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UCONN

Chemistry 2e.

Atoms First

Chemistry: Atoms First 2e
1: Essential Ideas
1.1: Chemistry in Context

1. Explain how you could experimentally determine whether the outside temperature is higher or lower than 0 °C (32 °F) without using a thermometer.

Solution
Place a glass of water outside. It will freeze if the temperature is below 0 °C.

2. Identify each of the following statements as being most similar to a hypothesis, a law, or a theory. Explain your reasoning.
(a) Falling barometric pressure precedes the onset of bad weather.
(b) All life on earth has evolved from a common, primitive organism through the process of natural selection.
(c) My truck's gas mileage has dropped significantly, probably because it's due for a tune-up.

Solution
(a) law (states a consistently observed phenomenon, can be used for prediction); (b) theory (a widely accepted explanation of the origin of species); (c) hypothesis (a tentative explanation, can be investigated by experimentation)

3. Identify each of the following statements as being most similar to a hypothesis, a law, or a theory. Explain your reasoning.
(a) The pressure of a sample of gas is directly proportional to the temperature of the gas.
(b) Matter consists of tiny particles that can combine in specific ratios to form substances with specific properties.
(c) At a higher temperature, solids (such as salt or sugar) will dissolve better in water.

Solution
(a) law (states a consistently observed phenomenon, can be used for prediction); (b) theory (a widely accepted explanation of the behavior of matter); (c) hypothesis (a tentative explanation, can be investigated by experimentation)

4. Identify each of the underlined items as a part of either the macroscopic domain, the microscopic domain, or the symbolic domain of chemistry. For any in the symbolic domain, indicate whether they are symbols for a macroscopic or a microscopic feature.
(a) The mass of a lead pipe is 14 lb.
(b) The mass of a certain chlorine atom is 35 amu.
(c) A bottle with a label that reads Al contains aluminum metal.
(d) Al is the symbol for an aluminum atom.

Solution
(a) macroscopic; (b) microscopic; (c) symbolic, macroscopic; (d) symbolic, microscopic

5. Identify each of the underlined items as a part of either the macroscopic domain, the microscopic domain, or the symbolic domain of chemistry. For those in the symbolic domain, indicate whether they are symbols for a macroscopic or a microscopic feature.
(a) A certain molecule contains one H atom and one Cl atom.
(b) Copper wire has a density of about 8 g/cm^3.
(c) The bottle contains 15 grams of Ni powder.
(d) A sulfur molecule is composed of eight sulfur atoms.

Solution
(a) symbolic, microscopic; (b) macroscopic; (c) symbolic, macroscopic; (d) microscopic

6. According to one theory, the pressure of a gas increases as its volume decreases, because the molecules in the gas have to move a shorter distance to hit the walls of the container. Does this theory follow a macroscopic or microscopic description of chemical behavior? Explain your answer.

Solution
Microscopic. The behavior is explained in terms of the behavior of microscopic particles (molecules).

7. The amount of heat required to melt 2 lbs of ice is twice the amount of heat required to melt 1 lb of ice. Is this observation a macroscopic or microscopic description of chemical behavior? Explain your answer.

Solution
Macroscopic. The heat required is determined from macroscopic properties.

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Chemistry: Atoms First 2e
1: Essential Ideas
1.2: Phases and Classification of Matter

8. Why do we use an object's mass, rather than its weight, to indicate the amount of matter it contains?

Solution
An object’s mass is used because the mass of the object is independent of outside forces on the object (that is, it is an intrinsic property of the object), whereas weight depends on the force of gravity and varies as gravity changes from location to location.

9. What properties distinguish solids from liquids? Liquids from gases? Solids from gases?

Solution
Liquids can change their shape (flow); solids can’t. Gases can undergo large volume changes as pressure changes; liquids do not. Gases flow and change volume; solids do not.

10. How does a heterogeneous mixture differ from a homogeneous mixture? How are they similar?

Solution
Mixtures are defined as systems containing two or more components that can be separated by physical means. When components mix and blend in such a manner that all regions are the same, the system is homogeneous; soft drinks, sugar water, gasoline, brass, and sterling silver are common examples of such mixtures. Most mixtures in the environment and in our experience are not homogeneous. Instead, mixtures such as deposits of rocks and minerals, river water, blood, and fruit salad are heterogeneous. The mixtures are alike in that physical methods, rather than chemical methods, can be used to separate the components.

11. How does a homogeneous mixture differ from a pure substance? How are they similar?

Solution
The mixture can have a variety of compositions; a pure substance has a definite composition. Both have the same composition from point to point.

12. How does an element differ from a compound? How are they similar?

Solution
Compounds can be broken down by chemical means, whereas elements cannot be decomposed by chemical changes. They are similar in that they both have properties associated with matter.

13. How do molecules of elements and molecules of compounds differ? In what ways are they similar?

Solution
Molecules of elements contain only one type of atom; molecules of compounds contain two or more types of atoms. They are similar in that both are comprised of two or more atoms chemically bonded together.

14. How does an atom differ from a molecule? In what ways are they similar?

Solution
An atom consists of only one particle; a molecule consists of two or more atoms. They are similar in that both are composed of the basic building block in chemistry, the atom.

15. Many of the items you purchase are mixtures of pure compounds. Select three of these commercial products and prepare a list of the ingredients that are pure compounds.

Solution
Answers will vary. Sample answer: Gatorade contains water, sugar, dextrose, citric acid, salt, sodium chloride, monopotassium phosphate, and sucrose acetate isobutyrate.

16. Classify each of the following as an element, a compound, or a mixture:
(a) copper
(b) water
(c) nitrogen
(d) sulfur
(e) air
(f) sucrose
(g) a substance composed of molecules each of which contains two iodine atoms
(h) gasoline

Solution
(a) element; (b) compound; (c) element; (d) element; (e) mixture; (f) compound; (g) element; (h) mixture

17. Classify each of the following as an element, a compound, or a mixture:
(a) iron
(b) oxygen
(c) mercury oxide
(d) pancake syrup
(e) carbon dioxide
(f) a substance composed of molecules each of which contains one hydrogen atom and one chlorine atom
(g) baking soda
(h) baking powder

Solution
(a) element; (b) element; (c) compound; (d) mixture, (e) compound; (f) compound; (g) compound; (h) mixture

18. A sulfur atom and a sulfur molecule are not identical. What is the difference?

Solution
A sulfur molecule is composed of eight sulfur atoms.

19. How are the molecules in oxygen gas, the molecules in hydrogen gas, and water molecules similar? How do they differ?

Solution
In each case, a molecule consists of two or more combined atoms. They differ in that the types of atoms change from one substance to the next.

20. We refer to astronauts in space as weightless, but not without mass. Why?

Solution
Because the force of gravity is extremely small in space, and the lack of attraction between bodies that gives weight to the astronauts is essentially absent. Therefore, they are weightless. They maintain their intrinsic mass, however.

21. As we drive an automobile, we don't think about the chemicals consumed and produced. Prepare a list of the principal chemicals consumed and produced during the operation of an automobile.

Solution
Gasoline (a mixture of compounds), oxygen, and to a lesser extent, nitrogen are consumed. Carbon dioxide and water are the principal products. Carbon monoxide and nitrogen oxides are produced in lesser amounts.

22. Matter is everywhere around us. Make a list by name of fifteen different kinds of matter that you encounter every day. Your list should include (and label at least one example of each) the following: a solid, a liquid, a gas, an element, a compound, a homogenous mixture, a heterogeneous mixture, and a pure substance.

Solution
There are many possible answers. Some include air (gas, homogenous mixture), aluminum foil (solid, pure substance), cereal with milk (heterogeneous mixture), distilled water (liquid, compound, pure substance), gold ingot (solid, element, pure substance), iron (element), milk (liquid, homogenous mixture), penny (solid), salt (solid, compound), soft drink (liquid, homogeneous mixture), sugar (solid, compound).

23. When elemental iron corrodes it combines with oxygen in the air to ultimately form red brown iron(III) oxide which we call rust. (a) If a shiny iron nail with an initial mass of 23.2 g is weighed after being coated in a layer of rust, would you expect the mass to have increased, decreased, or remained the same? Explain. (b) If the mass of the iron nail increases to 24.1 g, what mass of oxygen combined with the iron?

Solution
(a) Increased as it would have combined with oxygen in the air thus increasing the amount of matter and therefore the mass. (b) 24.1 g – 23.2 g = 0.9 g

24. As stated in the text, convincing examples that demonstrate the law of conservation of matter outside of the laboratory are few and far between. Indicate whether the mass would increase, decrease, or stay the same for the following scenarios where chemical reactions take place:
(a) Exactly one pound of bread dough is placed in a baking tin. The dough is cooked in an oven at 350 °F releasing a wonderful aroma of freshly baked bread during the cooking process. Is the mass of the baked loaf less than, greater than, or the same as the one pound of original dough? Explain.
(b) When magnesium burns in air a white flaky ash of magnesium oxide is produced. Is the mass of magnesium oxide less than, greater than, or the same as the original piece of magnesium? Explain.

(c) Antoine Lavoisier, the French scientist credited with first stating the law of conservation of matter, heated a mixture of tin and air in a sealed flask to produce tin oxide. Did the mass of the sealed flask and contents decrease, increase, or remain the same after the heating?

Solution
(a) The mass would be less than one pound as water vapor and other molecules (aroma) are released from the cooking dough. (b) The mass of the magnesium oxide product would be greater than the original magnesium metal as the amount of magnesium remains the same, but having combined with oxygen, the total amount of matter increases. (c) The mass of the sealed flask and contents would remain the same as no reactants or products leave the flask, and therefore the quantity of matter in the flask does not change.

25. Yeast converts glucose to ethanol and carbon dioxide during anaerobic fermentation as depicted in the simple chemical equation below:

$$\text{glucose} \longrightarrow \text{ethanol} + \text{carbon dioxide}$$

(a) If 200.0 g of glucose is fully converted, what will be the total mass of ethanol and carbon dioxide produced?
(b) If the fermentation is carried out in an open container, would you expect the mass of the container and contents after fermentation to be less than, greater than, or the same as the mass of the container and contents before fermentation? Explain.
(c) If 97.7 g of carbon dioxide is produced, what mass of ethanol is produced?

Solution
(a) 200.0 g; (b) The mass of the container and contents would decrease as carbon dioxide is a gaseous product and would leave the container. (c) 200.0 g – 97.7 g = 102.3 g

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Chemistry: Atoms First 2e
1: Essential Ideas
1.3: Physical and Chemical Properties

26. Classify the six underlined properties in the following paragraph as chemical or physical: Fluorine is a pale yellow gas that reacts with most substances. The free element melts at –220 °C and boils at –188 °C. Finely divided metals burn in fluorine with a bright flame. Nineteen grams of fluorine will react with 1.0 gram of hydrogen.

Solution
physical; chemical; physical; physical; chemical; chemical

27. Classify each of the following changes as physical or chemical:
(a) condensation of steam
(b) burning of gasoline
(c) souring of milk
(d) dissolving of sugar in water
(e) melting of gold

Solution
(a) physical; (b) chemical; (c) chemical; (d) physical; (e) physical

28. Classify each of the following changes as physical or chemical:
(a) coal burning

(b) ice melting
(c) mixing chocolate syrup with milk
(d) explosion of a firecracker
(e) magnetizing of a screwdriver

Solution
(a) chemical; (b) physical; (c) physical; (d) chemical; (e) physical

29. The volume of a sample of oxygen gas changed from 10 mL to 11 mL as the temperature changed. Is this a chemical or physical change?

Solution
physical

30. A 2.0-liter volume of hydrogen gas combined with 1.0 liter of oxygen gas to produce 2.0 liters of water vapor. Does oxygen undergo a chemical or physical change?

Solution
Two different elements combine to form a different substance. The change is chemical.

31. Explain the difference between extensive properties and intensive properties.

Solution
The value of an extensive property depends upon the amount of matter being considered, whereas the value of an intensive property is the same regardless of the amount of matter being considered.

32. Identify the following properties as either extensive or intensive.
(a) volume
(b) temperature
(c) humidity
(d) heat
(e) boiling point

Solution
(a) extensive; (b) intensive; (c) intensive; (d) extensive; (e) intensive

33. The density (d) of a substance is an intensive property that is defined as the ratio of its mass (m) to its volume (V).

$$\text{density} = \frac{\text{mass}}{\text{volume}} \qquad d = \frac{m}{V}$$

Considering that mass and volume are both extensive properties, explain why their ratio, density, is intensive.

Solution
Being extensive properties, both mass and volume are directly proportional to the amount of substance under study. Dividing one extensive property by another will in effect “cancel” this dependence on amount, yielding a ratio that is independent of amount (an intensive property).

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Chemistry: Atoms First 2e
1: Essential Ideas
1.4: Measurements

34. Is one liter about an ounce, a pint, a quart, or a gallon?

Solution
a quart

35. Is a meter about an inch, a foot, a yard, or a mile?

Solution
about a yard

36. Indicate the SI base units or derived units that are appropriate for the following measurements:
(a) the length of a marathon race (26 miles 385 yards)
(b) the mass of an automobile
(c) the volume of a swimming pool
(d) the speed of an airplane
(e) the density of gold
(f) the area of a football field
(g) the maximum temperature at the South Pole on April 1, 1913

Solution
(a) meters; (b) kilograms; (c) cubic meters; (d) meters/second; (e) kilograms/cubic meter; (f) square meters; (g) kelvin

37. Indicate the SI base units or derived units that are appropriate for the following measurements:
(a) the mass of the moon
(b) the distance from Dallas to Oklahoma City
(c) the speed of sound
(d) the density of air
(e) the temperature at which alcohol boils
(f) the area of the state of Delaware
(g) the volume of a flu shot or a measles vaccination

Solution
(a) kilograms; (b) meters; (c) meters/second; (d) kilograms/cubic meter; (e) kelvin; (f) square meters; (g) cubic meters

38. Give the name and symbol of the prefixes used with SI units to indicate multiplication by the following exact quantities.
(a) 10^3
(b) 10^{-2}
(c) 0.1
(d) 10^{-3}
(e) 1,000,000
(f) 0.000001

Solution
(a) kilo-, k; (b) centi-, c; (c) deci-, (d) d; milli-, (e) m; mega-, M; (f) micro-, μ

39. Give the name of the prefix and the quantity indicated by the following symbols that are used with SI base units.
(a) c
(b) d
(c) G
(d) k
(e) m
(f) n
(g) p

(h) T

Solution

(a) centi-, $\times 10^{-2}$; (b) deci-, $\times 10^{-1}$; (c) Giga-, $\times 10^{9}$; (d) kilo-, $\times 10^{3}$; (e) milli-, $\times 10^{-3}$; (f) nano-, $\times 10^{-9}$; (g) pico-, $\times 10^{-12}$; (h) tera-, $\times 10^{12}$

40. A large piece of jewelry has a mass of 132.6 g. A graduated cylinder initially contains 48.6 mL water. When the jewelry is submerged in the graduated cylinder, the total volume increases to 61.2 mL.
(a) Determine the density of this piece of jewelry.
(b) Assuming that the jewelry is made from only one substance, what substance is it likely to be? Explain.

Solution

(a) 10.5 g/cm^3; (b) silver, because silver has density = 10.5 g/cm^3 (Table 1.4)

41. Visit https://www.simbucket.com/density/ and click the "turn fluid into water" button to adjust the density of liquid in the beaker to 1.00 g/mL.
(a) Use the water displacement approach to measure the mass and volume of the unknown material (select the green block with question marks).
(b) Use the measured mass and volume data from step (a) to calculate the density of the unknown material.
(c) Assuming this material is a widely available copper-containing gemstone, what is its likely identity? Compare the measured density to the values tabulated at https://www.gemsociety.org/article/select-gems-ordered-density/.

Solution

(a) m = 18.58 g, V = 5.7 mL; (b) d = 3.3 g/mL; (c) malachite (basic copper carbonate, d = 3.25-4.10 g/mL)

42. Visit https://www.simbucket.com/density/ and click the "reset" button to ensure all simulator parameters are at their default values.
(a) Use the water displacement approach to measure the mass and volume of the red block.
(b) Use the measured mass and volume data from step (a) to calculate the density of the red block.
(c) Use the vertical green slide control to adjust the fluid density to values well above, then well below, and finally nearly equal to the density of the red block, reporting your observations.

Solution

(a) m = 2.5 g, V = 4.1 mL; (b) d = 0.61 g/mL; (c) The block sinks in the fluid when $d_{block} > d_{fluid}$, it floats on the fluid surface when $d_{block} < d_{fluid}$, and it remains suspended within the fluid when $d_{block} \approx d_{fluid}$.

43. Visit https://www.simbucket.com/density/ and click the "turn fluid into water" button to adjust the density of liquid in the beaker to 1.00 g/mL. Change the block material to foam, and then wait patiently until the foam block stops bobbing up and down in the water.
(a) The foam block should be floating on the surface of the water (that is, only partially submerged). What is the volume of water displaced?
(b) Use the water volume from part (a) and the density of water (1.0 g/mL) to calculate the mass of water displaced.
(c) Remove and weigh the foam block. How does the block's mass compare the mass of displaced water from part (b)?

Solution

(a) displaced water volume = 2.8 mL; (b) displaced water mass = 2.8 g; (c) The block mass is 2.76 g, essentially equal to the mass of displaced water (2.8 g) and consistent with Archimedes' principle of buoyancy.

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Chemistry: Atoms First 2e
1: Essential Ideas
1.5: Measurement Uncertainty, Accuracy, and Precision

44. Express each of the following numbers in scientific notation with correct significant figures:
(a) 711.0
(b) 0.239
(c) 90743
(d) 134.2
(e) 0.05499
(f) 10000.0
(g) 0.000000738592

Solution
(a) three significant figures 7.110×10^2; (b) three significant figures 2.39×10^{-1}; (c) five significant figures 9.0743×10^4; (d) four significant figures 1.342×10^2; (e) four significant figures 5.499×10^{-2}; (f) six significant figures 1.00000×10^4; (g) six significant figures 7.38592×10^{-7}

45. Express each of the following numbers in exponential notation with correct significant figures:
(a) 704
(b) 0.03344
(c) 547.9
(d) 22086
(e) 1000.00
(f) 0.0000000651
(g) 0.007157

Solution
(a) 7.04×10^2; (b) 3.344×10^{-2}; (c) 5.479×10^2; (d) 2.2086×10^4; (e) 1.00000×10^3; (f) 6.51×10^{-8}; (g) 7.157×10^{-3}

46. Indicate whether each of the following can be determined exactly or must be measured with some degree of uncertainty:
(a) the number of eggs in a basket
(b) the mass of a dozen eggs
(c) the number of gallons of gasoline necessary to fill an automobile gas tank
(d) the number of cm in 2 m
(e) the mass of a textbook
(f) the time required to drive from San Francisco to Kansas City at an average speed of 53 mi/h

Solution
(a) exact; (b) uncertain; (c) uncertain; (d) exact; (e) uncertain; (f) uncertain

47. Indicate whether each of the following can be determined exactly or must be measured with some degree of uncertainty:
(a) the number of seconds in an hour
(b) the number of pages in this book
(c) the number of grams in your weight
(d) the number of grams in 3 kilograms
(e) the volume of water you drink in one day
(f) the distance from San Francisco to Kansas City

Solution
(a) exact; (b) exact; (c) uncertain; (d) exact; (e) uncertain; (f) uncertain

48. How many significant figures are contained in each of the following measurements?
(a) 38.7 g
(b) 2×10^{18} m
(c) 3,486,002 kg
(d) 9.74150×10^{-4} J
(e) 0.0613 cm^3
(f) 17.0 kg
(g) 0.01400 g/mL

Solution
(a) three; (b) one; (c) seven; (d) six; (e) three; (f) three; (g) four

49. How many significant figures are contained in each of the following measurements?
(a) 53 cm
(b) 2.05×10^8 m
(c) 86,002 J
(d) 9.740×10^4 m/s
(e) 10.0613 m^3
(f) 0.17 g/mL
(g) 0.88400 s

Solution
(a) two; (b) three; (c) five; (d) four; (e) six; (f) two; (g) five

50. The following quantities were reported on the labels of commercial products. Determine the number of significant figures in each.
(a) 0.0055 g active ingredients
(b) 12 tablets
(c) 3% hydrogen peroxide
(d) 5.5 ounces
(e) 473 mL
(f) 1.75% bismuth
(g) 0.001% phosphoric acid
(h) 99.80% inert ingredients

Solution
(a) two; (b) this is an exact number, so the concept of significant figures does not apply; (c) one; (d) two; (e) three; (f) three; (g) one; (h) four

51. Round off each of the following numbers to two significant figures:
(a) 0.436
(b) 9.000

(c) 27.2
(d) 135
(e) 1.497×10^{-3}
(f) 0.445

Solution
(a) 0.44; (b) 9.0; (c) 27; (d) 140; (e) 1.5×10^{-3}; (f) 0.44

52. Round off each of the following numbers to two significant figures:
(a) 517
(b) 86.3
(c) 6.382×10^{3}
(d) 5.0008
(e) 22.497
(f) 0.885

Solution
(a) 5.2×10^{2}; (b) 86; (c) 6.4×10^{3}; (d) 5.0; (e) 22; (f) 0.88

53. Perform the following calculations and report each answer with the correct number of significant figures.
(a) 628×342
(b) $(5.63 \times 10^{2}) \times (7.4 \times 10^{3})$
(c) $\dfrac{28.0}{13.483}$
(d) 8119×0.000023
(e) 14.98 + 27,340 + 84.7593
(f) 42.7 + 0.259

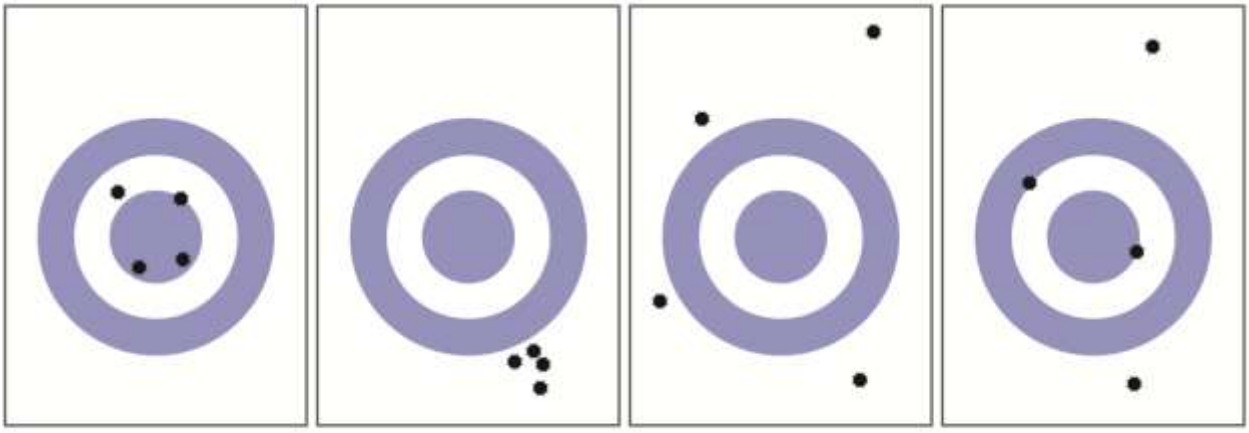
Solution
(a) 2.15×10^{5}; (b) 4.2×10^{6}; (c) 2.08; (d) 0.19; (e) 27,440; (f) 43.0

54. Perform the following calculations and report each answer with the correct number of significant figures.
(a) 62.8×34
(b) 0.147 + 0.0066 + 0.012
(c) $38 \times 95 \times 1.792$
(d) 15 – 0.15 – 0.6155
(e) $8.78 \times \left(\dfrac{0.0500}{0.478}\right)$
(f) 140 + 7.68 + 0.014
(g) 28.7 – 0.0483
(h) $\dfrac{(88.5 - 87.57)}{45.13}$

Solution
(a) 2.1×10^{3}; (b) 0.166 or 1.66×10^{-1}; (c) 6.5×10^{3}; (d) 14 or 1.4×10^{1}; (e) 0.918 or 9.18×10^{-1}; (f) either 148 or 150, depending on whether the ambiguous ones-place zero in 140 is significant (148) or not (150); (g) 28.7; (h) 0.02

55. Consider the results of the archery contest shown in this figure.
(a) Which archer is most precise?
(b) Which archer is most accurate?

(c) Who is both least precise and least accurate?



Solution
(a) Archer X; (b) Archer W; (c) Archer Y

56. Classify the following sets of measurements as accurate, precise, both, or neither.
(a) Checking for consistency in the weight of chocolate chip cookies: 17.27 g, 13.05 g, 19.46 g, 16.92 g
(b) Testing the volume of a batch of 25-mL pipettes: 27.02 mL, 26.99 mL, 26.97 mL, 27.01 mL
(c) Determining the purity of gold: 99.9999%, 99.9998%, 99.9998%, 99.9999%

Solution
(a) neither; (b) precise but not accurate; (c) both accurate and precise

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Chemistry: Atoms First 2e
1: Essential Ideas
1.6: Mathematical Treatment of Measurement Results

57. Write conversion factors (as ratios) for the number of:
(a) yards in 1 meter
(b) liters in 1 liquid quart
(c) pounds in 1 kilogram

Solution
(a) $\frac{1.0936\ \text{yd}}{1\ \text{m}}$; (b) $\frac{0.94635\ \text{L}}{1\ \text{qt}}$; (c) $\frac{2.2046\ \text{lb}}{1\ \text{kg}}$

58. Write conversion factors (as ratios) for the number of:
(a) kilometers in 1 mile
(b) liters in 1 cubic foot
(c) grams in 1 ounce

Solution
(a) $\frac{1.609\ \text{km}}{1\ \text{mi}}$; (b) $\frac{28.317\ \text{L}}{1\ \text{ft}^3}$; (c) $\frac{28.349\ \text{g}}{1\ \text{oz}}$

59. The label on a soft drink bottle gives the volume in two units: 2.0 L and 67.6 fl oz. Use this information to derive a conversion factor between the English and metric units. How many significant figures can you justify in your conversion factor?

Solution
Divide the total number of liters by the total number of fluid ounces.

$$0.030 \text{ L} = 1 \text{ fl oz}$$

$$\frac{2.0 \text{ L}}{67.6 \text{ fl oz}} = \frac{0.030 \text{ L}}{1 \text{ fl oz}}$$

Only two significant figures are justified.

60. The label on a box of cereal gives the mass of cereal in two units: 978 grams and 34.5 oz. Use this information to find a conversion factor between the English and metric units. How many significant figures can you justify in your conversion factor?

Solution
28.3 g = (exactly) 1 oz, three significant figures

61. Soccer is played with a round ball having a circumference between 27 and 28 in. and a weight between 14 and 16 oz. What are these specifications in units of centimeters and grams?

Solution
68–71 cm; 400–450 g

62. A woman's basketball has a circumference between 28.5 and 29.0 inches and a maximum weight of 20 ounces (two significant figures). What are these specifications in units of centimeters and grams?

Solution
72.4–73.7 cm; max. 5.7×10^2 g

63. How many milliliters of a soft drink are contained in a 12.0-oz can?

Solution
355 mL

64. A barrel of oil is exactly 42 gal. How many liters of oil are in a barrel?

Solution

$$1 \text{ qt} = 0.94635 \text{ L} = \frac{1}{4} \text{ gal}$$

$$42 \cancel{\text{ gal}} \text{ (exact)} \times \frac{4 \cancel{\text{ qt}}}{1 \cancel{\text{ gal}}} \times \frac{0.9463 \text{ L}}{1 \cancel{\text{ qt}}} = 159.00 \text{ L}$$

65. The diameter of a red blood cell is about 3×10^{-4} in. What is its diameter in centimeters?

Solution
8×10^{-4} cm

66. The distance between the centers of the two oxygen atoms in an oxygen molecule is 1.21×10^{-8} cm. What is this distance in inches?

Solution
1 in. = 2.54 cm

$$1.21 \times 10^{-8} \cancel{\text{ cm}} \times \frac{1 \text{ in.}}{2.54 \cancel{\text{ cm}}} = 4.76 \times 10^{-9} \text{ in.}$$

67. Is a 197-lb weight lifter light enough to compete in a class limited to those weighing 90 kg or less?

Solution
yes; weight = 89.4 kg

68. A very good 197-lb weight lifter lifted 192 kg in a move called the clean and jerk. What was the mass of the weight lifted in pounds?

Solution
1 lb = 0.45359 kg

$$192\ \cancel{\text{kg}} \times \frac{1\ \text{lb}}{0.45359\ \cancel{\text{kg}}} = 423\ \text{lb} = 4.23 \times 10^{2}\ \text{lb}$$

69. Many medical laboratory tests are run using 5.0 μL blood serum. What is this volume in milliliters?

Solution
5.0×10^{-3} mL

70. If an aspirin tablet contains 325 mg aspirin, how many grams of aspirin does it contain?

Solution

$$\frac{325\ \cancel{\text{mg}} \times 1\ \text{g}}{1000\ \cancel{\text{mg}}} = 0.325\ \text{g}$$

71. Use scientific (exponential) notation to express the following quantities in terms of the SI base units in Table 1.3:
(a) 0.13 g
(b) 232 Gg
(c) 5.23 pm
(d) 86.3 mg
(e) 37.6 cm
(f) 54 μm
(g) 1 Ts
(h) 27 ps
(i) 0.15 mK

Solution
(a) 1.3×10^{-4} kg; (b) 2.32×10^{8} kg; (c) 5.23×10^{-12} m; (d) 8.63×10^{-5} kg; (e) 3.76×10^{-1} m; (f) 5.4×10^{-5} m; (g) 1×10^{12} s; (h) 2.7×10^{-11} s; (i) 1.5×10^{-4} K

72. Complete the following conversions between SI units.
(a) 612 g = _____ mg
(b) 8.160 m = _____ cm
(c) 3779 μg = _____ g
(d) 781 mL = _____ L
(e) 4.18 kg = _____ g
(f) 27.8 m = _____ km
(g) 0.13 mL = _____ L
(h) 1738 km = _____ m
(i) 1.9 Gg = _____ g

Solution
See Table 1.6

(a) $612\ \cancel{\text{g}} \times \frac{1000\ \text{mg}}{1\ \cancel{\text{g}}} = 6.12 \times 10^{5}\ \text{mg}$ 1 g = 1000 mg

(b) $8.160\ \cancel{\text{m}} \times \frac{100\ \text{cm}}{\cancel{\text{m}}} = 8.160 \times 10^{2}\ \text{cm}$ 1 m = 100 cm

(c) $3779\ \cancel{\mu g} \times \frac{10^{-6}\ g}{1\ \cancel{\mu g}} = 3.779 \times 10^{-3}\ g$ $\quad 1\mu g = 10^{-6}\ g$

(d) $781\ \cancel{mL} \times \frac{10^{-3}\ L}{1\ \cancel{mL}} = 7.81 \times 10^{-1}\ L$ $\quad 1\ mL = 10^{-3}\ L$

(e) $4.18\ \cancel{kg} \times \frac{1000\ g}{1\ \cancel{kg}} = 4.18 \times 10^{3}\ g$ $\quad 1\ kg = 1000\ g$

(f) $2.78\ \cancel{m} \times \frac{10^{-3}\ km}{1\ \cancel{m}} = 2.78 \times 10^{-2}\ m$ $\quad 1\ m = 10^{-3}\ L$

(g) $0.13\ \cancel{mL} \times \frac{10^{-3}\ L}{1\ \cancel{mL}} = 1.3 \times 10^{-4}\ L$ $\quad 1\ mL = 10^{-3}\ L$

(h) $1738\ \cancel{km} \times \frac{1000\ m}{1\ \cancel{km}} = 1.738 \times 10^{6}\ m$ $\quad 1\ km = 1000\ m$

(i) $1.9\ \cancel{Gg} \times \frac{10^{9}\ g}{1\ \cancel{Gg}} = 1.9 \times 10^{9}\ g$ $\quad 1\ Gg = 10^{9}\ g$

73. Gasoline is sold by the liter in many countries. How many liters are required to fill a 12.0-gal gas tank?

Solution
45.4 L

74. Milk is sold by the liter in many countries. What is the volume of exactly 1/2 gal of milk in liters?

Solution

$1\ L = 1.0567\ qt;\ 1\ gal = 4\ qt;\ \frac{1}{2}\ gal = 2\ qt$

$2\ \cancel{qt} \times \frac{1\ L}{1.0567\ \cancel{qt}} = 1.892\ L$

75. A long ton is defined as exactly 2240 lb. What is this mass in kilograms?

Solution

$2240\ \cancel{lb}\ (\text{exactly}) \times \frac{0.45359\ kg}{1\ \cancel{lb}} = 1016.0\ kg = 1.0160 \times 10^{3}\ kg$

76. Make the conversion indicated in each of the following:

(a) the men's world record long jump, 29 ft $4\frac{1}{4}$ in., to meters

(b) the greatest depth of the ocean, about 6.5 mi, to kilometers

(c) the area of the state of Oregon, 96,981 mi^2, to square kilometers

(d) the volume of 1 gill (exactly 4 oz) to milliliters

(e) the estimated volume of the oceans, 330,000,000 mi^3, to cubic kilometers.

(f) the mass of a 3525-lb car to kilograms

(g) the mass of a 2.3-oz egg to grams

Solution

(a) 8.95 m; (b) 1.0×10^{1} km; (c) $2.5118 \times 10^{5}\ km^2$; (d) 118.3 mL; (e) $1.4 \times 10^{9}\ km^3$;, (f) 1,599 kg; (g) 65 g

77. Make the conversion indicated in each of the following:

(a) the length of a soccer field, 120 m (three significant figures), to feet

(b) the height of Mt. Kilimanjaro, at 19,565 ft the highest mountain in Africa, to kilometers
(c) the area of an 8.5 × 11-inch sheet of paper in cm^2
(d) the displacement volume of an automobile engine, 161 $in.^3$, to liters
(e) the estimated mass of the atmosphere, 5.6×10^{15} tons, to kilograms
(f) the mass of a bushel of rye, 32.0 lb, to kilograms
(g) the mass of a 5.00-grain aspirin tablet to milligrams (1 grain = 0.00229 oz)

Solution

(a) $120 \cancel{\text{ m}} \times \frac{1.0936 \cancel{\text{ yd}}}{1 \cancel{\text{ m}}} \times \frac{3 \text{ ft}}{1 \cancel{\text{ yd}}} = 394 \text{ ft}$

(b) $19{,}565 \cancel{\text{ ft}} \times \frac{12 \cancel{\text{ in.}}}{1 \cancel{\text{ ft}}} \times \frac{2.54 \cancel{\text{ cm}}}{1 \cancel{\text{ in.}}} \times \frac{1 \cancel{\text{ m}}}{100 \cancel{\text{ cm}}} \times \frac{1 \text{ km}}{1000 \cancel{\text{ m}}} = 5.9634 \text{ km}$

(c) $8.5 \text{ in.} \times 11 \text{ in.} = 93.5 \cancel{\text{ in.}^2} \times \frac{(2.54 \text{ cm})^2}{(1 \cancel{\text{ in.}})^2} = 6.0 \times 10^2$

(d) $161 \cancel{\text{ in.}^3} \times \left(\frac{2.54 \cancel{\text{ cm}}}{1 \cancel{\text{ in.}}}\right)^3 \times \frac{1 \text{ L}}{1000 \cancel{\text{ cm}^3}} = 2.64 \text{ L}$

(e) $5.6 \times 10^{15} \cancel{\text{ short tons}} \times 907.185 \text{ kg}/\cancel{\text{ short tons}} = 5.1 \times 10^{18} \text{ kg}$

(f) $32.0 \cancel{\text{ lb}} \times \frac{0.45359 \text{ kg}}{1 \cancel{\text{ lb}}} = 14.5 \text{ kg}$

(g) $5.00 \cancel{\text{ grain}} \times \frac{0.00229 \cancel{\text{ oz}}}{1 \cancel{\text{ grain}}} \times \frac{28.349 \text{ g}}{1 \cancel{\text{ oz}}} = 0.324 \text{ g}$

$0.411 \cancel{\text{ g}} \times \frac{1000 \text{ mg}}{1 \cancel{\text{ g}}} = 324 \text{ mg}$

78. Many chemistry conferences have held a 50-Trillion Angstrom Run (two significant figures). How long is this run in kilometers and in miles? ($1 \text{ Å} = 1 \times 10^{-10} \text{ m}$)

Solution

5.0 km, 3.1 mi

79. A chemist's 50-Trillion Angstrom Run (see Exercise 78) would be an archeologist's 10,900 cubit run. How long is one cubit in meters and in feet? ($1 \text{ Å} = 1 \times 10^{-8} \text{ cm}$)

Solution

$5.0 \times \frac{10^3 \text{ m}}{10{,}900 \text{ cubit}} = 0.46 \text{ m/cubit or 1 cubit} = 0.46 \text{ m}$

$\frac{5000 \text{ m}}{10{,}900 \text{ cubit}} \times \frac{1 \text{ yd}}{0.9744 \text{ m}} \times 3 \text{ ft/yd} = 1.5 \text{ ft/cubit}$

80. The gas tank of a certain luxury automobile holds 22.3 gallons according to the owner's manual. If the density of gasoline is 0.8206 g/mL, determine the mass in kilograms and pounds of the fuel in a full tank.

Solution

1 gal = 4 qt; 1 qt = 0.94635 L

$1 \cancel{\text{ gal}} \times \frac{4 \cancel{\text{ qt}}}{1 \cancel{\text{ gal}}} \times 0.94635 \text{ L}/\cancel{\text{ qt}} = 3.7852 \text{ L}$

$$22.3\ \cancel{\text{gal}} \times 3.7852\ \cancel{\text{L}}/\cancel{\text{gal}} \times 0.8206\ \cancel{\text{g}}/\cancel{\text{mL}} \times \frac{1\ \text{kg}}{1000\ \cancel{\text{g}}} \times 1000\ \cancel{\text{mL}}/\cancel{\text{L}} = 69.3\ \text{kg}$$

$$69.3\ \cancel{\text{kg}} \times \frac{1\ \text{lb}}{0.45359\ \cancel{\text{kg}}} = 153\ \text{lb}$$

81. As an instructor is preparing for an experiment, he requires 225 g phosphoric acid. The only container readily available is a 150-mL Erlenmeyer flask. Is it large enough to contain the acid, whose density is 1.83 g/mL?

Solution
Yes, the acid's volume is 123 mL.

82. To prepare for a laboratory period, a student lab assistant needs 125 g of a compound. A bottle containing 1/4 lb is available. Did the student have enough of the compound?

Solution
Determine the number of grams in 1/4 lb; assume the same number of significant figures as in the 125-g sample, that is, 3.

$$0.250\ \cancel{\text{lb}} \times 453.59\ \text{g}/\cancel{\text{lb}} = 113\ \text{g}$$

And so, the student does not have enough compound.

83. A chemistry student is 159 cm tall and weighs 45.8 kg. What is her height in inches and weight in pounds?

Solution
62.6 in (about 5 ft 3 in.) and 101 lb

84. In a recent Grand Prix, the winner completed the race with an average speed of 229.8 km/h. What was his speed in miles per hour, meters per second, and feet per second?

Solution
142.8 mi/h, 63.84 m/s, 209.4 ft/s

85. Solve these problems about lumber dimensions.
(a) To describe to a European how houses are constructed in the US, the dimensions of "two-by-four" lumber must be converted into metric units. The thickness × width × length dimensions are 1.50 in. × 3.50 in. × 8.00 ft in the US. What are the dimensions in cm × cm × m?
(b) This lumber can be used as vertical studs, which are typically placed 16.0 in. apart. What is that distance in centimeters?

Solution
(a) 3.81 cm × 8.89 cm × 2.44 m; (b) 40.6 cm

86. The mercury content of a stream was believed to be above the minimum considered safe—1 part per billion (ppb) by weight. An analysis indicated that the concentration was 0.68 parts per billion. What quantity of mercury in grams was present in 15.0 L of the water, the density of which is 0.998 g/ml? $\left(1\ \text{ppb Hg} = \frac{1\ \text{ng Hg}}{1\ \text{g water}}\right)$

Solution
1.0×10^{-5} g

87. Calculate the density of aluminum if 27.6 cm^3 has a mass of 74.6 g.

Solution
2.70 g/cm^3

88. Osmium is one of the densest elements known. What is its density if 2.72 g has a volume of 0.121 cm^3

Solution

$\text{density} = \frac{\text{mass}}{\text{volume}}; \frac{2.7\ \text{g}}{0.121\ \text{cm}^3} = 22.5\ \text{g/cm}^3$

89. Calculate these masses.
(a) What is the mass of 6.00 cm^3 of mercury, density = 13.5939 g/cm^3?
(b) What is the mass of 25.0 mL octane, density = 0.702 g/cm^3?

Solution
(a) 81.6 g; (b) 17.6 g

90. Calculate these masses.
(a) What is the mass of 4.00 cm^3 of sodium, density = 0.97 g/cm?
(b) What is the mass of 125 mL gaseous chlorine, density = 3.16 g/L?

Solution
$\text{mass} = \text{volume} \times \text{density}$; (a) $\text{Mass} = 4.00\ \cancel{\text{cm}^3} \times 0.97\ \text{g}/\cancel{\text{cm}^3} = 3.9\ \text{g}$; (b)
$\text{Mass} = 125\ \cancel{\text{mL}} \times 3.16\ \text{g}/\cancel{\text{L}} \times \frac{1\ \cancel{\text{L}}}{1000\ \cancel{\text{mL}}} = 0.395\ \text{g}$

91. Calculate these volumes.
(a) What is the volume of 25 g iodine, density = 4.93 g/cm^3?
(b) What is the volume of 3.28 g gaseous hydrogen, density = 0.089 g/L?

Solution
(a) 5.1 mL; (b) 37 L

92. Calculate these volumes.
(a) What is the volume of 11.3 g graphite, density = 2.25 g/cm^3?
(b) What is the volume of 39.657 g bromine, density = 2.928 g/cm^3

Solution
$\text{volume} = \frac{\text{mass}}{\text{density}}$; (a) $\frac{11.3\ \cancel{\text{g}}}{2.25\ \cancel{\text{g}}/\text{cm}^3} = 5.02\ \text{cm}^3 = 5.02\ \text{mL}$; (b)
$\text{Volume} = \frac{39.657\ \cancel{\text{g}}}{2.2928\ \cancel{\text{g}}/\text{cm}^3} = 13.54\ \text{cm}^3 = 13.54\ \text{mL}$

93. Convert the boiling temperature of gold, 2966 °C, into degrees Fahrenheit and kelvin.

Solution
5371 °F, 3239 K

94. Convert the temperature of scalding water, 54 °C, into degrees Fahrenheit and kelvin.

Solution
$°\text{F} = \frac{9}{5}(°\text{C}) + 32$; $\text{K} = °\text{C} + 273.15$; $°\text{F} = \frac{9}{5}(54) + 32 = 129\ °\text{F}$; $\text{K} = 54\ ºC + 273.15 = 327\ \text{K}$

95. Convert the temperature of the coldest area in a freezer, –10 °F, to degrees Celsius and kelvin.

Solution
–23 °C, 250 K

96. Convert the temperature of dry ice, –77 °C, into degrees Fahrenheit and kelvin.

Solution
$°\text{F} = \frac{9}{5}(°\text{C}) + 32$; $\text{K} = °\text{C} + 273.15$; $°\text{F} = \frac{9}{5}(-77) + 32 = -138.6 + 32 = -107\ °\text{F}$; $\text{K} = -77\ ºC + 273.15 = 196\ \text{K}$

97. Convert the boiling temperature of liquid ammonia, –28.1 °F, into degrees Celsius and kelvin.

Solution
–33.4 °C, 239.8 K

98. The label on a pressurized can of spray disinfectant warns against heating the can above 130 °F. What are the corresponding temperatures on the Celsius and kelvin temperature scales?

Solution
$°C = \frac{5}{9}(°F - 32)$; $K = °C + 273.15$; $°C = \frac{5}{9}(130 - 32) = \frac{5}{9}(98) = 54\ °C$; $K = 54 + 273.15 = 327\ K$

99. The weather in Europe was unusually warm during the summer of 1995. The TV news reported temperatures as high as 45 °C. What was the temperature on the Fahrenheit scale?

Solution
113 °F

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Chemistry: Atoms First 2e
2: Atoms, Molecules, and Ions
2.1: Early Ideas in Atomic Theory

1. In the following drawing, the green spheres represent atoms of a certain element. The purple spheres represent atoms of another element. If the spheres of different elements touch, they are part of a single unit of a compound. The following chemical change represented by these spheres may violate one of the ideas of Dalton's atomic theory. Which one?



Solution
The starting materials consist of one green sphere and two purple spheres. The products consist of two green spheres and two purple spheres. This violates Dalton's postulate that that atoms are not created during a chemical change, but are merely redistributed.

2. Which postulate of Dalton's theory is consistent with the following observation concerning the weights of reactants and products? When 100 grams of solid calcium carbonate is heated, 44 grams of carbon dioxide and 56 grams of calcium oxide are produced.

Solution
Atoms are neither created nor destroyed during a chemical change; they are rearranged. This explains why the mass of the reactant equals the mass of the products.

3. Identify the postulate of Dalton's theory that is violated by the following observations: 59.95% of one sample of titanium dioxide is titanium; 60.10% of a different sample of titanium dioxide is titanium.

Solution
This statement violates Dalton's fourth postulate: In a given compound, the numbers of atoms of each type (and thus also the percentage) always have the same ratio.

4. Samples of compound X, Y, and Z are analyzed, with results shown below.

Compound	Description	Mass of Carbon	Mass of Hydrogen
X	clear, colorless, liquid with strong odor	1.776 g	0.148 g
Y	clear, colorless, liquid with strong odor	1.974 g	0.329 g
Z	clear, colorless, liquid with strong odor	7.812 g	0.651 g

Do these data provide example(s) of the law of definite proportions, the law of multiple proportions, neither, or both? What do these data tell you about compounds X, Y, and Z?

Solution
The carbon-to-hydrogen mass ratio in X is 12:1, in Y is 6:1, and in Z is 12:1. Compounds X and Z have the same mass ratio, so they could be the same compound; that would be an example of the law of definite proportions. The ratio of the mass ratios of X:Y as well as Z:Y are both 12:6 = 2:1, which are examples of the law of multiple proportions.

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Chemistry: Atoms First 2e
2: Atoms, Molecules, and Ions
2.2: Evolution of Atomic Theory

5. The existence of isotopes violates one of the original ideas of Dalton's atomic theory. Which one?

Solution

Dalton originally thought that all atoms of a particular element had identical properties, including mass. Thus, the concept of isotopes, in which an element has different masses, was a violation of the original idea. To account for the existence of isotopes, the second postulate of his atomic theory was modified to state that atoms of the same element must have identical chemical properties.

6. How are electrons and protons similar? How are they different?

Solution

Both are charged particles that are components of an atom. Although charges are the same size, the signs of the charges are opposite. Protons are much more massive than electrons. Protons are located within an atom's nucleus, whereas electrons are located outside the nucleus.

7. How are protons and neutrons similar? How are they different?

Solution

Both are subatomic particles that reside in an atom's nucleus. Both have approximately the same mass. Protons are positively charged, whereas neutrons are uncharged.

8. Predict and test the behavior of α particles fired at a "plum pudding" model atom.

(a) Predict the paths taken by α particles that are fired at atoms with a Thomson's plum pudding model structure. Explain why you expect the α particles to take these paths.

(b) If α particles of higher energy than those in (a) are fired at plum pudding atoms, predict how their paths will differ from the lower-energy α particle paths. Explain your reasoning.

(c) Now test your predictions from (a) and (b). Open the URL http://phet.colorado.edu/en/simulation/rutherford-scattering and select the "Plum Pudding Atom" tab. Set "Alpha Particles Energy" to "min," and select "show traces." Click on the gun to start firing α particles. Does this match your prediction from (a)? If not, explain why the actual path would be that shown in the simulation. Hit the pause button, or "Reset All." Set "Alpha Particles Energy" to "max," and start firing α particles. Does this match your prediction from (b)? If not, explain the effect of increased energy on the actual paths as shown in the simulation.

Solution

(a) The plum pudding model indicates that the positive charge is spread uniformly throughout the atom, so we expect the α particles to (perhaps) be slowed somewhat by the positive-positive repulsion, but to follow straight-line paths (i.e., not to be deflected) as they pass through the atoms. (b) Higher-energy α particles will be traveling faster (and perhaps slowed less) and will also follow straight-line paths through the atoms. (c) The α particles followed straight-line paths through the plum pudding atom. There was no apparent slowing of the α particles as they passed through the atoms.

9. Predict and test the behavior of α particles fired at a Rutherford atom model.

(a) Predict the paths taken by α particles that are fired at atoms with a Rutherford atom model structure. Explain why you expect the α particles to take these paths.

(b) If α particles of higher energy than those in (a) are fired at Rutherford atoms, predict how their paths will differ from the lower-energy α particle paths. Explain your reasoning.

(c) Predict how the paths taken by the α particles will differ if they are fired at Rutherford atoms of elements other than gold. What factor do you expect to cause this difference in paths, and why?

(d) Now test your predictions from (a), (b), and (c). Open the URL: http://phet.colorado.edu/en/simulation/rutherford-scattering and select the "Rutherford Atom" tab. Due to the scale of the simulation, it is best to start with a small nucleus, so select "20" for both protons and neutrons, "min" for energy, show traces, and then start firing α particles. Does this match your prediction from (a)? If not, explain why the actual path would be that shown in the simulation. Pause or reset, set energy to "max," and start firing α particles. Does this match your prediction from (b)? If not, explain the effect of increased energy on the actual path as shown in the simulation. Pause or reset, select "40" for both protons and neutrons, "min" for energy, show traces, and fire away. Does this match your prediction from (c)? If not, explain why the actual path would be that shown in the simulation. Repeat this with larger numbers of protons and neutrons. What generalization can you make regarding the type of atom and effect on the path of α particles? Be clear and specific.

Solution

(a) The Rutherford atom has a small, positively charged nucleus, so most α particles will pass through empty space far from the nucleus and be undeflected. Those α particles that pass near the nucleus will be deflected from their paths due to positive-positive repulsion. The more directly toward the nucleus the α particles are headed, the larger the deflection angle will be. (b) Higher-energy α particles that pass near the nucleus will still undergo deflection, but the faster they travel, the less the expected angle of deflection. (c) If the nucleus is smaller, the positive charge is smaller and the expected deflections are smaller—both in terms of how closely the α particles pass by the nucleus undeflected and the angle of deflection. If the nucleus is larger, the positive charge is larger and the expected deflections are larger—more α particles will be deflected, and the deflection angles will be larger. (d) The paths followed by the α particles match the predictions from (a), (b), and (c).

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Chemistry: Atoms First 2e
2: Atoms, Molecules, and Ions
2.3: Atomic Structure and Symbolism

10. In what way are isotopes of a given element always different? In what way(s) are they always the same?

Solution

Isotopes of a given element by definition always exhibit different mass numbers (numbers of neutrons in their atoms' nuclei) and, consequently, different atomic masses. They always exhibit the same atomic number (number of protons in their atoms' nuclei), however, as this is the trait that defines their elemental identity.

11. Write the symbol for each of the following ions:
(a) the ion with a 1+ charge, atomic number 55, and mass number 133
(b) the ion with 54 electrons, 53 protons, and 74 neutrons
(c) the ion with atomic number 15, mass number 31, and a 3– charge
(d) the ion with 24 electrons, 30 neutrons, and a 3+ charge

Solution

(a) $^{133}Cs^{+}$; (b) $^{127}I^{-}$; (c) $^{31}P^{3-}$; (d) $^{57}Co^{3+}$

12. Write the symbol for each of the following ions:
(a) the ion with a 3+ charge, 28 electrons, and a mass number of 71
(b) the ion with 36 electrons, 35 protons, and 45 neutrons
(c) the ion with 86 electrons, 142 neutrons, and a 4+ charge
(d) the ion with a 2+ charge, atomic number 38, and mass number 87

Solution
In the following symbols, both atomic number and mass number are given if available from the problem. (a) Gallium has an atomic number of 31 and would form a 3+ ion with 28 electrons. The complete symbol is $^{71}Ga^{3+}$. (b) The element with 35 protons is bromine. Its 36 electrons are consistent with a single negative charge. The complete symbol is $^{80}Br^{-}$. (c) With 86 electrons and a 4+ charge, the neutral atom must have 90 electrons and 90 protons. The element with 90 protons is thorium (Th). The symbol is $^{232}Th^{4+}$. (d) Strontium has atomic number 38 and the symbol is $^{87}Sr^{2+}$.

13. Open the URL: http://phet.colorado.edu/en/simulation/build-an-atom and click on the Atom icon.
(a) Pick any one of the first 10 elements that you would like to build and state its symbol.
(b) Drag protons, neutrons, and electrons onto the atom template to make an atom of your element.
State the numbers of protons, neutrons, and electrons in your atom, as well as the net charge and mass number.
(c) Click on "Net Charge" and "Mass Number," check your answers to (b), and correct, if needed.
(d) Predict whether your atom will be stable or unstable. State your reasoning.
(e) Check the "Stable/Unstable" box. Was your answer to (d) correct? If not, first predict what you can do to make a stable atom of your element, and then do it and see if it works. Explain your reasoning.

Solution
(a) Carbon-12, ^{12}C; (b) This atom contains six protons and six neutrons. There are six electrons in a neutral ^{12}C atom. The net charge of such a neutral atom is zero, and the mass number is 12. (c) The above answers are correct. (d) The atom will be stable since C-12 is a stable isotope of carbon. (e) The above answer is correct. Other answers for this exercise are possible if a different element of isotope is chosen.

14. Open the URL: http://phet.colorado.edu/en/simulation/build-an-atom.
(a) Drag protons, neutrons, and electrons onto the atom template to make a neutral atom of Oxygen-16 and give the isotope symbol for this atom.
(b) Now add two more electrons to make and ion and give the symbol for the ion you have created.

Solution
(a) Oxygen-16 contains eight protons, eight neutrons, and eight electrons. The isotope symbol ^{16}O or $^{16}_{8}O$. (b) $^{16}O^{2-}$ or $^{16}_{8}O^{2-}$

15. Open the URL: http://phet.colorado.edu/en/simulation/build-an-atom.
(a) Drag protons, neutrons, and electrons onto the atom template to make a neutral atom of Lithium-6 and give the isotope symbol for this atom.
(b) Now remove one electron to make an ion and give the symbol for the ion you have created.

Solution

(a) Lithium-6 contains three protons, three neutrons, and three electrons. The isotope symbol is 6Li or ${}^{6}_{3}\text{Li}$. (b) ${}^{6}_{3}\text{Li}$ or ${}^{6}_{3}\text{Li}$

16. Determine the number of protons, neutrons, and electrons in the following isotopes that are used in medical diagnoses:
(a) atomic number 9, mass number 18, charge of 1–
(b) atomic number 43, mass number 99, charge of 7+
(c) atomic number 53, atomic mass number 131, charge of 1–
(d) atomic number 81, atomic mass number 201, charge of 1+
(e) Name the elements in parts (a), (b), (c), and (d).

Solution
(a) 9 protons, 10 electrons, 9 neutrons; (b) 43 protons, 36 electrons, 56 neutrons; (c) 53 protons, 54 electrons, 78 neutrons; (d) 81 protons, 80 electrons, 120 neutrons; (e) fluorine, technetium, iodine, thallium

17. The following are properties of isotopes of two elements that are essential in our diet. Determine the number of protons, neutrons and electrons in each and name them.
(a) atomic number 26, mass number 58, charge of 2+
(b) atomic number 53, mass number 127, charge of 1–

Solution
(a) Iron, 26 protons, 24 electrons, and 32 neutrons; (b) iodine, 53 protons, 54 electrons, and 74 neutrons

18. Give the number of protons, electrons, and neutrons in neutral atoms of each of the following isotopes:
(a) ${}^{10}_{5}\text{B}$
(b) ${}^{199}_{80}\text{Hg}$
(c) ${}^{63}_{29}\text{Cu}$
(d) ${}^{13}_{6}\text{C}$
(e) ${}^{77}_{34}\text{Se}$

Solution
(a) 5 protons, 5 electrons, 5 neutrons; (b) 80 protons, 80 electrons, 119 neutrons; (c) 29 protons, 29 electrons, 34 neutrons; (d) 6 protons, 6 electrons, 7 neutrons; (e) 34 protons, 34 electrons, 43 neutrons

19. Give the number of protons, electrons, and neutrons in neutral atoms of each of the following isotopes:
(a) ${}^{7}_{3}\text{Li}$
(b) ${}^{125}_{52}\text{Te}$
(c) ${}^{109}_{47}\text{Ag}$
(d) ${}^{15}_{7}\text{N}$
(e) ${}^{31}_{15}\text{P}$

Solution
(a) 3 protons, 3 electrons, 4 neutrons; (b) 52 protons, 52 electrons, 73 neutrons; (c) 47 protons, 47 electrons, 62 neutrons; (d) 7 protons, 7 electrons, 8 neutrons; (e) 15 protons, 15 electrons, 16 neutrons

20. Click on the URL: http://phet.colorado.edu/en/simulation/isotopes-and-atomic-mass and select the "Mix Isotopes" tab, hide the "Percent Composition" and "Average Atomic Mass" boxes, and then select the element boron.
(a) Write the symbols of the isotopes of boron that are shown as naturally occurring in significant amounts.
(b) Predict the relative amounts (percentages) of these boron isotopes found in nature. Explain the reasoning behind your choice.
(c) Add isotopes to the black box to make a mixture that matches your prediction in (b). You may drag isotopes from their bins or click on "More" and then move the sliders to the appropriate amounts.
(d) Reveal the "Percent Composition" and "Average Atomic Mass" boxes. How well does your mixture match with your prediction? If necessary, adjust the isotope amounts to match your prediction.
(e) Select "Nature's" mix of isotopes and compare it to your prediction. How well does your prediction compare with the naturally occurring mixture? Explain. If necessary, adjust your amounts to make them match "Nature's" amounts as closely as possible.

Solution
(a) ^{10}B and ^{11}B; (b) The atomic mass for boron is 10.8. Thus, it makes sense to predict that naturally occurring boron contains about 80% of Boron-11 and about 20% of Boron-10. (c) and (d) After using four atoms of Boron-11 and one atom of Boron-10, the atomic mass is 10.81003 amu, which is not too far from the experimental number of 10.811 amu. (e) The natural composition is 80.1% of Boron-11 and 19.9% of Boron-10, which is close to our prediction.

21. Repeat Exercise 20 using an element that has three naturally occurring isotopes.

Solution
Let us use neon as an example. Since there are three isotopes, there is no way to be sure to accurately predict the abundances to make the total of 20.18 amu average atomic mass. Let us guess that the abundances are 9% Ne-22, 91% Ne-20, and only a trace of Ne-21. The average mass would be 20.18 amu. Checking the nature's mix of isotopes shows that the abundances are 90.48% Ne-20, 9.25% Ne-22, and 0.27% Ne-21, so our guessed amounts have to be slightly adjusted.

22. An element has the following natural abundances and isotopic masses: 90.92% abundance with 19.99 amu, 0.26% abundance with 20.99 amu, and 8.82% abundance with 21.99 amu. Calculate the average atomic mass of this element.

Solution
In problems in which the percentage composition is given, multiply each percentage (expressed as a decimal) by its isotopic mass. Then add to find the sum of all components. The resulting number is the average atomic mass.

$$\begin{aligned}\text{average atomic mass} &= (0.9092 \times 19.99\ \text{amu}) + (0.0026 \times 20.99\ \text{amu}) + (0.0882 \times 21.99\ \text{amu}) \\ &= 18.1749\ \text{amu} + 0.0546\ \text{amu} + 1.9395\ \text{amu} \\ &= 20.169\ \text{amu}\end{aligned}$$

The element is likely Ne.

23. Average atomic masses listed by IUPAC are based on a study of experimental results. Bromine has two isotopes, ^{79}Br and ^{81}Br, whose masses (78.9183 and 80.9163 amu, respectively) and abundances (50.69% and 49.31%, respectively) were determined in earlier experiments. Calculate the average atomic mass of bromine based on these experiments.

Solution

$$\begin{aligned}\text{average atomic mass} &= (0.5069 \times 78.9183 \text{ amu}) + (0.4931 \times 80.9163 \text{ amu}) \\ &= 79.90 \text{ amu}\end{aligned}$$

24. Variations in average atomic mass may be observed for elements obtained from different sources. Lithium provides an example of this. The isotopic composition of lithium from naturally occurring minerals is 7.5% ^{6}Li and 92.5% ^{7}Li, which have masses of 6.01512 amu and 7.01600 amu, respectively. A commercial source of lithium, recycled from a military source, was 3.75% ^{6}Li (and the rest 7Li). Calculate the average atomic mass values for each of these two sources.

Solution
Mineral sources:

$$\begin{aligned}\text{average atomic mass} &= (0.075 \times 6.01512 \text{ amu}) + (0.925 \times 7.01600 \text{ amu}) \\ &= 6.9 \text{ amu}\end{aligned}$$

Recycled military source:

$$\begin{aligned}\text{average atomic mass} &= (0.0375 \times 6.01512 \text{ amu}) + (0.9625 \times 7.01600 \text{ amu}) \\ &= 6.98 \text{ amu}\end{aligned}$$

25. The average atomic masses of some elements may vary, depending upon the sources of their ores. Naturally occurring boron consists of two isotopes with accurately known masses (^{10}B, 10.0129 amu and ^{11}B, 11.00931 amu). The actual atomic mass of boron can vary from 10.807 to 10.819, depending on whether the mineral source is from Turkey or the United States. Calculate the percent abundances leading to the two values of the average atomic masses of boron from these two countries.

Solution
Two items, the percentage of each isotope, are unknown. As both unknowns are related through an equation that says that the sum of the two fractions is equal to 1, we can write:
Turkey source:

$$\begin{aligned}10.807 \text{ amu} &= 10.0129\,(1-x) + 11.00931x \\ 10.807 - 10.0129 &= -10.0129x + 11.00931x \\ x &= 0.735 \text{ (of 11.00931 amu isotope)} \\ 1-x &= 0.203 \text{ (of 10.0129 amu isotope)}\end{aligned}$$

US source:

$$\begin{aligned}10.819 \text{ amu} &= 10.0129\,(1-x) + 11.00931x \\ 10.819 - 10.0129 &= -10.0129x + 11.00931x \\ x &= 0.809 \text{ (of 11.00931 amu isotope)} \\ 1-x &= 0.191 \text{ (of 10.0129 amu isotope)}\end{aligned}$$

26. The ^{18}O:^{16}O abundance ratio in some meteorites is greater than that used to calculate the average atomic mass of oxygen on earth. Is the average mass of an oxygen atom in these meteorites greater than, less than, or equal to that of a terrestrial oxygen atom?

Solution
The greater relative abundance of the heavier oxygen isotope found in meteorites will result in a greater contribution of its larger isotopic mass to the (*weighted*) average atomic mass for oxygen. And so, the average atomic mass computed for oxygen in the meteorite will be greater than that for terrestrial oxygen.

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Chemistry: Atoms First 2e
2: Atoms, Molecules, and Ions
2.4: Chemical Formulas

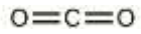
27. Explain why the symbol for an atom of the element oxygen and the formula for a molecule of oxygen differ.

Solution
The symbol for the element oxygen, O, represents both the element and one atom of oxygen. A molecule of oxygen, O_2, contains two oxygen atoms; the subscript 2 in the formula must be used to distinguish the diatomic molecule from two single oxygen atoms.

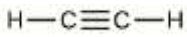
28. Explain why the symbol for the element sulfur and the formula for a molecule of sulfur differ.

Solution
The symbol for the sulfur atom, S, represents the element and one atom of the element. The sulfur molecule (S_8) consists of eight sulfur atoms linked in a ring. Thus, S without a subscript would be an inadequate representation of the molecule.

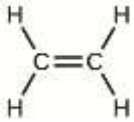
29. Write the molecular and empirical formulas of the following compounds:
(a)



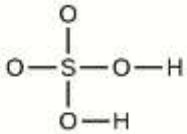
(b)



(c)

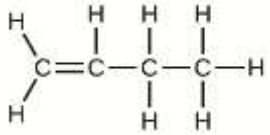


(d)

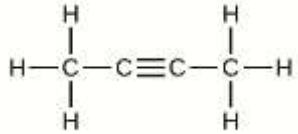


Solution
(a) molecular CO_2, empirical CO_2; (b) molecular C_2H_2, empirical CH; (c) molecular C_2H_4, empirical CH_2; (d) molecular H_2SO_4, empirical H_2SO_4

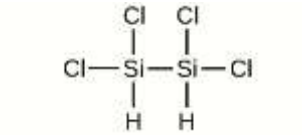
30. Write the molecular and empirical formulas of the following compounds:
(a)



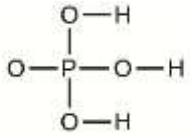
(b)



(c)



(d)



Solution
(a) molecular C_4H_8, empirical CH_2; (b) molecular C_4H_6, empirical C_2H_3; (c) molecular $Si_2H_2Cl_4$, empirical $SiHCl_2$; (d) molecular H_3PO_4, empirical H_3PO_4

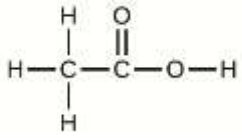
31. Determine the empirical formulas for the following compounds:
(a) caffeine, $C_8H_{10}N_4O_2$
(b) sucrose, $C_{12}H_{22}O_{11}$
(c) hydrogen peroxide, H_2O_2
(d) glucose, $C_6H_{12}O_6$
(e) ascorbic acid (vitamin C), $C_6H_8O_6$

Solution
(a) $C_4H_5N_2O$; (b) $C_{12}H_{22}O_{11}$; (c) HO; (d) CH_2O; (e) $C_3H_4O_3$

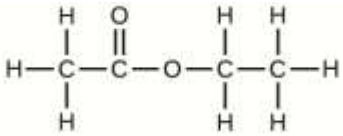
32. Determine the empirical formulas for the following compounds:
(a) acetic acid, $C_2H_4O_2$
(b) citric acid, $C_6H_8O_7$
(c) hydrazine, N_2H_4
(d) nicotine, $C_{10}H_{14}N_2$
(e) butane, C_4H_{10}

Solution
(a) CH_2O; (b) $C_6H_8O_7$; (c) NH_2; (d) C_5H_7N; (e) C_2H_5

33. Write the empirical formulas for the following compounds:
(a)



(b)

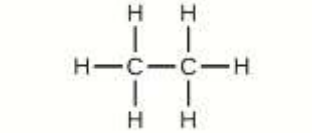


Solution
(a) CH_2O; (b) C_2H_4O

34. Open the URL: http://phet.colorado.edu/en/simulation/build-a-molecule and select the "Larger Molecules" tab. Select an appropriate atom's "Kit" to build a molecule with two carbon and six hydrogen atoms. Drag atoms into the space above the "Kit" to make a molecule. A name will appear when you have made an actual molecule that exists (even if it is not the one you want). You can use the scissors tool to separate atoms if you would like to change the connections. Click on "3D" to see the molecule, and look at both the space-filling and ball-and-stick possibilities.

(a) Draw the structural formula of this molecule and state its name.
(b) Can you arrange these atoms in any way to make a different compound?

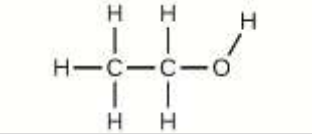
Solution
(a) ethane



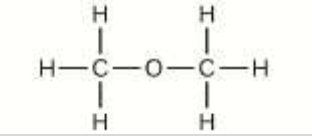
(b) No, unless more than one molecule can be made, such as, $C_2H_4 + H_2$. The carbon atoms have to be connected to each other, and then there is only one way to place the hydrogens.

35. Use the URL: http://phet.colorado.edu/en/simulation/build-a-molecule to repeat Exercise 34, but build a molecule with two carbons, six hydrogens, and one oxygen.
(a) Draw the structural formula of this molecule and state its name.
(b) Can you arrange these atoms to make a different molecule? If so, draw its structural formula and state its name.
(c) How are the molecules drawn in (a) and (b) the same? How do they differ? What are they called (the type of relationship between these molecules, not their names)?

Solution
(a) ethanol



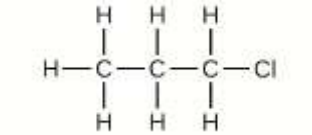
(b) methoxymethane, more commonly known as dimethyl ether



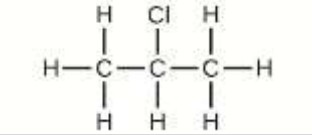
(c) These molecules have the same chemical composition (types and number of atoms) but different chemical structures. They are structural isomers.

36. Use the URL http://phet.colorado.edu/en/simulation/build-a-molecule to repeat Exercise 34, but build a molecule with three carbons, seven hydrogens, and one chlorine.
(a) Draw the structural formula of this molecule and state its name.
(b) Can you arrange these atoms to make a different molecule? If so, draw its structural formula and state its name.
(c) How are the molecules drawn in (a) and (b) the same? How do they differ? What are they called (the type of relationship between these molecules, not their names)?

Solution
(a) 1-chloropropane



(b) 2-chloropropane



(c) These molecules have the same chemical composition (types and number of atoms) but different chemical structures. They are structural isomers.

37. Write a sentence that describes how to determine the number of moles of a compound in a known mass of the compound if we know its molecular formula.

Solution

Use the molecular formula to find the molar mass; to obtain the number of moles, divide the mass of compound by the molar mass of the compound expressed in grams.

38. Compare 1 mole of H_2, 1 mole of O_2, and 1 mole of F_2.

(a) Which has the largest number of molecules? Explain why.

(b) Which has the greatest mass? Explain why.

Solution

(a) All three have the same number of molecules, since a mole is defined as a specific number of particles. (b) F_2 has the largest molar mass, so it has the greatest mass of the three.

39. Which contains the greatest mass of oxygen: 0.75 mol of ethanol (C_2H_5OH), 0.60 mol of formic acid (HCO_2H), or 1.0 mol of water (H_2O)? Explain why.

Solution

Formic acid. Its formula has twice as many oxygen atoms as the other two compounds (one each). Therefore, 0.60 mol of formic acid would be equivalent to 1.20 mol of a compound containing a single oxygen atom.

40. Which contains the greatest number of moles of oxygen atoms: 1 mol of ethanol (C_2H_5OH), 1 mol of formic acid (HCO_2H), or 1 mol of water (H_2O)? Explain why.

Solution

One mole of formic acid. Formic acid has two moles of oxygen atoms per formula unit, whereas the other two compounds have only one mole of oxygen atoms per mole.

41. How are the molecular mass and the molar mass of a compound similar and how are they different?

Solution

The two masses have the same numerical value, but the units are different: The molecular mass is the mass of 1 molecule while the molar mass is the mass of 6.022×10^{23} molecules.

42. Calculate the molar mass of each of the following compounds:

(a) hydrogen fluoride, HF

(b) ammonia, NH_3

(c) nitric acid, HNO_3

(d) silver sulfate, Ag_2SO_4

(e) boric acid, $B(OH)_3$

Solution

(a) HF:

$$1H = 1 \times 1.00794 = 1.00794$$

$$1F = 1 \times 18.9984 = \underline{18.9984} \quad ;$$

$$= 20.0063 \text{ g}$$

(b) NH_3:

1N = 1 × 14.0067 = 14.0067
3H = 3 × 1.00794 = 3.02382 ;
= 17.0305 g

(c) HNO_3:
1N = 1 × 14.0067 = 14.0067
1H = 1 × 1.00794 = 1.00794
3O = 3 × 15.9994 = 47.9982 ;
= 63.0128 g

(d) Ag_2SO_4
2Ag = 2 × 107.8682 = 215.736
1S = 1 × 32.066 = 32.066
4O = 4 × 15.994 = 63.976 ;
311.800 g

(e) $B(OH)_3$:
1B = 1 × 10.81 = 10.81
3O = 3 × 15.9994 = 47.9982
3H = 3 × 1.00794 = 3.02382
= 61.83 g

43. Calculate the molar mass of each of the following:
(a) S_8
(b) C_5H_{12}
(c) $Sc_2(SO_4)_3$
(d) CH_3COCH_3 (acetone)
(e) $C_6H_{12}O_6$ (glucose)

Solution
(a) S_8
8S = 8 × 32.06 = 256.48 g/mol;
(b) C_5H_{12}
5C = 5 × 12.011 = 60.055 g mol^{-1}
12H = 12 × 1.00794 = 12.09528 g mol^{-1} ;
= 72.150 g mol^{-1}

(c) $Sc_2(SO_4)_3$
2Sc = 2 × 44.9559109 = 89.9118218 g mol^{-1}
3S = 3 × 32.066 = 96.198 g mol^{-1}
12O = 12 × 15.99943 = 191.99316 g mol^{-1} ;
= 378.103 g mol^{-1}

(d) CH_3COCH_3

$3C = 3 \times 12.011 = 36.033\ g\ mol^{-1}$
$1O = 1 \times 15.9994 = 15.9994\ g\ mol^{-1}$
$6H = 6 \times 1.00794 = 6.04764\ g\ mol^{-1}$;
$= 58.080\ g\ mol^{-1}$

(e) $C_6H_{12}O_6$
$6C = 6 \times 12.011 = 72.066\ g\ mol^{-1}$
$12H = 12 \times 1.00794 = 12.09528\ g\ mol^{-1}$
$6O = 6 \times 15.9994 = 95.9964\ g\ mol^{-1}$
$= 180.158\ g\ mol^{-1}$

44. Calculate the empirical or molecular formula mass and the molar mass of each of the following minerals:
(a) limestone, $CaCO_3$
(b) halite, NaCl
(c) beryl, $Be_3Al_2Si_6O_{18}$
(d) malachite, $Cu_2(OH)_2CO_3$
(e) turquoise, $CuAl_6(PO_4)_4(OH)_8(H_2O)_4$

Solution
(a) $CaCO_3$
$1Ca = 1 \times 40.078 = 40.078\ g\ mol^{-1}$
$1C = 1 \times 12.011 = 12.011\ g\ mol^{-1}$
$3O = 3 \times 15.9994 = 47.9982\ g\ mol^{-1}$;
$= 100.087\ g\ mol^{-1}$

(b) NaCl
$1Na = 1 \times 22.989768 = 22.989768\ g\ mol^{-1}$
$1Cl = 1 \times 35.4527 = 35.4527\ g\ mol^{-1}$;
$= 58.4425\ g\ mol^{-1}$

(c) $Be_3Al_2Si_6O_{18}$
$3Be = 3 \times 9.01218 = 27.03654\ g\ mol^{-1}$
$2Al = 2 \times 26.98154 = 53.96308\ g\ mol^{-1}$
$6Si = 6 \times 28.0855 = 168.513\ g\ mol^{-1}$;
$18O = 18 \times 15.9994 = 287.9892\ g\ mol^{-1}$
$= 537.502\ g\ mol^{-1}$

(d) $Cu_2(OH)_2CO_3$

$2C = 2 \times 63.546 = 127.092\ g\ mol^{-1}$

$5O = 5 \times 15.9994 = 79.997\ g\ mol^{-1}$

$2H = 2 \times 1.00794 = 2.01588\ g\ mol^{-1}$;

$1H = 1 \times 12.011 = 12.011\ g\ mol^{-1}$

$= 221.116\ g\ mol^{-1}$

(e) $CuAl_6(PO_4)_4(OH)_8(H_2O)_4$

$1Cu = 1 \times 63.546 = 63.546\ g\ mol^{-1}$

$6Al = 6 \times 26.98154 = 161.88924\ g\ mol^{-1}$

$4P = 4 \times 30.9737624 = 123.89505\ g\ mol^{-1}$

$28O = 28 \times 15.9994 = 447.9832\ g\ mol^{-1}$

$16H = 16 \times 1.00794 = 16.12704\ g\ mol^{-1}$

$= 813.441\ g\ mol^{-1}$

45. Calculate the molar mass of each of the following:
(a) the anesthetic halothane, $C_2HBrClF_3$
(b) the herbicide paraquat, $C_{12}H_{14}N_2Cl_2$
(c) caffeine, $C_8H_{10}N_4O_2$
(d) urea, $CO(NH_2)_2$
(e) a typical soap, $C_{17}H_{35}CO_2Na$

Solution
(a) $C_2HBrClF_3$

$2C = 2 \times 12.011 = 24.022\ g\ mol^{-1}$

$1H = 1 \times 1.00794 = 1.00794\ g\ mol^{-1}$

$1Br = 1 \times 79.904 = 79.904\ g\ mol^{-1}$

$1Cl = 1 \times 35.453 = 35.453\ g\ mol^{-1}$;

$3F = 3 \times 18.998403 = 56.995209\ g\ mol^{-1}$

$= 197.382\ g\ mol^{-1}$

(b) $C_{12}H_{14}N_2Cl_2$

$12C = 12 \times 12.011 = 144.132\ g\ mol^{-1}$

$14H = 14 \times 1.00794 = 14.111\ g\ mol^{-1}$

$2N = 2 \times 14.0067 = 28.0134\ g\ mol^{-1}$;

$2Cl = 2 \times 35.453 = 70.906\ g\ mol^{-1}$

$= 257.163\ g\ mol^{-1}$

(c) $C_8H_{10}N_4O_2$

$8C = 8 \times 12.011 = 96.088\ g\ mol^{-1}$

$10H = 10 \times 1.007 = 10.079\ g\ mol^{-1}$

$4N = 4 \times 14.0067 = 56.027\ g\ mol^{-1}$;

$2O = 2 \times 15.9994 = 31.999\ g\ mol^{-1}$

$= 194.193\ g\ mol^{-1}$

(d) $CO(NH_2)_2$

$1C = 1 \times 12.011 = 12.011\ g\ mol^{-1}$

$1O = 1 \times 15.9994 = 15.9994\ g\ mol^{-1}$

$2N = 2 \times 14.0067 = 28.0134\ g\ mol^{-1}$;

$4H = 4 \times 1.00794 = \underline{4.03176\ g\ mol^{-1}}$

$= 60.056\ g\ mol^{-1}$

(e) $C_{17}H_{35}CO_2Na$

$18C = 18 \times 12.011 = 216.198\ g\ mol^{-1}$

$35H = 35 \times 1.00794 = 35.2779\ g\ mol^{-1}$

$2O = 2 \times 15.9994 = 31.9988\ g\ mol^{-1}$

$1Na = 1 \times 22.98977 = \underline{22.98977\ g\ mol^{-1}}$

$= 306.464\ g\ mol^{-1}$

46. Determine the number of moles of compound and the number of moles of each type of atom in each of the following:

(a) 25.0 g of propylene, C_3H_6

(b) 3.06×10^{-3} g of the amino acid glycine, $C_2H_5NO_2$

(c) 25 lb of the herbicide Treflan, $C_{13}H_{16}N_2O_4F$ (1 lb = 454 g)

(d) 0.125 kg of the insecticide Paris Green, $Cu_4(AsO_3)_2(CH_3CO_2)_2$

(e) 325 mg of aspirin, $C_6H_4(CO_2H)(CO_2CH_3)$

Solution

(a) C_3H_6

$3C = 3 \times 12.011 = 36.033$

$6H = 6 \times 1.00794 = \underline{6.04764}$

molar mass = $42.081\ g\ mol^{-1}$

$$\text{mol propylene} = \frac{25.0\ \cancel{g}}{42.081\ \cancel{g}\ mol^{-1}} = 0.594\ mol$$

$3C = 3 \times 12.011 = 36.033$

$6H = 6 \times 1.00794 = \underline{6.04764}$

molar mass = $42.081\ g\ mol^{-1}$

$$\text{mol propylene} = \frac{25.0\ \cancel{g}}{42.081\ \cancel{g}\ mol^{-1}} = 0.594\ mol$$

1.78 mol C, 3.56 mol H;

(b) $C_2H_5NO_2$

$2C = 2 \times 12.011 = 24.022$

$5H = 5 \times 1.00794 = 5.0397$

$1N = 1 \times 14.0067 = 14.0067$

$2O = 2 \times 15.9994 = \underline{31.9988}$

molar mass = 75.067 g mol^{-1}

$$\text{mol glycine} = \frac{3.06 \times 10^{-3}\ \cancel{\text{g}}}{75.067\ \cancel{\text{g}}\ \text{mol}^{-1}} = 4.08 \times 10^{-5}\ \text{mol}$$

8.16×10^{-5} mol C and mol O, 2.04×10^{-4} mol H, 4.08×10^{-5} mol N;
(c) $C_{13}H_{16}N_2O_4F$

$13C = 13 \times 12.011 = 156.143$

$16H = 16 \times 1.00794 = 16.12704$

$2N = 2 \times 14.0067 = 28.0134$

$4O = 4 \times 15.9994 = 63.9976$

$1F = 1 \times 18.9984032 = \underline{18.9984032}$

molar mass = 283.270 g mol^{-1}

Convert lb to g: 25 lb × 454 lb^{-1} = 11,350 g

$$\text{mol Treflan} = \frac{11{,}380\ \cancel{\text{g}}}{283.270\ \cancel{\text{g}}\ \text{mol}^{-1}} = 40.20\ \text{mol}$$

5.2×10^2 mol C, 6.4×10^2 mol H, 80.2 mol N, 1.6×10^2 mol O, 40 mol F;
(d) $Cu_4(AsO_3)_2(CH_3CO_2)_2$

$4Cu = 4 \times 63.546 = 254.184$

$2As = 2 \times 74.92159 = 149.84318$

$10O = 10 \times 15.9994 = 159.9940$

$4C = 4 \times 12.011 = 48.044$

$6H = 6 \times 1.00794 = \underline{6.04764}$

molar mass = 618.113 g mol^{-1}

$$\text{mol Paris Green} = \frac{125\ \cancel{\text{g}}}{618.113\ \cancel{\text{g}}\ \text{mol}^{-1}} = 0.202\ \text{mol}$$

0.808 mol Cu and mol C, 0.404 mol As, 1.21 mol H, 2.02 mol O;
(e) $C_6H_4(CO_2H)(COCH_3)$

$9C = 9 \times 12.011 = 108.099$

$8H = 8 \times 1.00794 = 8.06352$

$4O = 4 \times 15.9994 = \underline{63.9976}$

molar mass = 180.160 g mol^{-1}

$$\text{mol aspirin} = \frac{0.325\ \cancel{\text{g}}}{180.160\ \cancel{\text{g}}\ \text{mol}^{-1}} = 1.80 \times 10^{-3}\ \text{mol}$$

1.62×10^{-2} mol C, 1.44×10^{-2} mol H, 7.20×10^{-3} mol O

47. Determine the mass of each of the following:
(a) 0.0146 mol KOH
(b) 10.2 mol ethane, C_2H_6
(c) 1.6×10^{-3} mol Na_2SO_4
(d) 6.854×10^3 mol glucose, $C_6H_{12}O_6$
(e) 2.86 mol $Co(NH_3)_6Cl_3$

Solution
(a) KOH:
$1K = 1 \times 39.0983 = 39.0983$
$1O = 1 \times 15.9994 = 15.9994$
$1H = 1 \times 1.00794 = \underline{1.00794}$
molar mass = 56.1056 g mol^{-1}
Mass = 0.0146 mol × 56.1056 g/mol = 0.819 g;
(b) C_2H_6
$2C = 2 \times 12.011 = 24.022$
$6H = 6 \times 1.00794 = \underline{6.04764}$
molar mass = 30.070 g mol^{-1}
Mass = 10.2 mol × 30.070 g/mol = 307 g;
(c) Na_2SO_4:
$2Na = 2 \times 22.990 = 45.98$
$1S = 1 \times 32.066 = 32.066$
$4O = 4 \times 15.9994 = \underline{63.9976}$
molar mass = 142.044 g mol^{-1}
Mass = 1.6×10^{-3} mol × 142.044 g/mol = 0.23 g;
(d) $C_6H_{12}O_6$
$6C = 6 \times 12.011 = 72.066$
$12H = 12 \times 1.00794 = 12.0953$
$6O = 6 \times 15.9994 = \underline{95.9964}$
molar mass = 180.158 g mol^{-1}
Mass = 6.854×10^3 mol × 180.158 g/mol = 1.235×10^6 g (1235 kg);
(e) $Co(NH_3)_6Cl_3$
$Co = 1 \times 58.99320 = 58.99320$
$6N = 6 \times 14.0067 = 84.0402$
$18H = 18 \times 1.00794 = 18.1429$
$3Cl = 3 \times 35.4527 = \underline{106.358}$
molar mass = 267.5344 g mol^{-1}
Mass = 2.86 mol × 267.5344 g/mol = 765 g

48. Determine the number of moles of the compound and determine the number of moles of each type of atom in each of the following:
(a) 2.12 g of potassium bromide, KBr

(b) 0.1488 g of phosphoric acid, H_3PO_4
(c) 23 kg of calcium carbonate, $CaCO_3$
(d) 78.452 g of aluminum sulfate, $Al_2(SO_4)_3$
(e) 0.1250 mg of caffeine, $C_8H_{10}N_4O_2$

Solution
(a) Molar mass of KBr:

$1K = 1 \times 39.0893 = 39.0893$
$1Br = 1 \times 79.904 = \underline{79.904}$
$= 118.9933\ g\ mol^{-1}$

$$\frac{2.12\ \cancel{g}}{118.9933\ \cancel{g}\ mol^{-1}} = 1.78 \times 10^{-2}\ mol\ KBr$$

$1 \times 1.78 \times 10^{-2} = 1.78 \times 10^{-2}\ mol\ K$;
$1 \times 1.78 \times 10^{-2} = 1.78 \times 10^{-2}\ mol\ Br$

(b) Molar mass of H_3PO_4

$1P = 1 \times 30.973762 = 30.973762$
$4O = 4 \times 15.9994 = 63.9976$
$3H = 3 \times 1.0079 = \underline{3.0237}$
$= 97.9951\ g\ mol^{-1}$

$$\frac{0.1488\ \cancel{g}}{97.9951\ \cancel{g}\ mol^{-1}} = 1.518 \times 10^{-3}\ mol\ H_3PO_4$$

$3 \times 1.518 \times 10^{-3} = 4.555 \times 10^{-3}\ mol\ H$
$1 \times 1.518 \times 10^{-3} = 1.518 \times 10^{-3}\ mol\ P$;
$4 \times 1.518 \times 10^{-3} = 6.073 \times 10^{-3}\ mol\ O$

(c) Molar mass of $CaCO_3$

$1Ca = 1 \times 40.078 = 40.078$
$1C = 1 \times 12.011 = 12.011$
$3O = 3 \times 15.9994 = \underline{47.9982}$
$= 100.087\ g\ mol^{-1}$

$$\frac{2.3 \times 10^{4}\ \cancel{g}}{100.087\ \cancel{g}\ mol^{-1}} = 2.3 \times 10^{2}\ mol\ CaCO_3$$

$1 \times 2.3 \times 10^{2}\ mol = 2.3 \times 10^{2}\ mol\ Ca$
$1 \times 2.3 \times 10^{2}\ mol = 2.3 \times 10^{2}\ mol\ C$;
$3 \times 2.3 \times 10^{2}\ mol = 6.9 \times 10^{2}\ mol\ O$

(d) Molar mass of $Al_2(SO_4)_3$

$2Al = 2 \times 26.981539 = 53.963078$
$3S = 3 \times 32.066 = 96.198$
$12O = 12 \times 15.9994 = \underline{191.9928}$;
$= 342.154\ g\ mol^{-1}$

$$\frac{78.452\ \cancel{g}}{315.172\ \cancel{g}\ mol^{-1}} = 0.22929\ mol\ Al_2(SO4)_3$$

$2 \times 0.22929 = 0.45858$ mol Al
$3 \times 0.22929 = 0.68787$ mol S
$12 \times 0.22929 = 2.75148$ mol O
(e) Molar mass of $C_8H_{10}N_4O_2$:
$8C = 8 \times 12.011 = 96.088$
$10H = 10 \times 1.00794 = 10.0794$
$4N = 4 \times 14.0067 = 56.0268$
$2O = 2 \times 15.9994 = \underline{31.9988}$
$= 194.193$ g mol^{-1}

$$\frac{0.1250\ \cancel{\text{mg}}}{(194.193\ \cancel{\text{g}}\ \text{mol}^{-1} \times 1000\ \cancel{\text{mg}}\ \cancel{\text{g}}^{-1})} = 6 \times 10^{-7}\ \text{mol}\ C_8H_{10}N_4O_2$$

$8 \times 6.437 \times 10^{-7}$ mol $C_8H_{10}N_4O_2 = 5.150 \times 10^{-6}$ mol C
$10 \times 6.437 \times 10^{-7}$ mol $C_8H_{10}N_4O_2 = 6.437 \times 10^{-6}$ mol H
$4 \times 6.437 \times 10^{-7}$ mol $C_8H_{10}N_4O_2 = 2.575 \times 10^{-6}$ mol N
$2 \times 6.437 \times 10^{-7}$ mol $C_8H_{10}N_4O_2 = 1.287 \times 10^{-6}$ mol O

49. Determine the mass of each of the following:
(a) 2.345 mol LiCl
(b) 0.0872 mol acetylene, C_2H_2
(c) 3.3×10^{-2} mol Na_2CO_3
(d) 1.23×10^3 mol fructose, $C_6H_{12}O_6$
(e) 0.5758 mol $FeSO_4(H_2O)_7$

Solution
(a) molar mass $(LiCl) = 1 \times 6.941 + 1 \times 35.4527 = 42.394$ g mol^{-1};
mass $= 2.345\ \cancel{\text{mol}} \times 42.394\ \text{g}\ \cancel{\text{mol}^{-1}} = 99.41$ g

(b) molar mass $(C_2H_2) = 2 \times 12.011 + 2 \times 1.00794 = 26.038$ g mol^{-1};
mass $= 0.0872\ \cancel{\text{mol}} \times 26.038\ \text{g}\ \cancel{\text{mol}^{-1}} = 2.27$ g

(c) molar mass $(Na_2CO_3) = 2 \times 22.989768 + 1 \times 12.011 + 3 \times 15.9994 = 105.989$ g mol^{-1};
mass $= 3.3 \times 10^{-2}\ \cancel{\text{mol}} \times 105.989\ \text{g}\ \cancel{\text{mol}^{-1}} = 3.5$ g

(d) molar mass $(C_6H_{12}O_6) = 6 \times 12.011 + 12 \times 1.00794 + 6 \times 15.9994 = 180.158$ g mol^{-1};
mass $= 1.23 \times 10^3\ \cancel{\text{mol}} \times 180.158\ \text{g}\ \cancel{\text{mol}^{-1}} = 2.22 \times 10^5$ g $= 222$ kg

(e) molar mass $[FeSO_4(H_2O)_7] = 1 \times 55.847 + 1 \times 32.066 + 4 \times 15.999 + 7(2 \times 1.00794 + 15.9994) = 278.018$ g mol^{-1}
mass $= 0.5758\ \cancel{\text{mol}} \times 278.018\ \text{g}\ \cancel{\text{mol}^{-1}} = 160.1$ g

50. The approximate minimum daily dietary requirement of the amino acid leucine, $C_6H_{13}NO_2$, is 1.1 g. What is this requirement in moles?

Solution
Molar mass $= 6 \times 12.011 + 13 \times 1.00794 + 1 \times 14.0067 + 2 \times 15.9994 = 131.175$ g/mol;

$$\text{mass} = \frac{1.1\ \text{g}}{131.175\ \text{g mol}^{-1}} = 8.4 \times 10^{-3}\ \text{mol}$$

51. Determine the mass in grams of each of the following:
(a) 0.600 mol of oxygen atoms
(b) 0.600 mol of oxygen molecules, O_2

(c) 0.600 mol of ozone molecules, O_3

Solution

(a) 0.600 ~~mol~~ × 15.9994 g/~~mol~~ = 9.60 g; (b) 0.600 ~~mol~~ × 2 × 15.994 g/~~mol~~ = 19.2 g; (c) 0.600 ~~mol~~ × 3 × 15.994 g/~~mol~~ = 28.8 g

52. A 55-kg woman has 7.5×10^{-3} mol of hemoglobin (molar mass = 64,456 g/mol) in her blood. How many hemoglobin molecules is this? What is this quantity in grams?

Solution

7.5×10^{-3} mol × 6.022×10^{23} mol^{-1} = 4.5×10^{21} molecules; 7.5×10^{-3} mol × 64,456 g/mol = 4.8×10^{2} g

53. Determine the number of atoms and the mass of zirconium, silicon, and oxygen found in 0.3384 mol of zircon, $ZrSiO_4$, a semiprecious stone.

Solution

Determine the number of moles of each component. From the moles, calculate the number of atoms and the mass of the elements involved. Zirconium: 0.3384 ~~mol~~ × 6.022×10^{23} ~~mol^{-1}~~ = 2.038×10^{23} atoms; 0.3384 ~~mol~~ × 91.224 g/~~mol~~ = 30.87 g; Silicon: 0.3384 ~~mol~~ × 6.022×10^{23} ~~mol^{-1}~~ = 2.038×10^{23} atoms; 0.3384 ~~mol~~ × 28.0855 g/~~mol~~ = 9.504 g; Oxygen: 4 × 0.3384 ~~mol~~ × 6.022×10^{23} ~~mol^{-1}~~ = 8.151×10^{23} atoms; 4 × 0.3384 ~~mol~~ × 15.9994 g/~~mol~~ = 21.66 g

54. Determine which of the following contains the greatest mass of hydrogen: 1 mol of CH_4, 0.6 mol of C_6H_6, or 0.4 mol of C_3H_8.

Solution

Multiply each amount of substance (mol) by the number of moles of hydrogen per mole of compound as shown in the compound formula. The result is the molar amount of H in the compound: the greater this molar amount, the greater the mass of H in the compound. CH_4: 1 × 4 = 4; C_6H_6: 0.6 × 6 = 2.4; C_3H_8: 0.4 × 8 = 3.2; 1 mol of CH_4 has the most mass of hydrogen.

55. Determine which of the following contains the greatest mass of aluminum: 122 g of $AlPO_4$, 266 g of $A1_2C1_6$, or 225 g of $A1_2S_3$.

Solution

Determine the molar mass and, from the grams present, the moles of each substance. The compound with the greatest number of moles of Al has the greatest mass of Al.

Molar mass $AlPO_4$: 26.981539 + 30.973762 + 4(15.9994) = 121.9529 g/mol

Molar mass Al_2Cl_6: 2(26.981539) + 6(35.4527) = 266.6793 g/mol

Molar mass Al_2S_3: 2(26.981539) + 3(32.066) = 150.161 g/mol

$AlPO_4$: $\frac{122\ \cancel{g}}{121.9529\ \cancel{g}\ mol^{-1}} = 1.000$ mol

mol Al = 1 × 1.000 mol = 1.000 mol, or 26.98 g Al

Al_2Cl_6: $\frac{266\ g}{266.6793\ g\ mol^{-1}} = 0.997$ mol

mol Al = 2 × 0.997 mol = 1.994 mol, or 53.74 g Al

Al_2S_3: $\frac{225\ \cancel{g}}{150.161\ \cancel{g}\ mol^{-1}} = 1.50$ mol

mol Al = 2 × 1.50 mol = 3.00 mol, or 80.94 g Al

The Al_2S_3 sample thus contains the greatest mass of Al.

56. Diamond is one form of elemental carbon. An engagement ring contains a diamond weighing 1.25 carats (1 carat = 200 mg). How many atoms are present in the diamond?

Solution

Determine the number of grams present in the diamond and from that the number of moles. From the number of moles, find the number of carbon atoms by multiplying by Avogadro's number:

$$1.25 \cancel{\text{ carats}} \times 200 \cancel{\text{ mg}} \cancel{\text{ carat}^{-1}} \times \frac{1 \text{ g}}{1000 \cancel{\text{ mg}}} = 0.250 \text{ g}$$

$$\frac{0.250 \cancel{\text{ g}}}{12.011 \cancel{\text{ g mol}^{-1}}} \times 6.022 \times 10^{23} \cancel{\text{ mol}^{-1}} = 1.25 \times 10^{22} \text{ atoms}$$

57. The Cullinan diamond was the largest natural diamond ever found (January 25, 1905). It weighed 3104 carats (1 carat = 200 mg). How many carbon atoms were present in the stone?

Solution

Determine the number of grams present in the diamond and from that the number of moles. Find the number of carbon atoms by multiplying Avogadro's number by the number of moles:

$$\frac{3104 \cancel{\text{ carats}} \times \frac{200 \cancel{\text{ mg}}}{1 \cancel{\text{ carat}}} \times \frac{1 \cancel{\text{ g}}}{1000 \cancel{\text{ mg}}}}{12.011 \cancel{\text{ g}} \cancel{\text{ mol}^{-1}} (6.022 \times 10^{23} \cancel{\text{ mol}^{-1}})} = 3.113 \times 10^{25} \text{C atoms}$$

58. One 55-gram serving of a particular cereal supplies 270 mg of sodium, 11% of the recommended daily allowance. How many moles and atoms of sodium are in the recommended daily allowance?

Solution

Assume that the sodium mass of 270 mg is in an ionic form:

$$\frac{270 \text{ mg} \times 1 \text{ g}}{1000 \text{ mg}} = 0.270 \text{ g of Na}$$

$$\text{Total sodium required} = \frac{0.270 \text{ g}}{0.11} = 2.4545 \text{ g of ionic sodium. This amount is}$$

$$\frac{2.4545 \cancel{\text{ g}}}{22.989768 \cancel{\text{ g}} \text{ mol}^{-1}} = 0.1068 \text{ mol Na}$$

$$0.1068 \text{ mol} \times 6.022 \times 10^{23} \text{ mol}^{-1} = 6.4 \times 10^{22} \text{ atoms}$$

59. A certain nut crunch cereal contains 11.0 grams of sugar (sucrose, $C_{12}H_{22}O_{11}$) per serving size of 60.0 grams. How many servings of this cereal must be eaten to consume 0.0278 moles of sugar?

Solution

Determine the molar mass of sugar. 12(12.011) + 22(1.00794) + 11(15.9994) = 342.300 g/mol;

Then 0.0278 mol × 342.300 g/mol = 9.52 g sugar. This 9.52 g of sugar represents $\frac{11.0}{60.0}$ of one serving or $\frac{60.0 \text{ g serving}}{11.0 \cancel{\text{ g sugar}}} \times 9.52 \cancel{\text{ g sugar}} = 51.9$ g cereal.

This amount is $\frac{51.9 \text{ g cereal}}{60.0 \text{ g serving}} = 0.865$ servings, or about 1 serving.

60. A tube of toothpaste contains 0.76 g of sodium monofluorophosphate (Na_2PO_3F) in 100 mL.
(a) What mass of fluorine atoms in mg was present?
(b) How many fluorine atoms were present?

Solution

Molar mass of Na_2PO_3F = 2(22.9898) + 1(18.9984) + 1(30.9738) + 3(15.9994) = 143.95 g/mol;

(a) mol $Na_2PO_3F = \frac{0.76\ g}{143.95\ g\ mol^{-1}} = 0.00528$ mol . Since there is only one F atom in the formula, the number of moles of fluorine is also 5.28×10^{-3} mol.

Mass F = 5.28×10^{-3} mol × 18.9984 g/mol × 1000 mg/g = 1.0×10^2 mg;

(b) $\text{atoms of F} = 100\ \cancel{\text{mg}}\ \text{F} \times \frac{1\ \cancel{\text{g}}}{1000\ \cancel{\text{mg}}} \times \frac{1\ \text{mol F}}{18.9984\ \cancel{\text{g}}\ \text{F}} \times 6.022 \times 10^{23}\ \text{atoms mol}^{-1}$

$= 3.2 \times 10^{21}$ atoms F

61. Which of the following represents the least number of molecules?
(a) 20.0 g of H_2O (18.02 g/mol)
(b) 77.0 g of CH_4 (16.06 g/mol)
(c) 68.0 g of C_3H_6 (42.08 g/mol)
(d) 100.0 g of N_2O (44.02 g/mol)
(e) 84.0 g of HF (20.01 g/mol)

Solution
Calculate the number of moles of each species, then remember that 1 mole of anything = 6.022×10^{23} species. (a) 20.0 g = 1.11 mol H_2O; (b) 77.0 g CH_4 = 4.79 mol CH_4; (c) 68.0 g C_3H_6= 1.62 mol C_3H_6; (d) 100.0 g N_2O = 2.27 mol N_2O; (e) 84.0 g HF = 4.20 mol HF. Therefore, 20.0 g H_2O represents the least number of molecules since it has the least number of moles.

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Chemistry: Atoms First 2e
3: Electronic Structure and Periodic Properties of Elements
3.1: Electromagnetic Energy

1. The light produced by a red neon sign is due to the emission of light by excited neon atoms. Qualitatively describe the spectrum produced by passing light from a neon lamp through a prism.

Solution
The spectrum consists of colored lines, at least one of which (probably the brightest) is red.

2. An FM radio station found at 103.1 on the FM dial broadcasts at a frequency of $1.031 \times 10^8\ s^{-1}$ (103.1 MHz). What is the wavelength of these radio waves in meters?

Solution

$$c = \lambda\nu$$

$$= \lambda \times 1.031 \times 10^8\ s^{-1}$$

$$\lambda = \frac{2.998 \times 10^8\ m\ s^{-1}}{1.031 \times 10^8\ s^{-1}} = 2.908\ m$$

3. FM–95, an FM radio station, broadcasts at a frequency of $9.51 \times 10^7\ s^{-1}$ (95.1 MHz). What is the wavelength of these radio waves in meters?

Solution

$$\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^8\ m\ s^{-1}}{9.51 \times 10^7\ s^{-1}} = 3.15\ m$$

4. A bright violet line occurs at 435.8 nm in the emission spectrum of mercury vapor. What amount of energy, in joules, must be released by an electron in a mercury atom to produce a photon of this light?

Solution

$$c = \lambda\nu$$

$$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^8\ \cancel{m}\ s^{-1}}{435.8 \times 10^{-9}\ \cancel{m}} = 6.879 \times 10^{14}\ s^{-1}$$

$$E = h\nu = 6.626 \times 10^{-34}\ J\ \cancel{s} \times 6.879 \times 10^{14}\ \cancel{s^{-1}}$$

$$= 4.558 \times 10^{-19}\ J$$

5. Light with a wavelength of 614.5 nm looks orange. What is the energy, in joules, per photon of this orange light? What is the energy in eV ($1\ eV = 1.602 \times 10^{-19}\ J$)?

Solution

$$c = \lambda\nu$$

$$\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^8\ \cancel{m}\ s^{-1}}{614.5 \times 10^{-9}\ \cancel{m}} = 4.879 \times 10^{14}\ s^{-1}$$

$$E = h\nu = 6.626 \times 10^{-34}\ J\ \cancel{s} \times 4.879 \times 10^{14}\ \cancel{s^{-1}} = 3.233 \times 10^{-19}\ J$$

$$E = \frac{3.233 \times 10^{-19}\ \cancel{J}}{1.602 \times 10^{-19}\ \cancel{J}\ eV^{-1}} = 2.018\ eV$$

6. Heated lithium atoms emit photons of light with an energy of 2.961×10^{-19} J. Calculate the frequency and wavelength of one of these photons. What is the total energy in 1 mole of these photons? What is the color of the emitted light?

Solution

$E = 2.961 \times 10^{-19}\ \text{J} = h\nu = 6.626 \times 10^{-34}\ \text{J s} \times \nu$

$$\nu = 2.961 \times 10^{-19} \frac{\cancel{\text{J}}}{6.626 \times 10^{-34}\ \cancel{\text{J}}} = 4.4688 \times 10^{14}\ \text{s}^{-1}$$

$$c = \lambda\nu;\ \lambda = \frac{c}{\nu} = 2.998 \times 10^{8} \frac{\cancel{\text{s}^{-1}}}{4.4699 \times 10^{14}\ \cancel{\text{s}^{-1}}} = 6.709 \times 10^{-7}\ \text{m}$$

This is a red light wavelength.

$E = 2.961 \times 10^{-19}\ \text{J} \times 6.022 \times 10^{23}\ \text{mol}^{-1} = 178.3\ \text{kJ mol}^{-1}$

7. A photon of light produced by a surgical laser has an energy of 3.027×10^{-19} J. Calculate the frequency and wavelength of the photon. What is the total energy in 1 mole of photons? What is the color of the emitted light?

Solution

$E = h\nu$

$$\nu = \frac{3.027 \times 10^{-19}\ \cancel{\text{J}}}{6.626 \times 10^{-34}\ \cancel{\text{J}}\ \text{s}^{-1}} = 4.568 \times 10^{14}\ \text{s}^{-1}$$

$$\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^{8}\ \text{m}\ \cancel{\text{s}^{-1}}}{4.568 \times 10^{14}\ \cancel{\text{s}^{-1}}} = 6.563 \times 10^{-7}\ \text{m} = 6563\ \text{Å} = 656.3\ \text{nm}$$

Energy $\text{mol}^{-1} = 3.027 \times 10^{-19}\ \text{J} \times 6.022 \times 10^{23}\ \text{mol}^{-1} = 1.823 \times 10^{5}\ \text{J mol}^{-1}$; red.

8. When rubidium ions are heated to a high temperature, two lines are observed in its line spectrum at wavelengths (a) 7.9×10^{-7} m and (b) 4.2×10^{-7} m. What are the frequencies of the two lines? What color do we see when we heat a rubidium compound?

Solution

(a) $\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^{8}\ \cancel{\text{m}}\ \text{s}^{-1}}{7.9 \times 10^{-7}\ \cancel{\text{m}}} = 3.8 \times 10^{14}\ \text{s}^{-1}$; this has a color of blue to violet. (b)

$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^{8}\ \cancel{\text{m}}\ \text{s}^{-1}}{4.2 \times 10^{-7}\ \cancel{\text{m}}} = 7.1 \times 10^{14}\ \text{s}^{-1}$; This has a color or red. Unseparated, the blue-violet color predominates and we see blue-violet.

9. The emission spectrum of cesium contains two lines whose frequencies are (a) 3.45×10^{14} Hz and (b) 6.53×10^{14} Hz. What are the wavelengths and energies per photon of the two lines? What color are the lines?

Solution

From $c = \lambda\nu$

(a) $\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^{8}\ \text{m}\ \cancel{\text{s}^{-1}}}{7.9 \times 10^{-7}\ \cancel{\text{s}^{-1}}} = 8.69 \times 10^{-7}\ \text{m}$

$E = h\nu = 6.626 \times 10^{-34}\ \text{J}\ \cancel{\text{s}} \times 3.45 \times 10^{14}\cancel{\text{s}^{-1}} = 2.29 \times 10^{-19}\ \text{J}$

(b) $\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^{8}\ \text{m}\ \cancel{\text{s}^{-1}}}{6.53 \times 10^{14}\ \cancel{\text{s}^{-1}}} = 4.59 \times 10^{-7}\ \text{m}$

$E = h\nu = 6.626 \times 10^{-34}\ \text{J}\ \cancel{\text{s}} \times 6.53 \times 10^{14}\cancel{\text{s}^{-1}} = 4.33 \times 10^{-19}\ \text{J}$

The color of (a) is red; (b) is blue.

10. Photons of infrared radiation are responsible for much of the warmth we feel when holding our hands before a fire. These photons will also warm other objects. How many infrared photons with a wavelength of 1.5×10^{-6} m must be absorbed by the water to warm a cup of water (175 g) from 25.0 °C to 40 °C?

Solution

The heat required is $q = cm\Delta T = 4.184 \text{ J } \cancel{\text{g}}^{-1}\cancel{^\circ\text{C}}^{-1} \times 175 \cancel{\text{g}} \times (40.0 - 25.0) \cancel{^\circ\text{C}} = 1.1 \times 10^4 \text{ J}$
The wavelength corresponds to energy of

$$E = h\nu = h\frac{c}{\lambda} = 6.626 \times 10^{-34} \text{ J } \cancel{\text{s}} \times \frac{2.998 \times 10^8 \ \cancel{\text{m}}\ \text{s}^{-1}}{1.5 \times 10^{-6} \cancel{\text{m}}} = 1.3 \times 10^{-19} \text{ J photon}^{-1}$$

$$\text{Number of photons} = \frac{1.1 \times 10^4 \ \cancel{\text{J}}}{1.3 \times 10^{-19} \ \cancel{\text{J}}\ \text{photons}^{-1}} = 8.5 \times 10^{22} \text{ photons}$$

11. One of the radiographic devices used in a dentist's office emits an X-ray of wavelength 2.090×10^{-11} m. What is the energy, in joules, and frequency of this X-ray?

Solution
$c = \lambda\nu$,

$$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^8 \ \cancel{\text{m}}\ \text{s}^{-1}}{2.090 \times 10^{-11} \ \cancel{\text{m}}} = 1.434 \times 10^{19} \text{ s}^{-1}$$

$E = h\nu = 6.626 \times 10^{-34} \text{ J } \cancel{\text{s}} \times 1.434 \times 10^{19} \cancel{\text{s}}^{-1} = 9.502 \times 10^{-15} \text{ J}$

12. The eyes of certain reptiles pass a single visual signal to the brain when the visual receptors are struck by photons of a wavelength of 850 nm. If a total energy of 3.15×10^{-14} J is required to trip the signal, what is the minimum number of photons that must strike the receptor?

Solution
Determine the frequency of the photons and then their energy. Divide the total energy by the energy per photon to determine the number of photons needed.
$850 \text{ nm} = 8.5 \times 10^{-7}$ m

$$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^8 \ \cancel{\text{m}}\ \text{s}^{-1}}{8.50 \times 10^{-7} \ \cancel{\text{m}}} = 3.527 \times 10^{14} \text{ s}^{-1}$$

$E = h\nu = 6.626 \times 10^{34} \text{ J } \cancel{\text{s}}^{-1} \times 3.527 \times 10^{14} \text{ s}^{-1} = 2.337 \times 10^{-19} \text{ J}$

$$\text{Total energy/energy per photon} = \frac{3.15 \times 10^{-14} \ \cancel{\text{J}}}{2.337 \times 10^{-19} \cancel{\text{J}}\ \text{photon}^{-1}} = 1.35 \times 10^5 \text{ photons}\ ]$$

13. RGB color television and computer displays use cathode ray tubes that produce colors by mixing red, green, and blue light. If we look at the screen with a magnifying glass, we can see individual dots turn on and off as the colors change. Using a spectrum of visible light, determine the approximate wavelength of each of these colors. What is the frequency and energy of a photon of each of these colors?

Solution
See Figure 3.13. Red: 660 nm; 4.54×10^{14} Hz; 3.01×10^{-19} J. Green: 520 nm; 5.77×10^{14} Hz; 3.82×10^{-19} J. Blue: 440 nm; 6.81×10^{14} Hz; 4.51×10^{-19} J. Somewhat different numbers are also possible.

14. Answer the following questions about a Blu-ray laser:
(a) The laser on a Blu-ray player has a wavelength of 405 nm. In what region of the electromagnetic spectrum is this radiation? What is its frequency?
(b) A Blu-ray laser has a power of 5 milliwatts (1 watt = 1 J s^{-1}). How many photons of light are produced by the laser in 1 hour?
(c) The ideal resolution of a player using a laser (such as a Blu-ray player), which determines how close together data can be stored on a compact disk, is determined using the following formula: Resolution = $0.60(\lambda/\text{NA})$, where λ is the wavelength of the laser and NA is the numerical aperture. Numerical aperture is a measure of the size of the spot of light on the disk; the larger the NA, the smaller the spot. In a typical Blu-ray system, NA = 0.95. If the 405-nm

laser is used in a Blu-ray player, what is the closest that information can be stored on a Blu-ray disk?
(d) The data density of a Blu-ray disk using a 405-nm laser is 1.5×10^7 bits mm^{-2}. Disks have an outside diameter of 120 mm and a hole of 15-mm diameter. How many data bits can be contained on the disk? If a Blu-ray disk can hold 9,400,000 pages of text, how many data bits are needed for a typed page? (Hint: Determine the area of the disk that is available to hold data. The area inside a circle is given by $A = \pi r^2$, where the radius r is one-half of the diameter.)

Solution
(a) The laser is in the visible spectrum range (violet) with a frequency of 7.40×10^{14} s^{-1}. (b) The energy per one photon is 4.90×10^{-19} J. $\frac{0.005 \text{ W}}{4.90 \times 10^{-19} \text{ J}} = 1.02 \times 10^{16}$ photons s^{-1}. $1.02 \times 10^{16} \times 3600 = 3.67 \times 10^{19}$ photons/h. (c) 2.6×10^{-7} m. (d) 1.7×10^{11} bits; a page requires 1.8×10^4 bits.

15. What is the threshold frequency for sodium metal if a photon with frequency 6.66×10^{14} s^{-1} ejects a photon with 7.74×10^{-20} J kinetic energy? Will the photoelectric effect be observed if sodium is exposed to orange light?

Solution
$E_{photon} = h\nu = (6.626 \times 10^{-34} \text{ J s}) \times (6.66 \times 10^{14} \text{ s}^{-1}) = 4.41 \times 10^{-19}$ J
$E_{photon} = E_{kinetic} + E_{threshold}$,.which means that $4.41 \times 10^{-19} \text{ J} = 7.74 \times 10^{-20} \text{ J} + E_{threshold}$, thus $E_{threshold} = 3.64 \times 10^{-19}$ J, which corresponds to a threshold frequency of 5.49×10^{14} s^{-1}. Orange light is roughly 620 nm or 4.84×10^{14} s^{-1}, which is less than the threshold, so no electrons will be ejected.

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Chemistry: Atoms First 2e
3: Electronic Structure and Periodic Properties of Elements
3.2: The Bohr Model

16. Why is the electron in a Bohr hydrogen atom bound less tightly when it has a quantum number of 3 than when it has a quantum number of 1?

Solution
The electron with $n = 3$ is farther from the nucleus and, since the Coulomb potential varies inversely with the distance between the electron and the nucleus, the electrostatic attraction between it and the nucleus is less than for an electron with $n = 1$.

17. What does it mean to say that the energy of the electrons in an atom is quantized?

Solution
Quantized energy means that the electrons can possess only certain discrete energy values; values between those quantized values are not permitted.

18. Using the Bohr model, determine the energy, in joules, necessary to ionize a ground-state hydrogen atom. Show your calculations.

Solution
$$\Delta E = E_i - E_f = R_\infty \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) = R_\infty \left(\frac{1}{1^2} - 0 \right) = R_\infty = 2.179 \times 10^{-18} \text{ J}$$

19. The electron volt (eV) is a convenient unit of energy for expressing atomic-scale energies. It is the amount of energy that an electron gains when subjected to a potential of 1 volt; 1 eV = 1.602×10^{-19} J. Using the Bohr model, determine the energy, in electron volts, of the photon produced when an electron in a hydrogen atom moves from the orbit with $n = 5$ to the orbit with $n = 2$. Show your calculations.

Solution

$$\Delta E = E_2 - E_5 = 2.179 \times 10^{-18}\left(\frac{1}{n_2^2} - \frac{1}{n_5^2}\right) \text{J}$$

$$= 2.179 \times 10^{-18}\left(\frac{1}{2^2} - \frac{1}{5^2}\right) = 4.576 \times 10^{-19} \text{ J}$$

$$= \frac{4.576 \times 10^{-19} \cancel{\text{J}}}{1.602 \times 10^{-19} \cancel{\text{J}}\ \text{eV}^{-1}} = 2.856 \text{ eV}$$

20. Using the Bohr model, determine the lowest possible energy, in joules, for the electron in the Li^{2+} ion.

Solution

$E = -2.179 \times 10^{-18}$ J $(Z^2)\left(\frac{1}{n^2}\right)$. Since Z is the number of protons in the nucleus, $Z = 3$ for Li.

$E = -2.179 \times 10^{-18}$ J$(9)\left(\frac{1}{1}\right) = 1.961 \times 10^{-17}$ J

21. Using the Bohr model, determine the lowest possible energy for the electron in the He^+ ion.

Solution

$E = -2.179 \times 10^{-18}$ J$\left(Z^2\right)\left(\frac{1}{n^2}\right)$. Since Z is the number of protons in the nucleus, $Z = 2$ for He. $E = -2.179 \times 10^{-18}$ J$(4)\left(\frac{1}{1}\right) = -8.716 \times 10^{-18}$ J

22. Using the Bohr model, determine the energy of an electron with $n = 6$ in a hydrogen atom.

Solution

$E = -2.179 \times 10^{-18}$ J$\left(Z^2\right)\left(\frac{1}{n^2}\right)$. Since Z is the number of protons in the nucleus, $Z = 1$ for H.

$E = -2.179 \times 10^{-18}$ J$(1)\left(\frac{1}{36}\right) = -6.053 \times 10^{-20}$ J

23. Using the Bohr model, determine the energy of an electron with $n = 8$ in a hydrogen atom.

Solution

$E = -2.179 \times 10^{-18}$ J$\left(Z^2\right)\left(\frac{1}{n^2}\right)$. Since Z is the number of protons in the nucleus, $Z = 1$ for H.

$E = -2.179 \times 10^{-18}$ J$(1)\left(\frac{1}{64}\right) = -3.405 \times 10^{-20}$ J

24. How far from the nucleus in angstroms (1 angstrom = 1×10^{-10} m) is the electron in a hydrogen atom if it has an energy of -8.72×10^{-20} J?

Solution

$E = -2.179 \times 10^{-18}\ \text{J}\left(Z^2\right)\left(\frac{1}{n^2}\right)$; $-8.72 \times 10^{-20}\ \text{J} = -2.179 \times 10^{-18}\ \text{J}(1)\left(\frac{1}{n^2}\right)$. So,

$n = \sqrt{\frac{-2.179 \times 10^{-18}\text{J}(1)}{8.72 \times 10^{-20}\ \text{J}}} = 5$, and

$r = \frac{n^2}{Z}a_0 = \frac{5^2}{1} \times 5.292 \times 10^{-11}\ \text{m} = 1.32 \times 10^{-9}\ \cancel{\text{m}} \times \frac{10^{10}\ \text{Å}}{1\ \cancel{\text{m}}} = 13.2\ \text{Å}$.

25. What is the radius, in angstroms, of the orbital of an electron with $n = 8$ in a hydrogen atom?

Solution

$r = \frac{n^2 a_0}{Z}$. For hydrogen, Z = 1; $a_0 = 0.529\ \text{Å}$; $n = 8$.

$r = \frac{8^2(0.529\ \text{Å})}{1} = 64(0.529) = 33.9\ \text{Å}$

26. Using the Bohr model, determine the energy in joules of the photon produced when an electron in a He^+ ion moves from the orbit with $n = 5$ to the orbit with $n = 2$.

Solution

$E = 2.179 \times 10^{-18}\ \text{J}(Z^2)\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

$= 2.179 \times 10^{-18}\ \text{J}(2^2)\left(\frac{1}{2^2} - \frac{1}{5^2}\right)$ $1.830 \times 10^{-18}\ \text{J}$

$= 1.830 \times 10^{-18}\ \text{J}$

27. Using the Bohr model, determine the energy in joules of the photon produced when an electron in a Li^{2+} ion moves from the orbit with $n = 2$ to the orbit with $n = 1$.

Solution

$E = 2.179 \times 10^{-18}\ \text{J}(Z^2)\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

$= 2.179 \times 10^{-18}\ \text{J}(3^2)\left(\frac{1}{1^2} - \frac{1}{2^2}\right)$

$= 1.471 \times 10^{-17}\ \text{J}$

28. Consider a large number of hydrogen atoms with electrons randomly distributed in the $n = 1$, 2, 3, and 4 orbits.
(a) How many different wavelengths of light are emitted by these atoms as the electrons fall into lower-energy orbits?
(b) Calculate the lowest and highest energies of light produced by the transitions described in part (a).
(c) Calculate the frequencies and wavelengths of the light produced by the transitions described in part (b).

Solution

(a) 6; (b) the lowest energy transition will be $4 \longrightarrow 3$ $4 \longrightarrow 3$, which emits 1.059×10^{-19} J: the highest energy transition will be $4 \longrightarrow 1$, which emits 2.043×10^{-18} J; (c) low: $1.598 \times 10^{14}\ \text{s}^{-1}$, 1876 nm; high: $3.083 \times 10^{15}\ \text{s}^{-1}$, 97.23 nm

29. How are the Bohr model and the Rutherford model of the atom similar? How are they different?

Solution
Both involve a relatively heavy nucleus with electrons moving around it, although strictly speaking, the Bohr model works only for one-electron atoms or ions. According to classical mechanics, the Rutherford model predicts a miniature "solar system" with electrons moving about the nucleus in circular or elliptical orbits that are confined to planes. If the requirements of classical electromagnetic theory that electrons in such orbits would emit electromagnetic radiation are ignored, such atoms would be stable, having constant energy and angular momentum, but would not emit any visible light (contrary to observation). If classical electromagnetic theory is applied, then the Rutherford atom would emit electromagnetic radiation of continually increasing frequency (contrary to the observed discrete spectra), thereby losing energy until the atom collapsed in an absurdly short time (contrary to the observed long-term stability of atoms). The Bohr model retains the classical mechanics view of circular orbits confined to planes having constant energy and angular momentum, but restricts these to quantized values dependent on a single quantum number, n. The orbiting electron in Bohr's model is assumed not to emit any electromagnetic radiation while moving about the nucleus in its stationary orbits, but the atom can emit or absorb electromagnetic radiation when the electron changes from one orbit to another. Because of the quantized orbits, such "quantum jumps" will produce discrete spectra, in agreement with observations.

30. The spectra of hydrogen and of calcium are shown in Figure 3.13. What causes the lines in these spectra? Why are the colors of the lines different? Suggest a reason for the observation that the spectrum of calcium is more complicated than the spectrum of hydrogen.

Solution
The lines are caused by the transition of electrons between different energy states. The lines have different colors because the energies of transition vary for different states, resulting in a variety of wavelengths and colors. The spectrum for calcium is more complicated because calcium has many more electrons than hydrogen and, therefore, many more possible electronic states and transitions.

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Chemistry: Atoms First 2e
3: Electronic Structure and Periodic Properties of Elements
3.3: Development of Quantum Theory

31. How are the Bohr model and the quantum mechanical model of the hydrogen atom similar? How are they different?

Solution
Both models have a central positively charged nucleus with electrons moving about the nucleus in accordance with the Coulomb electrostatic potential. The Bohr model *assumes* that the electrons move in circular orbits that have quantized energies, angular momentum, and radii that are specified by a single quantum number, n = 1,2,3,…, but this quantization is an ad hoc assumption made by Bohr to incorporate quantization into an essentially classical mechanics description of the atom. Bohr also assumed that electrons orbiting the nucleus normally do not emit or absorb electromagnetic radiation, but do so when the electron switches to a different orbit. In the quantum mechanical model, the electrons do not move in precise orbits (such orbits

violate the Heisenberg uncertainty principle) and, instead, a probabilistic interpretation of the electron's position at any given instant is used, with a mathematical function ψ called a wave function that can be used to determine the electron's spatial probability distribution. These wave functions, or orbitals, are three-dimensional stationary waves that can be specified by three quantum numbers that arise naturally from their underlying mathematics (no ad hoc assumptions required): the principal quantum number, n (the same one used by Bohr), which specifies shells such that orbitals having the same n all have the same energy and approximately the same spatial extent; the angular momentum quantum number l, which is a measure of the orbital's angular momentum and corresponds to the orbitals' general shapes, as well as specifying subshells such that orbitals having the same l (and n) all have the same energy; and the orientation quantum number m, which is a measure of the z component of the angular momentum and corresponds to the orientations of the orbitals. The Bohr model gives the same expression for the energy as the quantum mechanical expression and, hence, both properly account for hydrogen's discrete spectrum (an example of getting the right answers for the wrong reasons, something that many chemistry students can sympathize with), but gives the wrong expression for the angular momentum (Bohr orbits necessarily all have non-zero angular momentum, but some quantum orbitals [s orbitals] can have zero angular momentum).

32. What are the allowed values for each of the four quantum numbers: n, l, m_l, and m_s?

Solution

$n = 1...\infty$; $l = 0...n - 1$; $m_l = -l, -1 + 1,...,l - 1, l$; $m_s = \pm\frac{1}{2}$

33. Describe the properties of an electron associated with each of the following four quantum numbers: n, l, m_l, and m_s.

Solution

n determines the general range for the value of energy and the probable distances that the electron can be from the nucleus. l determines the shape of the orbital. m_l determines the orientation of the orbitals of the same l value with respect to one another. m_s determines the spin of an electron.

34. Answer the following questions:

(a) Without using quantum numbers, describe the differences between the shells, subshells, and orbitals of an atom.

(b) How do the quantum numbers of the shells, subshells, and orbitals of an atom differ?

Solution

(a) A shell consists of one or more subshells; each subshell contains a different type of orbital. A subshell consists of one or more orbitals of the same type with the same energy, unless an external magnetic field is applied. An orbital describes a region of space that can be occupied by a maximum of two electrons. (b) Quantum numbers of shells give the overall energy of the electrons in the respective shell. Those subshells define the shape and volume of spaces that the electrons can occupy. The quantum numbers for individual orbitals of an atom distinguish the orbitals' orientation in space.

35. Identify the subshell in which electrons with the following quantum numbers are found:

(a) $n = 2$, $l = 1$

(b) $n = 4$, $l = 2$

(c) $n = 6$, $l = 0$

Solution

(a) 2p, (b) 4d, (c) 6s

36. Which of the subshells described in Exercise 35 contain degenerate orbitals? How many degenerate orbitals are in each?

Solution
(a) Three, (b) five, (c) one orbital, but degeneracy does not apply to single orbitals.

37. Identify the subshell in which electrons with the following quantum numbers are found:
(a) $n = 3$, $l = 2$
(b) $n = 1$, $l = 0$
(c) $n = 4$, $l = 3$

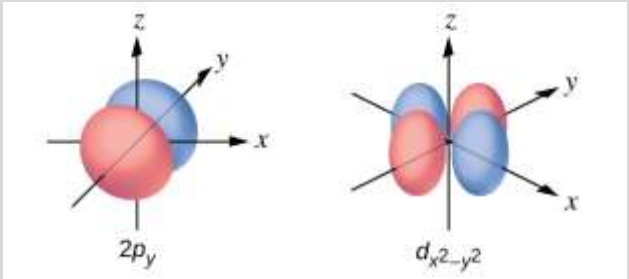
Solution
(a) 3*d;* (b) 1*s;* (c) 4*f*

38. Which of the subshells described in Exercise 37 contain degenerate orbitals? How many degenerate orbitals are in each?

Solution
(a) 3*d* and 4*f*; (b) five in 3*d*, seven in 4*f*

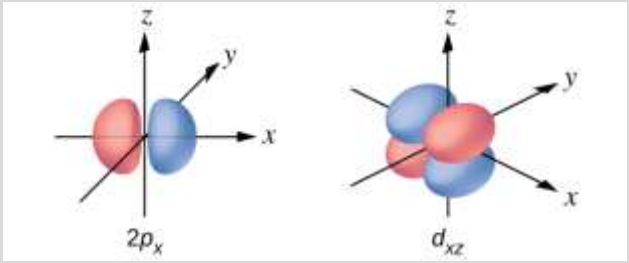
39. Sketch the boundary surface of a $d_{x^2-y^2}$ and a p_y orbital. Be sure to show and label the axes.

Solution

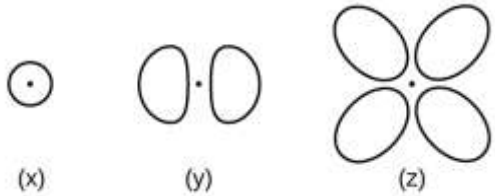


40. Sketch the p_x and d_{xz} orbitals. Be sure to show and label the coordinates.

Solution



41. Consider the orbitals shown here in outline.



(a) What is the maximum number of electrons contained in an orbital of type (x)? Of type (y)? Of type (z)?
(b) How many orbitals of type (x) are found in a shell with $n = 2$? How many of type (y)? How many of type (z)?
(c) Write a set of quantum numbers for an electron in an orbital of type (x) in a shell with $n = 4$. Of an orbital of type (y) in a shell with $n = 2$. Of an orbital of type (z) in a shell with $n = 3$.
(d) What is the smallest possible n value for an orbital of type (x)? Of type (y)? Of type (z)?

(e) What are the possible l and m_l values for an orbital of type (x)? Of type (y)? Of type (z)?

Solution

(a) x. 2, y. 2, z. 2; (b) x. 1, y. 3, z. 0; (c) x. 4 0 0 $\frac{1}{2}$, y. 2 1 0 $\frac{1}{2}$, z. 3 2 0 $\frac{1}{2}$; (d) x. 1, y. 2, z. 3; (e) x. $l = 0$, $m_l = 0$, y. $l = 1$, $m_l = -1$ 0 or +1, z. $l = 2$, $m_l = -2$ –1 0 +1 +2

42. State the Heisenberg uncertainty principle. Describe briefly what the principle implies.

Solution

The Heisenberg uncertainty principle states that it is impossible to precisely determine both the momentum and the position of a particle at the same time. The uncertainty principle means that the more exactly you learn either the momentum or the position of a quantum particle, the less exactly you can know the other quantity. A similar relationship with energy and time is covered by the uncertainty principle: The better that we know the energy of a particle, the less knowledge we have of the time of its emission from an atom.

43. How many electrons could be held in the second shell of an atom if the spin quantum number m_s could have three values instead of just two? (Hint: Consider the Pauli exclusion principle.)

Solution

In the second subshell ($n = 2$), there are two possible angular momentum (l) values (0 and 1). When $l = 0$, the magnetic quantum number (m_l) can only be 0. When $l = 1$, the magnetic quantum number (m_l) can be equal to –1, 0, or 1. Therefore, in the second shell, there are four orbitals (the number of orbitals in a shell is equal to n^2). If there were three possible values for the spin quantum number, each orbital could hold three different electrons and still obey the Pauli exclusion principle. In other words, each orbital could hold three electrons and none of those three electrons would have the exact same four quantum numbers. If each orbital could hold three electrons, the second shell, which has four orbitals, could hold a total of 12 electrons.

44. Which of the following equations describe particle-like behavior? Which describe wavelike behavior? Do any involve both types of behavior? Describe the reasons for your choices.

(a) $c = \lambda v$

(b) $E = \frac{mv^2}{2}$

(c) $r = \frac{n^2 a_0}{Z}$

(d) $E = hv$

(e) $\lambda = \frac{h}{mv}$

Solution

(a) Wavelike behavior. This is the formula for a wave of electromagnetic radiation (it can be applied to other waves if c is modified to be the speed of the wave, not necessarily of light). (b) Particle-like behavior. This is the formula for energy of a particle of rest mass m using a definite velocity value of v. (c) This is a formula for particle-like behavior, as it assumes that an electron is moving around the nucleus at a distance r; thus, it has a definite trajectory. (d) Wavelike behavior. This is a formula for energy of an electromagnetic wave. (e) Both wave and particle, since it shows that there is a wavelength that belongs to a particle with a rest mass m.

45. Write a set of quantum numbers for each of the electrons with an n of 4 in a Se atom.

Solution

n	l	m_l	s
4	0	0	$+\frac{1}{2}$
4	0	0	$-\frac{1}{2}$
4	1	−1	$+\frac{1}{2}$
4	1	0	$+\frac{1}{2}$
4	1	+1	$+\frac{1}{2}$
4	1	−1	$-\frac{1}{2}$

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Chemistry: Atoms First 2e
3: Electronic Structure and Periodic Properties of Elements
3.4: Electronic Structure of Atoms (Electron Configurations)

46. Read the labels of several commercial products and identify monatomic ions of at least four transition elements contained in the products. Write the complete electron configurations of these cations.

Solution
For example, Fe^{3+}: $1s^22s^22p^63s^23p^63d^5$; Cu^{2+}: $1s^22s^22p^63s^23p^63d^9$; Ti^{4+}: $1s^22s^22p^63s^23p^6$; Cr^{3+}: $1s^22s^22p^63s^23p^63d^3$

47. Read the labels of several commercial products and identify monatomic ions of at least six main group elements contained in the products. Write the complete electron configurations of these cations and anions.

Solution
For example, $Na^{+:}$ $1s^22s^22p^6$; Ca^{2+}: $1s^22s^22p^63s^23p^6$; Sn^{2+}: $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^2$; F^-: $1s^22s^22p^6$; O^{2-}: $1s^22s^22p^6$; Cl^-: $1s^22s^22p^63s^23p^6$

48. Using complete subshell notation (not abbreviations, $1s^22s^22p^6$, and so forth), predict the electron configuration of each of the following atoms:
(a) C
(b) P
(c) V
(d) Sb
(e) Sm

Solution
(a) $1s^2 2s^2 2p^2$; (b) $1s^2 2s^2 2p^6 3s^2 3p^3$; (c) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$; (d) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^3$; (e) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2 4f^6$

49. Using complete subshell notation ($1s^2 2s^2 2p^6$, and so forth), predict the electron configuration of each of the following atoms:
(a) N
(b) Si
(c) Fe
(d) Te
(e) Tb

Solution
(a) $1s^2 2\ s^2 2p^3$; (b) $1s^2 2\ s^2 2p^6 3s^2 3p^2$; (c) $1s^2 2\ s^2 2p^6 3s^2 3p^6 4s^2 3d^6$; (d) $1s^2 2\ s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^4$; (e) $1s^2 2\ s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^9$

50. Is $1s^2 2s^2 2p^6$ the symbol for a macroscopic property or a microscopic property of an element? Explain your answer.

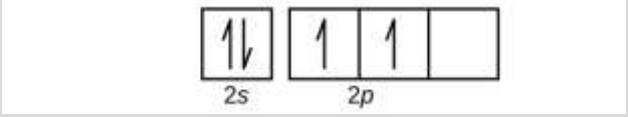
Solution
A microscopic property; it describes the electronic configuration, which is a property of an atom.

51. What additional information do we need to answer the question "Which ion has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6$""?

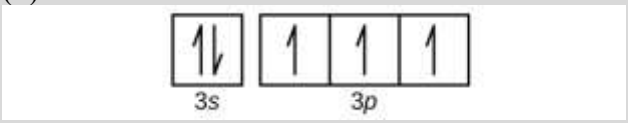
Solution
The charge on the ion.

52. Draw the orbital diagram for the valence shell of each of the following atoms:
(a) C
(b) P
(c) V
(d) Sb
(e) Ru

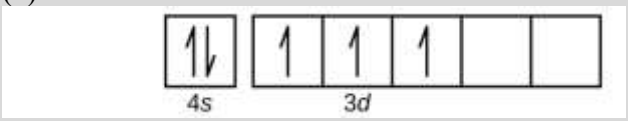
Solution
(a)



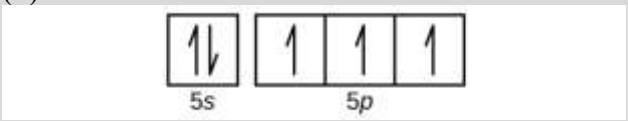
(b)



(c)



(d)

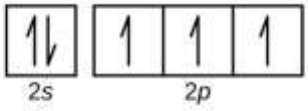


(e)

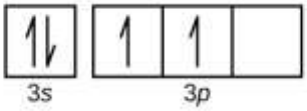


53. Use an orbital diagram to describe the electron configuration of the valence shell of each of the following atoms:
(a) N
(b) Si
(c) Fe
(d) Te
(e) Mo

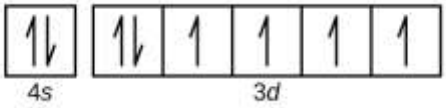
Solution
(a)



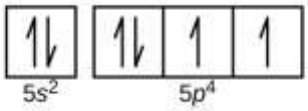
(b)



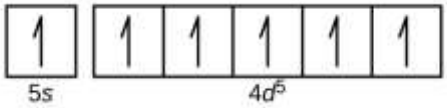
(c)



(d)



(e)



54. Using complete subshell notation ($1s^22s^22p^6$, and so forth), predict the electron configurations of the following ions.
(a) N^{3-}
(b) Ca^{2+}
(c) S^{-}
(d) Cs^{2+}
(e) Cr^{2+}
(f) Gd^{3+}

Solution
(a) $1s^22s^22p^6$; (b) $1s^22s^22p^63s^23p^6$; (c) $1s^22s^22p^63s^23p^5$; (d) $1s^22s^22p^63s^23p^63d^{10}4s^24p^65s^24d^{10}5p^5$; (e) $1s^22s^22p^63s^23p^63d^4$; (f) $1s^22s^22p^63s^23p^63d^{10}4s^24p^65s^24d^{10}5s^25p^64f^5$

55. Which atom has the electron configuration $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^2$?

Solution
Zr

56. Which atom has the electron configuration $1s^22s^22p^63s^23p^63d^74s^2$?

Solution
Co

57. Which ion with a +1 charge has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$? Which ion with a –2 charge has this configuration?

Solution
Rb^+, Se^{2-}

58. Which of the following atoms contains only three valence electrons: Li, B, N, F, Ne?

Solution
B

59. Which of the following has two unpaired electrons?
(a) Mg
(b) Si
(c) S
(d) Both Mg and S
(e) Both Si and S.

Solution
Although both (b) and (c) are correct, (e) encompasses both and is the best answer.

60. Which atom would be expected to have a half-filled 6*p* subshell?

Solution
Bi

61. Which atom would be expected to have a half-filled 4*s* subshell?

Solution
K

62. In one area of Australia, the cattle did not thrive despite the presence of suitable forage. An investigation showed the cause to be the absence of sufficient cobalt in the soil. Cobalt forms cations in two oxidation states, Co^{2+} and Co^{3+}. Write the electron structure of the two cations.

Solution
Co^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7$; Co^{3+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$

63. Thallium was used as a poison in the Agatha Christie mystery story “The Pale Horse.” Thallium has two possible cationic forms, +1 and +3. The +1 compounds are the more stable. Write the electron structure of the +1 cation of thallium.

Solution
$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10}$

64. Write the electron configurations for the following atoms or ions:
(a) B^{3+}
(b) O^-
(c) Cl^{3+}
(d) Ca^{2+}
(e) Ti

Solution
(a) $1s^2$; (b) $1s^2 2s^2 2p^5$; (c) $1s^2 2s^2 2p^6 3s^2 3p^2$; (d) $1s^2 2s^2 2p^6 3s^2 3p^6$; (e) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$

65. Cobalt–60 and iodine–131 are radioactive isotopes commonly used in nuclear medicine. How many protons, neutrons, and electrons are in atoms of these isotopes? Write the complete electron configuration for each isotope.

Solution
Co has 27 protons, 27 electrons, and 33 neutrons: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$.

I has 53 protons, 53 electrons, and 78 neutrons: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^5$.

66. Write a set of quantum numbers for each of the electrons with an n of 3 in a Sc atom.

Solution

$n = 3, l = 0, m_l = 0, m_s = \frac{1}{2}$; $n = 3, l = 0, m_l = 0, m_s = -\frac{1}{2}$; $n = 3, l = 1, m_l = -1, m_s = \frac{1}{2}$; $n = 3, l = 1, m_l = -1, m_s = -\frac{1}{2}$; $n = 3, l = 1, m_l = 0, m_s = \frac{1}{2}$; $n = 3, l = 1, m_l = 0, m_s = -\frac{1}{2}$; $n = 3, l = 1, m_l = 1, m_s = \frac{1}{2}$; $n = 3, l = 1, m_l = 1, m_s = -\frac{1}{2}$; $n = 3, l = 2, m_l = -2, -1, 0, 1,$ or 2, $m_s = \pm\frac{1}{2}$

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Chemistry: Atoms First 2e
3: Electronic Structure and Periodic Properties of Elements
3.5: Periodic Variations in Element Properties

67. Based on their positions in the periodic table, predict which has the smallest atomic radius: Mg, Sr, Si, Cl, I.

Solution

Cl

68. Based on their positions in the periodic table, predict which has the largest atomic radius: Li, Rb, N, F, I.

Solution

Rb

69. Based on their positions in the periodic table, predict which has the largest first ionization energy: Mg, Ba, B, O, Te.

Solution

O

70. Based on their positions in the periodic table, predict which has the smallest first ionization energy: Li, Cs, N, F, I.

Solution

Cs

71. Based on their positions in the periodic table, rank the following atoms in order of increasing first ionization energy: F, Li, N, Rb.

Solution

Rb < Li < N < F

72. Based on their positions in the periodic table, rank the following atoms or compounds in order of increasing first ionization energy: Mg, O, S, Si.

Solution

Mg < Si < S < O

73. Atoms of which group in the periodic table have a valence shell electron configuration of ns^2np^3?

Solution

15 (5A)

74. Atoms of which group in the periodic table have a valence shell electron configuration of ns^2?

Solution
2 (2A)

75. Based on their positions in the periodic table, list the following atoms in order of increasing radius: Mg, Ca, Rb, Cs.

Solution
Mg < Ca < Rb < Cs

76. Based on their positions in the periodic table, list the following atoms in order of increasing radius: Sr, Ca, Si, Cl.

Solution
Cl < Si < Ca < Sr

77. Based on their positions in the periodic table, list the following ions in order of increasing radius: K^+, Ca^{2+}, Al^{3+}, Si^{4+}.

Solution
$Si^{4+} < Al^{3+} < Ca^{2+} < K^+$

78. List the following ions in order of increasing radius: Li^+, Mg^{2+}, Br^-, Te^{2-}.

Solution
$Mg^{2+} < Li^+ < Br^- < Te^{2-}$

79. Which atom and/or ion is (are) isoelectronic with Br^+: Se^{2+}, Se, As^-, Kr, Ga^{3+}, Cl^-?

Solution
Se, As^-

80. Which of the following atoms and ions is (are) isoelectronic with S^{2+}: Si^{4+}, Cl^{3+}, Ar, As^{3+}, Si, Al^{3+}?

Solution
Cl^{3+}, Si

81. Compare both the numbers of protons and electrons present in each to rank the following ions in order of increasing radius: As^{3-}, Br^-, K^+, Mg^{2+}.

Solution
$Mg^{2+} < K^+ < Br^- < As^{3-}$

82. Of the five elements Al, Cl, I, Na, Rb, which has the most exothermic reaction? (E represents an atom.) What name is given to the energy for the reaction? (Hint: Note the process depicted does *not* correspond to electron affinity.)

$$E^+(g) + e^- \longrightarrow E(g)$$

Solution
Cl, this is the reverse of first ionization energy, $-IE_1$. It is not EA_1.

83. Of the five elements Sn, Si, Sb, O, Te, which has the most endothermic reaction? (E represents an atom.) What name is given to the energy for the reaction?

$$E(g) \longrightarrow E^+(g) + e^-$$

Solution
O, IE_1

84. The ionic radii of the ions S^{2-}, Cl^-, and K^+ are 184, 181, 138 pm respectively. Explain why these ions have different sizes even though they contain the same number of electrons.

Solution
The S^{2-} ion has the smallest nuclear charge and attracts the electrons least strongly.

85. Which main group atom would be expected to have the lowest second ionization energy?

Solution
Ra

86. Explain why Al is a member of group 13 rather than group 3?

Solution
Al is a member of group 13 to allow space for the 10 groups that contain *d* orbitals that are being filled after group 2.

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Chemistry: Atoms First 2e
3: Electronic Structure and Periodic Properties of Elements
3.6: The Periodic Table

87. Using the periodic table, classify each of the following elements as a metal or a nonmetal, and then further classify each as a main-group (representative) element, transition metal, or inner transition metal:
(a) uranium
(b) bromine
(c) strontium
(d) neon
(e) gold
(f) americium
(g) rhodium
(h) sulfur
(i) carbon
(j) potassium

Solution
(a) metal, inner transition metal; (b) nonmetal, representative element; (c) metal, representative element; (d) nonmetal, representative element; (e) metal, transition metal; (f) metal, inner transition metal; (g) metal, transition metal; (h) nonmetal, representative element; (i) nonmetal, representative element; (j) metal, representative element

88. Using the periodic table, classify each of the following elements as a metal or a nonmetal, and then further classify each as a main-group (representative) element, transition metal, or inner transition metal:
(a) cobalt
(b) europium
(c) iodine
(d) indium
(e) lithium
(f) oxygen
(g) cadmium
(h) terbium
(i) rhenium

Solution
(a) metal, transition metal; (b) metal, inner transition metal; (c) nonmetal, representative element; (d) metal, representative element; (e) metal, representative element; (f) nonmetal, representative element; (g) metal, representative element; (h) metal, representative element; (i) metal, inner transition metal; (j) metal, transition metal

89. Using the periodic table, identify the lightest member of each of the following groups:
(a) noble gases
(b) alkaline earth metals
(c) alkali metals
(d) chalcogens

Solution
(a) He; (b) Be; (c) Li; (d) O

90. Using the periodic table, identify the heaviest member of each of the following groups:
(a) alkali metals
(b) chalcogens
(c) noble gases
(d) alkaline earth metals

Solution
(a) Fr; (b) Po; (c) Rn; (d) Ra

91. Use the periodic table to give the name and symbol for each of the following elements:
(a) the noble gas in the same period as germanium
(b) the alkaline earth metal in the same period as selenium
(c) the halogen in the same period as lithium
(d) the chalcogen in the same period as cadmium

Solution
(a) krypton, Kr; (b) calcium, Ca; (c) fluorine, F; (d) tellurium, Te

92. Use the periodic table to give the name and symbol for each of the following elements:
(a) the halogen in the same period as the alkali metal with 11 protons
(b) the alkaline earth metal in the same period with the neutral noble gas with 18 electrons
(c) the noble gas in the same row as an isotope with 30 neutrons and 25 protons
(d) the noble gas in the same period as gold

Solution
(a) chlorine, Cl; (b) magnesium, Mg; (c) krypton, Kr; (d) radon, Rn

93. Write a symbol for each of the following neutral isotopes. Include the atomic number and mass number for each.
(a) the alkali metal with 11 protons and a mass number of 23
(b) the noble gas element with and 75 neutrons in its nucleus and 54 electrons in the neutral atom
(c) the isotope with 33 protons and 40 neutrons in its nucleus
(d) the alkaline earth metal with 88 electrons and 138 neutrons

Solution
(a) ${}^{23}_{11}\text{Na}$; (b) ${}^{129}_{54}\text{Xe}$; (c) ${}^{73}_{33}\text{As}$; (d) ${}^{226}_{88}\text{Ra}$

94. Write a symbol for each of the following neutral isotopes. Include the atomic number and mass number for each.
(a) the chalcogen with a mass number of 125
(b) the halogen whose longest-lived isotope is radioactive
(c) the noble gas, used in lighting, with 10 electrons and 10 neutrons

(d) the lightest alkali metal with three neutrons

Solution

(a) $^{125}_{52}\text{Te}$; (b) $^{210}_{85}\text{At}$; (c) $^{20}_{10}\text{Ne}$; (d) $^{6}_{3}\text{Li}$

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Chemistry: Atoms First 2e
3: Electronic Structure and Periodic Properties of Elements
3.7: Molecular and Ionic Compounds

95. Using the periodic table, predict whether the following chlorides are ionic or covalent: KCl, NCl_3, ICl, $MgCl_2$, PCl_5, and CCl_4.

Solution

In general, those elements that are widely separated in the periodic table—that is, at the extreme left and extreme right—will form compounds that are ionic. Those elements that are near one another in the periodic table generally will form covalent compounds. More specifically, when a metal is combined with one or more nonmetals, the compound is usually ionic. Covalent compounds are usually formed by a combination of nonmetals. Ionic: KCl, $MgCl_2$; Covalent: NCl_3, ICl, PCl_5, CCl_4

96. Using the periodic table, predict whether the following chlorides are ionic or covalent: $SiCl_4$, PCl_3, $CaCl_2$, CsCl, $CuCl_2$, and $CrCl_3$.

Solution

Covalent compounds are usually formed by a combination of nonmetals. Ionic compounds are usually formed when a metal is combined with one or more nonmetals. Ionic: $CaCl_2$, CsCl, $CuCl_2$; Covalent: $SiCl_4$, PCI_3

97. For each of the following compounds, state whether it is ionic or covalent. If it is ionic, write the symbols for the ions involved:
(a) NF_3
(b) BaO
(c) $(NH_4)_2CO_3$
(d) $Sr(H_2PO_4)_2$
(e) IBr
(f) Na_2O

Solution

(a) covalent; (b) ionic, Ba^{2+}, O^{2-}; (c) ionic, NH_4^+, CO_3^{2-} ; (d) ionic, Sr^{2+}, $H_2PO_4^-$; (e) covalent; (f) ionic, Na^+, O^{2-}

98. For each of the following compounds, state whether it is ionic or covalent, and if it is ionic, write the symbols for the ions involved:
(a) $KClO_4$
(b) $Mg(C_2H_3O_2)_2$
(c) H_2S
(d) Ag_2S
(e) N_2Cl_4
(f) $Co(NO_3)_2$

Solution

(a) ionic, K^+, ClO_4^-; (b) ionic, Mg^{2+}, $C_2H_3O_2$, charge 2–; (c) covalent; (d) ionic, Ag^+, S^{2-}; (e) covalent; (f) ionic, Co^{2+}, NO_3^-

99. For each of the following pairs of ions, write the symbol for the formula of the compound they will form:
(a) Ca^{2+}, S^{2-}
(b) NH_4^+, SO_4^{2-}
(c) Al^{3+}, Br^-
(d) Na^+, HPO_4^{2-}
(e) Mg^{2+}, PO_4^{3-}

Solution
(a) CaS; (b) $(NH_4)_2SO_4$; (c) $AlBr_3$; (d) Na_2HPO_4; (e) $Mg_3(PO_4)_2$

100. For each of the following pairs of ions, write the symbol for the formula of the compound they will form:
(a) K^+, O^{2-}
(b) NH_4^+, PO_4^{3-}
(c) Al^{3+}, O^{2-}
(d) Na^+, CO_3^{2-}
(e) Ba^{2+}, PO_4^{3-}

Solution
(a) K_2O; (b) $(NH_4)_3PO_4$; (c) Al_2O_3; (d) Na_2CO_3; (e) $Ba_3(PO_4)_2$

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Chemistry: Atoms First 2e
4: Chemical Bonding and Molecular Geometry
4.1: Ionic Bonding

1. Does a cation gain protons to form a positive charge or does it lose electrons?

Solution
The protons in the nucleus do not change during normal chemical reactions. Only the outer electrons move. Positive charges form when electrons are lost.

2. Iron(III) sulfate [$Fe_2(SO_4)_3$] is composed of Fe^{3+} and SO_4^{2-} ions. Explain why a sample of iron(III) sulfate is uncharged.

Solution
The Fe^{3+} ions and SO_4^{2-} ions are combined in a 2:3 ratio. The positive and negative charges cancel, yielding a neutral compound: $[2 \times (+3)] + [3 \times (-2)] = 0$.

3. Which of the following atoms would be expected to form negative ions in binary ionic compounds and which would be expected to form positive ions: P, I, Mg, Cl, In, Cs, O, Pb, Co?

Solution
P, I, Cl, and O would form anions because they are nonmetals. Mg, In, Cs, Pb, and Co would form cations because they are metals.

4. Which of the following atoms would be expected to form negative ions in binary ionic compounds and which would be expected to form positive ions: Br, Ca, Na, N, F, Al, Sn, S, Cd?

Solution
Br, N, F, and S would form anions. Ca, Na, Al, Sn, and Cd would form cations.

5. Predict the charge on the monatomic ions formed from the following atoms in binary ionic compounds:
(a) P
(b) Mg
(c) Al
(d) O
(e) Cl
(f) Cs

Solution
(a) P^{3-}; (b) Mg^{2+}; (c) Al^{3+}; (d) O^{2-}; (e) Cl^{-}; (f) Cs^{+}

6. Predict the charge on the monatomic ions formed from the following atoms in binary ionic compounds:
(a) I
(b) Sr
(c) K
(d) N
(e) S
(f) In

Solution
(a) I^{-}; (b) Sr^{2+}; (c) K^{+}; (d) N^{3-}; (e) S^{2-}; (f) In^{+}

7. Write the electron configuration for each of the following ions:
(a) As^{3-}
(b) I^{-}
(c) Be^{2+}

(d) Cd^{2+}
(e) O^{2-}
(f) Ga^{3+}
(g) Li^{+}
(h) N^{3-}
(i) Sn^{2+}
(j) Co^{2+}
(k) Fe^{2+}

(l) As^{3+}

Solution
(a) [Ar]$4s^2 3d^{10} 4p^6$; (b) [Kr]$4d^{10} 5s^2 5p^6$; (c) $1s^2$; (d) [Kr]$4d^{10}$; (e) [He]$2s^2 2p^6$; (f) [Ar]$3d^{10}$; (g) $1s^2$; (h) [He]$2s^2 2p^6$; (i) [Kr]$d^{10} 5s^2$; (j) [Ar]$3d^7$; (k) [Ar]$3d^6$; (l) [Ar]$3d^{10} 4s^2$

8. Write the electron configuration for the monatomic ions formed from the following elements (which form the greatest concentration of monatomic ions in seawater):
(a) Cl
(b) Na
(c) Mg
(d) Ca
(e) K
(f) Br
(g) Sr
(h) F

Solution
(a) Cl^-, [Ne]$3s^2 3p^6$; (b) Na^+, [Ne]; (c) Mg^{2+}, $1s^2 2s^2 2p^6$, [Ne]; (d) Ca^{2+}, [Ar]; (e) K^+, [Ar]; (f) Br^-, [Kr]; (g) Sr^{2+}, [Kr]; (h) F^-, [Ne] noble gas

9. Write out the full electron configuration for each of the following atoms and for the monatomic ion found in binary ionic compounds containing the element:
(a) Al
(b) Br
(c) Sr
(d) Li
(e) As
(f) S

Solution
(a) $1s^2 2s^2 2p^6 3s^2 3p^1$; Al^{3+}: $1s^2 2s^2 2p^6$; (b) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$; $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$; (c) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$; Sr^{2+}:$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$; (d) $1s^2 2s^1$; Li^+ $1s^2$; (e) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$; $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$; (f) $1s^2 2s^2 2p^6 3s^2 3p^4$; $1s^2 2s^2 2p^6 3s^2 3p^6$

10. From the labels of several commercial products, prepare a list of six ionic compounds in the products. For each compound, write the formula. (You may need to look up some formulas in a suitable reference.)

Solution
Examples include sodium chloride (salt), NaCl; sodium hydrogen carbonate (baking soda), $NaHCO_3$; sodium hydroxide, NaOH; potassium chloride (a salt substitute), KCl; tin(II) fluoride (in toothpaste), SnF_2; calcium carbonate (antacid), $CaCO_3$; ammonium nitrate (fertilizer) NH_4NO_3.

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Chemistry: Atoms First 2e
4: Chemical Bonding and Molecular Geometry
4.2: Covalent Bonding

11. Why is it incorrect to speak of a molecule of solid NaCl?

Solution
NaCl consists of discrete ions arranged in a crystal lattice, not covalently bonded molecules.

12. What information can you use to predict whether a bond between two atoms is covalent or ionic?

Solution
If the elements in a compound are the same or close to one another in the periodic table, the compound is likely to be covalent; if they are far apart, then the compound will likely be ionic. If electronegativity values are available, the difference in electronegativity can indicate whether a bond is likely to be ionic or covalent.

13. Predict which of the following compounds are ionic and which are covalent, based on the location of their constituent atoms in the periodic table:
(a) Cl_2CO
(b) MnO
(c) NCl_3
(d) $CoBr_2$
(e) K_2S
(f) CO
(g) CaF_2
(h) HI
(i) CaO
(j) IBr
(k) CO_2

Solution
ionic: (b), (d), (e), (g), and (i); covalent: (a), (c), (f), (h), (j), and (k)

14. Explain the difference between a nonpolar covalent bond, a polar covalent bond, and an ionic bond.

Solution
In an ionic bond, an electron or electrons are transferred from one atom to another, making one negative and the other positive. The electrostatic attraction holds them together. In a covalent bond, electrons are shared between the two atoms, resulting in a bond. A polar covalent bond is one in which the electrons are shared unequally. In this case, one atom has a greater electronegativity and a greater attraction for the electrons in the bond. In a pure covalent bond, the electrons are shared equally. In this case, the two atoms have very similar, if not the same, electronegativities and attract the electrons in the bond equally.

15. From its position in the periodic table, determine which atom in each pair is more electronegative:
(a) Br or Cl
(b) N or O
(c) S or O

(d) P or S
(e) Si or N
(f) Ba or P
(g) N or K

Solution
(a) Cl; (b) O; (c) O; (d) S; (e) N; (f) P; (g) N

16. From its position in the periodic table, determine which atom in each pair is more electronegative:
(a) N or P
(b) N or Ge
(c) S or F
(d) Cl or S
(e) H or C
(f) Se or P
(g) C or Si

Solution
(a) N; (b) N; (c) F; (d) Cl; (e) C; (f) P; (g) C

17. From their positions in the periodic table, arrange the atoms in each of the following series in order of increasing electronegativity:
(a) C, F, H, N, O
(b) Br, Cl, F, H, I
(c) F, H, O, P, S
(d) Al, H, Na, O, P
(e) Ba, H, N, O, As

Solution
(a) H, C, N, O, F; (b) H, I, Br, Cl, F; (c) H, P, S, O, F; (d) Na, Al, H, P, O; (e) Ba, H, As, N, O

18. From their positions in the periodic table, arrange the atoms in each of the following series in order of increasing electronegativity:
(a) As, H, N, P, Sb
(b) Cl, H, P, S, Si
(c) Br, Cl, Ge, H, Sr
(d) Ca, H, K, N, Si
(e) Cl, Cs, Ge, H, Sr

Solution
(a) H, Sb, As, P, N; (b) H, Si, P, S, Cl; (c) Sr, H, Ge, Br, Cl; (d) K, Ca, H, Si, N; (e) Cs, Sr, H, Ge, Cl

19. Which atoms can bond to sulfur so as to produce a positive partial charge on the sulfur atom?

Solution
N, O, F, and Cl

20. Which is the most polar bond?
(a) C–C
(b) C–H
(c) N–H
(d) O–H
(e) Se–H

Solution

O–H

21. Identify the more polar bond in each of the following pairs of bonds:
(a) HF or HCl
(b) NO or CO
(c) SH or OH
(d) PCl or SCl
(e) CH or NH
(f) SO or PO
(g) CN or NN

Solution
(a) HF; (b) CO; (c) OH; (d) PCl; (e) NH; (f) PO; (g) CN

22. Which of the following molecules or ions contain polar bonds?
(a) O_3
(b) S_8
(c) O_2^{2-}
(d) NO_3^-
(e) CO_2
(f) H_2S
(g) BH_4^-

Solution
(d) NO_3^-; (e) CO_2; (f) H_2S; (g) BH_4^-

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Chemistry: Atoms First 2e
4: Chemical Bonding and Molecular Geometry
4.3: Chemical Nomenclature

23. Name the following compounds:
(a) CsCl
(b) BaO
(c) K_2S
(d) $BeCl_2$
(e) HBr
(f) AlF_3

Solution
(a) cesium chloride; (b) barium oxide; (c) potassium sulfide; (d) beryllium chloride; (e) hydrogen bromide; (f) aluminum fluoride

24. Name the following compounds:
(a) NaF
(b) Rb_2O
(c) BCl_3
(d) H_2Se
(e) P_4O_6

(f) ICl_3

Solution

(a) sodium fluoride; (b) rubidium oxide; (c) boron trichloride; (d) hydrogen selenide; (e) tetraphosphorushexaoxide; (f) iodine trichloride

25. Write the formulas of the following compounds:
(a) rubidium bromide
(b) magnesium selenide
(c) sodium oxide
(d) calcium chloride
(e) hydrogen fluoride
(f) gallium phosphide
(g) aluminum bromide
(h) ammonium sulfate

Solution

(a) RbBr; (b) MgSe; (c) Na_2O; (d) $CaCl_2$; (e) HF; (f) GaP; (g) $AlBr_3$; (h) $(NH_4)_2SO_4$

26. Write the formulas of the following compounds:
(a) lithium carbonate
(b) sodium perchlorate
(c) barium hydroxide
(d) ammonium carbonate
(e) sulfuric acid
(f) calcium acetate
(g) magnesium phosphate
(h) sodium sulfite

Solution

(a) Li_2CO_3; (b) $NaClO_4$; (c) $Ba(OH)_2$; (d) $(NH_4)_2CO_3$;(e) H_2SO_4; (f) $Ca(C_2H_3O_2)_2$; (g) $Mg_3(PO_4)_2$; (h) Na_2SO_3

27. Write the formulas of the following compounds:
(a) chlorine dioxide
(b) dinitrogentetraoxide
(c) potassium phosphide
(d) silver sulfide
(e) aluminum fluoride trihydrate
(f) silicon dioxide

Solution

(a) ClO_2; (b) N_2O_4; (c) K_3P; (d) Ag_2S; (e) $AlF_3 \cdot 3H_2O$; (f) SiO_2

28. Write the formulas of the following compounds:
(a) barium chloride
(b) magnesium nitride
(c) sulfur dioxide
(d) nitrogentrichloride
(e) dinitrogen trioxide
(f) tin(IV) chloride

Solution

(a) $BaCl_2$; (b) Mg_3N_2; (c) SO_2; (d) NCl_3; (e) N_2O_3; (f) $SnCl_4$

29. Each of the following compounds contains a metal that can exhibit more than one ionic charge. Name these compounds:
(a) Cr_2O_3
(b) $FeCl_2$
(c) CrO_3
(d) $TiCl_4$
(e) $CoCl_2 \cdot 6H_2O$
(f) MoS_2

Solution
(a) chromium(III) oxide; (b) iron(II) chloride; (c) chromium(VI) oxide; (d) titanium(IV) chloride; (e) cobalt(II) chloride hexahydrate; (f) molybdenum(IV) sulfide

30. Each of the following compounds contains a metal that can exhibit more than one ionic charge. Name these compounds:
(a) $NiCO_3$
(b) MoO_3
(c) $Co(NO_3)_2$
(d) V_2O_5
(e) MnO_2
(f) Fe_2O_3

Solution
(a) nickel(II) carbonate; (b) molybdenum(VI) oxide; (c) cobalt(II) nitrate; (d) vanadium(V) oxide; (e) manganese(IV) oxide; (f) iron(III) oxide

31. The following ionic compounds are found in common household products. Write the formulas for each compound:
(a) potassium phosphate
(b) copper(II) sulfate
(c) calcium chloride
(d) titanium(IV) oxide
(e) ammonium nitrate
(f) sodium bisulfate (the common name for sodium hydrogen sulfate)

Solution
(a) K_3PO_4; (b) $CuSO_4$; (c) $CaCl_2$; (d) TiO_2; (e) NH_4NO_3; (f) $NaHSO_4$

32. The following ionic compounds are found in common household products. Name each of the compounds:
(a) $Ca(H_2PO_4)_2$
(b) $FeSO_4$
(c) $CaCO_3$
(d) MgO
(e) $NaNO_2$
(f) KI

Solution
(a) calcium dihydrogen phosphate; (b) iron(II) sulfate; (c) calcium carbonate; (d) magnesium oxide; (e) sodium nitrite; (f) potassium iodide

33. What are the IUPAC names of the following compounds?
(a) manganese dioxide
(b) mercurous chloride (Hg_2Cl_2)

(c) ferric nitrate [$Fe(NO_3)_3$]
(d) titanium tetrachloride
(e) cupric bromide ($CuBr_2$)

Solution
(a) manganese(IV) oxide; (b) mercury(I) chloride; (c) iron(III) nitrate; (d) titanium(IV) chloride; (e) copper(II) bromide

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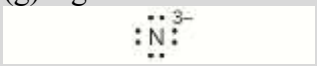
Chemistry: Atoms First 2e
4: Chemical Bonding and Molecular Geometry
4.4: Lewis Symbols and Structures

34. Write the Lewis symbols for each of the following ions:
(a) As^{3-}
(b) I^-
(c) Be^{2+}
(d) O^{2-}
(e) Ga^{3+}
(f) Li^+
(g) N^{3-}

Solution
(a) eight electrons:

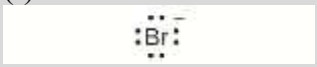
;
(b) eight electrons:

;
(c) no electrons
Be^{2+};
(d) eight electrons:

;
(e) no electrons
Ga^{3+};
(f) no electrons
Li^+;
(g) eight electrons:


35. Many monatomic ions are found in seawater, including the ions formed from the following list of elements. Write the Lewis symbols for the monatomic ions formed from the following elements:
(a) Cl
(b) Na
(c) Mg

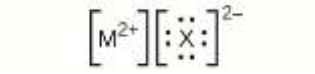
(d) Ca
(e) K
(f) Br
(g) Sr
(h) F

Solution
(a)  ;
(b) Na^+;
(c) Mg^{2+};
(d) Ca^{2+};
(e) K^+;
(f)  ;
(g) Sr^{2+};
(h) 

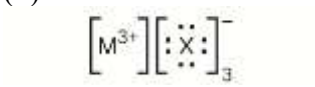
36. Write the Lewis symbols of the ions in each of the following ionic compounds and the Lewis symbols of the atom from which they are formed:
(a) MgS
(b) Al_2O_3
(c) $GaCl_3$
(d) K_2O
(e) Li_3N
(f) KF

Solution
(a)  ;
(b)  ;
(c)  ;
(d)  ;
(e)  ;
(f) 

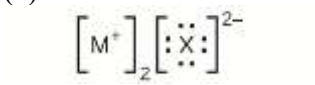
37. In the Lewis structures listed below, M and X represent various elements in the third period of the periodic table. Write the formula of each compound using the chemical symbols of each element:
(a)



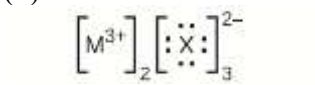
(b)



(c)



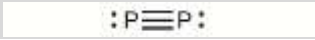
(d)



Solution
(a) MgS; (b) $AlCl_3$; (c) Na_2S; (d) Al_2S_3

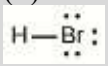
38. Write the Lewis structure for the diatomic molecule P_2, an unstable form of phosphorus found in high-temperature phosphorus vapor.

Solution

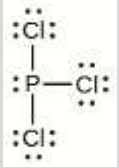


39. Write Lewis structures for the following:
(a) H_2
(b) HBr
(c) PCl_3
(d) SF_2
(e) H_2CCH_2
(f) HNNH
(g) H_2CNH
(h) NO^-
(i) N_2
(j) CO
(k) CN^-

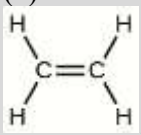
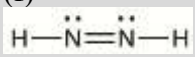
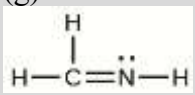
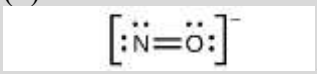
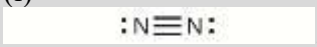
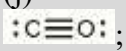
Solution
(a) H–H;
(b)



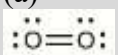
;
(c)

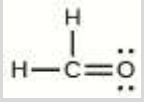
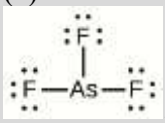
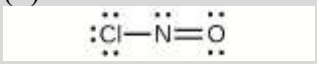
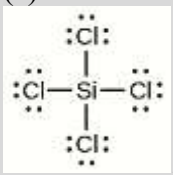
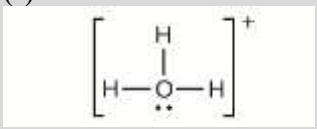
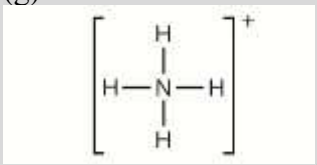
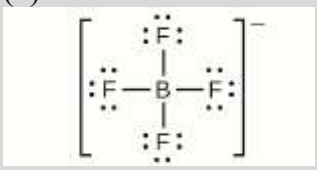
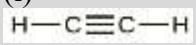
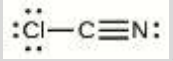
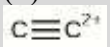


;
(d)

 ;
(e)
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(f)
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(g)
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(h)
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(i)
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(j)
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(k)

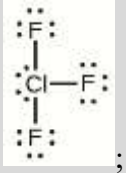
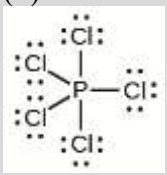

40. Write Lewis structures for the following:
(a) O_2
(b) H_2CO
(c) AsF_3
(d) ClNO
(e) $SiCl_4$
(f) H_3O^+
(g) NH_4^+
(h) BF_4^-
(i) HCCH
(j) ClCN
(k) C_2^{2+}

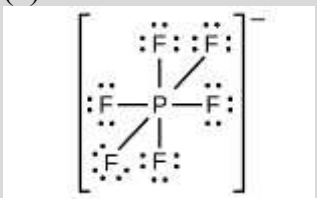
Solution
(a)

In this case, the Lewis structure is inadequate to depict the fact that experimental studies have shown two unpaired electrons in each oxygen molecule.
(b)

 ;
(c)
 ;
(d)
 ;
(e)
 ;
(f)
 ;
(g)
 ;
(h)
 ;
(i)
 ;
(j)
 ;
(k)


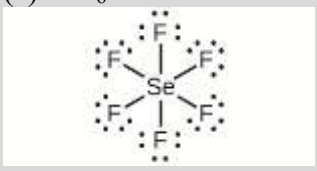
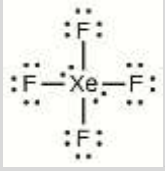
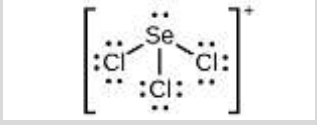
41. Write Lewis structures for the following:
(a) ClF_3
(b) PCl_5
(c) BF_3
(d) PF_6^-

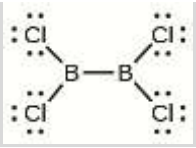
Solution
(a)


;
(b)

;
(c)

;
(d)


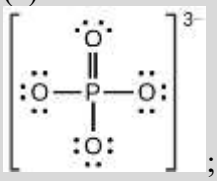
42. Write Lewis structures for the following:
(a) SeF_6
(b) XeF_4
(c) $SeCl_3^+$
(d) Cl_2BBCl_2 (contains a B–B bond)

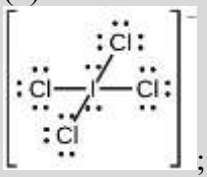
Solution
(a) SeF_6:

;
(b) XeF_4:

;
(c) $SeCl_3^+$:

;
(d) Cl_2BBCl_2:

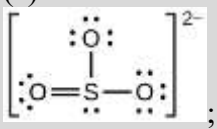


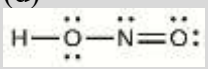
43. Write Lewis structures for:
(a) PO_4^{3-}
(b) ICl_4^-
(c) SO_3^{2-}
(d) HONO

Solution
(a)


;
(b)


;
(c)


;
(d)

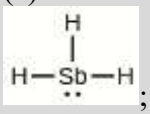


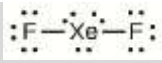
44. Correct the following statement: "The bonds in solid $PbCl_2$ are ionic; the bond in a HCl molecule is covalent. Thus, all of the valence electrons in $PbCl_2$ are located on the Cl^- ions, and all of the valence electrons in a HCl molecule are shared between the H and Cl atoms."

Solution
Two valence electrons per Pb atom are transferred to Cl atoms; the resulting Pb^{2+} ion has a $6s^2$ valence shell configuration. Two of the valence electrons in the HCl molecule are shared, and the other six are located on the Cl atom as lone pairs of electrons.

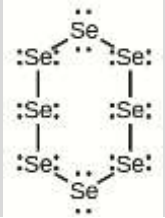
45. Write Lewis structures for the following molecules or ions:
(a) SbH_3
(b) XeF_2
(c) Se_8 (a cyclic molecule with a ring of eight Se atoms)

Solution
(a)


;
(b)

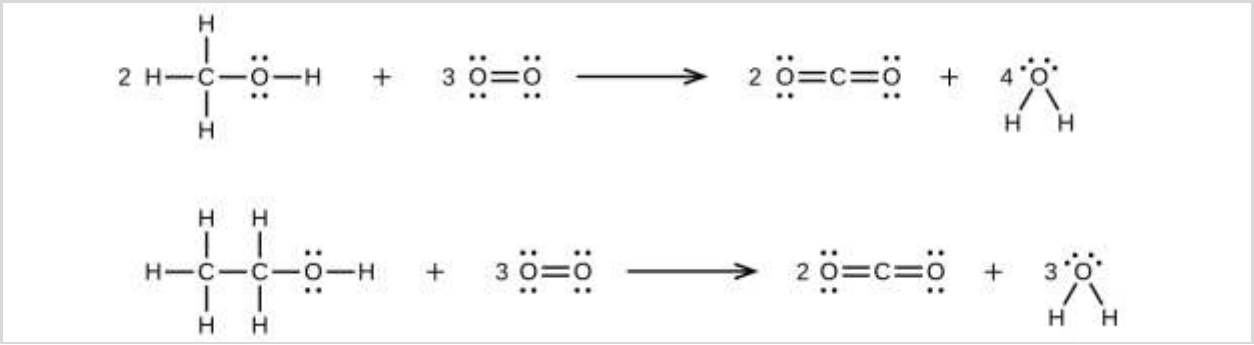
 ;

(c)



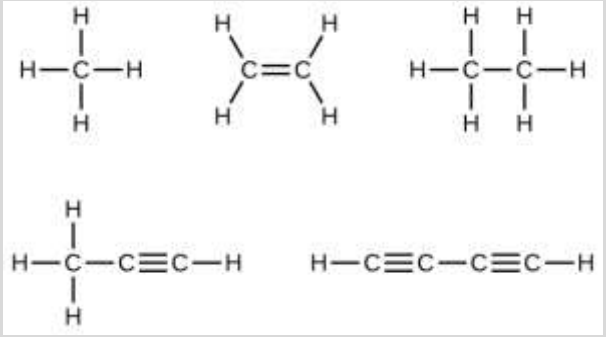
46. Methanol, H_3COH, is used as the fuel in some race cars. Ethanol, C_2H_5OH, is used extensively as motor fuel in Brazil. Both methanol and ethanol produce CO_2 and H_2O when they burn. Write the chemical equations for these combustion reactions using Lewis structures instead of chemical formulas

Solution



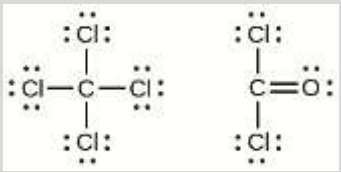
47. Many planets in our solar system contain organic chemicals including methane (CH_4) and traces of ethylene (C_2H_4), ethane (C_2H_6), propyne (H_3CCCH), and diacetylene (HCCCCH). Write the Lewis structures for each of these molecules.

Solution



48. Carbon tetrachloride was formerly used in fire extinguishers for electrical fires. It is no longer used for this purpose because of the formation of the toxic gas phosgene, Cl_2CO. Write the Lewis structures for carbon tetrachloride and phosgene.

Solution



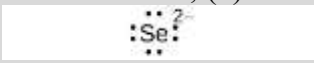
49. Identify the atoms that correspond to each of the following electron configurations. Then, write the Lewis symbol for the common ion formed from each atom:

(a) $1s^2 2s^2 2p^5$
(b) $1s^2 2s^2 2p^6 3s^2$
(c) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$
(d) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^4$
(e) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^1$

Solution
(a) atom: F, common ion F^-, Lewis structure:

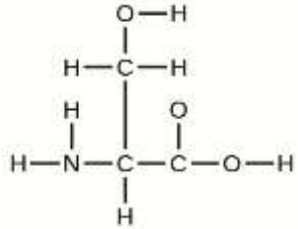


;
(b) atom: Mg, common ion Mg^{2+}, Lewis structure Mg^{2+}; (c) atom: Zn, common ion: Zn^{2+}, Lewis structure: Zn^{2+}; (d) atom: Se, common ion Se^{2-}, Lewis structure:

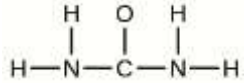


;
(e) atom: Ga, common ion: Ga^{3+}, Lewis structure: Ga^{3+}

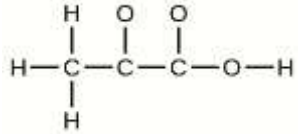
50. The arrangement of atoms in several biologically important molecules is given below. Complete the Lewis structures of these molecules by adding multiple bonds and lone pairs. Do not add any more atoms.
(a) the amino acid serine:



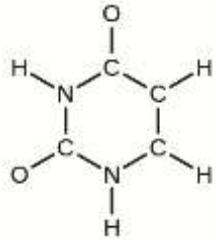
(b) urea:



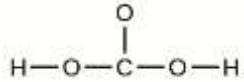
(c) pyruvic acid:



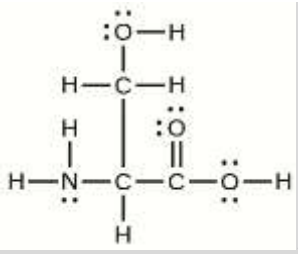
(d) uracil:



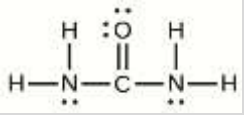
(e) carbonic acid:



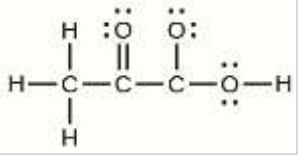
Solution
(a)

 ;

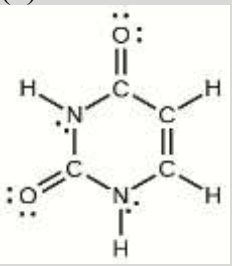
(b)

 ;

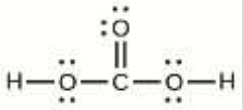
(c)

 ;

(d)

 ;

(e)



51. A compound with a molar mass of about 28 g/mol contains 85.7% carbon and 14.3% hydrogen by mass. Write the Lewis structure for a molecule of the compound.

Solution

There are 85.7 g C and 14.3 g H in a 100.0-g sample:

$$\frac{85.7\text{ g}}{12.011\text{ g mol}^{-1}} = 7.14\text{ mol C} \qquad \frac{7.14\text{ mol}}{7.14\text{ mol}} = 1 \qquad 1\text{ C}$$

$$\frac{14.3\text{ g}}{1.0079\text{ g mol}^{-1}} = 14.19\text{ mol H} \qquad \frac{14.19\text{ mol}}{7.14\text{ mol}} = 2 \qquad 2\text{ H}$$

52. A compound with a molar mass of about 42 g/mol contains 85.7% carbon and 14.3% hydrogen by mass. Write the Lewis structure for a molecule of the compound.

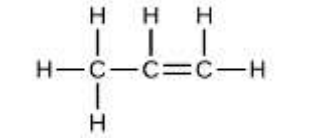
Solution

A 100.0-g sample of this compound would contain 85.7 g C and 14.3 g H:

$$\frac{85.7\text{ g}}{12.011\text{ g mol}^{-1}} = 7.14\text{ mol C}$$

$$\frac{14.3\text{ g}}{1.00794\text{ g mol}^{-1}} = 14.19\text{ mol H}$$

This is a ratio of 2 H to 1 C, or an empirical formula of CH_2 with a formula mass of approximately 14. As $\frac{42}{14} = 3$, the formula is $3 \times CH_2$ or C_3H_6. The Lewis structure is:



53. Two arrangements of atoms are possible for a compound with a molar mass of about 45 g/mol that contains 52.2% C, 13.1% H, and 34.7% O by mass. Write the Lewis structures for the two molecules.

Solution

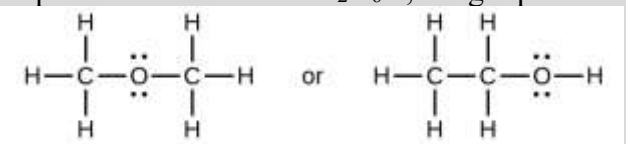
There are 52.2 g C, 13.1 g H, and 34.7 g O in a 100.0-g sample.

$\frac{52.2}{12.011} = 4.346 \text{ mol}$ $\quad \frac{4.346 \text{ mol}}{4.346 \text{ mol}} = 2 \quad 2 \text{ C}$

$\frac{13.1}{1.0079} = 12.997 \text{ mol}$ $\quad \frac{12.997 \text{ mol}}{2.1688 \text{ mol}} = 6 \quad 6 \text{ H}$

$\frac{34.7}{15.9994} = 2.1668 \text{ mol}$ $\quad \frac{2.1688 \text{ mol}}{2.1688 \text{ mol}} = 1 \quad 1 \text{ O}$

Experimental formula = C_2H_6O; weight per formula unit = 46. The compound may be:



54. How are single, double, and triple bonds similar? How do they differ?

Solution

Each bond includes a sharing of electrons between atoms. Two electrons are shared in a single bond; four electrons are shared in a double bond; and six electrons are shared in a triple bond.

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Chemistry: Atoms First 2e
4: Chemical Bonding and Molecular Geometry
4.5: Formal Charges and Resonance

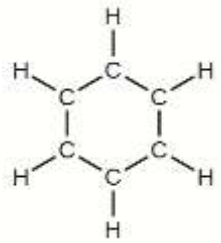
55. Write resonance forms that describe the distribution of electrons in each of the molecules or ions given below:

(a) selenium dioxide, OSeO

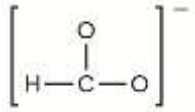
(b) nitrate ion, NO_3^-

(c) nitric acid, HNO_3 (N is bonded to an OH group and two O atoms)

(d) benzene, C_6H_6:



(e) the formate ion:



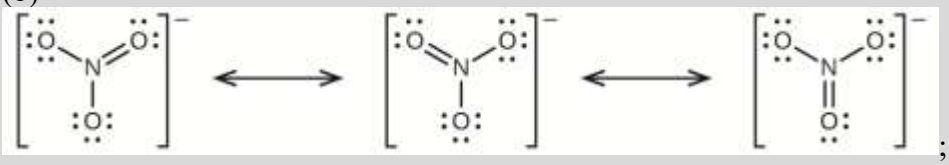
Solution

(a)



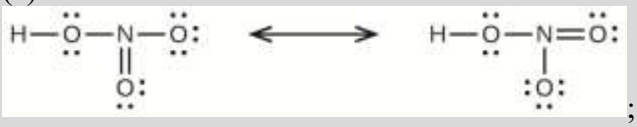
;

(b)



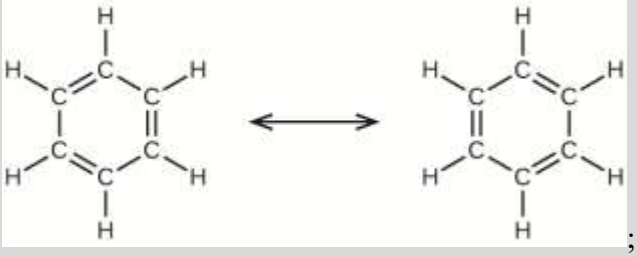
;

(c)



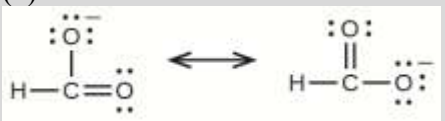
;

(d)



;

(e)



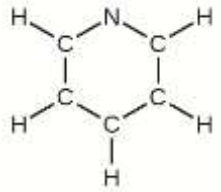
56. Write resonance forms that describe the distribution of electrons in each of the molecules or ions given below:

(a) sulfur dioxide, SO_2

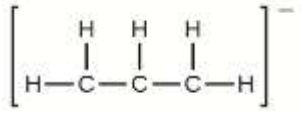
(b) carbonate ion, CO_3^{2-}

(c) hydrogen carbonate ion, HCO_3^- (C is bonded to an OH group and two O atoms)

(d) pyridine:



(e) the allyl ion:



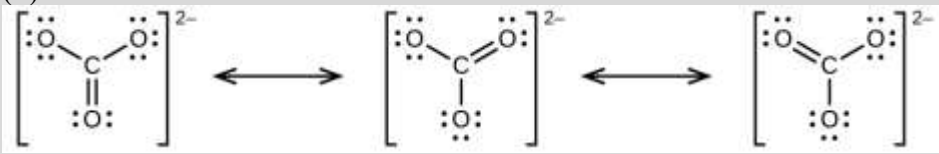
Solution

(a)



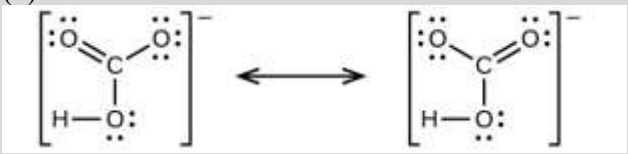
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(b)



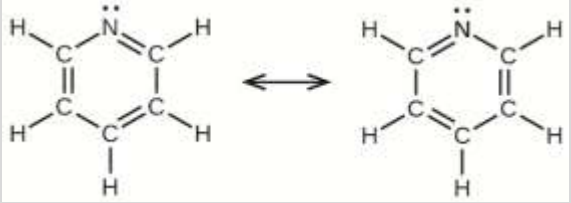
;

(c)



;

(d)



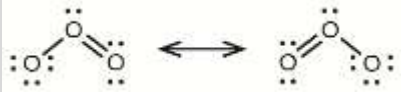
;

(e)



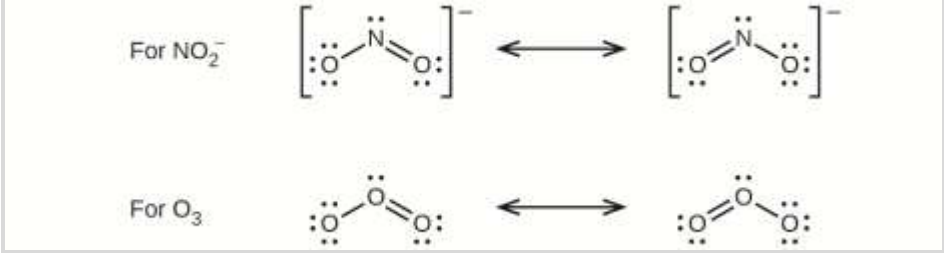
57. Write the resonance forms of ozone, O_3, the component of the upper atmosphere that protects the Earth from ultraviolet radiation.

Solution

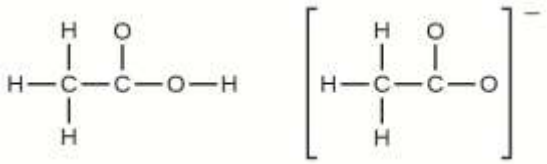


58. Sodium nitrite, which has been used to preserve bacon and other meats, is an ionic compound. Write the resonance forms of the nitrite ion, NO_2^-.

Solution



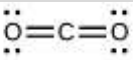
59. In terms of the bonds present, explain why acetic acid, CH_3CO_2H, contains two distinct types of carbon-oxygen bonds, whereas the acetate ion, formed by loss of a hydrogen ion from acetic acid, only contains one type of carbon-oxygen bond. The skeleton structures of these species are shown:



Solution
The acetic acid molecule contains a C–O double bond and a C–O single bond. The acetate ion is described by two resonance structures that average the two C–O bonds.

60. Write the Lewis structures for the following, and include resonance structures where appropriate. Indicate which of the three has the strongest carbon-oxygen bond.
(a) CO_2
(b) CO

Solution
(a)



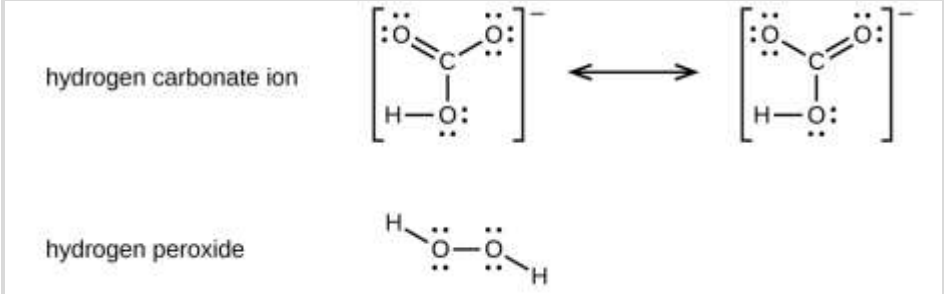
(b)



CO has the strongest carbon-oxygen bond, because there are is a triple bond joining C and O. CO_2 has double bonds, and carbonate has 1.3 bonds.

61. Toothpastes containing sodium hydrogen carbonate (sodium bicarbonate) and hydrogen peroxide are widely used. Write Lewis structures for the hydrogen carbonate ion and hydrogen peroxide molecule, with resonance forms where appropriate.

Solution



62. Determine the formal charge of each element in the following:
(a) HCl
(b) CF_4
(c) PCl_3

(d) PF_5

Solution

	Element	Bonding Electrons	Nonbonded Electrons	Valence Electrons	Formal Charge
(a)	H Cl	1 1	0 6	1 7	0 0
(b)	C F	4 1	0 6	4 7	0 0
(c)	P Cl	3 1	2 6	5 7	0 0
(d)	P F	5 1	0 6	5 7	0 0

63. Determine the formal charge of each element in the following:

(a) H_3O^+

(b) SO_4^{2-}

(c) NH_3

(d) O_2^{2-}

(e) H_2O_2

Solution

	Element	Bonding Electrons	Nonbonded Electrons	Valence Electrons	Formal Charge
(a)	H O	1 3	0 2	1 6	0 +1
(b)	S O	4 1	0 6	6 6	+2 −1
(c)	N H	3 1	2 0	5 1	0 0
(d)	O	1	6	6	−1
(e)	O H	2 1	4 0	6 1	0 0

64. Calculate the formal charge of chlorine in the molecules Cl_2, $BeCl_2$, and ClF_5.

Solution

	Element	Bonding Electrons	Nonbonded Electrons	Valence Electrons	Formal Charge
Cl_2	Cl	1	6	7	0
$BeCl_2$	Be Cl	2 1	0 6	2 7	0 0
ClF_5	Cl F	5 1	2 6	7 7	0 0

65. Calculate the formal charge of each element in the following compounds and ions:

(a) F_2CO

(b) NO^-

(c) BF_4^-

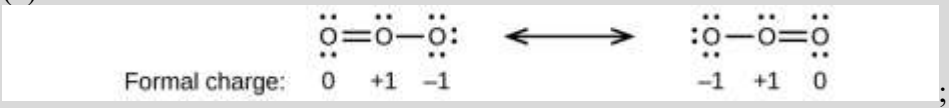
(d) $SnCl_3^-$
(e) H_2CCH_2
(f) ClF_3
(g) SeF_6
(h) PO_4^{3-}

Solution

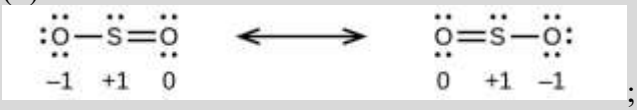
	Element	Bonding Electrons	Nonbonded Electrons	Valence Electrons	Formal Charge
(a)	F C O	1 4 2	6 0 4	7 4 6	0 0 0
(b)	N O	2 2	4 4	5 6	−1 0
(c)	B F	4 1	0 6	3 7	−1 0
(d)	Sn Cl	3 1	2 6	4 7	−1 0
(e)	C H	4 1	0 0	4 1	0 0
(f)	Cl F	3 1	4 6	7 7	0 0
(g)	Se F	6 1	0 6	6 7	0 0
(h)	P O	4 1	0 6	5 6	+1 −1

66. Draw all possible resonance structures for each of the compounds below. Determine the formal charge on each atom in each of the resonance structures:
(a) O_3
(b) SO_2
(c) NO_2^-
(d) NO_3^-

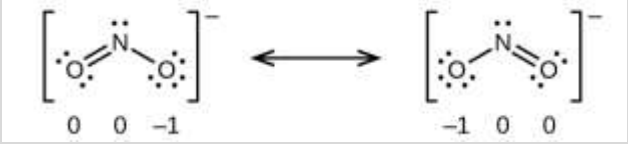
Solution
(a)



;
(b)

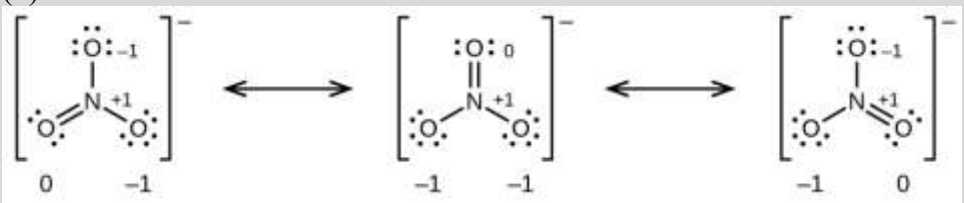


;
(c)



;

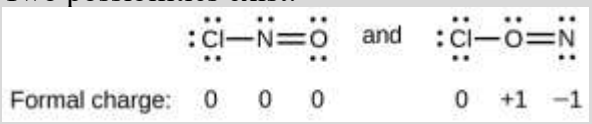
(d)



67. Based on formal charge considerations, which of the following would likely be the correct arrangement of atoms in nitrosyl chloride: ClNO or ClON?

Solution

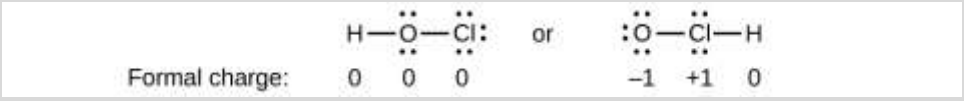
Two possibilities exist:



The first representation, having no formal charges, is more likely to occur than the second representation, which has formal charges at both N and O. The latter arrangement is even less favored because the formal negative charge is on the more electropositive ion.

68. Based on formal charge considerations, which of the following would likely be the correct arrangement of atoms in hypochlorous acid: HOCl or OClH?

Solution

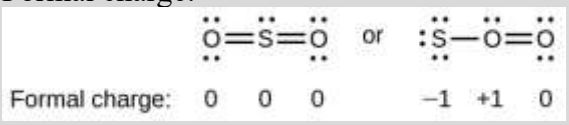


The structure with formal charges of 0 is the most stable and would therefore be the correct arrangement of atoms.

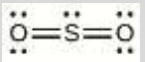
69. Based on formal charge considerations, which of the following would likely be the correct arrangement of atoms in sulfur dioxide: OSO or SOO?

Solution

Formal charge:



Correct arrangement:

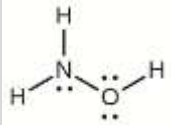


This form has no formal charges. The second form has a positive charge on the more electronegative element, an unfavorable situation.

70. Draw the structure of hydroxylamine, H_3NO, and assign formal charges; look up the structure. Is the actual structure consistent with the formal charges?

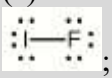
Solution

The structure that gives zero formal charges is consistent with the actual structure:



71. Iodine forms a series of fluorides (listed below). Write Lewis structures for each of the four compounds and determine the formal charge of the iodine atom in each molecule:
(a) IF
(b) IF_3
(c) IF_5
(d) IF_7

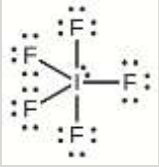
Solution
(a) formal charge 0:



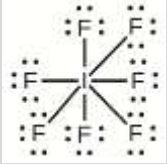
;
(b) formal charge 0:



;
(c) formal charge 0:



;
(d) formal charge 0:



72. Write the Lewis structure and chemical formula of the compound with a molar mass of about 70 g/mol that contains 19.7% nitrogen and 80.3% fluorine by mass, and determine the formal charge of the atoms in this compound.

Solution
There are 19.7 g N and 80.3 g F in a 100.0-g sample:

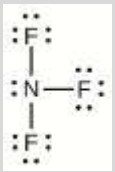
$$\frac{19.7\text{ g}}{14.0067\text{ g mol}^{-1}} = 1.406\text{ mol}$$

$$\frac{1.406\text{ mol}}{1.406\text{ mol}} = 1\text{ N}$$

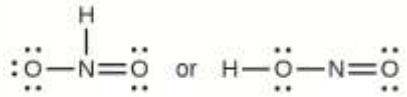
$$\frac{80.3\text{ g}}{18.9984\text{ g mol}^{-1}} = 4.2267\text{ mol}$$

$$\frac{4.2267\text{ mol}}{1.406\text{ mol}} = 3\text{ F}$$

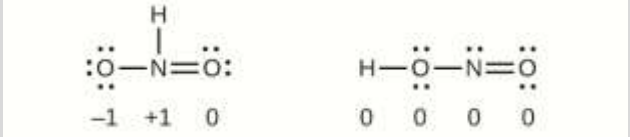
The empirical formula is NF_3 and its molar mass is 71.00 g/mol, which is consistent with the stated molar mass.
Oxidation states: N = +3, F = –1.
Formal charges: N = 0, F = 0:



73. Which of the following structures would we expect for nitrous acid? Determine the formal charges:

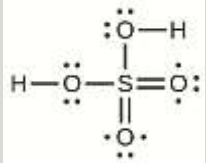


Solution
The second form, having all zero formal charges, is more likely:



74. Sulfuric acid is the industrial chemical produced in greatest quantity worldwide. About 90 billion pounds are produced each year in the United States alone. Write the Lewis structure for sulfuric acid, H_2SO_4, which has two oxygen atoms and two OH groups bonded to the sulfur.

Solution



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Chemistry: Atoms First 2e
4: Chemical Bonding and Molecular Geometry
4.6: Molecular Structure and Polarity

75. Explain why the HOH molecule is bent, whereas the HBeH molecule is linear.

Solution
The placement of the two sets of unpaired electrons in water forces the bonds to assume a tetrahedral arrangement, and the resulting HOH molecule is bent. The HBeH molecule (in which Be has only two electrons to bond with the two electrons from the hydrogens) must have the electron pairs as far from one another as possible and is therefore linear.

76. What feature of a Lewis structure can be used to tell if a molecule's (or ion's) electron-pair geometry and molecular structure will be identical?

Solution
The presence or absence of lone pairs on the central atom.

77. Explain the difference between electron-pair geometry and molecular structure.

Solution
Space must be provided for each pair of electrons whether they are in a bond or are present as lone pairs. Electron-pair geometry considers the placement of all electrons. Molecular structure considers only the bonding-pair geometry.

78. Why is the H–N–H angle in NH_3 smaller than the H–C–H bond angle in CH_4? Why is the H–N–H angle in NH_4^+ identical to the H–C–H bond angle in CH_4?

Solution
NH_3 contains three bonding pairs of electrons and a lone pair of electrons. The lone pair takes up more room than the bonding pairs. Both CH_4 and NH_4^+ contain four bonding pairs and no lone pairs.

79. Explain how a molecule that contains polar bonds can be nonpolar.

Solution
As long as the polar bonds are compensated (for example. two identical atoms are found directly across the central atom from one another), the molecule can be nonpolar.

80. As a general rule, MX_n molecules (where M represents a central atom and X represents terminal atoms; n = 2 – 5) are polar if there is one or more lone pairs of electrons on M. NH_3 (M = N, X = H, n = 3) is an example. There are two molecular structures with lone pairs that are exceptions to this rule. What are they?

Solution
MX_2E_3 (linear) and MX_4E_2 (square planar), where E represents an unshared pair of electrons; XeF_2 and XeF_4 are examples

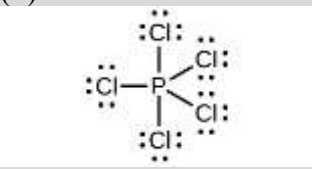
81. Predict the electron pair geometry and the molecular structure of each of the following molecules or ions:
(a) SF_6
(b) PCl_5
(c) BeH_2
(d) CH_3^+

Solution
(a) Number of valence electrons: S = 6, F = 7 each, total 48. A single line bond represents two electrons:



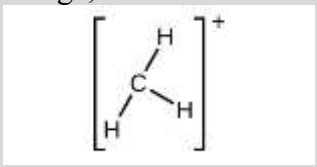
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The total number of electrons used is 48; six bonds are formed and no nonbonded pairs exist. Therefore the molecule includes six regions of electron density and, from the table, the electron geometry is octahedral. Since no lone pairs exist, the electron geometry and molecular structure are the same.
(b) Number of valence electrons: P = 5, Cl = 7 each, total 40:



.

The total number of electrons is 40; there are five regions of electron density and, from the table, the geometry is trigonal bipyramid. Since no lone pairs exist on P, the electron geometry and molecular structure are the same.
(c) Number of valence electrons: Be = 2, H = 1 each, total 4:
H:Be:H .
There are only two regions of electron density and they must have a linear arrangement. These regions also correspond to the location of the bonds. Both the electron and molecular structures are linear.
(d) Number of valence electrons: C = 4, H = 1 each, less one electron because of the positive charge, for a total of six electrons:



.
There are three regions of electron density coincident with the three bonds. Therefore the shape is trigonal planar for both the electron geometry and molecular structure.

82. Identify the electron pair geometry and the molecular structure of each of the following molecules or ions:
(a) IF_6^+
(b) CF_4
(c) BF_3
(d) SiF_5^-
(e) $BeCl_2$

Solution

		Regions of High Electron Density		Structure	
Formula	Electrons	Total	Lone pairs	Electron	Molecular
(a) IF_6^+	48	6	0	octahedral	octahedral
(b) CF_4	32	4	0	tetrahedral	tetrahedral
(c) BF_3	24	3	0	trigonal	trigonal
(d) SiF_5^-	40	5	0	trigonal bipyramidal	trigonal bipyramidal
(e) $BeCl_2$	16	2	0	linear	linear

83. What are the electron-pair geometry and the molecular structure of each of the following molecules or ions?
(a) ClF_5
(b) ClO_2^-
(c) $TeCl_4^{2-}$
(d) PCl_3
(e) SeF_4
(f) PH_2^-

Solution

		Regions of High Electron Density		Structure	
Formula	Electrons	Total	Lone pairs	Electron	Molecular
(a) ClF_5	42	6	1	octahedral	square pyramidal
(b) ClO_2^-	20	4	2	tetrahedral	bent
(c) $TeCl_4^{2-}$	36	6	2	octahedral	square planar
(d) PCl_3	26	4	1	tetrahedral	trigonal pyramidal
(e) SeF_4	34	5	1	trigonal bipyramidal	seesaw
(f) PH_2^-	8	4	2	tetrahedral	bent (109°)

84. Predict the electron pair geometry and the molecular structure of each of the following ions:
(a) H_3O^+
(b) PCl_4^-
(c) $SnCl_3^+$
(d) $BrCl_4^-$
(e) ICl_3
(f) XeF_4
(g) SF_2

Solution

		Regions of High Electron Density		Structure	
Formula	Electrons	Bonding pairs	Lone pairs	Electron	Molecular
(a) H_3O^+	8	3	1	tetrahedral	trigonal pyramidal
(b) PCl_4^-	34	4	1	trigonal bipyramidal	sawhorse
(c) $SnCl_3^-$	24	3	0	trigonal planar	trigonal planar
(d) $BrCl_4^-$	36	4	2	octahedral	square planar
(e) ICl_3	28	3	2	trigonal bipyramidal	T-shaped
(f) XeF_4	36	4	2	octahedral	square planar
(g) SF_2	20	2	2	tetrahedral	bent (109°)

85. Identify the electron pair geometry and the molecular structure of each of the following molecules:
(a) ClNO (N is the central atom)
(b) CS_2
(c) Cl_2CO (C is the central atom)
(d) Cl_2SO (S is the central atom)
(e) SO_2F_2 (S is the central atom)
(f) XeO_2F_2 (Xe is the central atom)
(g) $ClOF_2^+$ (Cl is the central atom)

Solution

	Regions of High Electron Density	Structure

Formula	Electrons	Total	Lone pairs	Electron	Molecular
(a) ClNO	18	3	1	trigonal planar	bent (120°)
(b) CS_2	16	2	0	linear	linear
(c) Cl_2CO	24	3	0	trigonal planar	trigonal planar
(d) Cl_2SO	26	4	1	tetrahedral	trigonal pyramidal
(e) SO_2F_2	32	4	0	tetrahedral	tetrahedral
(f) XeO_2F_2	34	5	1	trigonal bipyramidal	seesaw
(g) $ClOF_2^+$	26	4	1	tetrahedral	trigonal pyramidal

86. Predict the electron pair geometry and the molecular structure of each of the following:
(a) IOF_5 (I is the central atom)
(b) $POCl_3$ (P is the central atom)
(c) Cl_2SeO (Se is the central atom)
(d) $ClSO^+$ (S is the central atom)
(e) F_2SO (S is the central atom)
(f) NO_2^-
(g) SiO_4^{4-}

Solution

		Regions of High Electron Density		Structure	
Formula	Electrons	Bonding pairs	Lone pairs	Electron	Molecular
(a) IOF_5	48	6	0	octahedral	octahedral
(b) $POCl_3$	32	4	0	tetrahedral	tetrahedral
(c) Cl_2SeO	26	3	1	tetrahedral	trigonal pyramidal
(d) $ClSO^+$	18	2	1	trigonal	Bent (120°)
(e) F_2SO	26	3	1	tetrahedral	trigonal pyramidal
(f) NO_2^-	18	2	1	trigonal planar	bent (120°)
(g) SiO_4^{4-}	32	4	0	tetrahedral	tetrahedral

87. Which of the following molecules and ions contain polar bonds? Which of these molecules and ions have dipole moments?
(a) ClF_5
(b) ClO_2^-
(c) $TeCl_4^{2-}$
(d) PCl_3
(e) SeF_4
(f) PH_2^-
(g) XeF_2

Solution
All of these molecules and ions contain polar bonds. Only ClF_5, ClO_2^-, PCl_3, SeF_4, and PH_2^- have dipole moments.

88. Which of these molecules and ions contain polar bonds? Which of these molecules and ions have dipole moments?
(a) H_3O^+
(b) PCl_4^-
(c) $SnCl_3^-$
(d) $BrCl_4^-$
(e) ICl_3
(f) XeF_4
(g) SF_2

Solution
All of these molecules and ions contain polar bonds. Only H_3O^+, PCI_4^-, and SF_2 have dipole moments.

89. Which of the following molecules have dipole moments?
(a) CS_2
(b) SeS_2
(c) CCl_2F_2
(d) PCl_3 (P is the central atom)
(e) ClNO (N is the central atom)

Solution
(a) CS_2 is linear and has no dipole moment. (b) SeS_2 is bent. This leads to an overall dipole moment. (c) The C–Cl and C–F bonds are not balanced—that is, the dipoles do not completely cancel. Therefore, it has a dipole moment. (d) PCl3 is trigonal pyramidal. Due to this shape, the dipoles of the bonds do not cancel and there is an overall dipole moment. (e) The ClNO molecule is bent, leading to a dipole moment.

90. Identify the molecules with a dipole moment:
(a) SF_4
(b) CF_4
(c) Cl_2CCBr_2
(d) CH_3Cl
(e) H_2CO

Solution
(a) SF_4; (c) Cl_2CCBr_2; (d) CH_3Cl; (e) H_2CO

91. The molecule XF_3 has a dipole moment. Is X boron or phosphorus?

Solution
P

92. The molecule XCl_2 has a dipole moment. Is X beryllium or sulfur?

Solution
X is sulfur because XCl_2 is bent; $BeCl_2$ does not have a dipole moment because it is linear.

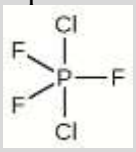
93. Is the Cl_2BBCl_2 molecule polar or nonpolar?

Solution
nonpolar

94. There are three possible structures for PCl_2F_3 with phosphorus as the central atom. Draw them and discuss how measurements of dipole moments could help distinguish among them.

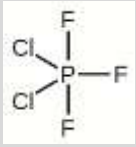
Solution

(a) The dipole moments resulting from the P–F and P–Cl bonds cancel one another so that no dipole moment is expected:



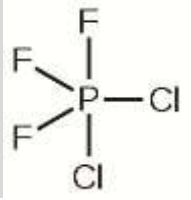
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(b) The two F atoms, at 180° cancel one another's effects. The two Cl atoms at 120° will have less influence on the dipole moment than the two F atoms at 120° in (c):



.

(c) The two P–F bond dipoles at 120° are only partially cancelled by the single P–Cl bond dipole at 120°. Likewise, the P–F bond 180° to the P–Cl bond only results in a minor cancellation of the dipole along the axis.

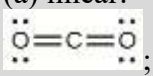


95. Describe the molecular structure around the indicated atom or atoms:
(a) the sulfur atom in sulfuric acid, H_2SO_4 [$(HO)_2SO_2$]
(b) the chlorine atom in chloric acid, $HClO_3$ [$HOClO_2$]
(c) the oxygen atom in hydrogen peroxide, HOOH
(d) the nitrogen atom in nitric acid, HNO_3 [$HONO_2$]
(e) the oxygen atom in the OH group in nitric acid, HNO_3 [$HONO_2$]
(f) the central oxygen atom in the ozone molecule, O_3
(g) each of the carbon atoms in propyne, CH_3CCH
(h) the carbon atom in Freon, CCl_2F_2
(i) each of the carbon atoms in allene, H_2CCCH_2

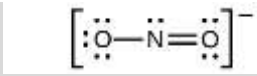
Solution
(a) tetrahedral; (b) trigonal pyramidal; (c) bent (109°); (d) trigonal planar; (e) bent (109°); (f) bent (<120°); (g) $\underline{C}H_3C\underline{C}H$ tetrahedral, $CH_3\underline{CC}H$ linear; (h) tetrahedral, (i) $H_2C\underline{C}CH_2$ linear; $H_2\underline{CC}\underline{C}H_2$ trigonal planar

96. Draw the Lewis structures and predict the shape of each compound or ion:
(a) CO_2
(b) NO_2^-
(c) SO_3
(d) SO_3^{2-}

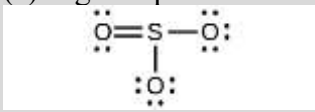
Solution
(a) linear:



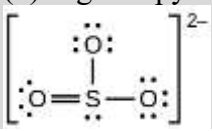
;
(b) bent:


;

(c) trigonal planar:

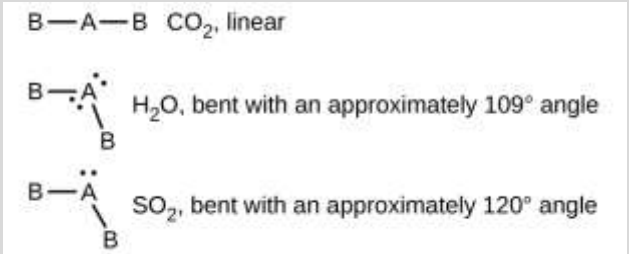

;

(d) trigonal pyramidal:



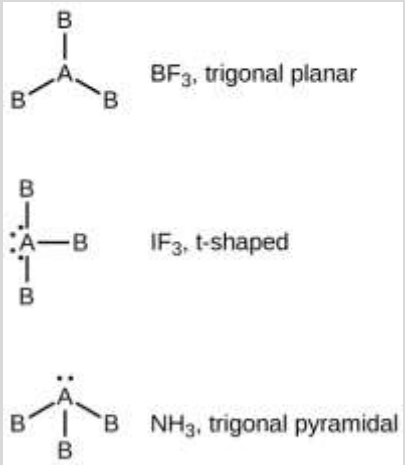
97. A molecule with the formula AB_2, in which A and B represent different atoms, could have one of three different shapes. Sketch and name the three different shapes that this molecule might have. Give an example of a molecule or ion for each shape.

Solution



98. A molecule with the formula AB_3, in which A and B represent different atoms, could have one of three different shapes. Sketch and name the three different shapes that this molecule might have. Give an example of a molecule or ion that has each shape.

Solution



99. Draw the Lewis electron dot structures for these molecules, including resonance structures where appropriate:

(a) CS_3^{2-}

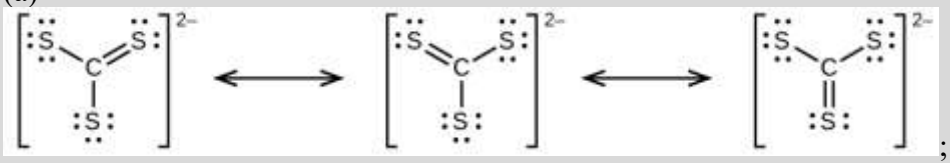
(b) CS_2

(c) CS

(d) predict the molecular shapes for CS_3^{2-} and CS_2 and explain how you arrived at your predictions

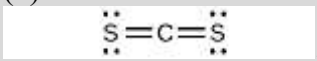
Solution

(a)



;

(b)



;

(c)



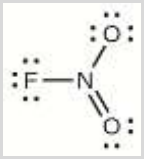
;

(d) CS_3^{2-} includes three regions of electron density (all are bonds with no lone pairs); the shape is trigonal planar; CS_2 has only two regions of electron density (all bonds with no lone pairs); the shape is linear

100. What is the molecular structure of the stable form of FNO_2? (N is the central atom.)

Solution

The Lewis dot structure is:



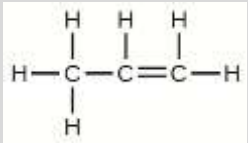
.

There are three regions of electron density and three bonds. The molecule is trigonal planar.

101. A compound with a molar mass of about 42 g/mol contains 85.7% carbon and 14.3% hydrogen. What is its molecular structure?

Solution

The empirical formula is CH_2 with a unit mass of14. $\frac{42}{14} = 3$. Therefore, the Lewis structure is made from three units, but the atoms must be rearranged:



102. Use this link: http://phet.colorado.edu/en/simulation/molecule-polarity to perform the following exercises for a two-atom molecule:
(a) Adjust the electronegativity value so the bond dipole is pointing toward B. Then determine what the electronegativity values must be to switch the dipole so that it points toward A.
(b) With a partial positive charge on A, turn on the electric field and describe what happens.
(c) With a small partial negative charge on A, turn on the electric field and describe what happens.
(d) Reset all, and then with a large partial negative charge on A, turn on the electric field and describe what happens.

Solution

(a) The electronegativity of A must be greater than B. (b) Nothing happens. (c) The molecule slowly rotates to align with the field. (d) The molecule quickly rotates to align with the field.

103. Use this link: http://phet.colorado.edu/en/simulation/molecule-polarity to perform the following exercises for a real molecule. You may need to rotate the molecules in three dimensions to see certain dipoles.

(a) Sketch the bond dipoles and molecular dipole (if any) for O_3. Explain your observations.
(b) Look at the bond dipoles for NH_3. Use these dipoles to predict whether N or H is more electronegative.
(c) Predict whether there should be a molecular dipole for NH_3 and, if so, in which direction it will point. Check the molecular dipole box to test your hypothesis.

Solution
The molecular dipole points away from the hydrogen atoms.

104. Use this link: http://phet.colorado.edu/en/simulation/molecule-shapes to build a molecule. Starting with the central atom, click on the double bond to add one double bond. Then add one single bond and one lone pair. Rotate the molecule to observe the complete geometry. Name the electron group geometry and molecular structure and predict the bond angle. Then click the check boxes at the bottom and right of the simulator to check your answers.

Solution
electron group geometry: trigonal planar; molecular structure: bent, bond angle 120°

105. Use this link: http://phet.colorado.edu/en/simulation/molecule-shapes to explore real molecules. On the Real Molecules tab, select H_2O. Switch between the "real" and "model" modes. Explain the difference observed.

Solution
The structures are very similar. In the model mode, each electron group occupies the same amount of space, so the bond angle is shown as 109.5°. In the "real" mode, the lone pairs are larger, causing the hydrogens to be compressed. This leads to the smaller angle of 104.5°.

106. Use this link: http://phet.colorado.edu/en/simulation/molecule-shapes to explore real molecules. On the Real Molecules tab, select "model" mode and S_2O. What is the model bond angle? Explain whether the "real" bond angle should be larger or smaller than the ideal model angle.

Solution
The model angle is 120°, as expected for a trigonal planar electron-group geometry. The real angle should be smaller, because the lone pair occupies more space and compresses the bonds to 119°.

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Chemistry: Atoms First 2e
6: Composition of Substances and Solutions
6.1: Formula Mass and the Mole Concept

1. What is the total mass (amu) of carbon in each of the following molecules?
(a) CH_4
(b) $CHCl_3$
(c) $C_{12}H_{10}O_6$
(d) $CH_3CH_2CH_2CH_2CH_3$

Solution
(a) 1 × 12.01 amu = 12.01 amu; (b) 1 × 12.01 amu = 12.01 amu; (c) 12 × 12.01 amu = 144.12 amu; (d) 5 × 12.01 amu = 60.05 amu

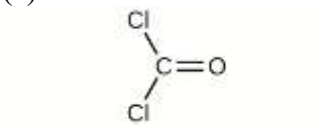
2. What is the total mass of hydrogen in each of the molecules?
(a) CH_4
(b) $CHCl_3$
(c) $C_{12}H_{10}O_6$
(d) $CH_3CH_2CH_2CH_2CH_3$

Solution
(a) 4 × 1.008 amu = 4.032 amu; (b) 1 × 1.008 amu = 1.008 amu; (c) 10 × 1.008 amu = 10.080 (significant figures) amu; (d) 12 × 1.008 amu = 12.096 amu

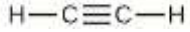
3. Calculate the molecular or formula mass of each of the following:
(a) P_4
(b) H_2O
(c) $Ca(NO_3)_2$
(d) CH_3CO_2H (acetic acid)
(e) $C_{12}H_{22}O_{11}$ (sucrose, cane sugar)

Solution
(a) 4 × 30.974 amu = 123.896 amu; (b) 2 × 1.008 amu + 15.999 amu = 18.015 amu; (c) 40.078 amu + 2 × 14.007 amu + 6 × 15.999 amu = 164.086 amu; (d) 2 × 12.011 amu + 4 × 1.008 amu + 2 × 15.999 amu = 60.052 amu; (e) 12 × 12.011 amu + 22 × 1.008 amu × 11 × 15.999 amu = 342.297 amu

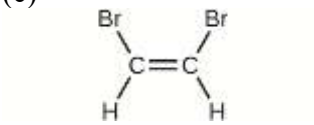
4. Determine the molecular mass of the following compounds:
(a)



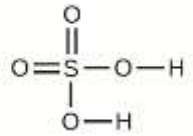
(b)



(c)



(d)



Solution

(a) Cl_2CO

$1C \times 12.011 = 12.011\ g\ mol^{-1}$

$1O \times 15.9994 = 15.9994\ g\ mol^{-1}$

$2Cl \times 35.4527 = \underline{70.9054\ g\ mol^{-1}}$;

$= 98.916\ g\ mol^{-1}$

(b) C_2H_2

$2C \times 12.011 = 24.022\ g\ mol^{-1}$

$2H \times 1.0079 = \underline{2.0158\ g\ mol^{-1}}$;

$= 26.038\ g\ mol^{-1}$

(c) $C_2H_2Br_2$

$2C \times 12.011 = 24.022\ g\ mol^{-1}$

$2H \times 1.0079 = 2.0158\ g\ mol^{-1}$

$4O \times 79.904 = \underline{159.808\ g\ mol^{-1}}$;

$= 185.846\ g\ mol^{-1}$

(d) H_2SO_4

$2H \times 1.0079 = 2.0158\ g\ mol^{-1}$

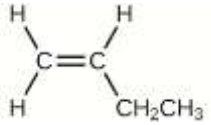
$1S \times 32.066 = 32.066\ g\ mol^{-1}$

$2Br \times 15.9994 = \underline{63.9976\ g\ mol^{-1}}$

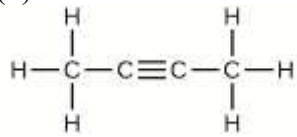
$= 98.079\ g\ mol^{-1}$

5. Determine the molecular mass of the following compounds:

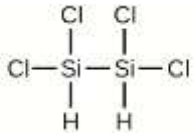
(a)



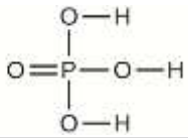
(b)



(c)

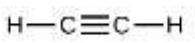


(d)

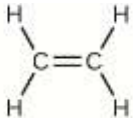


Solution
(a) C_4H_8
$4C \times 12.011 = 48.044$ amu
$8H \times 1.0079 = \underline{8.06352 \text{ amu}}$;
$= 56.107$ amu
(b) C_4H_6
$4C \times 12.011 = 48.044$ amu
$6H \times 1.0079 = \underline{6.0474 \text{ amu}}$;
$= 54.091$ amu
(c) $H_2Si_2Cl_4$
$2H \times 1.0079 = 2.01558$ amu
$2Si \times 28.0855 = 56.1710$ amu ;
$4Cl \times 35.4527 = \underline{141.8108 \text{ amu}}$
$= 199.9976$ amu
(d) H_3PO_4
$3H \times 1.0079 = 3.0237$ amu
$1P \times 30.973762 = 30.973762$ amu
$4O \times 15.9994 = \underline{63.9976 \text{ amu}}$
$= 97.9950$ amu

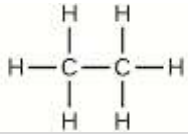
6. Which molecule has a molecular mass of 28.05 amu?
(a)



(b)



(c)



Solution
(b) 2×12.011 amu $+ 4 \times 1.008$ amu $= 28.05$ amu C_2H_4

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7. What information is needed to determine the molecular formula of a compound from the empirical formula?

Solution
After determining the empirical formula, additional information such as the molar mass, or the moles of an element per mole of the compound, must be given.

8. Calculate the following to four significant figures:
(a) the percent composition of ammonia, NH_3
(b) the percent composition of photographic fixer solution ("hypo"), $Na_2S_2O_3$
(c) the percent of calcium ion in $Ca_3(PO_4)_2$

Solution
In each of these exercises asking for the percent composition, divide the molecular weight of the desired element or group of elements (the number of times it/they occur in the formula times the molecular weight of the desired element or elements) by the molecular weight of the compound.

(a)
$$\%\ \mathrm{N} = \frac{14.0067\ \mathrm{g\ mol^{-1}} \times 100\%}{[3(1.007940 + 14.0067)]\ \mathrm{g\ mol^{-1}}} = \frac{14.0067\ \mathrm{g\ mol^{-1}}}{17.0305\ \mathrm{g\ mol^{-1}}} = 82.24\%$$
;
$$\%\ \mathrm{H} = \frac{3 \times 1.00794\ \mathrm{g\ mol^{-1}}}{17.0305\ \mathrm{g\ mol^{-1}}} \times 100\% = 17.76\%$$

(b)
$$\%\ \mathrm{Na} = \frac{2 \times 22.989768}{2 \times 22.989768 + 2 \times 32.066 + 3 \times 15.9994} \times 100\% = \frac{45.9795}{158.1097} \times 100 = 29.08\%$$
;
$$\%\ \mathrm{S} = \frac{64.132}{158.1097} \times 100\% = 40.56\%$$
$$\%\ \mathrm{O} = \frac{47.9982}{158.1097} \times 100\% = 30.36\%$$

(c)
$$\%\ \mathrm{Ca^{2+}} = \frac{3 \times 40.078}{3 \times 40.078 + 2 \times 30.973762 + 8 \times 15.9994} \times 100\% = \frac{120.234}{310.1816} \times 100\% = 38.76\%$$

9. Determine the following to four significant figures:
(a) the percent composition of hydrazoic acid, HN_3
(b) the percent composition of TNT, $C_6H_2(CH_3)(NO_2)_3$
(c) the percent of SO_4^{2-} in $Al_2(SO_4)_3$

Solution
(a)
$$\%\ \mathrm{H} = \frac{1.008}{43.029} \times 100 = 2.34\%$$
;
$$\%\ \mathrm{N} = \frac{42.021}{43.029} \times 100 = 97.66\%$$

(b)

$$\%\ C = \left(\frac{84.077}{227.132}\right) \times 100 = 37.01\%\ C$$

$$\%\ H = \left(\frac{5.040}{227.132}\right) \times 100 = 2.219\%\ H$$

;

$$\%\ O = \left(\frac{95.994}{227.132}\right) \times 100 = 42.26\%\ O$$

$$\%\ N = \left(\frac{42.021}{227.132}\right) \times 100 = 18.50\%\ N$$

(c) $\%\ SO_4^{2-} = \frac{3(32.066 + 4 \times 15.999) \times 100\%}{2 \times 26.982 + 3(32.066 + 4 \times 15.999)} = \frac{288.186 \times 100\%}{342.15} = 84.23\%$

10. Determine the percent ammonia, NH_3, in $Co(NH_3)_6Cl_3$, to three significant figures.

Solution

$$\%\ NH_3 = \frac{6(14.007 + 3 \times 1.008)}{58.933 + 6(14.007 + 3 \times 1.008) + 3(35.453)} \times 100\% = \frac{102.186}{267.478} \times 100\% = 38.2\%$$

11. Determine the percent water in $CuSO_4 \cdot 5H_2O$ to three significant figures.

Solution

$$\%\ H_2O = \frac{5(2 \times 1.008 + 15.999)}{63.546 + 32.066 + 4(15.999) + 5(2 \times 1.008 + 15.999)}$$

$$= \frac{90.075}{159.608 + 90.075} = \frac{90.075}{249.683} \times 100\% = 36.1\%$$

12. Determine the empirical formulas for compounds with the following percent compositions:
(a) 15.8% carbon and 84.2% sulfur
(b) 40.0% carbon, 6.7% hydrogen, and 53.3% oxygen

Solution

(a) The percent of an element in a compound indicates the percent by mass. The mass of an element in a 100.0-g sample of a compound is equal in grams to the percent of that element in the sample; hence, 100.0 g of the sample contains 15.8 g of C and 84.2 g of S. The relative number of moles of C and S atoms in the compound can be obtained by converting grams to moles as shown.

Step 1:

$$\text{C: } 15.8\ \text{g} \times \frac{1\ \text{mol}}{12.011\ \text{g}} = 1.315\ \text{mol}$$

$$\text{S: } 84.2\ \text{g} \times \frac{1\ \text{mol}}{32.066\ \text{g}} = 2.626\ \text{mol}$$

Step 2:

$$\text{C: } \frac{1.315\ \text{mol}}{1.315\ \text{mol}} = 1.000$$

$$\text{S: } \frac{2.626\ \text{mol}}{1.315\ \text{mol}} = 1.997$$

The empirical formula is CS_2.

(b) Step 1:

C: $40.0\ \text{g} \times \frac{1\ \text{mol}}{12.011\ \text{g}} = 3.330\ \text{mol}$

H: $6.7\ \text{g} \times \frac{1\ \text{mol}}{1.00794\ \text{g}} = 6.647\ \text{mol}$

O: $53.3\ \text{g} \times \frac{1\ \text{mol}}{15.9994\ \text{g}} = 3.331\ \text{mol}$

Step 2:

C: $\frac{3.330\ \text{mol}}{3.330\ \text{mol}} = 1.0$

H: $\frac{6.647\ \text{mol}}{3.330\ \text{mol}} = 2$

O: $\frac{3.331\ \text{mol}}{3.330\ \text{mol}} = 1.0$

The empirical formula is CH_2O.

13. Determine the empirical formulas for compounds with the following percent compositions:
(a) 43.6% phosphorus and 56.4% oxygen
(b) 28.7% K, 1.5% H, 22.8% P, and 47.0% O

Solution
(a) Step 1:

P: $43.6\ \cancel{\text{g}} \times \frac{1\ \text{mol}}{30.97376\ \cancel{\text{g}}} = 1.4076\ \text{mol}$

O: $56.4\ \cancel{\text{g}} \times \frac{1\ \text{mol}}{15.9994\ \cancel{\text{g}}} = 3.525\ \text{mol}$

Step 2:

P: $\frac{1.4076\ \cancel{\text{mol}}}{1.4076\ \cancel{\text{mol}}} = 1.000$ $\quad 1.0 \times 2 = 2.0$

O: $\frac{3.525\ \cancel{\text{mol}}}{1.4076\ \cancel{\text{mol}}} = 2.504$ $\quad 2.5 \times 2 = 5.0$

The empirical formula is P_2O_5.
(b)
Step 1:

K: $28.7\ \cancel{\text{g}} \times \frac{1\ \text{mol}}{39.0983\ \cancel{\text{g}}} = 0.7340\ \text{mol}$

H: $1.5\ \cancel{\text{g}} \times \frac{1\ \text{mol}}{1.00794\ \cancel{\text{g}}} = 1.4882\ \text{mol}$

P: $22.8\ \cancel{\text{g}} \times \frac{1\ \text{mol}}{30.9738\ \cancel{\text{g}}} = 0.7361\ \text{mol}$

O: $47.0\ \cancel{\text{g}} \times \frac{1\ \text{mol}}{15.9994\ \cancel{\text{g}}} = 2.9376\ \text{mol}$

Step 2:

K: $\frac{0.7340 \cancel{\text{ mol}}}{0.7340 \cancel{\text{ mol}}} = 1.00$

H: $\frac{1.4882 \cancel{\text{ mol}}}{0.7340 \cancel{\text{ mol}}} = 2.03$

P: $\frac{0.7361 \cancel{\text{ mol}}}{0.7340 \cancel{\text{ mol}}} = 1.00$

O: $\frac{2.9376 \cancel{\text{ mol}}}{0.7340 \cancel{\text{ mol}}} = 4.00$

The empirical formula is KH_2PO_4.

14. A compound of carbon and hydrogen contains 92.3% C and has a molar mass of 78.1 g/mol. What is its molecular formula?

Solution

To determine the empirical formula, a relationship between percent composition and atom composition must be established. The percent composition of each element in a compound can be found either by dividing its mass by the total mass of compound or by dividing the molar mass of that element as it appears in the formula (atomic mass times the number of times the element appears in the formula) by the formula mass of the compound. From this latter perspective, the percent composition of an element can be converted into a mass by assuming that we start with a 100-g sample. Then, multiplying the percentage times 100 g gives the mass in grams of that component. Division of each mass by its respective atomic mass gives the relative ratio of atoms in the formula. From the numbers so obtained, the whole-number ratio of elements in the compound can be found by dividing each ratio by the number representing the smallest ratio. Generally, this process can be done in two simple steps (a third step is needed if the ratios are not whole numbers).

Step 1: Divide each element's percentage (converted to grams) by its atomic mass:

C: $\frac{92.3 \text{ g}}{12.011 \text{ g mol}^{-1}} = 7.68 \text{ mol}$

H: $\frac{7.7 \text{ g}}{1.00794 \text{ g mol}^{-1}} = 7.6 \text{ mol}$

This operation established the relative ration of carbon to hydrogen in the formula.

Step 2: To establish a whole-number ratio of carbon to hydrogen, divide each factor by the smallest factor. In this case, both factors are essentially equal; thus the ration of atoms is 1 to 1:

C: $\frac{7.68}{7.6} = 1$

H: $\frac{7.6}{7.6} = 1$

The empirical formula is CH.

Since the molecular mass of the compound is 78.1 amu, some integer times the sum of the mass of 1C and 1H in atomic mass units (12.011 amu + 1.00794 amu = 13.019 amu) must be equal to 78.1 amu. To find this number, divide 78.1 amu by 13.019 amu:

$\frac{78.1 \text{ amu}}{13.019 \text{ amu}} = 5.9989 \longrightarrow 6$

The molecular formula is $(CH)_6 = C_6H_6$.

15. Dichloroethane, a compound that is often used for dry cleaning, contains carbon, hydrogen, and chlorine. It has a molar mass of 99 g/mol. Analysis of a sample shows that it contains 24.3% carbon and 4.1% hydrogen. What is its molecular formula?

Solution

The molecular formula is a whole-number multiple of the empirical formula, and the molecular mass is a whole-number multiple of the empirical mass. The solution sequence is to determine the empirical formula, the formula mass, and then the molecular formula.

Step 1:

$\text{C}: \dfrac{24.3}{12.011} = 2.02 \text{ mol}$

$\text{H}: \dfrac{4.1}{1.0079} = 4.07 \text{ mol}$

$\text{Cl}: \dfrac{71.6}{35.453} = 2.02 \text{ mol}$

Step 2:

$\text{C}: \dfrac{2.02}{2.02} = 1.0$

$\text{H}: \dfrac{4.07}{2.02} = 2.0$

$\text{Cl}: \dfrac{2.02}{2.02} = 1.0$

The empirical formula is CH_2Cl; the empirical formula mass is 49.5.

Molecular mass = (empirical formula mass) $\times$ (number of formula units)

$99 = 49.5 \times$ no. of formula units

Solve for the number of formula units: $\dfrac{99}{49.5} = 2$

Molecular formula: $2(CH_2Cl) = C_2H_4Cl_2$

16. Determine the empirical and molecular formula for chrysotile asbestos. Chrysotile has the following percent composition: 28.03% Mg, 21.60% Si, 1.16% H, and 49.21% O. The molar mass for chrysotile is 520.8 g/mol.

Solution

$(28.03 \text{ g Mg})\left(\dfrac{1 \text{ mol Mg}}{24.30 \text{ g}}\right) = 1.153 \text{ mol Mg} \qquad \dfrac{1.153}{0.769} = 1.512 \text{ mol Mg}$

$(21.60 \text{ g Si})\left(\dfrac{1 \text{ mol Si}}{28.09 \text{ g Si}}\right) = 0.769 \text{ mol Si} \qquad \dfrac{0.769}{0.769} = 1.00 \text{ mol Si}$

$(1.16 \text{ g H})\left(\dfrac{1 \text{ mol H}}{1.01 \text{ g H}}\right) = 1.149 \text{ mol H} \qquad \dfrac{1.149}{0.769} = 1.49 \text{ mol H}$

$(49.21 \text{ g O})\left(\dfrac{1 \text{ mol O}}{16.00 \text{ g O}}\right) = 3.076 \text{ mol O} \qquad \dfrac{3.076}{0.769} = 4.00 \text{ mol O}$

$(2)(Mg_{1.5}Si_1H_{1.5}O_4) = Mg_3Si_2H_3O_8$ (empirical formula), empirical mass of 260.1 g/unit

$\dfrac{\text{MM}}{\text{EM}} = \dfrac{520.8}{260.1} = 2.00$, so $(2)(Mg_3Si_2H_3O_8) = Mg_6Si_4H_6O_{16}$

17. Polymers are large molecules composed of simple units repeated many times. Thus, they often have relatively simple empirical formulas. Calculate the empirical formulas of the following polymers:
(a) Lucite (Plexiglas); 59.9% C, 8.06% H, 32.0% O
(b) Saran; 24.8% C, 2.0% H, 73.1% Cl
(c) polyethylene; 86% C, 14% H
(d) polystyrene; 92.3% C, 7.7% H
(e) Orlon; 67.9% C, 5.70% H, 26.4% N

Solution
(a)

Step 1:

$$\text{C: } 59.9 \cancel{\text{g}} \times \frac{1 \text{ mol}}{12.011 \cancel{\text{g}}} = 4.99 \text{ mol}$$

$$\text{H: } 8.06 \cancel{\text{g}} \times \frac{1 \text{ mol}}{1.00794 \cancel{\text{g}}} = 8.00 \text{ mol}$$

$$\text{O: } 32.0 \cancel{\text{g}} \times \frac{1 \text{ mol}}{15.9994 \cancel{\text{g}}} = 2.00 \text{ mol}$$

Step 2:

$$\text{C: } \frac{4.99}{2.00} = 2.5$$

$$\text{H: } \frac{8.00}{2.00} = 4.0$$

$$\text{O: } \frac{2.00}{2.00} = 1.0$$

Step 3:

$$\text{C: } 2.5 \times 2 = 5.0$$
$$\text{H: } 4.0 \times 2 = 8.0$$
$$\text{O: } 1.0 \times 2 = 2.0$$

The empirical formula is $C_5H_8O_2$.

(b)

Step 1:

$$\text{C: } 24.8 \cancel{\text{g}} \times \frac{1 \text{ mol}}{12.011 \cancel{\text{g}}} = 2.06 \text{ mol}$$

$$\text{H: } 2.0 \cancel{\text{g}} \times \frac{1 \text{ mol}}{1.00794 \cancel{\text{g}}} = 2.0 \text{ mol}$$

$$\text{Cl: } 73.1 \cancel{\text{g}} \times \frac{1 \text{ mol}}{35.453 \cancel{\text{g}}} = 2.06 \text{ mol}$$

Step 2:

$$\text{C: } \frac{2.06\ \cancel{\text{mol}}}{2.06\ \cancel{\text{mol}}} = 1$$

$$\text{H: } \frac{2.0\ \cancel{\text{mol}}}{2.06\ \cancel{\text{mol}}} = 1$$

$$\text{Cl: } \frac{2.06\ \cancel{\text{mol}}}{2.06\ \cancel{\text{mol}}} = 1$$

The empirical formula is CHCl.

(c)

Step 1:

$$\text{C: } \frac{86\ \cancel{\text{g}}}{12.011\ \cancel{\text{g}}\ \text{mol}^{-1}} = 7.2\ \text{mol}$$

$$\text{H: } \frac{14\ \cancel{\text{g}}}{1.00794\ \cancel{\text{g}}\ \text{mol}^{-1}} = 14\ \text{mol}$$

Step 2:

$$\text{C: } \frac{7.2\ \cancel{\text{mol}}}{7.2\ \cancel{\text{mol}}} = 1$$

$$\text{H: } \frac{14\ \text{mol}}{7.2\ \text{mol}} = 1.9 \approx 2$$

The empirical formula is CH_2.

(d)

Step 1:

$$\text{C: } 92.3\ \cancel{\text{g}} \times \frac{1\ \text{mol}}{12.011\ \cancel{\text{g}}} = 7.68\ \text{mol}$$

$$\text{H: } 7.7\ \cancel{\text{g}} \times \frac{1\ \text{mol}}{1.00794\ \cancel{\text{g}}} = 7.64\ \text{mol}$$

Step 2:

$$\text{C: } \frac{7.68\ \cancel{\text{mol}}}{7.64\ \cancel{\text{mol}}} = 1$$

$$\text{H: } \frac{7.64\ \text{mol}}{7.64\ \text{mol}} = 1$$

The empirical formula is CH.

(e)

Step 1:

C: $\frac{67.9\ \cancel{g}}{12.011\ \cancel{g}\ \text{mol}^{-1}} = 5.65\ \text{mol}$

H: $\frac{5.70\ \cancel{g}}{1.00794\ \cancel{g}\ \text{mol}^{-1}} = 5.66\ \text{mol}$

N: $\frac{26.4\ \text{g}}{14.0067\ \text{g mol}^{-1}} = 1.88\ \text{mol}$

Step 2:

C: $\frac{5.65\ \cancel{\text{mol}}}{1.88\ \cancel{\text{mol}}} = 3.01$

H: $\frac{5.66\ \cancel{\text{mol}}}{1.88\ \cancel{\text{mol}}} = 3.01$

N: $\frac{1.88\ \cancel{\text{mol}}}{1.88\ \cancel{\text{mol}}} = 1.00$

The empirical formula is C_3H_3N.

18. A major textile dye manufacturer developed a new yellow dye. The dye has a percent composition of 75.95% C, 17.72% N, and 6.33% H by mass with a molar mass of about 240 g/mol. Determine the molecular formula of the dye.

Solution
Assume 100.0 g; the percentages of the elements are then the same as their mass in grams. Divide each mass by the molar mass to find the number of moles.
Step 1:

$\frac{75.95\ \cancel{g}}{12.011\ \cancel{g}\,\text{mol}^{-1}} = 6.323\ \text{mol C}$

$\frac{17.72\ \cancel{g}}{14.0067\ \cancel{g}\,\text{mol}^{-1}} = 1.265\ \text{mol N}$

$\frac{6.33\ \cancel{g}}{1.00794\ \cancel{g}\,\text{mol}^{-1}} = 6.28\ \text{mol H}$

Step 2: Divide each by the smallest number. The answers are 5C, 1N, and 5H. The empirical formula is C_5H_5N, which has a molar mass of 79.10 g/mol. To find the actual molecular formula, divide 240, the molar mass of the compound, by 79.10 to obtain 3. So the formula is three times the empirical formula, or $C_{15}H_{15}N_3$.

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19. Explain what changes and what stays the same when 1.00 L of a solution of NaCl is diluted to 1.80 L.

Solution
The mass and number of moles of NaCl stay the same. The volume of the solution and the concentration of NaCl change.

20. What information is needed to calculate the molarity of a sulfuric acid solution?

Solution
We need to know the number of moles of sulfuric acid dissolved in the solution and the volume of the solution.

21. A 200-mL sample and a 400-mL sample of a solution of salt have the same molarity. In what ways are the two samples identical? In what ways are these two samples different?

Solution
When a 200-mL and a 400-mL sample have the same concentration, both solutions have the same amount of salt per unit volume. The solutions are different in that the 400 mL solution contains twice as much salt.

22. Determine the molarity for each of the following solutions:
(a) 0.444 mol of $CoCl_2$ in 0.654 L of solution
(b) 98.0 g of phosphoric acid, H_3PO_4, in 1.00 L of solution
(c) 0.2074 g of calcium hydroxide, $Ca(OH)_2$, in 40.00 mL of solution
(d) 10.5 kg of $Na_2SO_4 \cdot 10H_2O$ in 18.60 L of solution
(e) 7.0×10^{-3} mol of I_2 in 100.0 mL of solution
(f) 1.8×10^4 mg of HCl in 0.075 L of solution

Solution
(a) $\dfrac{0.444 \text{ mol}}{0.654 \text{ L}} = 0.679 \text{ mol L}^{-1} = 0.679\ M$;
(b) First convert mass in grams to moles, and then substitute the proper terms into the definition.
Molar mass of H_3PO_4 = 97.995 g/mol

$$\text{mol } (H_3PO_4) = 98.0 \text{ g} \times \frac{1 \text{ mol}}{97.995 \text{ g}} = 1.00 \text{ mol}$$

$$M = \frac{1.00 \text{ mol}}{1.00 \text{ L}} = 1.00\ M;$$

(c) Molar mass $[Ca(OH)_2]$ = 74.09 g/mol

$$0.2074 \text{ g} \times \frac{1 \text{ mol}}{74.09 \text{ g}} = 0.002799 \text{ mol } Ca(OH)_2$$

$$\frac{0.002799 \text{ mol}}{0.0400 \text{ L}} = 0.06998 \text{ mol L}^{-1} = 0.06998\ M;$$

(d) Molar mass $(Na_2SO_4 \cdot 10H_2O)$ = 322.20 g/mol

$$10{,}500 \times \frac{1 \text{ mol}}{322.20 \text{ g}} = 32.6 \text{ mol}$$

$$\frac{32.6 \text{ mol}}{18.60 \text{ L}} = 1.75\ M;$$

(e) $M = \dfrac{\text{millimoles solute}}{\text{volume of solution in milliliters}}$

$\frac{7.00 \text{ mmol } I_2}{100 \text{ mL}} = 0.070\ M$;
(f) Molar mass (HCl) = 36.46 g/mol

$$\text{mass (HCl)} = 1.8 \times 10^1 \text{ g HCl} \times \frac{1 \text{ mol}}{36.46 \text{ g}} = 0.49 \text{ mol HCl}$$

$$\frac{0.49 \text{ mol HCl}}{0.075 \text{ L}} = 6.6\ M$$

23. Determine the molarity of each of the following solutions:
(a) 1.457 mol KCl in 1.500 L of solution
(b) 0.515 g of H_2SO_4 in 1.00 L of solution
(c) 20.54 g of $Al(NO_3)_3$ in 1575 mL of solution
(d) 2.76 kg of $CuSO_4 \cdot 5H_2O$ in 1.45 L of solution
(e) 0.005653 mol of Br_2 in 10.00 mL of solution
(f) 0.000889 g of glycine, $C_2H_5NO_2$, in 1.05 mL of solution

Solution
Make any conversions of units as necessary before setting up the problem and calculate the molar mass where necessary.

(a) $\frac{1.457 \text{ mol KCl}}{1.500 \text{ L}} = 0.9713\ M$;

(b) $\frac{\frac{0.515 \text{ g}}{98.079 \text{ g mol}^{-1}}}{1.00 \text{ L}} = 0.00525\ M$;

(c) $\frac{\frac{20.54 \text{ g}}{213.00 \text{ g mol}^{-1}}}{1.575 \text{ L}} = 0.06123\ M$;

(d) $\frac{\frac{2.76 \times 10^3 \text{ g}}{429.69 \text{ g mol}^{-1}}}{1.45 \text{ L}} = 7.62\ M$;

(e) $\frac{0.005653 \text{ mol}}{0.01000 \text{ L}} = 0.5653\ M$;

(f) $\frac{\frac{0.000889 \text{ g}}{75.0675 \text{ g mol}^{-1}}}{0.00105 \text{ L}} = 0.0113\ M$

24. Consider this question: What is the mass of the solute in 0.500 L of 0.30 *M* glucose, $C_6H_{12}O_6$, used for intravenous injection?
(a) Outline the steps necessary to answer the question.
(b) Answer the question.

Solution
(a) determine the number of moles of glucose in 0.500 L of solution; determine the molar mass of glucose; determine the mass of glucose from the number of moles and its molar mass; (b) 0.500 L contains 0.30 $M \times 0.500$ L = 1.5×10^{-1} mol. Molar mass (glucose): 6×12.0011 g + 12×1.00794 g + 6×15.9994 g = 180.158 g, 1.5×10^{-1} ~~mol~~ × 180.158 g/~~mol~~ = 27 g.

25. Consider this question: What is the mass of solute in 200.0 L of a 1.556-*M* solution of KBr?

(a) Outline the steps necessary to answer the question.
(b) Answer the question.

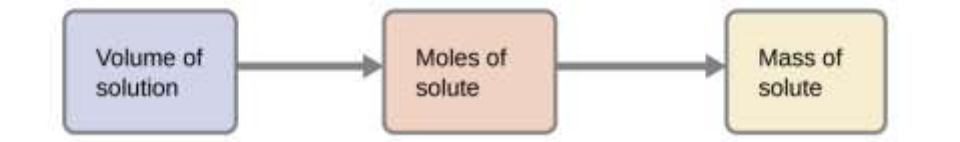
Solution

(a) Determine the number of moles of KBr in 200.0 L of a 1.556-*M* solution. Determine the formula mass of KBr. Then determine the mass of KBr from the number of moles and its formula mass. (b) mol KBr = 200.0 L × 1.556 *M* = 311.2 mol
Mass (formula) = 39.0983 g/mol + 79.904 g/mol = 119.002 g/mol
Mass (KBr) = 311.2 mol × 119.002 g/mol = 3.703×10^4 g

26. Calculate the number of moles and the mass of the solute in each of the following solutions:
(a) 2.00 L of 18.5 *M* H_2SO_4, concentrated sulfuric acid
(b) 100.0 mL of 3.8×10^{-6} *M* NaCN, the minimum lethal concentration of sodium cyanide in blood serum
(c) 5.50 L of 13.3 *M* H_2CO, the formaldehyde used to "fix" tissue samples
(d) 325 mL of 1.8×10^{-6}*M* $FeSO_4$, the minimum concentration of iron sulfate detectable by taste in drinking water

Solution

The molarity must be converted to moles of solute, which is then converted to grams of solute:



$$M = \frac{\text{mol}}{\text{liter}} \text{ or mol} = M \times \text{liter}$$

(a)
$$\text{mol } H_2SO_4 = 2.00 \cancel{\text{ L}} \times \frac{18.5 \text{ mol}}{\cancel{\text{L}}} = 37.0 \text{ mol } H_2SO_4$$
$$37.0 \cancel{\text{ mol } H_2SO_4} \times \frac{98.08 \text{ g } H_2SO_4}{1 \cancel{\text{ mol } H_2SO_4}} = 3.63 \times 10^3 \text{ g } H_2SO_4 ;$$

(b)
$$\text{mol NaCN} = 0.1000 \cancel{\text{ L}} \times \frac{3.8 \times 10^{-6} \text{ mol}}{\cancel{\text{L}}} = 3.8 \times 10^{-7} \text{ mol NaCN}$$
$$3.8 \times 10^{-7} \cancel{\text{ mol NaCN}} \times \frac{49.01 \text{ g}}{1 \cancel{\text{ mol NaCN}}} = 1.9 \times 10^{-5} \text{ g NaCN} ;$$

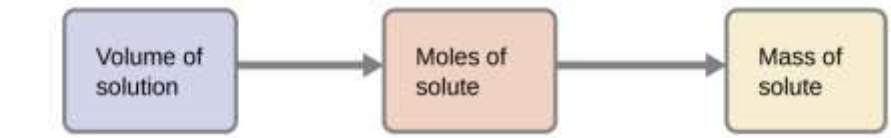
(c)
$$\text{mol } H_2CO = 5.50 \cancel{\text{ L}} \times \frac{13.3 \text{ mol}}{\cancel{\text{L}}} = 73.2 \text{ mol } H_2CO$$
$$73.2 \cancel{\text{ mol } H_2CO} \times \frac{30.026 \text{ g}}{1 \cancel{\text{ mol } H_2CO}} = 2198 \text{ g } H_2CO = 2.20 \text{ kg } H_2CO ;$$

(d)
$$\text{mol } FeSO_4 = 0.325 \cancel{\text{ L}} \times \frac{1.8 \times 10^{-6} \text{ mol}}{\cancel{\text{L}}} = 5.9 \times 10^{-7} \text{ mol } FeSO_4$$
$$5.85 \times 10^{-7} \cancel{\text{ mol } FeSO_4} \times \frac{151.9 \text{ g}}{1 \cancel{\text{ mol } FeSO_4}} = 8.9 \times 10^{-5} \text{ g } FeSO_4$$

27. Calculate the number of moles and the mass of the solute in each of the following solutions:
(a) 325 mL of 8.23×10^{-5}*M* KI, a source of iodine in the diet
(b) 75.0 mL of 2.2×10^{-5} *M* H_2SO_4, a sample of acid rain
(c) 0.2500 L of 0.1135 *M* K_2CrO_4, an analytical reagent used in iron assays

(d) 10.5 L of 3.716 *M* $(NH_4)_2SO_4$, a liquid fertilizer

Solution



M = mol/L or mol = *M* × L; convert mL to L to begin;

(a) mol KI = 0.325 L × $8.23 \times 10^{-5} M = 2.67 \times 10^{-5}$ mol KI

$$2.67 \times 10^{-5} \text{ mol KI} \times \frac{166.0028 \text{ g}}{1 \text{ mol KI}} = 4.43 \times 10^{-3} \text{ g KI};$$

(b) mol H_2SO_4 = 0.0750 L × $2.2 \times 10^{-5} M = 1.6 \times 10^{-6}$mol H_2SO_4

$$1.6 \times 10^{-6} \text{ mol } H_2SO_4 \times \frac{98.079 \text{ g}}{1 \text{ mol } H_2SO_4} = 1.6 \times 10^{-6} \text{ g } H_2SO_4;$$

(c) mol K_2CrO_4 = 0.2500 L × 0.1135 *M* = 0.02838 mol K_2CrO_4

$$0.02838 \text{ mol } K_2CrO_4 \times \frac{194.1903 \text{ g}}{1 \text{ mol } K_2CrO_4} = 5.511 \text{ g } K_2CrO_4;$$

(d) mol $(NH_4)_2SO_4$ = 10.5 L × 3.716 *M* = 39.0 mol $(NH_4)_2SO_4$

$$39.0 \text{ mol } (NH_4)_2SO_4 \times \frac{132.141 \text{ g}}{\text{mol } (NH_4)_2SO_4} = 5.15 \times 10^3 \text{ g } (NH_4)_2SO_4$$

28. Consider this question: What is the molarity of $KMnO_4$ in a solution of 0.0908 g of $KMnO_4$ in 0.500 L of solution?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

Solution

(a) determine the molar mass of $KMnO_4$; determine the number of moles of $KMnO_4$ in the solution; from the number of moles and the volume of solution, determine the molarity; (b) Molar mass of $KMnO_4$ = 158.0264 g/mol

$$\text{mol } KMnO_4 = 0.0908 \text{ g } KMnO_4 \times \frac{1 \text{ mol}}{158.0264 \text{ g } KMnO_4} = 5.746 \times 10^{-4} \text{ mol}$$

$$M \text{ } KMnO_4 = \frac{5.746 \times 10^{-4} \text{ mol}}{0.500 \text{ L}} = 1.15 \times 10^{-3} \text{ } M$$

29. Consider this question: What is the molarity of HCl if 35.23 mL of a solution of HCl contain 0.3366 g of HCl?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

Solution

(a) Determine the molar mass of HCl. Determine the number of moles of HCl in the solution. From the number of moles and the volume of solution, determine the molarity. (b) Molar mass of HCl = 36.4606

$$\text{mol HCl} = 0.3366 \text{ g HCl} \times \frac{1 \text{ mol}}{36.4606 \text{ g HCl}} = 9.232 \times 10^{-3} \text{ mol}$$

$$M \text{ HCl} = \frac{9.232 \times 10^{-3} \text{ mol}}{0.03523 \text{ L}} = 0.2620 \text{ } M$$

30. Calculate the molarity of each of the following solutions:
(a) 0.195 g of cholesterol, $C_{27}H_{46}O$, in 0.100 L of serum, the average concentration of cholesterol in human serum
(b) 4.25 g of NH_3 in 0.500 L of solution, the concentration of NH_3 in household ammonia
(c) 1.49 kg of isopropyl alcohol, C_3H_7OH, in 2.50 L of solution, the concentration of isopropyl alcohol in rubbing alcohol
(d) 0.029 g of I_2 in 0.100 L of solution, the solubility of I_2 in water at 20 °C

Solution

(a) $M\ C_{27}H_{46}O = \frac{\text{mol}}{V} = \frac{\frac{0.195\ \cancel{\text{g}}\ C_{27}H_{46}O}{386.660\ \cancel{\text{g}}\ \text{mol}^{-1}\ C_{27}H_{46}O}}{0.100\ \text{L}} = 5.04 \times 10^{-3}\ M$;

(b) $M\ NH_3 = \frac{\text{mol}}{V} = \frac{\frac{4.25\ \cancel{\text{g}}\ NH_3}{17.0304\ \cancel{\text{g}}\ \text{mol}^{-1}\ NH_3}}{0.500\ \text{L}} = 0.499\ M$;

(c) $M\ C_3H_7OH = \frac{\text{mol}}{V} = \frac{1.49\ \cancel{\text{kg}}\ C_3H_7OH \times \frac{1000\ \cancel{\text{g}}}{1\ \cancel{\text{kg}}} \times \frac{1\ \text{mol}\ C_3H_7OH}{60.096\ \cancel{\text{g}}}}{2.50\ \text{L}} = 9.92\ M$;

(d) $M\ I_2 = \frac{\text{mol}}{V} = \frac{\frac{0.029\ \cancel{\text{g}}\ I_2}{253.8090\ \cancel{\text{g}}\ \text{mol}^{-1}\ I_2}}{0.100\ \text{L}} = 1.1 \times 10^{-3}\ M$

31. Calculate the molarity of each of the following solutions:
(a) 293 g HCl in 666 mL of solution, a concentrated HCl solution
(b) 2.026 g $FeCl_3$ in 0.1250 L of a solution used as an unknown in general chemistry laboratories
(c) 0.001 mg Cd^{2+} in 0.100 L, the maximum permissible concentration of cadmium in drinking water
(d) 0.0079 g $C_7H_5SNO_3$ in one ounce (29.6 mL), the concentration of saccharin in a diet soft drink.

Solution

(a) $M\ HCl = \frac{\text{mol}}{V} = \frac{293\ \cancel{\text{g HCl}} \times \frac{1\ \text{mol}}{36.4606\ \cancel{\text{g HCl}}}}{0.666\ \text{L}} = 12.1\ M$;

(b) $M\ FeCl_3 = \frac{\text{mol}}{V} = \frac{2.026\ \cancel{\text{g FeCl}_3} \times \frac{1\ \text{mol}}{162.205\ \cancel{\text{g FeCl}_3}}}{0.1250\ \text{L}} = 0.09992\ M$;

(c) $M\ Cd^{2+} = \frac{\text{mol}}{V} = \frac{0.001\ \cancel{\text{g Cd}}^{2+} \times \frac{0.001\ \cancel{\text{g}}}{1\ \cancel{\text{mg}}} \times \frac{1\ \text{mol}}{112.411\ \cancel{\text{g Cd}}^{2+}}}{0.100\ \text{L}} = 9 \times 10^{-8}\ M$;

(d) $M\ C_7H_5SNO_3 = \frac{\text{mol}}{V} = \frac{0.0079\ \cancel{\text{g C}_7\text{H}_5\text{SNO}_3} \times \frac{1\ \text{mol}}{183.188\ \cancel{\text{g C}_7\text{H}_5\text{SNO}_3}}}{0.0296\ \text{L}} = 1.5 \times 10^{-3}\ M$

32. There is about 1.0 g of calcium, as Ca^{2+}, in 1.0 L of milk. What is the molarity of Ca^{2+} in milk?

Solution

$$M = \frac{\text{mol}}{V} = \frac{\frac{1.0\ \cancel{\text{g}}}{40.08\ \cancel{\text{g}}\ \text{mol}^{-1}}}{1.0\ \text{L}} = 0.025\ M$$

33. What volume of a 1.00-*M* $Fe(NO_3)_3$ solution can be diluted to prepare 1.00 L of a solution with a concentration of 0.250 *M*?

Solution

$$V_1 = \frac{V_2 \times M_2}{M_2} = 1.00\ \text{L} \times \frac{0.250\ M}{1.00\ M} = 0.250\ \text{L}$$

34. If 0.1718 L of a 0.3556-*M* C_3H_7OH solution is diluted to a concentration of 0.1222 *M*, what is the volume of the resulting solution?

Solution

$$\frac{C_1V_1}{C_2} = V_2$$

$$\frac{\frac{0.3556\ \text{mol}}{\text{L}} \times 0.1718\ \text{L}}{\frac{0.1222\ \text{mol}}{\text{L}}} = V_2$$

$$0.5000\ \text{L} = V_2$$

35. If 4.12 L of a 0.850 *M*-H_3PO_4 solution is be diluted to a volume of 10.00 L, what is the concentration the resulting solution?

Solution

$$\frac{C_1V_1}{V_2} = C_2$$

$$\frac{\frac{0.850\ \text{mol}}{\text{L}} \times 4.12\ \text{L}}{10.00\ \text{L}} = C_2$$

$$0.350\ M = C_2$$

36. What volume of a 0.33-*M* $C_{12}H_{22}O_{11}$ solution can be diluted to prepare 25 mL of a solution with a concentration of 0.025 *M*?

Solution

$$V_1 = \frac{V_2 \times M_2}{M_2} = 25\ \text{mL} \times \frac{0.025\ M}{0.33\ M} = 1.9\ \text{mL}$$

37. What is the concentration of the NaCl solution that results when 0.150 L of a 0.556-*M* solution is allowed to evaporate until the volume is reduced to 0.105 L?

Solution

$$M_2 = \frac{V_1 \times M_1}{V_2} = 0.150\ \text{L} \times \frac{0.556\ M}{0.105\ \text{L}} = 0.794\ M$$

38. What is the molarity of the diluted solution when each of the following solutions is diluted to the given final volume?

(a) 1.00 L of a 0.250-*M* solution of $Fe(NO_3)_3$is diluted to a final volume of 2.00 L

(b) 0.5000 L of a 0.1222-*M* solution of C_3H_7OH is diluted to a final volume of 1.250 L

(c) 2.35 L of a 0.350-*M* solution of H_3PO_4 is diluted to a final volume of 4.00 L

(d) 22.50 mL of a 0.025-*M* solution of $C_{12}H_{22}O_{11}$ is diluted to 100.0 mL

Solution

(a) $C_2 = \frac{V_1 \times C_1}{V_2} = 1.00 \cancel{\text{L}} \times \frac{0.250M}{2.00 \cancel{\text{L}}} = 0.125\ M$;

(b) $C_2 = \frac{V_1 \times C_1}{V_2} = 0.5000 \cancel{\text{L}} \times \frac{0.1222\ M}{1.250 \cancel{\text{L}}} = 0.04888\ M$;

(c) $C_2 = \frac{V_1 \times C_1}{V_2} = 2.35 \cancel{\text{L}} \times \frac{0.350M}{4.00 \cancel{\text{L}}} = 0.206\ M$;

(d) $C_2 = \frac{V_1 \times C_1}{V_2} = 22.50\ \text{L} \times \frac{0.025\ M}{100\ \text{L}} = 0.0056\ M$

39. What is the final concentration of the solution produced when 225.5 mL of a 0.09988-*M* solution of Na_2CO_3 is allowed to evaporate until the solution volume is reduced to 45.00 mL?

Solution

$C_2 = \frac{V_1 \times C_1}{V_2} = 225.5 \cancel{\text{mL}} \times \frac{0.09988\ M}{45.00 \cancel{\text{mL}}} = 0.5005$

40. A 2.00-L bottle of a solution of concentrated HCl was purchased for the general chemistry laboratory. The solution contained 868.8 g of HCl. What is the molarity of the solution?

Solution

Determine the number of moles in 434.4 g of HCl: 1.00794 + 35.4527 = 36.4606 g/mol

$\text{mol HCl} = \frac{434.4 \cancel{\text{g}}}{36.4606 \cancel{\text{g}}\ \text{mol}^{-1}} = 11.91\ \text{mol}$

This HCl is present in 1.00 L, so the molarity is 11.9 *M*.

41. An experiment in a general chemistry laboratory calls for a 2.00-*M* solution of HCl. How many mL of 11.9 *M* HCl would be required to make 250 mL of 2.00 *M* HCl?

Solution

Use $C_1V_1 = C_2V_2$.

$V_1 = \frac{250\ \text{mL} \times 2.00\ M}{11.9\ M} = 42.0\ \text{mL}$

42. What volume of a 0.20-*M* K_2SO_4 solution contains 57 g of K_2SO_4?

Solution

$57\ \text{g}\ K_2SO_4 \times \frac{1\ \text{mol}}{174.26\ \text{g}} \times \frac{1\ \text{L}}{0.20\ \text{mol}} = 1.6\ \text{L}$

43. The US Environmental Protection Agency (EPA) places limits on the quantities of toxic substances that may be discharged into the sewer system. Limits have been established for a variety of substances, including hexavalent chromium, which is limited to 0.50 mg/L. If an industry is discharging hexavalent chromium as potassium dichromate ($K_2Cr_2O_7$), what is the maximum permissible molarity of that substance?

Solution

$\frac{0.50\ \text{mg}}{\text{L}} \times \frac{1\ \text{g}}{1000\ \text{mg}} \times \frac{1\ \text{mol}}{294.1846\ \text{g}} = 1.7 \times 10^{-6}\ M$

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Chemistry: Atoms First 2e
6: Composition of Substances and Solutions
6.4: Other Units for Solution Concentrations

44. Consider this question: What mass of a concentrated solution of nitric acid (68.0% HNO_3 by mass) is needed to prepare 400.0 g of a 10.0% solution of HNO_3 by mass?
(a) Outline the steps necessary to answer the question.
(b) Answer the question.

Solution
(a) The dilution equation can be used, appropriately modified to accommodate mass-based concentration units:
$\%\text{mass}_1 \times \text{mass}_1 = \%\text{mass}_2 \times \text{mass}_2$
This equation can be rearranged to isolate mass_1 and the given quantities substituted into this equation.

(b) $\text{mass}_1 = \dfrac{\%\text{mass}_2 \times \text{mass}_2}{\%\text{mass}_1} = \dfrac{10.0\ \% \times 400.0\ \text{g}}{68.0\ \%} = 58.8\ \text{g}$

45. What mass of a 4.00% NaOH solution by mass contains 15.0 g of NaOH?

Solution

$$\text{mass (NaOH solution)} \times \frac{4.00\%}{100.0\%} = 15.0\ \text{g}$$

$$\text{mass (NaOH solution)} \times \frac{15.0\ \text{g}}{0.0400} = 375\ \text{g}$$

46. What mass of solid NaOH (97.0% NaOH by mass) is required to prepare 1.00 L of a 10.0% solution of NaOH by mass? The density of the 10.0% solution is 1.109 g/mL.

Solution

$$1000\ \cancel{\text{cm}}^3 \times \frac{1.109\ \text{g}}{\cancel{\text{cm}}^3} = 1.11 \times 10^3\ \text{g}.$$

The mass of pure NaOH required is

$$\text{mass}\ (\text{NaOH}) = \frac{10.0\%}{100.0\%} \times 1.11 \times 10^3\ \text{g} = 1.11 \times 10^2\ \text{g}.$$

This mass of NaOH must come from the 97.0% solution:

$$\text{mass (NaOH solution)} \times \frac{97.0\%}{100.0\%} = 1.11 \times 10^2\ \text{g}$$

$$\text{mass (NaOH solution)} = \frac{1.11 \times 10^2\ \text{g}}{0.970} = 114\ \text{g}$$

47. What mass of HCl is contained in 45.0 mL of an aqueous HCl solution that has a density of 1.19 g cm^{-3} and contains 37.21% HCl by mass?

Solution
The solution contains 37.21% HCl by mass, and the remainder is water. Calculate the mass of the 45.0-mL sample, and then multiply by the percentage to obtain the mass of HCl. Since 1 cm^3 = 1 mL. Mass (sample) = 45.0 $\cancel{\text{mL}}$ × 1.19 g/$\cancel{\text{mL}}$ = 53.55 g; Mass (HCl) = 53.55 g × 0.3721 = 19.9 g

48. The hardness of water (hardness count) is usually expressed in parts per million (by mass) of $CaCO_3$, which is equivalent to milligrams of $CaCO_3$ per liter of water. What is the molar concentration of Ca^{2+} ions in a water sample with a hardness count of 175 mg $CaCO_3$/L?

Solution
Since $CaCO_3$ contains 1 mol Ca^{2+} per mol of $CaCO_3$, the molar concentration of Ca^{2+} equals the molarity of $CaCO_3$:

$$M\ \mathrm{Ca}^{2+} = \frac{\text{mol CaCO}_3}{\text{L}} = \frac{175\ \cancel{\text{mg}} \times \left(\frac{1\ \text{mol}}{100.0792\ \cancel{\text{g}}}\right) \times \left(\frac{1\ \cancel{\text{g}}}{1000\ \cancel{\text{mg}}}\right)}{1\ \text{L}} = 1.75 \times 10^{-3}\ M$$

49. The level of mercury in a stream was suspected to be above the minimum considered safe (1 part per billion by weight). An analysis indicated that the concentration was 0.68 parts per billion. Assume a density of 1.0 g/mL and calculate the molarity of mercury in the stream.

Solution
Convert 0.68 parts per billion to mass in grams:

$$\text{mass Hg} = \frac{0.68\ \cancel{\text{g}}\ \text{Hg}}{1 \times 10^{9}\ \cancel{\text{g}}\ \text{solution}} = 6.8 \times 10^{-10}\ \frac{\text{g Hg}}{\text{g solution}}$$

$$\text{mol Hg} = \frac{6.8 \times 10^{-10}\ \frac{\cancel{\text{g}}\ \text{Hg}}{\text{g solution}}}{200.59\ \cancel{\text{g}}\ \text{mol}^{-1}} = 3.4 \times 10^{-12}\ \frac{\text{mol Hg}}{\text{g solution}}$$

$$\text{molarity of Hg} = \frac{3.4 \times 10^{-12}\ \text{mol Hg}}{\text{g solution}} \times \frac{1.0\ \text{g solution}}{\text{mL solution}} \times \frac{1000\ \text{mL}}{1\ \text{L}} = 3.4 \times 10^{-9}\ M$$

50. In Canada and the United Kingdom, devices that measure blood glucose levels provide a reading in millimoles per liter. If a measurement of 5.3 m*M* is observed, what is the concentration of glucose ($C_6H_{12}O_6$) in mg/dL?

Solution
1 mg/dL = 0.01 g/L and 1 L = 10 dL
5.3 mmol/L × 180.158 mg/mmol = 9.5×10^2 mg/L

$$9.5 \times 10^2 \text{mg/L} \times \frac{1\ \text{L}}{10\ \text{dL}} = 95\ \text{mg/dL}$$

51. A throat spray is 1.40% by mass phenol, C_6H_5OH, in water. If the solution has a density of 0.9956 g/mL, calculate the molarity of the solution.

Solution
Assume 1.000 L of solution. Then
1000 mL × 0.9956 g/mL = 995.6 g
995.6 g × 1.40% = 995.6 g × 0.0140 = 13.9 g.
The molar mass of phenol is:
6 × C = 6 × 12.011 = 72.066
6 × H = 6 × 1.00794 = 6.04764
1 × O = 1 × 15.9994 = 15.9994
94.113 g mol^{-1}

$$\text{mol phenol} = \frac{13.9\ \cancel{\text{g}}}{94.113\ \cancel{\text{g}}\ \text{mol}^{-1}} = 0.148\ \text{mol};$$

Since this value is the number of moles in 1 L, the molarity is 0.148 *M*.

52. Copper(I) iodide (CuI)is often added to table salt as a dietary source of iodine. How many moles of CuI are contained in 1.00 lb (454 g) of table salt containing 0.0100% CuI by mass?

Solution
0.0100% of 454 g is (0.000100 × 454 g) = 0.0454 g;
Molar mass of CuI = 63.546 + 126.90447 = 190.450 g/mol;

$$\text{mol CuI} = \frac{0.0454\ \text{g}}{190.450\ \text{g mol}^{-1}} = 0.000238\ \text{mol} = 2.38 \times 10^{-4}\ \text{mol}$$

53. A cough syrup contains 5.0% ethyl alcohol, C_2H_5OH, by mass. If the density of the solution is 0.9928 g/mL, determine the molarity of the alcohol in the cough syrup.

Solution
Assume that we start with 1000 mL of liquid. Then

$$\frac{0.9928\ \text{g}}{\text{mL}^{-1}} \times 1000\ \text{mL} = 992.8\ \text{g};$$

992.8 g × 5.0% = 992.8 g × 0.050 = 49.64 g;
the molar mass of ethanol, C_2H_5OH, is:
2 × 12.011 + 6 × 1.00794 + 15.9994 = 46.069 g/mol;

$$\text{Mol ethanol} = \frac{49.64\ \text{g}}{46.069\ \text{g mol}^{-1}} = 1.1\ \text{mol};$$

since this amount of ethanol is present in a 1 L solution, the molarity is 1.1 *M*.

54. D5W is a solution used as an intravenous fluid. It is a 5.0% by mass solution of dextrose ($C_6H_{12}O_6$) in water. If the density of D5W is 1.029 g/mL, calculate the molarity of dextrose in the solution.

Solution
The molar mass of $C_6H_{12}O_6$ is 6 × 12.011 + 12 × 1.00794 + 6 × 15.9994 = 180.2 g/mol. In 1.000 L, there are:

$$(1000\ \cancel{\text{mL}} \times 1.029\ \text{g}\ \cancel{\text{mL}}^{-1}) = 1029\ \text{g}$$

$$\text{mol dextrose} = 1029\ \cancel{\text{g}} \times 0.050 \times \frac{1\ \text{mol}}{180.2\ \cancel{\text{g}}} = 0.29\ \text{mol}\ C_6H_{12}O_6.$$

Since we selected the volume to be 1.00 L, the molarity of dextrose is

$$\text{molarity} = \frac{\text{mol}}{\text{L}} = \frac{0.29\ \text{mol}}{1.00\ \text{L}} = 0.29\ \text{M}.$$

55. Find the molarity of a 40.0% by mass aqueous solution of sulfuric acid, H_2SO_4, for which the density is 1.3057 g/mL.

Solution
First, calculate the moles of sulfuric acid in a convenient, 100-g sample:

$$40.0\ \text{g}\ H_2SO_4 \times \frac{1\ \text{mol}}{98.0748\ \text{g}} = 0.407833\ \text{mol}\ H_2SO_4.$$

Next, use the given density to find the volume of a 100-g sample:

$$100\ \text{g solution} \times \frac{1\ \text{mL}}{1.3057\ \text{g solution}} \times \frac{1\ \text{L}}{1000\ \text{mL}} = 0.076587\ \text{L solution}.$$

Finally, use the calculated values to find the molarity:

$\frac{0.407833 \text{ mol } H_2SO_4}{0.076587 \text{ L solution}} = 5.33\ M\ H_2SO_4$.

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Chemistry: Atoms First 2e
7: Stoichiometry of Chemical Reactions
7.1: Writing and Balancing Chemical Equations

1. What does it mean to say an equation is balanced? Why is it important for an equation to be balanced?

Solution
An equation is balanced when the same number of each element is represented on the reactant and product sides. Equations must be balanced to accurately reflect the law of conservation of matter.

2. Consider molecular, complete ionic, and net ionic equations.
(a) What is the difference between these types of equations?
(b) In what circumstance would the complete and net ionic equations for a reaction be identical?

Solution
(a) Molecular equations are written without regard to the dissociation of any ionic reactants or products, with all formulas represented as neutral substances. Complete ionic equations more realistically represent all dissolved ions.Net ionic equations represent only those dissolved ions that are chemically or physically changed by the reaction, omitting any spectator ions.
(b) If there are no spectator ions involved in a reaction, its complete and net ionic equations will be the same.

3. Balance the following equations:

(a) $PCl_5(s) + H_2O(l) \longrightarrow POCl_3(l) + HCl(aq)$

(b) $Cu(s) + HNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + H_2O(l) + NO(g)$

(c) $H_2(g) + I_2(s) \longrightarrow HI(s)$

(d) $Fe(s) + O_2(g) \longrightarrow Fe_2O_3(s)$

(e) $Na(s) + H_2O(l) \longrightarrow NaOH(aq) + H_2(g)$

(f) $(NH_4)_2Cr_2O_7(s) \longrightarrow Cr_2O_3(s) + N_2(g) + H_2O(g)$

(g) $P_4(s) + Cl_2(g) \longrightarrow PCl_3(l)$

(h) $PtCl_4(s) \longrightarrow Pt(s) + Cl_2(g)$

Solution
(a) $PCl_5(s) + H_2O(l) \longrightarrow POCl_3(l) + 2HCl(aq)$; (b)
$3Cu(s) + 8HNO_3(aq) \longrightarrow 3Cu(NO_3)_2(aq) + 4H_2O(l) + 2NO(g)$; (c)
$H_2(g) + I_2(s) \longrightarrow 2HI(s)$; (d) $4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$; (e)
$2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g)$; (f)

$(NH_4)_2Cr_2O_7(s) \longrightarrow Cr_2O_3(s) + N_2(g) + 4H_2O(g)$; (g) $P_4(s) + 6Cl_2(g) \longrightarrow 4PCl_3(l)$; (h) $PtCl_4(s) \longrightarrow Pt(s) + 2Cl_2(g)$

4. Balance the following equations:

(a) $Ag(s) + H_2S(g) + O_2(g) \longrightarrow Ag_2S(s) + H_2O(l)$

(b) $P_4(s) + O_2(g) \longrightarrow P_4O_{10}(s)$

(c) $Pb(s) + H_2O(l) + O_2(g) \longrightarrow Pb(OH)_2(s)$

(d) $Fe(s) + H_2O(l) \longrightarrow Fe_3O_4(s) + H_2(g)$

(e) $Sc_2O_3(s) + SO_3(l) \longrightarrow Sc_2(SO_4)_3(s)$

(f) $Ca_3(PO_4)_2(aq) + H_3PO_4(aq) \longrightarrow Ca(H_2PO_4)_2(aq)$

(g) $Al(s) + H_2SO_4(aq) \longrightarrow Al_2(SO_4)_3(aq) + H_2(g)$

(h) $TiCl_4(s) + H_2O(g) \longrightarrow TiO_2(s) + HCl(g)$

Solution

(a) $4Ag(s) + 2H_2S(g) + O_2(g) \longrightarrow 2Ag_2S(s) + 2H_2O(l)$; (b) $P_4(s) + 5O_2(g) \longrightarrow P_4O_{10}(s)$; (c) $2Pb(s) + 2H_2O(l) + O_2(g) \longrightarrow 2Pb(OH)_2(s)$; (d) $3Fe(s) + 4H_2O(l) \longrightarrow Fe_3O_4(s) + 4H_2(g)$; (e) $Sc_2O_3(s) + 3SO_3(l) \longrightarrow Sc_2(SO_4)_3(s)$; (f) $Ca_3(PO_4)_2(aq) + 4H_3PO_4(aq) \longrightarrow 3Ca(H_2PO_4)_2(aq)$; (g) $2Al(s) + 3H_2SO_4(aq) \longrightarrow Al_2(SO_4)_3(aq) + 3H_2(g)$; (h) $TiCl_4(s) + 2H_2O(g) \longrightarrow TiO_2(s) + 4HCl(g)$]

5. Write a balanced molecular equation describing each of the following chemical reactions.

(a) Solid calcium carbonate is heated and decomposes to solid calcium oxide and carbon dioxide gas.

(b) Gaseous butane, C_4H_{10}, reacts with diatomic oxygen gas to yield gaseous carbon dioxide and water vapor.

(c) Aqueous solutions of magnesium chloride and sodium hydroxide react to produce solid magnesium hydroxide and aqueous sodium chloride.

(d) Water vapor reacts with sodium metal to produce solid sodium hydroxide and hydrogen gas.

Solution

(a) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$; (b) $2C_4H_{10}(g) + 13O_2(g) \longrightarrow 8CO_2(g) + 10H_2O(g)$; (c) $MgCl_2(aq) + 2NaOH(aq) \longrightarrow Mg(OH)_2(s) + 2NaCl(aq)$; (d) $2H_2O(g) + 2Na(s) \longrightarrow 2NaOH(s) + H_2(g)$

6. Write a balanced equation describing each of the following chemical reactions.

(a) Solid potassium chlorate, $KClO_3$, decomposes to form solid potassium chloride and diatomic oxygen gas.

(b) Solid aluminum metal reacts with solid diatomic iodine to form solid Al_2I_6.

(c) When solid sodium chloride is added to aqueous sulfuric acid, hydrogen chloride gas and aqueous sodium sulfate are produced.

(d) Aqueous solutions of phosphoric acid and potassium hydroxide react to produce aqueous potassium dihydrogen phosphate and liquid water.

Solution

(a) $2KClO_3(s) \xrightarrow{\Delta} 2KCl(s) + 3O_2(g)$; (b) $2Al(s) + 3I_2(s) \longrightarrow Al_2I_6(s)$; (c) $2NaCl(s) + H_2SO_4(aq) \xrightarrow{\Delta} 2HCl(g) + Na_2SO_4(aq)$; (d) $H_3PO_4(aq) + KOH(aq) \longrightarrow KH_2PO_4(aq) + H_2O(l)$

7. Colorful fireworks often involve the decomposition of barium nitrate and potassium chlorate and the reaction of the metals magnesium, aluminum, and iron with oxygen.
(a) Write the formulas of barium nitrate and potassium chlorate.
(b) The decomposition of solid potassium chlorate leads to the formation of solid potassium chloride and diatomic oxygen gas. Write an equation for the reaction.
(c) The decomposition of solid barium nitrate leads to the formation of solid barium oxide, diatomic nitrogen gas, and diatomic oxygen gas. Write an equation for the reaction.
(d) Write separate equations for the reactions of the solid metals magnesium, aluminum, and iron with diatomic oxygen gas to yield the corresponding metal oxides.(Assume the iron oxide contains Fe^{3+} ions.)

Solution
(a) $Ba(NO_3)_2$, $KClO_3$; (b) $2KClO_3(s) \longrightarrow 2KCl(s) + 3O_2(g)$; (c) $2Ba\left(NO_3\right)_2(s) \longrightarrow 2BaO(s) + 2N_2(g) + 5O_2(g)$;

$2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$

(d) $4Al(s) + 3O_2(g) \longrightarrow 2Al_2O_3(g)$

$4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$

8. Fill in the blank with a single chemical formula for a covalent compound that will balance the equation:



Solution
H_2O

9. Aqueous hydrogen fluoride (hydrofluoric acid) is used to etch glass and to analyze minerals for their silicon content. Hydrogen fluoride will also react with sand (silicon dioxide). (a) Write an equation for the reaction of solid silicon dioxide with hydrofluoric acid to yield gaseous silicon tetra fluoride and liquid water.
(b) The mineral fluorite (calcium fluoride) occurs extensively in Illinois. Solid calcium fluoride can also be prepared by the reaction of aqueous solutions of calcium chloride and sodium fluoride, yielding aqueous sodium chloride as the other product. Write complete and net ionic equations for this reaction.

Solution
(a) $4HF(aq) + SiO_2(s) \longrightarrow SiF_4(g) + 2\ H_2O(l)$; (b) complete ionic equation: $2Na^+(aq) + 2F^-(aq) + Ca^{2+}(aq) + 2Cl^-(aq) \longrightarrow CaF_2(s) + 2Na^+(aq) + 2Cl^-(aq)$, net ionic equation: $2F^-(aq) + Ca^{2+}(aq) \longrightarrow CaF_2(s)$

10. A novel process for obtaining magnesium from sea water involves several reactions. Write a balanced chemical equation for each step of the process.
(a) The first step is the decomposition of solid calcium carbonate from seashells to form solid

calcium oxide and gaseous carbon dioxide.
(b) The second step is the formation of solid calcium hydroxide as the only product from the reaction of the solid calcium oxide with liquid water.
(c) Solid calcium hydroxide is then added to the seawater, reacting with dissolved magnesium chloride to yield solid magnesium hydroxide and aqueous calcium chloride.
(d) The solid magnesium hydroxide is added to a hydrochloric acid solution, producing dissolved magnesium chloride and liquid water.
(e) Finally, the magnesium chloride is melted and electrolyzed to yield liquid magnesium metal and diatomic chlorine gas.

Solution
(a) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$; (b) $CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(aq)$; (c) $MgCl_2(aq) + Ca(OH)_2(aq) \longrightarrow Mg(OH)_2(s) + CaCl_2(aq)$; (d) $Mg(OH)_2(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + 2H_2O(l)$; (e) $MgCl_2(l) \xrightarrow{\Delta} Mg(l) + Cl_2(g)$

11. From the balanced molecular equations, write the complete ionic and net ionic equations for the following:
(a) $K_2C_2O_4(aq) + Ba(OH)_2(aq) \longrightarrow 2KOH(aq) + BaC_2O_2(s)$
(b) $Pb(NO_3)_2(aq) + H_2SO_4(aq) \longrightarrow PbSO_4(s) + 2HNO_3(aq)$
(c) $CaCO_3(s) + H_2SO_4(aq) \longrightarrow CaSO_4(s) + CO_2(g) + H_2O(l)$

Solution
(a)
$2K^+(aq) + C_2O_4^{2-}(aq) + Ba^{2+}(aq) + 2OH^-(aq) \longrightarrow 2K^+(aq) + 2OH^-(aq) + BaC_2O_4(s)$ (complete)
$Ba^{2+}(aq) + C_2O_4^{2-}(aq) \longrightarrow BaC_2O_4(s)$ (net)
(b)
$Pb^{2+}(aq) + 2NO_3^-(aq) + 2H^+(aq) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2H^+(aq) + 2NO_3^-(aq)$ (complete)
$Pb^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s)$ (net)
(c)
$CaCO_3(s) + 2H^+(aq) + SO_4^{2-}(aq) \longrightarrow CaSO_4(s) + CO_2(g) + H_2O(l)$ (complete)
$CaCO_3(s) + 2H^+(aq) + SO_4^{2-}(aq) \longrightarrow CaSO_4(s) + CO_2(g) + H_2O(l)$ (net)

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12. Use the following equations to answer the next five questions:
i. $H_2O(s) \longrightarrow H_2O(l)$

ii. $Na^+(aq) + Cl^-(aq) + Ag^+(aq) + NO_3^-(aq) \longrightarrow AgCl(s) + Na^+(aq) + NO_3^-(aq)$

iii. $CH_3OH(g) + O_2(g) \longrightarrow CO_2(g) + H_2O(g)$

iv. $2H_2O(l) \longrightarrow 2H_2(g) + O_2(g)$

v. $H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$

(a) Which equation describes a physical change?
(b) Which equation identifies the reactants and products of a combustion reaction?
(c) Which equation is not balanced?
(d) Which is a net ionic equation?

Solution
(a) i. The transition is from ice to liquid water. (b) iii. Combustion with oxygen generally produces both CO_2 and H_2O. (c) iii. The balanced equation is $2CH_3OH(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 4H_2O(g)$. (d) v. Only reacting ionic species are present.

13. Indicate what type, or types, of reaction each of the following represents:

(a) $Ca(s) + Br_2(l) \longrightarrow CaBr_2(s)$

(b) $Ca(OH)_2(aq) + 2HBr(aq) \longrightarrow CaBr_2(aq) + 2H_2O(l)$

(c) $C_6H_{12}(l) + 9O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(g)$

Solution
(a) oxidation-reduction (addition); (b) acid-base (neutralization); (c) oxidation-reduction (combustion)

14. Indicate what type, or types, of reaction each of the following represents:

(a) $H_2O(g) + C(s) \longrightarrow CO(g) + H_2(g)$

(b) $2KClO_3(s) \longrightarrow 2KCl(s) + 3O_2(g)$

(c) $Al(OH)_3(aq) + 3HCl(aq) \longrightarrow AlBr_3(aq) + 3H_2O(l)$

(d) $Pb(NO_3)_2(aq) + H_2SO_4(aq) \longrightarrow PbSO_4(s) + 2HNO_3(aq)$

Solution
(a) oxidation-reduction (combustion); (b) oxidation-reduction; (c) acid-base (neutralization); (d) precipitation

15. Silver can be separated from gold because silver dissolves in nitric acid while gold does not. Is the dissolution of silver in nitric acid an acid-base reaction or an oxidation-reduction reaction? Explain your answer.

Solution
An oxidation-reduction reaction, because the oxidation state of the silver changes during the reaction.

16. Determine the oxidation states of the elements in the following compounds:
(a) NaI
(b) $GdCl_3$
(c) $LiNO_3$
(d) H_2Se
(e) Mg_2Si
(f) RbO_2, rubidium superoxide

(g) HF

Solution

(a) Na +1, I –1; (b) Gd +3, Cl –1; (c) Li +1, N +5, O –2; (d) H +1, Se –2; (e) Mg +2, Si –4; (f) Rb +1; $\mathrm{O}\ -\frac{1}{2}$; (g) H +1, F –1

17. Determine the oxidation states of the elements in the compounds listed. None of the oxygen-containing compounds are peroxides or superoxides.

(a) H_3PO_4

(b) $Al(OH)_3$

(c) SeO_2

(d) KNO_2

(e) In_2S_3

(f) P_4O_6

Solution

(a) H +1, P +5, O –2; (b) Al +3, H +1, O –2; (c) Se +4, O –2; (d) K +1, N +3, O –2; (e) In +3, S –2; (f) P +3, O –2

18. Determine the oxidation states of the elements in the compounds listed. None of the oxygen-containing compounds are peroxides or superoxides.

(a) H_2SO_4

(b) $Ca(OH)_2$

(c) BrOH

(d) $ClNO_2$

(e) $TiCl_4$

(f) NaH

Solution

(a) H +1, S +6, O –2; (b) Ca +2, O –2, H +1; (c) Br +1, O –2, H +1; (d) Cl +1, N +3, O –2; (e) Ti +4, Cl –1; (f) Na +1, H –1

19. Classify the following as acid-base reactions or oxidation-reduction reactions:

(a) $\mathrm{Na_2S}(aq) + 2\mathrm{HCl}(aq) \longrightarrow 2\mathrm{NaCl}(aq) + \mathrm{H_2S}(g)$

(b) $2\mathrm{Na}(s) + 2\mathrm{HCl}(aq) \longrightarrow 2\mathrm{NaCl}(aq) + \mathrm{H_2}(g)$

(c) $\mathrm{Mg}(s) + \mathrm{Cl_2}(g) \longrightarrow \mathrm{MgCl_2}(s)$

(d) $\mathrm{MgO}(s) + 2\mathrm{HCl}(aq) \longrightarrow \mathrm{MgCl_2}(aq) + \mathrm{H_2O}(l)$

(e) $\mathrm{K_3P}(s) + 2\mathrm{O_2}(g) \longrightarrow \mathrm{K_3PO_4}(s)$

(f) $3\mathrm{KOH}(aq) + \mathrm{H_3PO_4}(aq) \longrightarrow \mathrm{K_3PO_4}(aq) + 3\mathrm{H_2O}(l)$

Solution

(a) acid-base; (b) oxidation-reduction: Na is oxidized, H^+ is reduced; (c) oxidation-reduction: Mg is oxidized, Cl_2 is reduced; (d) acid-base; (e) oxidation-reduction: P^{3-} is oxidized, O_2 is reduced; (f) acid-base

20. Identify the atoms that are oxidized and reduced, the change in oxidation state for each, and the oxidizing and reducing agents in each of the following equations:

(a) $\mathrm{Mg}(s) + \mathrm{NiCl_2}(aq) \longrightarrow \mathrm{MgCl_2}(aq) + \mathrm{Ni}(s)$

(b) $\mathrm{PCl_3}(l) + \mathrm{Cl_2}(g) \longrightarrow \mathrm{PCl_5}(s)$

(c) $C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(g)$

(d) $Zn(s) + H_2SO_4(aq) \longrightarrow ZnSO_4(aq) + H_2(g)$

(e) $2K_2S_2O_3(s) + I_2(s) \longrightarrow K_2S_4O_6(s) + 2KI(s)$

(f) $3Cu(s) + 8HNO_3(aq) \longrightarrow 3Cu\left(NO_3\right)_2(aq) + 2NO(g) + 4H_2O(l)$

Solution
(a) Mg is oxidized from 0 to +2 and is the reducing agent, Ni is reduced from +2 to 0 and is the oxidizing agent; (b) P is oxidized from +3 to +5 and is the reducing agent, Cl is reduced from 0 to –1 and is the oxidizing agent; (c) C is oxidized from −2 to +4 and is the reducing agent, O is reduced from 0 to –2 and is the oxidizing agent; (d) Zn is oxidized from 0 to +2 and is the reducing agent, H is reduced from +1 to 0 and is the oxidizing agent; (e) S is oxidized from +2 to +2.5 and is the reducing agent, I_2 is reduced from 0 to –1 and is the oxidizing agent; (f) Cu is oxidized from O to +2, N is reduced from +5 to +2]

21. Complete and balance the following acid-base equations:
(a) HCl gas reacts with solid $Ca(OH)_2(s)$.
(b) A solution of $Sr(OH)_2$ is added to a solution of HNO_3.

Solution
(a) $2HCl(g) + Ca\left(OH\right)_2(s) \longrightarrow CaCl_2(s) + 2H_2O(l)$; (b)
$Sr\left(OH\right)_2(aq) + 2HNO_3(aq) \longrightarrow Sr\left(NO_3\right)_2(aq) + 2H_2O(l)$

22. Complete and balance the following acid-base equations:
(a) A solution of $HClO_4$ is added to a solution of LiOH.
(b) Aqueous H_2SO_4 reacts with NaOH.
(c) $Ba(OH)_2$ reacts with HF gas.

Solution
(a) $HClO_4(aq) + LiOH(aq) \longrightarrow H_2O(l) + LiClO_4(aq)$; (b)
$H_2SO_4(aq) + 2NaOH(aq) \longrightarrow Na_2SO_4(aq) + 2H_2O(l)$; (c)
$Ba\left(OH\right)_2(aq) + 2HF(g) \longrightarrow BaF_2(aq) + 2H_2O(l)$

23. Complete and balance the following oxidation-reduction reactions, which give the highest possible oxidation state for the oxidized atoms.

(a) $Al(s) + F_2(g) \longrightarrow$

(b) $Al(s) + CuBr_2(aq) \longrightarrow$ (single displacement)

(c) $P_4(s) + O_2(g) \longrightarrow$

(d) $Ca(s) + H_2O(l) \longrightarrow$ (products are a strong base and a diatomic gas)

Solution
(a) $2Al(s) + 3F_2(g) \longrightarrow 2AlF_3(s)$; (b) $2Al(s) + 3CuBr_2(aq) \longrightarrow 3Cu(s) + 2AlBr_3(aq)$; (c)
$P_4(s) + 5O_2(g) \longrightarrow P_4O_{10}(s)$; (d) $Ca(s) + 2H_2O(l) \longrightarrow Ca\left(OH\right)_2(aq) + H_2(g)$

24. Complete and balance the following oxidation-reduction reactions, which give the highest possible oxidation state for the oxidized atoms.

(a) $K(s) + H_2O(l) \longrightarrow$

(b) $Ba(s) + HBr(aq) \longrightarrow$

(c) $Sn(s) + I_2(s) \longrightarrow$

Solution

(a) $2K(s) + 2H_2O(l) \longrightarrow 2KOH(aq) + H_2(g)$; (b)

$Ba(s) + 2HBr(aq) \longrightarrow BaBr_2(aq) + H_2(g)$; (c) $Sn(s) + 2I_2(s) \longrightarrow SnI_4(s)$

25. Complete and balance the equations for the following acid-base neutralization reactions. If water is used as a solvent, write the reactants and products as aqueous ions. In some cases, there may be more than one correct answer, depending on the amounts of reactants used.

(a) $Mg(OH)_2(s) + HClO_4(aq) \longrightarrow$

(b) $SO_3(g) + H_2O(l) \longrightarrow$ (assume an excess of water and that the product dissolves)

(c) $SrO(s) + H_2SO_4(l) \longrightarrow$

Solution

(a) $Mg(OH)_2(s) + 2HClO_4(aq) \longrightarrow Mg^{2+}(aq) + 2ClO_4^-(aq) + 2H_2O(l)$; (b)

$SO_3(g) + 2H_2O(l) \longrightarrow H_3O^+(aq) + HSO_4^-(aq)$, (a solution of H_2SO_4; (c)

$SrO(s) + H_2SO_4(l) \longrightarrow SrSO_4(s) + H_2O$

26. When heated to 700–800 °C, diamonds, which are pure carbon, are oxidized by atmospheric oxygen. (They burn!) Write the balanced equation for this reaction.

Solution

$C(s) + O_2(g) \longrightarrow CO_2(g)$

27. The military has experimented with lasers that produce very intense light when fluorine combines explosively with hydrogen. What is the balanced equation for this reaction?

Solution

$H_2(g) + F_2(g) \longrightarrow 2HF(g)$

28. Write the molecular, total ionic, and net ionic equations for the following reactions:

(a) $Ca(OH)_2(aq) + HC_2H_3O_2(aq) \longrightarrow$

(b) $H_3PO_4(aq) + CaCl_2(aq) \longrightarrow$

Solution

(a) $Ca(OH)_2(aq) + 2HC_2H_3O_2(aq) \longrightarrow Ca(C_2H_3O_2)_2(aq) + 2H_2O(l)$,

$Ca^{2+}(aq) + 2OH^-(aq) + 2HC_2H_3O_2(aq) \longrightarrow Ca^{2+}(aq) + 2C_2H_3O_2^-(aq) + 2H_2O(l)$,

$OH^-(aq) + HC_2H_3O_2(aq) \longrightarrow C_2H_3O_2^-(aq) + H_2O(l)$

(b) $2H_3PO_4(aq) + 3CaCl_2(aq) \longrightarrow Ca_3(PO_4)_2(s) + 6HCl(aq)$,

$2H_3PO_4(aq) + 3Ca^{2+}(aq) + 6Cl^-(aq) \longrightarrow Ca_3(PO_4)_2(s) + 6H^+(aq) + 6Cl^-(aq)$,

$2H_3PO_4(aq) + 3Ca^{2+}(aq) \longrightarrow Ca_3(PO_4)_2(s) + 6H^+(aq)$

29. Great Lakes Chemical Company produces bromine, Br_2, from bromide salts such as NaBr, in Arkansas brine by treating the brine with chlorine gas. Write a balanced equation for the reaction of NaBr with Cl_2.

Solution

$$2NaBr(aq) + Cl_2(g) \longrightarrow 2NaCl(aq) + Br_2(l)$$

30. In a common experiment in the general chemistry laboratory, magnesium metal is heated in air to produce MgO. MgO is a white solid, but in these experiments it often looks gray, due to small amounts of Mg_3N_2, a compound formed as some of the magnesium reacts with nitrogen. Write a balanced equation for each reaction.

Solution

$$2Mg(s) + O_2(g) \longrightarrow 2MgO(s)\,;\ 3Mg(s) + N_2(g) \longrightarrow Mg_3N_2(s)$$

31. Lithium hydroxide may be used to absorb carbon dioxide in enclosed environments, such as manned spacecraft and submarines. Write an equation for the reaction that involves 2 mol of LiOH per 1 mol of CO_2. (Hint: Water is one of the products.)

Solution

$$2LiOH(aq) + CO_2(g) \longrightarrow Li_2CO_3(aq) + H_2O(l)$$

32. Calcium propionate is sometimes added to bread to retard spoilage. This compound can be prepared by the reaction of calcium carbonate, $CaCO_3$, with propionic acid, $C_2H_5CO_2H$, which has properties similar to those of acetic acid. Write the balanced equation for the formation of calcium propionate.

Solution

$$CaCO_3(s) + 2C_2H_5CO_2H(aq) \longrightarrow Ca\left(C_2H_5CO_2\right)_2(aq) + CO_2(g) + H_2O(l)$$

33. Complete and balance the equations of the following reactions, each of which could be used to remove hydrogen sulfide from natural gas:

(a) $Ca\left(OH\right)_2(s) + H_2S(g) \longrightarrow$

(b) $Na_2CO_3(aq) + H_2S(g) \longrightarrow$

Solution

$Ca\left(OH\right)_2(s) + H_2S(g) \longrightarrow CaS(s) + 2H_2O(l)$; (b)

$Na_2CO_3(aq) + H_2S(g) \longrightarrow Na_2S(aq) + CO_2(g) + H_2O(l)$

34. Copper(II) sulfide is oxidized by molecular oxygen to produce gaseous sulfur trioxide and solid copper(II) oxide. The gaseous product then reacts with liquid water to produce liquid dihydrogen sulfate as the only product. Write the two equations that represent these reactions.

Solution

$$CuS(s) + 2O_2(g) \longrightarrow SO_2(g) + CuO(s)$$

$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(l)$$

35. Write balanced chemical equations for the reactions used to prepare each of the following compounds from the given starting material(s). In some cases, additional reactants may be required.

(a) solid ammonium nitrate from gaseous molecular nitrogen via a two-step process (first reduce the nitrogen to ammonia, then neutralize the ammonia with an appropriate acid)

(b) gaseous hydrogen bromide from liquid molecular bromine via a one-step redox reaction

(c) gaseous H_2S from solid Zn and S via a two-step process (first a redox reaction between the starting materials, then reaction of the product with a strong acid)

Solution

(a) step 1: $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$, step 2:

$NH_3(g) + HNO_3(aq) \longrightarrow NH_4NO_3(aq) \longrightarrow NH_4NO_3(s)$ (after drying); (b)

$H_2(g) + Br_2(l) \longrightarrow 2HBr(g)$; (c) $Zn(s) + S(s) \longrightarrow ZnS(s)$ and

$ZnS(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + H_2S(g)$

36. Calcium cyclamate $Ca(C_6H_{11}NHSO_3)_2$ is an artificial sweetener used in many countries around the world but is banned in the United States. It can be purified industrially by converting it to the barium salt through reaction of the acid $C_6H_{11}NHSO_3H$ with barium carbonate, treatment with sulfuric acid (barium sulfate is very insoluble), and then neutralization with calcium hydroxide. Write the balanced equations for these reactions.

Solution

$2C_6H_{11}NHSO_3H(aq) + BaCO_3(aq) \longrightarrow (C_6H_{11}NHSO_3)_2Ba(s) + H_2CO_3(aq)$

$(C_6H_{11}NHSO_3)_2Ba(s) + H_2SO_4(aq) \longrightarrow BaSO_4(s) + 2C_6H_{11}NHSO_3H(aq)$

$2C_6H_{11}NHSO_3H(aq) + Ca(OH)_2(aq) \longrightarrow Ca(C_6H_{11}NHSO_3)_2(s) + 2H_2O(l)$

37. Complete and balance each of the following half-reactions (steps 2–5 in half-reaction method):

(a) $Sn^{4+}(aq) \longrightarrow Sn^{2+}(aq)$

(b) $\left[Ag(NH_3)_2\right]^+(aq) \longrightarrow Ag(s) + NH_3(aq)$

(c) $Hg_2Cl_2(s) \longrightarrow Hg(l) + Cl^-(aq)$

(d) $H_2O(l) \longrightarrow O_2(g)$ (in acidic solution)

(e) $IO_3^-(aq) \longrightarrow I_2(s)$ (in basic solution)

(f) $SO_3^{2-}(aq) \longrightarrow SO_4^{2-}(aq)$ (in acidic solution)

(g) $MnO_4^-(aq) \longrightarrow Mn^{2+}(aq)$ (in acidic solution)

(h) $Cl^-(aq) \longrightarrow ClO_3^-(aq)$ (in basic solution)

Solution

(a) $Sn^{4+}(aq) \longrightarrow Sn^{2+}(aq)$
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$; (b) $\left[Ag(NH_3)_2\right]^+(aq) \longrightarrow Ag(s) + 2NH_3(aq)$
$\left[Ag(NH_3)_2\right]^+(aq) + e^- \longrightarrow Ag(s) + 2NH_3(aq)$; (c)

$Hg_2Cl_2(s) \longrightarrow Hg(l) + Cl^-(aq)$
$Hg_2Cl_2(s) \longrightarrow 2Hg(l) + 2Cl^-(aq)$
$Hg_2Cl_2(s) + 2e^- \longrightarrow 2Hg(l) + 2Cl^-(aq)$; (d)

$2H_2O(l) \longrightarrow O_2(g)$
$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq)$
$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$; (e)

$IO_3^-(aq) \longrightarrow I_2(s)$

$2IO_3^-(aq) \longrightarrow I_2(s)$

$2IO_3^-(aq) \longrightarrow I_2(s) + 6H_2O(l)$

$12H^+(aq) + 2IO_3^-(aq) \longrightarrow I_2(s) + 6H_2O(l)$

$12H^+(aq) + \mathbf{12OH^-(aq)} + 2IO_3^-(aq) \longrightarrow I_2(s) + 6H_2O(l) + \mathbf{12OH^-(aq)}$; (f)

$12H_2O(l) + 2IO_3^-(aq) \longrightarrow I_2(s) + 6H_2O(l) + 12OH^-(aq)$

$6H_2O(l) + 2IO_3^-(aq) \longrightarrow I_2(s) + 12OH^-(aq)$

$6H_2O(l) + 2IO_3^-(aq) + 10e^- \longrightarrow I_2(s) + 12OH^-(aq)$

$SO_3^{2-}(aq) \longrightarrow SO_4^{2-}(aq)$

$H_2O(l) + SO_3^{2-}(aq) \longrightarrow SO_4^{2-}(aq)$

$H_2O(l) + SO_3^{2-}(aq) \longrightarrow SO_4^{2-}(aq) + 2H^+(aq)$; (g)

$H_2O(l) + SO_3^{2-}(aq) \longrightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e^-$

$MnO_4^-(aq) \longrightarrow Mn^{2+}(aq)$

$MnO_4^-(aq) \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$

$8H^+(aq) + MnO_4^-(aq) \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$; (h)

$8H^+(aq) + MnO_4^-(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$

$Cl^-(aq) \longrightarrow ClO_3^-(aq)$

$3H_2O(l) + Cl^-(aq) \longrightarrow ClO_3^-(aq)$

$3H_2O(l) + Cl^-(aq) \longrightarrow ClO_3^-(aq) + 6H^+(aq)$

$3H_2O(l) + Cl^-(aq) + \mathbf{6OH^-(aq)} \longrightarrow ClO_3^-(aq) + 6H^+(aq) + \mathbf{6OH^-(aq)}$

$3H_2O(l) + Cl^-(aq) + 6OH^-(aq) \longrightarrow ClO_3^-(aq) + 6H_2O(l)$

$Cl^-(aq) + 6OH^-(aq) \longrightarrow ClO_3^-(aq) + 3H_2O(l) + 6e^-$

38. Complete and balance each of the following half-reactions (steps 2–5 in half-reaction method):

(a) $Cr^{2+}(aq) \longrightarrow Cr^{3+}(aq)$

(b) $Hg(l) + Br^-(aq) \longrightarrow HgBr_4^{2-}(aq)$

(c) $ZnS(s) \longrightarrow Zn(s) + S^{2-}(aq)$

(d) $H_2(g) \longrightarrow H_2O(l)$ (in basic solution)

(e) $H_2(g) \longrightarrow H_3O^+(aq)$ (in acidic solution)

(f) $NO_3^-(aq) \longrightarrow HNO_2(aq)$ (in acidic solution)

(g) $MnO_2(s) \longrightarrow MnO_4^-(aq)$ (in basic solution)

(h) $Cl^-(aq) \longrightarrow ClO_3^-(aq)$ (in acidic solution)

Solution

For an example of the fully worked out solution, see the solution to Exercise 37. (a) $Cr^{2+}(aq) \longrightarrow Cr^{3+}(aq) + e^-$; (b) $Hg(l) + 4Br^-(aq) \longrightarrow HgBr_4^{2-}(aq) + 2e^-$; (c) $ZnS(s) + 2e^- \longrightarrow Zn(s) + S^{2-}(aq)$; (d) $H_2(g) + 2OH^-(aq) \longrightarrow 2H_2O(l) + 2e^-$; (e) $H_2(g) + 2H_2O(l) \longrightarrow 2H_3O^+(aq) + 2e^-$; (f) $NO_3^-(aq) + 3H_3O^+(aq) + 2e^- \longrightarrow HNO_2(aq) + 4H_2O(l)$; (g) $MnO_2(s) + 4OH^-(aq) \longrightarrow MnO_4^-(aq) + 2H_2O(l) + 3e^-$; (h) $Cl^-(aq) + 3H_2O(l) \longrightarrow ClO_3^-(aq) + 6H_3O^+(aq) + 6e^-$

39. Balance each of the following equations according to the half-reaction method:

(a) $Sn^{2+}(aq) + Cu^{2+}(aq) \longrightarrow Sn^{4+}(aq) + Cu^+(aq)$

(b) $H_2S(g) + Hg_2^{2+}(aq) \longrightarrow Hg(l) + S(s)$ (in acid)

(c) $CN^-(aq) + ClO_2(aq) \longrightarrow CNO^-(aq) + Cl^-(aq)$ (in acid)

(d) $Fe^{2+}(aq) + Ce^{4+}(aq) \longrightarrow Fe^{3+}(aq) + Ce^{3+}(aq)$

(e) $HBrO(aq) \longrightarrow Br^-(aq) + O_2(g)$ (in acid)

Solution

For an example of the fully worked out solution, see the solution to Exercise 37. (a) $Sn^{2+}(aq) + 2Cu^{2+}(aq) \longrightarrow Sn^{4+}(aq) + 2Cu^+(aq)$; (b) $H_2S(g) + Hg_2^{2+}(aq) + 2H_2O(l) \longrightarrow 2Hg(l) + S(s) + 2H_3O^+(aq)$; (c) $5CN^-(aq) + 2ClO_2(aq) + 3H_2O(l) \longrightarrow 5CNO^-(aq) + 2Cl^-(aq) + 2H_3O^+(aq)$; (d) $Fe^{2+}(aq) + Ce^{4+}(aq) \longrightarrow Fe^{3+}(aq) + Ce^{3+}(aq)$; (e) $2HBrO(aq) + 2H_2O(l) \longrightarrow 2H_3O^+(aq) + 2Br^-(aq) + O_2(g)$

40. Balance each of the following equations according to the half-reaction method:

(a) $Zn(s) + NO_3^-(aq) \longrightarrow Zn^{2+}(aq) + N_2(g)$ (in acid)

(b) $Zn(s) + NO_3^-(aq) \longrightarrow Zn^{2+}(aq) + NH_3(aq)$ (in base)

(c) $CuS(s) + NO_3^-(aq) \longrightarrow Cu^{2+}(aq) + S(s) + NO(g)$ (in acid)

(d) $NH_3(aq) + O_2(g) \longrightarrow NO_2(g)$ (gas phase)

(e) $H_2O_2(aq) + MnO_4^-(aq) \longrightarrow Mn^{2+}(aq) + O_2(g)$ (in acid)

(f) $NO_2(g) \longrightarrow NO_3^-(aq) + NO_2^-(aq)$ (in base)

(g) $Fe^{3+}(aq) + I^-(aq) \longrightarrow Fe^{2+}(aq) + I_2(aq)$

Solution

For an example of the fully worked out solution, see the solution to Exercise 37.

(a) $5Zn(s) + 12H_3O^+(aq) + 2NO_3^-(aq) \longrightarrow 5Zn^{2+}(aq) + N_2(g) + 18H_2O(l)$;

(b) $4Zn(s) + NO_3^-(aq) + 6H_2O(l) \longrightarrow 4Zn^{2+}(aq) + NH_3(aq) + 9OH^-(aq)$;

(c) $3CuS(s) + 8H_3O^+(aq) + 2NO_3^-(aq) \longrightarrow 3Cu^{2+}(aq) + 3S(s) + 2NO(g) + 12H_2O(l)$;

(d) $4NH_3(aq) + 7O_2(g) \longrightarrow 4NO_2(g) + 6H_2O(l)$;

(e) $5H_2O_2(aq) + 2MnO_4^-(aq) + 6H_3O^+(aq) \longrightarrow 2Mn^{2+}(aq) + 5O_2(g) + 14H_2O(l)$;

(f) $2NO_2(g) + 2OH^-(aq) \longrightarrow NO_3^-(aq) + NO_2^-(aq) + H_2O(l)$;

(g) $2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(aq)$

41. Balance each of the following equations according to the half-reaction method:

(a) $MnO_4^-(aq) + NO_2^-(aq) \longrightarrow MnO_2(s) + NO_3^-(aq)$ (in base)

(b) $MnO_4^{2-}(aq) \longrightarrow MnO_4^-(aq) + MnO_2(s)$ (in base)

(c) $Br_2(l) + SO_2(g) \longrightarrow Br^-(aq) + SO_4^{2-}(aq)$ (in acid)

Solution

For an example of the fully worked out solution, see the solution to Exercise 37. (a)

$2MnO_4^-(aq) + 3NO_2^-(aq) + H_2O(l) \longrightarrow 2MnO_2(s) + 3NO_3^-(aq) + 2OH^-(aq)$; (b)

$3MnO_4^{2-}(aq) + 2H_2O(l) \longrightarrow 2MnO_4^-(aq) + 4OH^-(aq) + MnO_2(s)$ (in base); (c)

$Br_2(l) + SO_2(g) + 2H_2O(l) \longrightarrow 4H^+(aq) + 2Br^-(aq) + SO_4^{2-}(aq)$

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Chemistry: Atoms First 2e
7: Stoichiometry of Chemical Reactions
7.3: Reaction Stoichiometry

42. Write the balanced equation, then outline the steps necessary to determine the information requested in each of the following:

(a) The number of moles and the mass of chlorine, Cl_2, required to react with 10.0 g of sodium metal, Na, to produce sodium chloride, NaCl.

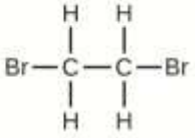
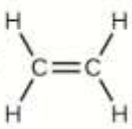
(b) The number of moles and the mass of oxygen formed by the decomposition of 1.252 g of mercury(II) oxide.

(c) The number of moles and the mass of sodium nitrate, $NaNO_3$, required to produce 128 g of oxygen. ($NaNO_2$ is the other product.)

(d) The number of moles and the mass of carbon dioxide formed by the combustion of 20.0 kg of carbon in an excess of oxygen.

(e) The number of moles and the mass of copper(II) carbonate needed to produce 1.500 kg of copper(II) oxide. (CO_2 is the other product.)

(f)

The number of moles and the mass of  formed by the reaction of 12.85 g of 

with an excess of Br_2.

Solution

(a) $2Na + Cl_2 \longrightarrow 2NaCl$,

mass of Na $\longrightarrow$ moles of Na $\longrightarrow$ moles of Cl_2 $\longrightarrow$ mass of Cl_2; (b)

$2HgO \longrightarrow 2Hg + O_2$,

Mass of HgO $\longrightarrow$ Moles of HgO $\longrightarrow$ Moles of O_2 $\longrightarrow$ Mass of O_2; (c)

$2NaNO_3 \longrightarrow 2NaNO_2 + O_2$,

Mass of $NaNO_3$ $\longrightarrow$ Moles of $NaNO_3$ $\longrightarrow$ Moles of O_2 $\longrightarrow$ Mass of O_2; (d)

$C + O_2 \longrightarrow CO_2$, Mass of C $\longrightarrow$ Moles of C $\longrightarrow$ Moles of CO_2 $\longrightarrow$ Mass of CO_2;

(e) $CuCO_3 \longrightarrow CuO + CO_2$,

Mass of $CuCO_3$ $\longrightarrow$ Moles of $CuCO_3$ $\longrightarrow$ Moles of CuO $\longrightarrow$ Mass of CuO; (f)

$C_2H_4 + Br_2 \longrightarrow C_2H_4Br_2$,

Mass of C_2H_4 $\longrightarrow$ Moles of C_2H_4 $\longrightarrow$ Moles of $C_2H_4Br_2$ $\longrightarrow$ Mass of $C_2H_4Br_2$

43. Determine the number of moles and the mass requested for each reaction in Exercise 42.

Solution

(a) The first step is to calculate the moles of sodium in 10.0 g.

$$\text{mol Na} = 10.0 \cancel{\text{g}} \times \frac{1 \text{ mol}}{22.989768 \cancel{\text{g}}} = 0.435 \text{ mol}$$

From the balanced equation, 2 mol Na reacts with 1 mol Cl_2: therefore,

$$\text{mol } Cl_2 = \frac{\text{mol Na}}{2} = \frac{0.435 \text{ mol}}{2} = 0.217 \text{ mol}$$

g Cl_2 = mol $\times$ molar mass = 0.217 mol $\times$ 2 $\times$ 35.4527 g mol^{-1} = 15.4 g Cl_2,0.217 mol Cl_2, 15.4 g Cl_2;(b)

$$\text{mol HgO} = 1.252 \cancel{\text{g}} \times \frac{1 \text{ mol}}{216.59 \cancel{\text{g HgO}}} = 0.005780 \text{ mol}$$

$$\text{mol } O_2 = 0.005780 \cancel{\text{mol HgO}} \times \frac{1 \text{ mol } O_2}{2 \cancel{\text{mol HgO}}} = 2.890 \times 10^{-3} \text{ mol}$$; (c) From the balanced

$$\text{mass } O_2 = 2.890 \times 10^{-3} \cancel{\text{mol}} \times \frac{31.9998 \text{ g}}{1 \cancel{\text{mol}}} = 9.248 \times 10^{-2} \text{ g}$$

equation, 2 mol of $NaNO_3$ is required to produce 1 mol O_2.

mol $NaNO_3$ required = 2 mol O_2 = 2(4.00 mol)= 8.00 mol $NaNO_3$

g $NaNO_3$ = 8.00 mol $NaNO_3$ $\times$ 84.9947 g mol^{-1} $NaNO_3$ = 6.80 $\times$ 10^2 g $NaNO_3$; (d)

$$\text{mol } CO_2 = 20.0 \cancel{\text{kg}} \times 100 \frac{\cancel{\text{g}}}{\cancel{\text{kg}}} \times \frac{1 \cancel{\text{mol C}}}{12.011 \cancel{\text{g C}}} \times \frac{1 \text{ mol } CO_2}{1 \cancel{\text{mol C}}} = 1665 \text{ mol } CO_2$$

;(e) Molar

$$\text{mass } CO_2 = 1665 \cancel{\text{mol } CO_2} \times \frac{44.009 \text{ g } CO_2}{1 \cancel{\text{mol } CO_2}} = 73.3 \text{ kg } CO_2$$

masses: CuO = 79.545 g mol^{-1}; $CuCO_3$ = 123.555 g mol^{-1}

$$\text{mol CuO} = 1500\ \text{g CuO} \times \frac{1\ \text{mol}}{79.545\ \text{g CuO}} = 18.86\ \text{mol}$$

$1\ \text{mol CuO} = 1\ \text{mol } CuO_3$

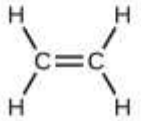
$$\text{kg } CuCO_3 = 18.86\ \cancel{\text{mol } CuCO_3} \times \frac{123.555\ \cancel{\text{g}}}{\cancel{\text{mol } CuCO_3}} \times \frac{1\ \text{kg}}{1000\ \cancel{\text{g}}} = 2.330\ \text{kg } CuCO_3\text{; (f)}$$

$$\text{mol } C_2H_4Br_2 = 12.85\ \cancel{\text{g } C_2H_4} \times \frac{1\ \cancel{\text{mol } C_2H_4}}{28.054\ \cancel{\text{g}}} \times \frac{1\ \text{mol } C_2H_4Br_2}{1\ \cancel{\text{mol } C_2H_4}} = 0.4580\ \text{mol } C_2H_4Br_2$$

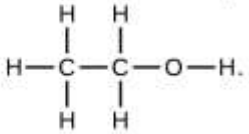
$$\text{g } C_2H_4Br_2 = 0.4580\ \cancel{\text{mol } C_2H_4Br_2} \times \frac{187.862\ \text{g } C_2H_4Br_2}{1\ \cancel{\text{mol } C_2H_4Br_2}} = 86.05\ \text{g } C_2H_4Br_2$$

44. Write the balanced equation, then outline the steps necessary to determine the information requested in each of the following:
(a) The number of moles and the mass of Mg required to react with 5.00 g of HCl and produce $MgCl_2$ and H_2.
(b) The number of moles and the mass of oxygen formed by the decomposition of 1.252 g of silver oxide.
(c) The number of moles and the mass of magnesium carbonate, $MgCO_3$, required to produce 283 g of carbon dioxide. (MgO is the other product.)
(d) The number of moles and the mass of water formed by the combustion of 20.0 kg ofacetylene, C_2H_2, in an excess of oxygen.
(e) The number of moles and the mass of barium peroxide, BaO_2, needed to produce 2.500 kg of barium oxide, BaO (O_2 is the other product.)
(f)

The number of moles and the mass of



required to react with H_2O to produce 9.55 g of



Solution

(a) $Mg + 2HCl \longrightarrow MgCl_2 + H_2$, g HCl $\longrightarrow$ mol HCl $\longrightarrow$ mol Mg $\longrightarrow$ g Mg;

(b) $2Ag_2O \longrightarrow 4Ag + O_2$, g $Ag_2O \longrightarrow$ mol $Ag_2O \longrightarrow$ mol O_2 g O_2;

(c) $MgCO_3 \longrightarrow CO_2 + MgO$, g $CO_2 \longrightarrow$ mol $CO_2 \longrightarrow$ mol $MgCO_3 \longrightarrow$ g $MgCO_3$;

(d) $C_2H_2 + 5O_2 \longrightarrow 4CO_2 + 2H_2O$, $C_2H_2 \longrightarrow$ mol $C_2H_2 \longrightarrow$ mol $H_2O \longrightarrow$ g H_2O;

(e) $2BaO_2 \longrightarrow 2BaO + O_2$,

kg BaO $\longrightarrow$ g BaO $\longrightarrow$ mol BaO $\longrightarrow$ mol $BaO_2 \longrightarrow$ g BaO_2; (f)

$C_2H_4 + H_2O \longrightarrow C_2H_6O$, g $C_2H_6O \longrightarrow$ mol $C_2H_6O \longrightarrow$ mol $C_2H_4 \longrightarrow$ g C_2H_4

45. Determine the number of moles and the mass requested for each reaction in Exercise 44.

Solution

(a) $\text{mol Mg} = 5.00\ \cancel{\text{g HCl}} \times \frac{1\ \cancel{\text{mol HCl}}}{36.4606\ \cancel{\text{g}}} \times \frac{1\ \text{mol Mg}}{2\ \cancel{\text{mol HCl}}} = 0.0686\ \text{mol}$,

$\text{g Mg} = 0.0686\ \cancel{\text{mol Mg}} \times \frac{24.305\ \text{g}}{1\ \cancel{\text{mol Mg}}} = 1.67\ \text{g}$;

(b) $\text{mol } O_2 = 1.252\ \cancel{\text{g } Ag_2O} \times \frac{1\ \cancel{\text{mol } Ag_2O}}{231.7358\ \cancel{\text{g}}} \times \frac{1\ \text{mol } O_2}{2\ \cancel{\text{mol } Ag_2O}} = 2.701 \times 10^{-3}$,

$\text{g } O_2 = 2.701 \times 10^{-3}\ \cancel{\text{mol } O_2} \times \frac{31.9988\ \text{g}}{1\ \cancel{\text{mol } O_2}} = 0.08644\ \text{g}$;(c)

$\text{mol } MgCO_3 = 283\ \cancel{\text{g } CO_2} \times \frac{1\ \cancel{\text{mol } CO_2}}{44.010\ \cancel{\text{g}}} \times \frac{1\ \text{mol } MgCO_3}{1\ \cancel{\text{mol } CO_2}} = 6.43\ \text{mol}$,

$\text{g } MgCO_3 = 6.43\ \cancel{\text{mol } MgCO_3} \times \frac{84.314\ \text{g}}{1\ \cancel{\text{mol } MgCO_3}} = 542\ \text{g}$;

(d) $\text{mol } H_2O = 2.00 \times 10^4\ \cancel{\text{g } C_2H_4} \times \frac{1\ \cancel{\text{mol } C_2H_2}}{26.04\ \cancel{\text{g}}} \times \frac{1\ \text{mol } H_2O}{1\ \cancel{\text{mol } C_2H_2}} = 768\ \text{mol}$,

$\text{g } H_2O = 768\ \cancel{\text{mol } H_2O} \times \frac{18.01528\ \cancel{\text{g}}}{1\ \cancel{\text{mol } H_2O}} \times \frac{1\ \text{kg}}{1000\ \cancel{\text{g}}} = 13.8\ \text{kg}$

(e) $2.500\ \cancel{\text{kg BaO}} \times \frac{1000\ \cancel{\text{g BaO}}}{1\ \cancel{\text{kg BaO}}} \times \frac{1\ \cancel{\text{mol BaO}}}{153.326\ \cancel{\text{g BaO}}} \times \frac{2\ \text{mol } BaO_2}{2\ \cancel{\text{mol BaO}}} = 16.31\ \text{mol } BaO_2$

$16.31\ \cancel{\text{mol } BaO_2} \times \frac{169.326\ \text{g } BaO_2}{1\ \cancel{\text{mol } BaO_2}} = 2762\ \text{g } BaO_2$

(f) $9.55\ \cancel{\text{g } C_2H_6O} \times \frac{1\ \cancel{\text{mol } C_2H_6O}}{46.068\ \cancel{\text{g } C_2H_6O}} \times \frac{1\ \text{mol } C_2H_4}{1\ \cancel{\text{mol } C_2H_6O}} = 0.207\ \text{mol } C_2H_4$

$0.207\ \cancel{\text{mol } C_2H_4} \times \frac{28.053\ \text{g } C_2H_4}{1\ \cancel{\text{mol } C_2H_4}} = 5.81\ \text{g } C_2H_4$

46. H_2 is produced by the reaction of 118.5 mL of a 0.8775-*M* solution of H_3PO_4 according to the following equation: $2Cr + 2H_3PO_4 \longrightarrow 3H_2 + 2CrPO_4$.

(a) Outline the steps necessary to determine the number of moles and mass of H_2.
(b) Perform the calculations outlined.

Solution

(a) volume of H_3PO_4 solution $\longrightarrow$ moles of H_3PO_4 $\longrightarrow$ moles of H_2 $\longrightarrow$ mass of H_2;

(b) multiply the volume in liters times the molarity to find the moles of H_3PO_4.

$\text{mol } H_3PO_4 = 0.1185\ \text{L} \times 0.8775\ M = 0.10398\ \text{mol}$

$\text{mol } H_2 = 0.10398\ \cancel{\text{mol } H_3PO_4} \times \frac{3\ \text{mol } H_2}{2\ \cancel{\text{mol } H_3PO_4}} = 0.1560\ \text{mol}$

$\text{g } H_2 = 0.1560\ \cancel{\text{mol } H_2} \times \frac{2.01588\ \text{g}}{1\ \cancel{\text{mol } H_2}} = 0.3144\ \text{g}$

47. Gallium chloride is formed by the reaction of 2.6 L of a 1.44 *M* solution of HCl according to

the following equation: $2Ga + 6HCl \longrightarrow 2GaCl_3 + 3H_2$.

(a) Outline the steps necessary to determine the number of moles and mass of gallium chloride.
(b) Perform the calculations outlined.

Solution

(a) volume HCl solution $\longrightarrow$ mol HCl $\longrightarrow$ mol $GaCl_3$; (b)

$$2.6 \cancel{\text{ L HCl}} \times \frac{1.44 \cancel{\text{ mol HCl}}}{1 \cancel{\text{ L HCl}}} \times \frac{2 \cancel{\text{ mol GaCl}_3}}{6 \cancel{\text{ mol HCl}}} \times \frac{176.1 \text{ g GaCl}_3}{1 \cancel{\text{ mol GaCl}_3}} = 2.2 \times 10^2 \text{ g GaCl}_3$$

48. I_2 is produced by the reaction of 0.4235 mol of $CuCl_2$ according to the following equation:

$2CuCl_2 + 4KI \longrightarrow 2CuI + 4KCl + I_2$.

(a) How many molecules of I_2 are produced?
(b) What mass of I_2 is produced?

Solution

(a) The calculation requires the following conversions:

mol $CuCl_2$ $\longrightarrow$ mol I_2 $\longrightarrow$ molecules of I_2

$$\text{molecules of } I_2 = 0.4235 \cancel{\text{ mol CuCl}_2} \times \frac{1 \cancel{\text{ mol I}_2}}{2 \cancel{\text{ mol CuCl}_2}} \times \frac{6.022 \times 10^{23} \text{ molecules}}{1 \cancel{\text{ mol I}_2}}$$

; (b) There

$$= 1.275 \times 10^{23} \text{ molecules of } I_2$$

are two possible ways to approach the problem.

Approach 1: Start with the number of moles. Since $2 \text{ mol } CuCl_2 \longrightarrow 1 \text{ mol } I_2$

$$0.4235 \cancel{\text{ mol CuCl}_2} \times \frac{1 \text{ mol I}_2}{2 \cancel{\text{ mol CuCl}_2}} = 0.21175 \text{ mol I}_2$$

$$0.21175 \cancel{\text{ mol I}_2} \times \frac{253.809 \text{ g}}{1 \cancel{\text{ mol I}_2}} = 53.74 \text{ g I}_2$$

Approach 2: Start with the number of molecules.

$$1.275 \times 10^{23} \cancel{\text{ molecules I}_2} \times \frac{253.809 \text{ g}}{6.022 \times 10^{23} \cancel{\text{ molecules I}_2}} = 53.74 \text{ g I}_2$$

49. Silver is often extracted from ores as $K[Ag(CN)_2]$ and then recovered by the reaction

$2K\left[Ag(CN)_2\right](aq) + Zn(s) \longrightarrow 2Ag(s) + Zn(CN)_2(aq) + 2KCN(aq)$

(a) How many molecules of $Zn(CN)_2$ are produced by the reaction of 35.27 g of $K[Ag(CN)_2]$?
(b) What mass of $Zn(CN)_2$ is produced?

Solution

The development requires the following:

mass $K\left[Ag(CN)_2\right]$ $\longrightarrow$ mol $K\left[Ag(CN)_2\right]$ $\longrightarrow$ mol $Zn(CN)_2$;

$\longrightarrow$ molecules of $Zn(CN)_2$ g $Zn(CN)_2$

(a)

$$35.27 \cancel{\text{ g K[Ag(CN)}_2\text{]}} \times \frac{1 \cancel{\text{ mol K[Ag(CN)}_2\text{]}}}{199.002 \cancel{\text{ g K[Ag(CN)}_2\text{]}}} \times \frac{1 \cancel{\text{ mol Zn(CN)}_2}}{2 \cancel{\text{ mol K[Ag(CN)}_2\text{]}}} \times \frac{6.022 \times 10^{23}}{1 \cancel{\text{ mol Zn(CN)}_2}}$$

$$= 5.337 \times 10^{22} \text{ molecules}$$

(b)

$$5.337 \times 10^{22}\ \cancel{\text{molecules}} \times \frac{1\ \cancel{\text{mol Zn(CN)}_2}}{6.022 \times 10^{23}\ \cancel{\text{molecules}}} \times \frac{117.43\ \text{g Zn(CN)}_2}{1\ \cancel{\text{mol Zn(CN)}_2}} = 10.41\ \text{g Zn(CN)}_2$$

50. What mass of silver oxide, Ag_2O, is required toproduce 25.0 g of silver sulfadiazine, $AgC_{10}H_9N_4SO_2$, from the reaction of silver oxide and sulfadiazine?

$$2C_{10}H_{10}N_4SO_2 + Ag_2O \longrightarrow 2AgC_{10}H_9N_4SO_2 + H_2O$$

Solution

The following conversions are needed:

$$\text{g } AgC_{10}H_9N_4SO_2 \longrightarrow \text{mol } AgC_{10}H_9N_4SO_2 \longrightarrow \text{mol } Ag_2O \longrightarrow \text{g } Ag_2O$$

$$\text{mass } Ag_2O = 25.0\ \cancel{\text{g AgC}_{10}\text{H}_9\text{N}_4\text{SO}_2} \times \frac{1\ \cancel{\text{mol AgC}_{10}\text{H}_9\text{N}_4\text{SO}_2}}{357.141\ \cancel{\text{g AgC}_{10}\text{H}_9\text{N}_4\text{SO}_2}} \times \frac{1\ \cancel{\text{mol Ag}_2\text{O}}}{2\ \cancel{\text{mol AgC}_{10}\text{H}_9\text{N}_4\text{SO}_2}}$$

$$\times \frac{231.735\ \text{g Ag}_2\text{O}}{1\ \cancel{\text{mol Ag}_2\text{O}}} = 8.11\ \text{g}$$

51. Carborundum is silicon carbide, SiC, a very hard material used as an abrasive on sandpaper and in other applications. It is prepared by the reaction of pure sand, SiO_2, with carbon at high temperature. Carbon monoxide, CO, is the other product of this reaction. Write the balanced equation for the reaction, and calculate how much SiO_2 is required to produce 3.00 kg of SiC.

Solution

$SiO_2 + 3C \longrightarrow SiC + 2CO$. From the balanced equation, 1 mol of SiO_2 produces 1 mol of SiC. The unknown is the mass of SiO_2 required to produce 3.00 kg (3000 g) of SiC. To calculate the mass of SiO_2 required, determine the molar masses of SiO_2 and SiC. Then calculate the number of moles of SiC required, and through the mole relation of SiO_2 to SiC, find the mass of SiO_2 required. The conversions required are:

$$\text{g SiC} \longrightarrow \text{mol SiC} \longrightarrow \text{mol } SiO_2 \longrightarrow \text{g } SiO_2$$

Molar masses: $SiO_2 = 60.0843\ \text{g mol}^{-1}$; $SiC = 40.0955\ \text{g mol}^{-1}$

$$\text{mass SiO2} = 3000\ \cancel{\text{g SiC}} \times \frac{1\ \cancel{\text{mol SiC}}}{40.955\ \cancel{\text{g SiC}}} \times \frac{1\ \cancel{\text{mol SiO}_2}}{1\ \cancel{\text{mol SiC}}} \times \frac{60.843\ \text{g SiO}_2}{1\ \cancel{\text{mol SiO}_2}} = 4496\ \text{g SiO}_2$$

$$= 4.50\ \text{kg SiO}_2$$

52. Automotive air bags inflate when a sample of sodium azide, NaN_3, is very rapidly decomposed.

$$2NaN_3(s) \longrightarrow 2Na(s) + 3N_2(g)$$

What mass of sodium azide is required to produce 2.6 ft^3 (73.6 L) of nitrogen gas with a density of 1.25 g/L?

Solution

$$\text{volume } N_2 \longrightarrow \text{mass } N_2 \longrightarrow \text{mol } N_2 \longrightarrow \text{mol } NaN_3 \longrightarrow \text{mass } NaN_3$$

$$368\ \cancel{\text{L}} \times \frac{1.25\ \cancel{\text{g}}}{\cancel{\text{L}}} \times \frac{1\ \cancel{\text{mol N}_2}}{28.02\ \cancel{\text{g}}} \times \frac{2\ \cancel{\text{mol NaN}_3}}{3\ \cancel{\text{mol N}_2}} \times \frac{65.02\ \text{g}}{1\ \cancel{\text{mol NaN}_3}} = 712\ \text{g}$$

53. Urea, $CO(NH_2)_2$, is manufactured on a large scale for use in producing urea-formaldehyde plastics and as a fertilizer. What is the maximum mass of urea that can be manufactured from the CO_2 produced by combustion of 1.00×10^3 kg of carbon followed by the reaction?

$$CO_2(g) + 2NH_3(g) \longrightarrow CO(NH_2)_2(s) + H_2O(l)$$

Solution
Molar mass urea = 12.011 + 15.9994 + 2(14.0067) + 4(1.0079) = 60.054 g mol^{-1}

$$1 \text{ mol C} \longrightarrow 1 \text{ mol } CO_2 \longrightarrow 1 \text{ mol urea}$$

$$\text{mass urea} = 1.00 \times 10^3 \text{ kg} \times \frac{1000 \text{ g}}{\text{kg}} \times \frac{1 \text{ mol C}}{12.0 \text{ g C}} \times \frac{1 \text{ mol urea}}{1 \text{ mol C}} \times \frac{60.054 \text{ g urea}}{1 \text{ mol urea}}$$

$$= 5.00 \times 10^6 \text{ g or } 5.00 \times 10^3 \text{ kg}$$

54. In an accident, a solution containing 2.5 kg of nitric acid was spilled. Two kilograms of Na_2CO_3 was quickly spread on the area and CO_2 was released by the reaction. Was sufficient Na_2CO_3 used to neutralize all of the acid?

Solution
The reaction is $Na_2CO_3 + 2HNO_3 \longrightarrow 2Na^+ + 2NO_3^- + 2CO_2 + H_2O$
Calculate the mass of Na_2CO_3 required for complete reaction of nitric acid using the process

$$\text{mass of acid} \longrightarrow \text{mol of acid} \longrightarrow \text{mol of } Na_2CO_3 \longrightarrow \text{mass of } Na_2CO_3$$

$$\text{mass of } Na_2CO_3 = 2.5 \text{ kg} \times 1000 \text{ g kg}^{-1} \times \frac{1 \text{ mol } HNO_3}{63.0 \text{ g}} \times \frac{1 \text{ mol } Na_2CO_3}{2 \text{ mol } HNO_3} \times \frac{106.0 \text{ g}}{\text{mol } Na_2CO_3}$$

$$= 2.1 \times 10^3 \text{ g} = 2.1 \text{ kg}$$

No, 2.1 kg is required.

55. A compact car gets 37.5 miles per gallon on the highway. If gasoline contains 84.2% carbonby mass and has a density of 0.8205 g/mL, determine the mass of carbon dioxide produced during a 500-mile trip (3.785 liters per gallon).

Solution
The balanced chemical equation is $C(s) + O_2(g) \longrightarrow CO_2(g)$

$$500 \text{ miles} \times \frac{1 \text{ gallon}}{37.5 \text{ miles}} \times \frac{3.785 \text{ L}}{1 \text{ gallon}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{0.8205 \text{ g gas}}{1 \text{ mL gas}} \times \frac{84.2 \text{ g C}}{100 \text{ g gas}}$$

$$\times \frac{1 \text{ mol C}}{12.01 \text{ g C}} \times \frac{1 \text{ mol } CO_2}{1 \text{ mol C}} \times \frac{44.01 \text{ g } CO_2}{1 \text{ mol } CO_2} = 1.28 \times 10^5 \text{ g } CO_2$$

56. What volume of a 0.750 M solution of hydrochloric acid, a solution of HCl, can be prepared from the HCl produced by the reaction of 25.0 g of NaCl with an excess of sulfuric acid?

$$NaCl(s) + H_2SO_4(l) \longrightarrow HCl(g) + NaHSO_4(s)$$

Solution

$$\text{mass NaCl} \longrightarrow \text{mol NaCl} \longrightarrow \text{mol HCl} \longrightarrow \text{Volume HCl}$$

$$25.0 \text{ g NaCl} \times \frac{1 \text{ mol NaCl}}{58.44 \text{ g NaCl}} \times \frac{1 \text{ mol HCl}}{1 \text{ mol NaCl}} \times \frac{1 \text{ L HCl}}{0.750 \text{ mol HCl}} = 0.570 \text{ L HCl}$$

57. What volume of a 0.2089 M KI solution contains enough KI to react exactly with the $Cu(NO_3)_2$ in 43.88 mL of a 0.3842 M solution of $Cu(NO_3)_2$?

$$2Cu(NO_3)_2 + 4KI \longrightarrow 2CuI + I_2 + 4KNO_3$$

Solution
Use molarity to convert. This solution involves the following steps:

1. Converting the volume of KI to moles of KI
2. Converting the moles of KI to moles of $Cu(NO_3)_2$
3. Converting the moles of $K \longrightarrow Cu(NO_3)_2$ to a volume of KI.$Cu(NO_3)_2$ solution

$$43.88 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.3842 \text{ mol Cu(NO}_3)_2}{1 \text{ L}} \times \frac{4 \text{ mol KI}}{2 \text{ mol Cu(NO}_3)_2} \times \frac{1 \text{ L KI}}{0.2089 \text{ mol KI}}$$

$= 161.4$ mL

All of these steps can be shown together, as follows:

$$\frac{43.88 \text{ mL Cu(NO}_3)_2}{1} \times \frac{0.3842 \text{ mol Cu(NO}_3)_2}{1000 \text{ mL Cu(NO}_3)_2} \times \frac{4 \text{ mol KI}}{2 \text{ mol Cu(NO}_3)_2} \times \frac{1000 \text{ mL KI}}{0.2089 \text{ mol KI}}$$

$= 161.4$ mL KI solution

58. A mordant is a substance that combines with a dye to produce a stable fixed color in a dyed fabric. Calcium acetate is used as a mordant. It is prepared by the reaction of acetic acid with calcium hydroxide.

$$2CH_3CO_2H + Ca(OH)_2 \longrightarrow Ca(CH_3CO_2)_2 + 2H_2O$$

What mass of $Ca(OH)_2$ is required to react with the acetic acid in 25.0 mL of a solution having a density of 1.065 g/mL and containing 58.0% acetic acid by mass?

Solution

Volume of solution $\longrightarrow$ mass solution $\longrightarrow$ mass acetic acid $\longrightarrow$ moles of acetic acid $\longrightarrow$ moles $Ca(OH)_2$ $\longrightarrow$ mass $Ca(OH)_2$

The last step is to determine the mass of $Ca(OH)_2$ from the moles:

$$25.0 \text{ mL} \times \frac{1.065 \text{ g solution}}{1 \text{ mL}} \times \frac{58.0 \text{ g acetic acid}}{100 \text{ g solution}} \times \frac{1 \text{ mol } CH_3COOH}{60.05 \text{ g } CH_3COOH} \times \frac{1 \text{ mol } Ca(OH)_2}{2 \text{ mol } CH_3COOH} \times \frac{74.093 \text{ g } Ca(OH)_2}{1 \text{ mol}} = 9.53 \text{ g}$$

59. The toxic pigment called white lead, $Pb_3(OH)_2(CO_3)_2$, has been replaced in white paints by rutile, TiO_2. How much rutile (g) can be prepared from 379 g of an ore that contains 88.3% ilmenite ($FeTiO_3$) by mass?

$$2FeTiO_3 + 4HCl + Cl_2 \longrightarrow 2FeCl_3 + 2TiO_2 + 2H_2O$$

Solution

Find from worked example, check your learning problem

$$\text{mass of ilmenite} = 379 \text{ g ore} \times \frac{0.883 \text{ g } FeTiO_3}{1 \text{ g ore}} = 334.6 \text{ g } FeTiO_3$$

$$\text{mass of rutile} = 334.6 \text{ g } FeTiO_3 \times \frac{1 \text{ mol } FeTiO_3}{151.7 \text{ g } FeTiO_3} \times \frac{2 \text{ mol } TiO_2}{2 \text{ mol } FeTiO_3} \times \frac{79.88 \text{ g } TiO_2}{1 \text{ mol } TiO_2}$$

$= 176$ g TiO_2

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7: Stoichiometry of Chemical Reactions
7.4: Reaction Yields

60. The following quantities are placed in a container: 1.5×10^{24} atoms of hydrogen, 1.0 mol of sulfur, and 88.0 g of diatomic oxygen.
(a) What is the total mass in grams for the collection of all three elements?
(b) What is the total number of moles of atoms for the three elements?
(c) If the mixture of the three elements formed a compound with molecules that contain two hydrogen atoms, one sulfur atom, and four oxygen atoms, which substance is consumed first?
(d) How many atoms of each remaining element would remain unreacted in the change described in (c)?

Solution
(a) Convert each quantity to grams.

For H: $\dfrac{1.5 \times 10^{24} \text{ atoms}}{6.022 \times 10^{23} \text{ atoms mol}^{-1}} \times 1.0079 \text{ g mol}^{-1} \text{ H} = 2.5 \text{ g}$

For S: $1.0 \text{ mol S} \times \dfrac{32.06 \text{ g S}}{1 \text{ mol S}} = 32 \text{ g S}$

Total mass = 2.5 g H + 32 g S + 88 g O_2 = 122 g
(b) Convert each quantity to moles.

For H: $\dfrac{1.5 \times 10^{24} \text{ atoms}}{6.022 \times 10^{23} \text{ atoms mol}^{-1}} = 2.5 \text{ mol H}$

For S: 1.0 mol S

For O_2: $88.0 \cancel{\text{ g O}_2} \times \dfrac{1 \cancel{\text{ mol O}_2}}{31.9988 \cancel{\text{ g O}_2}} \times \dfrac{2 \text{ mol O}}{1 \cancel{\text{ mol O}_2}} = 5.5 \text{ mol O}$

Total number of moles = 2.5 + 1.0 + 5.5 = 9.0 mol
(c) The moles of each element present are given in (b). The ratio is 2.5 H: 1.0 S: 11.0 O. The ratio in the compound is 2H: 1 S: 4 O. Comparing these two ratios shows that both H and O are provided in greater-than-stoichiometric amounts. For each mole of S, the compound requires 2 moles of H (2.5 are provided) and 4 moles of O (11.0 mol are provided). Sulfur, therefore, is the limiting reagent.
(d) H remaining = 2.5 mol – 2.0 mol = 0.5 mol H or 3.0×10^{23} H atoms; O atoms remaining = 11.0 mol – 4.0 mol = 7 mol O or 4.2×10^{24} O atoms

61. What is the limiting reactant in a reaction that produces sodium chloride from 8 g of sodium and 8 g of diatomic chlorine?

Solution
Write the balanced chemical equation and determine the number of moles of each reactant available.

The reaction is: $2\text{Na} + \text{Cl}_2 \longrightarrow 2\text{NaCl}$

$\text{Moles of Na} = 8 \text{ g Na} \times \dfrac{1 \text{ mol}}{23.0 \text{ g}} = 0.3 \text{ mol Na}$

$\text{Moles of Cl}_2 = 8 \text{ g} \times \dfrac{1 \text{ mol}}{70.9 \text{ g}} = 0.1 \text{ mol Cl}_2$

The stoichiometric ratio is 2 mol Na: 1 mol Cl_2; since the reactants are provided in a 0.3:0.1 or 3:1 ratio, Na is present in excess and Cl_2 is the limiting reactant.

62. Which of the postulates of Dalton's atomic theory explains why we can calculate a theoretical yield for a chemical reaction?

Solution

In a given compound, the number of atoms of each type always has the same ratio. Atoms are neither created nor destroyed during a chemical change.

63. A student isolated 25 g of a compound following a procedure that would theoretically yield 81 g. What was his percent yield?

$$\text{Percent yield} = \frac{25\text{ g}}{81\text{ g}} \times 100\% = 31\%$$

64. A sample of 0.53 g of carbon dioxide was obtained by heating 1.31 g of calcium carbonate. What is the percent yield for this reaction?

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(s)$$

Solution

Begin by calculating the mass of CO_2 that can be produced from 1.31 g of $CaCO_3$, assuming that all of the CO_2 can be recovered. The conversion is $\text{g } CaCO_3 \longrightarrow \text{mol } CaCO_3 \longrightarrow \text{mol } CO_2 \longrightarrow \text{g } CO_2$. This procedure gives the theoretical mass. Then divide the actual yield by the theoretical yield and multiply the result by 100% to obtain the percentage yield. Molar masses: $CaCO_3$ = 100.09 g/mol; CO_2 = 44.010 g/mol. For complete conversion,

$$\text{Mass } CO_2 = 1.31\text{ g } CaCO_3 \times \frac{1\text{ mol } CaCO_3}{100.09\text{ g } CaCO_3} \times \frac{1\text{ mol } CO_2}{1\text{ mol } CaCO_3} \times \frac{44.010\text{ g } CO_2}{1\text{ mol } CO_2}$$

$$= 0.576\text{ g } CO_2 \text{ (theoretical yield)}$$

65. Freon-12, CCl_2F_2, is prepared from CCl_4 by reaction with HF. The other product of this reaction is HCl. Outline the steps needed to determine the percent yield of a reaction that produces 12.5 g of CCl_2F_2 from 32.9 g of CCl_4. Freon-12 has been banned and is no longer used as a refrigerant because it catalyzes the decomposition of ozone and has a very long lifetime in the atmosphere. Determine the percent yield.

Solution

Write and balance the equation for the reaction: $CCl_4 + 2HF \longrightarrow CCl_2F_2 + 2HCl$. Molar masses: CCl_4 = 153.82 g/mol; CCl_2F_2 = 120.89 g/mol. The conversions required are $\text{g } CCl_4 \longrightarrow \text{mol } CCl_4 \longrightarrow \text{mol } CCl_2F_2 \longrightarrow \text{g } CCl_2F_2$. To find the percent yield, divide the 12.5 g of CCl_2F_2 by the theoretical mass, and multiply by 100%. For complete conversion,

$$\text{mass } CCl_2F_2 = 32.9\ \cancel{\text{g } CCl_4} \times \frac{1\ \cancel{\text{mol } CCl_4}}{153.82\ \cancel{\text{g } CCl_4}} \times \frac{1\ \cancel{\text{mol } CCl_2F_2}}{1\ \cancel{\text{mol } CCl_4}} \times \frac{120.89\text{ g } CCl_2F_2}{1\ \cancel{\text{mol } CCl_2F_2}}$$

$$= 25.86\text{ g } CCl_2F_2$$

$$\text{percent yield} = \frac{12.5\text{ g}}{25.86\text{ g}} \times 100\% = 48.3\%$$

66. Citric acid, $C_6H_8O_7$, a component of jams, jellies, and fruity soft drinks, is prepared industrially via fermentation of sucrose by the mold *Aspergillus niger*. The equation representing this reaction is

$$C_{12}H_{22}O_{11} + H_2O + 3O_2 \longrightarrow 2C_6H_8O_7 + 4H_2O$$

What mass of citric acid is produced from exactly 1 metric ton (1.000×10^3 kg) of sucrose if the yield is 92.30%?

Solution

Calculate the mass of citric acid by assuming 100% yield. The expected value is 92.30% of this amount. $C_{12}H_{22}O_{11} + H_2O + 3O_2 \longrightarrow 2C_6H_8O_7 + 4H_2O$

1 mol 2 mol

1.000×10^3 kg 100% yield?

Formula masses: $C_{12}H_{22}O_{11}$ = 342.30 g/mol; $C_6H_8O_7$ = 192.12 g/mol. Once the ratio of masses is established, the formula masses are independent of units; thus, mass either in grams or kilograms can be used, as long as the units are used consistently. One mole of $C_{12}H_{22}O_{11}$ (342.30 g), produces two moles of $C_6H_8O_7$: 2×192.12 g = 384.24. Using kilogram values, 342.30 kg of $C_{12}H_{22}O_{11}$ produces 2×192.12 kg of citric acid, or 384.24 kg.

For 100% yield,

$$\text{mass of } C_6H_8O_7 = 1.000 \times 10^3 \text{ kg sucrose} \times \frac{1 \text{ mol kg sucrose}}{342.30 \text{ kg sucrose}} \times \frac{2 \text{ mol-kg citric acid}}{1 \text{ mol-kg sucrose}} \times \frac{192.12 \text{ kg citric acid}}{\text{mol-kg citric acid}} = 1122 \text{ kg citric acid}$$

For 92.302% yield, mass of $C_6H_8O_7$ = 1122 kg $\times$ 0.9230 = 1036 kg

67. Toluene, $C_6H_5CH_3$, is oxidized by air under carefully controlled conditions to benzoic acid, $C_6H_5CO_2H$, which is used to prepare the food preservative sodium benzoate, $C_6H_5CO_2Na$. What is the percent yield of a reaction that converts 1.000 kg of toluene to 1.21 kg of benzoic acid?

$2C_6H_5CH_3 + 3O_2 \longrightarrow 2C_6H_5CO_2H + 2H_2O$

Solution

$$100 \cancel{\text{ g } C_6H_5CH_3} \times \frac{1 \cancel{\text{ mol toluene}}}{92.13 \cancel{\text{ g } C_6H_5CH_3}} \times \frac{1 \cancel{\text{ mol benzoic acid}}}{1 \cancel{\text{ mol toluene}}} \times \frac{122.1 \cancel{\text{ g benzoic acid}}}{1 \cancel{\text{ mol benzoic acid}}} \times \frac{1 \text{ kg}}{1000 \cancel{\text{ g benzoic acid}}} = 1.325 \text{ kg benzoic acid (theoretical yield)}$$

$$\text{percent yield} = \frac{1.21 \text{ kg}}{1.325 \text{ kg}} \times 100\% = 91.3\%$$

68. In a laboratory experiment, the reaction of 3.0 mol of H_2 with 2.0 mol of I_2 produced 1.0 mol of HI. Determine the theoretical yield in grams and the percent yield for this reaction.

Solution

$H_2 + I_2 \longrightarrow 2HI$

Because the balanced equation shows that H_2 and I_2 react on a 1:1 molar ratio, the I_2 in this problem is limiting.

$$2.0 \text{ mol } I_2 \times \frac{2 \text{ mol HI}}{1 \text{ mol } I_2} = 4.0 \text{ mol HI (theoretical yield)}$$

$$4.0 \text{ mol HI} \times \frac{127.9 \text{ g}}{\text{mol HI}} = 5.1 \times 10^2 \text{ HI}$$

$$\text{percent yield} = \frac{1.0 \text{ mol}}{4.0 \text{ mol}} \times 100\% = 25\%$$

69. Outline the steps needed to solve the following problem, then do the calculations. Ether, $(C_2H_5)_2O$, which was originally used as an anesthetic but has been replaced by safer and more effective medications, is prepared by the reaction of ethanol with sulfuric acid.

$$2C_2H_5OH + H_2SO_4 \longrightarrow (C_2H_5)_2O + H_2SO_4 \cdot H_2O$$

What is the percent yield of ether if 1.17 L (d = 0.7134 g/mL) is isolated from the reaction of 1.500 L of C_2H_5OH (d = 0.7894 g/mL)?

Solution

Convert mass of ethanol to moles of ethanol; relate the moles of ethanol to the moles of ether produced using the stoichiometry of the balanced equation. Convert moles of ether to grams; divide the actual grams of ether (determined through the density) by the theoretical mass to determine the percent yield.

$$d_{ether} = \frac{m}{V}$$

$$m = dV = 0.7134 \text{ g mL}^{-1} \times 1170 \text{ mL} = 834.7 \text{ g}$$

$$d_{ether} = \frac{m}{V}$$

$$m = dV = 0.7894 \text{ g mL}^{-1} \times 1500 \text{ mL} = 1184 \text{ g}$$

Mass ether = 1.184

$$\text{mass ether} = \cancel{\text{g ethanol}} \times \frac{1 \cancel{\text{ mol ethanol}}}{46.0688 \cancel{\text{ g ethanol}}} \times \frac{1 \cancel{\text{ mol ether}}}{2 \cancel{\text{ mol ethanol}}} \times \frac{74.1224 \text{ g ether}}{1 \cancel{\text{ mol ether}}}$$

$$= 0.9525 \text{ g}$$

$$\text{percent yield} = \frac{0.8347 \cancel{\text{ g}}}{0.9525 \cancel{\text{ g}}} \times 100\% = 87.6\%$$

70. Outline the steps needed to determine the limiting reactant when 30.0 g of propane, C_3H_8, is burned with 75.0 g of oxygen.

Determine the limiting reactant.

Solution

Determine the moles of CO_2 produced by 30.0 g of propane. Determine the moles of CO_2 produced by 75.0 g of oxygen. The limiting reagent is the one that produces the smaller amount of CO_2.

$$30.0 \text{ g } C_3H_8 \times \frac{1 \text{ mol } C_3H_8}{44.097 \text{ g } C_3H_8} \times \frac{5 \text{ mol } O_2}{1 \text{ mol } C_3H_8} = 3.40 \text{ mol } O_2$$

$$75.0 \text{ g } O_2 \times \frac{1 \text{ mol } O_2}{31.9988 \text{ g } O_2} = 2.34 \text{ mol } O_2$$

Only 2.34 mol O_2 is available. As 3.40 mol of O_2 are required to burn the propane, O_2 is limiting the reaction.

71. Outline the steps needed to determine the limiting reactant when 0.50 g of Cr and 0.75 g of H_3PO_4 react according to the following chemical equation?

$$2Cr + 2H_3PO_4 \longrightarrow 2CrPO_4 + 3H_2$$

Determine the limiting reactant.

Solution

The conversion needed is $\text{mol Cr} \longrightarrow \text{mol } H_3PO_4$. Then compare the amount of Cr to the amount of acid present.

$$0.50 \text{ mol Cr} \times \frac{2 \text{ mol } H_3PO_4}{2 \text{ mol Cr}} = 0.50 \ H_3PO_4$$

Thus, 0.25 mol H_3PO_4 is in excess, so Cr is the limiting reactant.

72. What is the limiting reactant when 1.50 g of lithium and 1.50 g of nitrogen combine to form lithium nitride, a component of advanced batteries, according to the following unbalanced equation?

$$Li + N_2 \longrightarrow Li_3N$$

Solution

Balance the equation. Then determine the number of moles of each component and compare with the mole requirement of the balanced equation.

$$6Li + N_2 \longrightarrow 2Li_3N$$

$$\text{mol Li} = 1.50 \text{ g Li} \times \frac{1 \text{ mol Li}}{6.941 \text{ g Li}} = 0.216 \text{ mol Li}$$

$$\text{mol } N_2 = 1.50 \text{ g } N_2 \times \frac{1 \text{ mol } N_2}{14.01348 \text{ g } N_2} = 0.107 \text{ mol } N_2$$

The ratio is six Li atoms to 1 mol N_2, the amount of Li is less than six times the number of moles of N_2; thus, Li is the limiting reagent.

73. Uranium can be isolated from its ores by dissolving it as $UO_2(NO_3)_2$, then separating it as solid $UO_2(C_2O_4) \cdot 3H_2O$. Addition of 0.4031 g of sodium oxalate, $Na_2C_2O_4$, to a solution containing 1.481 g of uranyl nitrate, $UO_2(NO_2)_2$, yields 1.073 g of solid $UO_2(C_2O_4) \cdot 3H_2O$.

$$Na_2C_2O_4 + UO_2\left(NO_3\right)_2 + 3H_2O \longrightarrow UO_2\left(C_2O_4\right)\bullet 3H_2O + 2NaNO_3$$

Determine the limiting reactant and the percent yield of this reaction.

Solution

Using the balanced equation, determine which reactant quantity produces the smallest theoretical yield. This quantity represents the largest amount of product that can be produced. Then calculate the percent yield. The conversions for reaction 1 using the nitrate as limiting reactant are

$$\text{g } UO_2\left(NO_3\right)_2 \longrightarrow UO_2\left(NO_3\right)_2 + 3H_2O \longrightarrow UO_2\left(C_2O_4\right)\bullet 3H_2O$$
$$\longrightarrow \text{g } UO_2\left(NO_3\right)_2\bullet 3H_2O.$$

The answer to this calculation should be compared with the answer from reaction 2 that uses sodium oxalate as the limiting reactant and requires the following conversions:

$$\text{g sodium oxalate} \longrightarrow \text{mol sodium oxalate} \longrightarrow \text{mol } UO_2\left(C_2O_4\right)\bullet 3H_2O$$
$$\longrightarrow \text{g } UO_2\left(C_2O_4\right)\bullet 3H_2O$$

Molar masses: $UO_2(NO_3)_2 = 394.04$ g/mol
$Na_2C_2O_4 = 134.00$ g/mol
$UO_2(C_2O_4)\cdot 3H_2O = 412.09$ g/mol

Reaction 1:

$$\text{mass (product)} = 1.48 \ \cancel{\text{g } UO_2(NO_3)_2} \times \frac{1 \ \cancel{\text{mol } UO_2(NO_3)_2}}{394.04 \ \cancel{\text{g } UO_2(NO_3)_2}} \times \frac{1 \ \cancel{\text{mol } UO_2(C_2O_4)\cdot 3H_2O}}{1 \ \cancel{\text{mol } UO_2(NO_3)_2}} \times \frac{412.09 \text{ g } UO_2(C_2O_4)\cdot 3H_2O}{1 \ \cancel{\text{mol } UO_2(C_2O_4)\cdot 3H_2O}} = 1.55 \text{ g } UO_2(C_2O_4)\cdot 3H_2O$$

Reaction 2:

$$\text{mass (product)} = 0.403 \ \cancel{\text{g } Na_2C_2O_4} \times \frac{1 \ \cancel{\text{mol } Na_2C_2O_4}}{134.00 \ \cancel{\text{g } Na_2C_2O_4}} \times \frac{1 \ \cancel{\text{mol } UO_2(C_2O_4)\cdot 3H_2O}}{1 \ \cancel{\text{mol } Na_2C_2O_4}} \times \frac{412.09 \text{ g } UO_2(C_2O_4)\cdot 3H_2O}{1 \ \cancel{\text{mol } UO_2(C_2O_4)\cdot 3H_2O}} = 1.239 \text{ g } UO_2(C_2O_4)\cdot 3H_2O$$

Based on the two masses, the smaller mass is the limiting reactant. Thus, $Na_2C_2O_4$ is the limiting reactant. An amount of $UO_2(NO_3)_2$ is left unreacted.

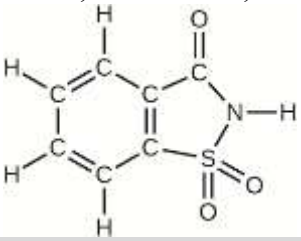
$$\text{percent yield} = \frac{1.073 \ \cancel{\text{g}}}{1.239 \ \cancel{\text{g}}} \times 100 = 86.56\%$$

74. How many molecules of $C_2H_4Cl_2$ can be prepared from 15 C_2H_4 molecules and 8 Cl_2 molecules?

Solution

Since multiplication of $C_2H_4Cl_2$ by eight gives the most Cl that can be accommodated consistent with the amount of Cl present, only eight C_2H_4 molecules are needed. Therefore, C_2H_4 is in excess and Cl_2 is the limiting reagent.

75. How many molecules of the sweetener saccharin can be prepared from 30 C atoms, 25 H atoms, 12 O atoms, 8 S atoms, and 14 N atoms?



Solution

Determine the number of atoms of each element in saccharin and then compare these numbers to the numbers of atoms available. The numbers of atoms in saccharin are seven C atoms, five H atoms, three O atoms, one S atom, and one N atom. Compare these to the numbers of atoms available. Divide each of the required number of atoms into the corresponding number of atoms available. These relationships are 30/7 C, 25/5 H, 12/3 O, 8/1 S, and 14/1 N. The smallest value is four for O, so only four molecules can be made.

76. The phosphorus pentoxide used to produce phosphoric acid for cola soft drinks is prepared by burning phosphorus in oxygen.

(a) What is the limiting reactant when 0.200 mol of P_4and0.200 mol of O_2 react according to

$$P_4 + 5O_2 \longrightarrow P_4O_{10}$$

(b) Calculate the percent yield if 10.0 g of P_4O_{10} is isolated from the reaction.

Solution

(a) The stoichiometry of this reaction requires 1 mole P_4 for each 5 moles of O_2, or an oxygen-to-phosphorus ratio of 5:1. The reactants are provided in equimolar amounts, 0.200 moles each, or

an oxygen-to-phosphorus ratio of 1:1. Oxygen is provided in a less-than-stoichiometric amount and is the limiting reactant.

(b) 0.200 mol O_2 will produce $\frac{1}{5} \times 0.200$ mol of P_4O_{10}. The molar mass of P_4O_{10} is $(4 \times 30.97376) + (10 \times 15.9994) = 283.889$ g/mol. Then $\frac{1}{5} \times 0.200 \times 283.889 \text{ g/mol} = 11.4 \text{ g}$.

$$\text{percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% = \frac{10.0 \text{ g}}{11.4 \text{ g}} \times 100\% = 87.7\%$$

77. Would you agree to buy 1 trillion (1,000,000,000,000) gold atoms for $5? Explain why or why not. Find the current price of gold at http://money.cnn.com/data/commodities/ (1 troy ounce = 31.1 g)

Solution

$$\text{mass Au} = \frac{1 \times 10^{12} \ \cancel{\text{atoms Au}}}{6.022 \times 10^{23} \ \cancel{\text{atoms mol}^{-1}}} \times 196.97 \text{ g } \cancel{\text{mol}^{-1}} = 3.27 \times 10^{-10} \text{ g}$$

This amount cannot be weighted by ordinary balances and is worthless.

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Chemistry: Atoms First 2e
7: Stoichiometry of Chemical Reactions
7.5: Quantitative Chemical Analysis

78. What volume of 0.0105-*M* HBr solution is be required to titrate 125 mL of a 0.0100-*M* $Ca(OH)_2$ solution?

$$Ca(OH)_2(aq) + 2HBr(aq) \longrightarrow CaBr_2(aq) + 2H_2O(l)$$

Solution

$$\text{Volume } Ca(OH)_2 \times \text{M } Ca(OH)_2 \longrightarrow \text{mol } Ca(OH)_2 \longrightarrow \text{mol HBr} \longrightarrow \text{volume HBr}$$

$0.0100\ M\ Ca(OH)_2 \times 0.125 \text{ L } Ca(OH)_2 = 1.25 \times 10^{-3} \text{ mol } Ca(OH)_2$

$$1.25 \times 10^{-3} \text{ mol } Ca(OH)_2 \times \frac{2 \text{ mol HBr}}{1 \text{ mol } Ca(OH)_2} = 2.50 \times 10^{-3} \text{ mol HBr}$$

$$\text{volume HBr} = \frac{2.50 \times 10^{-3} \text{ mol HBr}}{1.05 \times 10^{-2} \text{ mol L}^{-1}} = 0.238 \text{ L or } 238 \text{ mL}$$

79. Titration of a 20.0-mL sample of acid rain required 1.7 mL of 0.0811 *M* NaOH to reach the end point. If we assume that the acidity of the rain is due to the presence of sulfuric acid, what was the concentration of sulfuric acid in this sample of rain?

Solution

The balanced equation is

$$H_2SO_4(aq) + 2NaOH(aq) \longrightarrow Na_2SO_4(aq) + 2H_2O(l)$$

The steps to follow in solving this problem if we use volumes in milliliters are

$$\text{Volume NaOH} \longrightarrow \text{mmol NaOH} \longrightarrow \text{mmol } H_2SO_4 \longrightarrow \text{M } H_2SO_4$$

$$1.7 \cancel{\text{mL}} \times \frac{0.0811 \text{ mmol NaOH}}{\cancel{\text{mL}}} = 0.138 \text{ mmol NaOH}$$

$$\text{mmol } H_2SO_4 = 0.138 \cancel{\text{ mmol NaOH}} \times \frac{1 \text{ mmol } H_2SO_4}{2 \cancel{\text{ mmol NaOH}}} = 0.069 \text{ mmol}$$

$$M \ H_2SO_4 = \frac{0.069 \text{ mmol } H_2SO_4}{20.0 \text{ mL}} = 3.4 \times 10^{-3} \ M$$

80. What is the concentration of NaCl in a solution if titration of 15.00 mL of the solution with 0.2503 *M* $AgNO_3$ requires 20.22 mL of the $AgNO_3$ solution to reach the end point?

$$AgNO_3(aq) + NaCl(aq) \longrightarrow AgCl(s) + NaNO_3(aq)$$

Solution

The end point in the reaction occurs when all available $AgNO_3$ has reacted with the minimum NaCl added. From the balanced equation, $AgNO_3$ and NaCl react on a 1:1 molar basis. Thus, the moles of NaCl in 15.00 mL equal the moles of $AgNO_3$ present:

$$\text{mol } AgNO_3 = 0.250 \ M \times 20.22 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.005055 \text{ mol}$$

Therefore, in 15.00 mL, there are 0.005055 mol NaCl. Thus,

$$M \ \text{NaCl} = \frac{0.005055 \text{ mol}}{0.01500 \text{ L}} = 0.3370 \text{ M}$$

81. In a common medical laboratory determination of the concentration of free chloride ion in blood serum, a serum sample is titrated with a $Hg(NO_3)_2$ solution.

$$2Cl^-(aq) + Hg(NO3)_2(aq) \longrightarrow 2NO_3^-(aq) + HgCl_2(s)$$

What is the Cl^- concentration in a 0.25-mL sample of normal serum that requires 1.46 mL of $5.25 \times 10^{-4} M$ $Hg(NO_3)_2(aq)$ to reach the end point?

Solution

In this exercise, the volume is left in units of milliliters and the number of moles is expressed in units of millimoles to compensate for the factor of 1000 difference between units. This technique is often useful in calculations. The steps involved in solving the problem are

$$\text{Volume } Hg(NO_3)_2 \longrightarrow \text{mmol } Hg(NO_3)_2 \longrightarrow \text{mmol } Cl^- \longrightarrow M \ Cl^-$$

$$\text{mmol } Hg(NO_3)_2 = 1.46 \cancel{\text{ mL}} \times \left(8.25 \times 10^{-4} \text{ mmol}/\cancel{\text{mL}}\right) = 1.20 \times 10^{-3} \text{ mmol}$$

$$\text{mmol } Cl^- = [1.20 \times 10^{-3} \cancel{\text{ mmol } Hg(NO_3)_2}] \times \frac{2 \text{ mmol } Cl^-}{1 \cancel{\text{ mmol } Hg(NO_3)_2}} = 2.41 \times 10^{-3} \text{ mmol } Cl^-$$

$$M \ Cl^- = \frac{2.41 \times 10^{-3} \text{ mmol}}{0.25} = 9.6 \times 10^{-3} \ M$$

82. Potatoes can be peeled commercially by soaking them in a 3-*M* to 6-*M* solution of sodium hydroxide, then removing the loosened skins by spraying them with water. Does a sodium hydroxide solution have a suitable concentration if titration of 12.00 mL of the solution requires 30.6 mL of 1.65 *M* HCI to reach the end point?

Solution

The reaction is

$NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l)$

$1.65 \text{ mol } L^{-1} \times 0.0306 \text{ L} = 5.05 \times 10^{-2} \text{ mol HCl} = 5.05 \times 10^{-2} \text{ mol NaOH}$

$$M \text{ NaOH} = \frac{5.05 \times 10^{-2} \text{ mol NaOH}}{0.01200 \text{ L}} = 4.21 \, M$$

Yes, the concentration of NaOH falls in the suitable range of 3 M to 6 M.

83. A sample of gallium bromide, $GaBr_3$, weighing 0.165 g was dissolved in water and treated with silver nitrate, $AgNO_3$, resulting in the precipitation of 0.299 g AgBr. Use these data to compute the % Ga (by mass) $GaBr_3$.

Solution

The reaction is $GaBr_3(aq) + 3AgNO_3(aq) \longrightarrow 3AgBr(s) + Ga(NO_3)_3(aq)$.

Begin by considering the definition of mass percentage:

$$\%Ga = \frac{\text{g Ga}}{\text{g } GaBr_3} \times 100\%$$

Computing this concentration will require the following approach:

$\text{g AgBr} \longrightarrow \text{mol AgBr} \longrightarrow \text{mol } Ga(NO_3)_3 \longrightarrow \text{g Ga}$

Using the provided data yields

$$\text{mol Ga} = 0.299 \cancel{\text{ g AgBr}} \times \frac{1 \cancel{\text{ mol}}}{187.7722 \cancel{\text{ g AgBr}}} \times \frac{1 \cancel{\text{ mol } Ga(NO_3)_3}}{3 \cancel{\text{ mol AgBr}}} \times \frac{1 \cancel{\text{ mol Ga}}}{1 \cancel{\text{ mol } Ga(NO_3)_3}} \times \frac{69.723 \text{ g}}{1 \cancel{\text{ mol Ga}}} = 3.701 \times 10^{-2} \text{ g}$$

Finally, the gallium mass percentage is calculated as

$$\%Ga = \frac{3.701 \times 10^{-2} \cancel{\text{ g Ga}}}{0.165 \cancel{\text{ g } Ga_3}_3} = 100\% = 22.4\%$$

84. The principal component of mothballs is naphthalene, a compound with a molecular mass of about 130 amu, containing only carbon and hydrogen. A 3.000-mg sample of naphthalene burns to give 10.3 mg of CO_2. Determine its empirical and molecular formulas.

Solution

$$10.3 \cancel{\text{ mg } CO_2} \times \frac{12.0 \text{ mg C}}{44.0 \cancel{\text{ mg } CO_2}} = 2.81 \text{ mg C}$$

$3.00 \text{ mg} - 2.81 \text{ mg} = 0.19 \text{ mg H}$

$$2.81 \cancel{\text{ mg C}} \times \frac{1 \text{ mmol C}}{1.01 \cancel{\text{ mg C}}} = 0.234 \text{ mmol C}$$

$$0.19 \cancel{\text{ mg H}} \times \frac{1 \text{ mmol}}{1.01 \cancel{\text{ mg H}}} = 0.188 \text{ mmol H}$$

Find the mole ratios and then the lowest common denominator.

$$\frac{0.234}{0.188} = 1.24 \qquad 1.24 \times 4 = 4.96$$

$$\frac{0.188}{0.188} = 1.00 \qquad 1.00 \times 4 = 4.00$$

Empirical formula: C_5H_4

Empirical mass of C_5H_4: 64.1

Molecular mass = (empirical mass)(n)

$$n = \frac{\text{molecular mass}}{\text{empirical mass}} = \frac{130}{64.1} \approx 2$$

Molecular formula: (2)(C_5H_4) $C_{10}H_8$

85. A 0.025-g sample of a compound composed of boron and hydrogen, with a molecular mass of ~28 amu, burns spontaneously when exposed to air, producing 0.063 g of B_2O_3. What are the empirical and molecular formulas of the compound.

Solution

Calculate the mass of B in the 0.063-gsample of B_2O_3. The difference of the mass of this boron and the 0.025-g sample of boron and hydrogen gives the mass of the hydrogen present. Determine the moles of B and H in the sample. Divide by the smaller number of moles to find the empirical formula. Divide the mass of the empirical formula into the assumed molecular mass of ~28 amu. That number multiplied by the subscripts of the empirical formula gives the molecular formula.

$$\text{mass of B in } B_2O_3 = \frac{2 \times 10.811 \text{ g mol}^{-1} \text{ B}}{69.6202 \text{ g mol}^{-1} \text{ } B_2O_3} \times 0.063 \text{ g } B_2O_3 = 0.0196 \text{ g}$$

$$\text{mass of H in } B_2O_3 = 0.025 \text{ g B \& H} - 0.0196 \text{ g B} = 0.0054 \text{ g H}$$

$$\text{mol B} = \frac{0.0196 \text{ g}}{10.811 \text{ g mol}^{-1}} = 0.00181 \text{ mol}$$

$$\text{mol H} = \frac{0.0054 \text{ g}}{1.00794 \text{ g mol}^{-1}} = 0.00535 \text{ mol}$$

$$\text{mole ratio: 1 B to } \frac{0.00535 \text{ mol H}}{0.00181 \text{ mol B}} = 2.96$$

Because of rounding errors, this calculation gives a ratio of 1:3. Therefore, the empirical formula is BH_3, which has a molecular mass of ~13.8 amu. Multiplication of this value by 2 gives 27.6 amu, a number of very close to the approximate mass. Consequently, the molecular formula is B_2H_6.

86. Sodium bicarbonate (baking soda), $NaHCO_3$, can be purified by dissolving it in hot water (60 °C), filtering to remove insoluble impurities, cooling to 0 °C to precipitate solid $NaHCO_3$, and then filtering to remove the solid, leaving soluble impurities in solution. Any $NaHCO_3$ that remains in solution is not recovered. The solubility of $NaHCO_3$ in hot water of 60 °C is 164 g L. Its solubility in cold water of 0 °C is 69 g/L. What is the percent yield of $NaHCO_3$ when it is purified by this method?

Solution

Use 1 L as a basis for calculation: 164 – 69 = 95 g solid $NaHCO_3$

$$\text{percent yield} = \frac{95 \text{ g}}{1641 \text{ g}} \times 100 = 58\%$$

87. What volume of 0.600 *M* HCl is required to react completely with 2.50 g of sodium hydrogen carbonate?

$$NaHCO_3(aq) + HCl(aq) \longrightarrow NaCl(aq) + CO_2(g) + H_2O(l)$$

Solution

Convert the mass of $NaHCO_3$ to moles of Na_2CO_3, find the moles of HCl required to react with this number of moles of $NaHCO_3$, and find the volume of the solution of HCl that contains the required number of moles of HCl: 49.6 mL

88. What volume of 0.08892 *M* HNO_3 is required to react completely with 0.2352 g of potassium hydrogen phosphate?

$$2HNO_3(aq) + K_2HPO_4(aq) \longrightarrow H_3PO_4(aq) + 2KNO_3(aq)$$

Solution

The outline of three steps is as follows:

1. Convert the grams of potassium hydrogen phosphate to moles of K_2HPO_4 present; use potassium hydrogen phosphate.
2. Convert the balanced equation to convert moles of potassium hydrogen phosphate to moles of HNO_3; then use nitric acid.
3. Convert the given moles of HNO_3 to calculate the volume needed in milliliters of nitric acid.

$$0.2352 \text{ g } K_2HPO_4 \times \frac{1 \text{ mol } K_2HPO_4}{174.20 \text{ g}} \times \frac{2 \text{ mol } HNO_3}{1 \text{ mol } K_2HPO_4} \times \frac{1 \text{ L}}{0.08892 \text{ mol } HNO_3} = 30.37 \text{ mL}$$

All these steps can be combined into a single calculation:

$$\frac{0.2352 \text{ g } K_2HPO_4}{1} \times \frac{1 \text{ mol } K_2HPO_4}{174.20 \text{ g}} \times \frac{2 \text{ mol } NHO_3}{1 \text{ mol } K_2HPO_4} \times \frac{1000 \text{ mL } HNO_3}{0.08892 \text{ mol } HNO_3} = 30.37 \text{ mL } HNO_3$$

89. What volume of a 0.3300-*M* solution of sodium hydroxide would be required to titrate 15.00 mL of 0.1500 *M* oxalic acid?

$$C_2O_4H_2(aq) + 2NaOH(aq) \longrightarrow Na_2C_2O_4(aq) + 2H_2O(l)$$

Solution

Find the number of moles of oxalic acid contained in 15.0 mL of its solution, find the moles of NaOH required to react with this number of moles of oxalic acid, and find the volume of the solution of NaOH that contains the required number of moles of NaOH: 13.64 mL

90. What volume of a 0.00945-*M* solution of potassium hydroxide would be required to titrate 50.00 mL of a sample of acid rain with a H_2SO_4concentration of 1.23×10^{-4} *M*.

$$H_2SO_4(aq) + 2KOH(aq) \longrightarrow K_2SO_4(aq) + 2H_2O(l)$$

Solution

$$\text{mass KOH} \longrightarrow \text{mol KOH} \longrightarrow \text{mol } H_2SO_4 \longrightarrow \text{M } H_2SO_4 \longrightarrow \text{volume } H_2SO_4$$

$$\text{mol KOH} = 24.74 \cancel{\text{ g}} \text{ KOH} \times \frac{1 \cancel{\text{ mol KOH}}}{39.0983 \cancel{\text{ g}}} \times \frac{1 \text{ mol } H_2SO_4}{2 \cancel{\text{ mol KOH}}} = 0.031638 \text{ mol}$$

$$\text{volume } H_2SO_4 = \frac{0.031638 \text{ mol}}{0.3446 \text{ M}} = 0.09181 \text{ L}$$

91. A sample of solid calcium hydroxide, $Ca(OH)_2$, is allowed to stand in water until a saturated solution is formed. A titration of 75.00 mL of this solution with 5.00×10^{-2} *M* HCl requires 36.6 mL of the acid to reach the end point.

$$Ca(OH)_2(aq) + 2HCl(aq) \longrightarrow CaCl_2(aq) + 2H_2O(l)$$

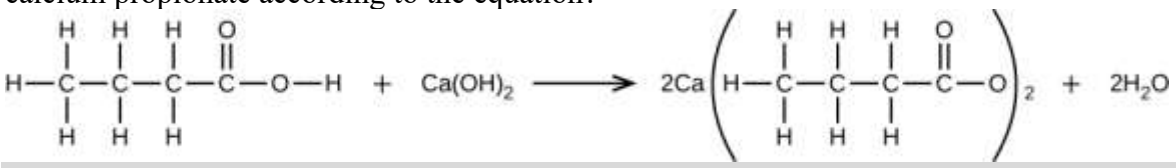
What is the molarity?

Solution

$$\text{Volume HCl} \longrightarrow \text{mol HCl} \longrightarrow \text{mol } Ca(OH)_2 \longrightarrow \text{Concentration } Ca(OH)2$$

$$36.6\ \cancel{\text{mL HCl}} \times \frac{5.00 \times 10^{-2}\ \cancel{\text{mol HCl}}}{1000\ \cancel{\text{mL HCl}}} \times \frac{1\ \text{mol Ca(OH)}_2}{2\ \cancel{\text{mol HCl}}} \times \frac{1}{0.07500\ \text{L Ca(OH)}_2} = 0.0122\ M$$

92. What mass of $Ca(OH)_2$ will react with 25.0 g of propionic acid to form the preservative calcium propionate according to the equation?



Solution
Determine the molar mass of $Ca(OH)_2$ and propionic acid.
Molar mass of $Ca(OH)_2$ = 74.093 g/mol
Molar mass of propionic acid = 88.106 g/mol

$$\text{mass of Ca}(\text{OH})_2 = 25.0\ \cancel{\text{g P.A.}} \times \frac{1\ \cancel{\text{mol P.A.}}}{88.106\ \cancel{\text{g P.A.}}} \times \frac{1\ \cancel{\text{mol Ca}(\text{OH})_2}}{\cancel{\text{mol P.A.}}} \times \frac{74.093\ \text{g}}{\cancel{\text{mol Ca}(\text{OH})_2}}$$

$$= 21.0\ \text{g}$$

93. How many milliliters of a 0.1500-*M* solution of KOH will be required to titrate 40.00 mL of a 0.0656-*M* solution of H_3PO_4?

$$H_3PO_4(aq) + 2KOH(aq) \longrightarrow K_2HPO_4(aq) + 2H_2O(l)$$

Solution

$$\text{Volume } H_3PO_4 \longrightarrow \text{mol KHP} \longrightarrow \text{mol NaOH} \longrightarrow \text{Concentration of NaOH}$$

$$40.00\ \cancel{\text{mL } H_3PO_4} \times \frac{0.0656\ \cancel{\text{mol } H_3PO_4}}{1000\ \cancel{\text{mL } H_3PO_4}} \times \frac{2\ \cancel{\text{mol KOH}}}{1\ \cancel{\text{mol } H_3PO_4}} \times \frac{1000\ \text{mL KOH}}{0.1500\ \cancel{\text{mol KOH}}}$$

$$= 34.99\ \text{mL KOH}$$

94. Potassium hydrogen phthalate, $KHC_8H_4O_4$, or KHP, is used in many laboratories, including general chemistry laboratories, to standardize solutions of base. KHP is one of only a few stable solid acids that can be dried by warming and weighed. A 0.3420-g sample of $KHC_8H_4O_4$ reacts with 35.73 mL of a NaOH solution in a titration. What is the molar concentration of the NaOH?

$$KHC_8H_4O_4(aq) + NaOH(aq) \longrightarrow KNaC_8H_4O_4(aq) + H_2O(aq)$$

Solution

$$\text{mass KHP} \longrightarrow \text{mol KHP} \longrightarrow \text{mol NaOH} \longrightarrow \text{Concentration of NaOH}$$

$$0.3420\ \cancel{\text{g KHP}} \times \frac{1\ \cancel{\text{mol KHP}}}{204.223\ \cancel{\text{g KHP}}} \times \frac{1\ \text{mol NaOH}}{1\ \cancel{\text{mol KHP}}} \times \frac{1}{0.03573\ \text{L}} = 4.687 \times 10^{-2}\ M$$

95. The reaction of WCl_6 with Al at ~400 °C gives black crystals of a compound containing only tungsten and chlorine. A sample of this compound, when reduced with hydrogen, gives 0.2232 g of tungsten metal and hydrogen chloride, which is absorbed in water. Titration of the hydrochloric acid thus produced requires 46.2 mL of 0.1051 *M* NaOH to reach the end point. What is the empirical formula of the black tungsten chloride?

Solution
The general solution follows these steps:

$$\text{Volume}(\text{NaOH}) \longrightarrow \text{mol NaOH} \longrightarrow \text{mol HC1} \longrightarrow \text{mol Cl and Mass W} \longrightarrow \text{mol W}$$

For Cl:

$$0.0462\ \text{L NaOH} \times 0.1051\ \text{M NaOH} = 4.86 \times 10^{-3}\ \text{mol NaOH}$$
$$= 4.86 \times 10^{-3}\ \text{mol HC1}$$
$$= 4.86 \times 10^{-3}\text{mol Cl}$$

For W:

$$\frac{0.2232\ \cancel{\text{g}}\ \text{W}}{183.85\ \cancel{\text{g}}\ \text{mol}^{-1}} = 1.214 \times 10^{-3}\ \text{mol W}$$

Then,

$$\frac{\text{mol Cl}}{\text{mol W}} = \frac{4.86 \times 10^{-3}\ \cancel{\text{mol}}}{1.214 \times 10^{-3}\ \cancel{\text{mol}}} = 4.00$$

The empirical formula is WCl_4.

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Chemistry: Atoms First 2e
8: Gases
8.1: Gas Pressure

1. Why are sharp knives more effective than dull knives? (Hint: Think about the definition of pressure.)

Solution

The cutting edge of a knife that has been sharpened has a smaller surface area than a dull knife. Since pressure is force per unit area, a sharp knife will exert a higher pressure with the same amount of force and cut through material more effectively.

2. Why do some small bridges have weight limits that depend on how many wheels or axles the crossing vehicle has?

Solution

The more axles/wheels a vehicle has, the more surface area it has that is in contact with the road. For a given weight of vehicle (force applied to the road), a higher area corresponds to a lower pressure, making vehicles with more axles/wheels less likely to damage the road surface.

3. Why should you roll or belly crawl rather than walk across a thinly frozen pond?

Solution

Lying down distributes your weight over a larger surface area, exerting less pressure on the ice compared to standing up. If you exert less pressure, you are less likely to break through thin ice.

4. A typical barometric pressure in Redding, California, is about 750 mm Hg. Calculate this pressure in atm and kPa.

Solution

$$750\ \cancel{\text{mm Hg}} \times \frac{1\ \text{atm}}{760\ \cancel{\text{mm Hg}}} = 0.987\ \text{atm}$$

$$0.987\ \cancel{\text{atm}} \times \frac{101.325\ \text{kPa}}{1\ \cancel{\text{atm}}} = 100\ \text{kPa}$$

5. A typical barometric pressure in Denver, Colorado, is 615 mm Hg. What is this pressure in atmospheres and kilopascals?

Solution
Convert 615 mm Hg to atmospheres using 760 mm Hg = 1 atm. Use 1 atm = 101.325 kPa in the second part.

$$615 \text{ mm Hg} \times \frac{1\text{atm}}{760\text{mmHg}} = 0.809 \text{ atm}$$

$$0.809 \text{ atm} \times \frac{101.325\text{kPa}}{1\text{atm}} = 82.0 \text{ kPa}$$

6. A typical barometric pressure in Kansas City is 740 torr. What is this pressure in atmospheres, in millimeters of mercury, and in kilopascals?

Solution
Convert 740 torr to the units required: 760 torr = 1 atm = 760 mmHg = 101.3 kPa.

$$P(\text{atm}) = 740 \cancel{\text{torr}} \times \frac{1 \text{ atm}}{760 \cancel{\text{torr}}} = 0.974 \text{ atm}$$

$$P(\text{mmHg}) = 740 \text{ torr} \times \frac{760 \text{ mmHg}}{760 \text{ torr}} = 740 \text{ mmHg}$$

$$P(\text{kPa}) = 740 \cancel{\text{torr}} \times \frac{101.3 \text{ kPa}}{760 \cancel{\text{torr}}} = 98.6 \text{ kPa}$$

7. Canadian tire pressure gauges are marked in units of kilopascals. What reading on such a gauge corresponds to 32 psi?

Solution

$$32.0 \cancel{\text{lb}}\ \cancel{\text{in}^{-2}} \times \frac{1 \cancel{\text{atm}}}{14.7 \cancel{\text{lb}}\ \cancel{\text{in}^{-2}}} \times \frac{101.325 \text{ kPa}}{1 \cancel{\text{atm}}} = 2.2 \times 10^{2} \text{ kPa}$$

8. During the Viking landings on Mars, the atmospheric pressure was determined to be on the average about 6.50 millibars (1 bar = 0.987 atm). What is that pressure in torr and kPa?

Solution

$$6.50 \cancel{\text{mbar}} \times \frac{1 \cancel{\text{bar}}}{1000 \cancel{\text{mbar}}} \times \frac{0.987 \cancel{\text{atm}}}{1 \cancel{\text{bar}}} \times \frac{760 \text{ torr}}{1 \cancel{\text{atm}}} = 4.88 \text{ torr}$$

$$6.50 \cancel{\text{mbar}} \times \frac{1 \cancel{\text{bar}}}{1000 \cancel{\text{mbar}}} \times \frac{0.987 \cancel{\text{atm}}}{1 \cancel{\text{bar}}} \times \frac{101.325 \text{ kPa}}{1 \cancel{\text{atm}}} = 0.650 \text{ kPa}$$

9. The pressure of the atmosphere on the surface of the planet Venus is about 88.8 atm. Compare that pressure in psi to the normal pressure on earth at sea level in psi.

Solution
Identify: 14.7 psi = 1 atm

$$88.8 \cancel{\text{atm}} \times \frac{14.7 \text{ psi}}{1 \cancel{\text{atm}}} = 1.30 \times 10^{3} \text{ psi}$$

10. A medical laboratory catalog describes the pressure in a cylinder of a gas as 14.82 MPa. What is the pressure of this gas in atmospheres and torr?

Solution
Convert 14.82 MPa into atm.

$$P(\text{atm}) = 14.82 \cancel{\text{MPa}} \times \frac{1000 \cancel{\text{kPa}}}{1 \cancel{\text{MPa}}} \times \frac{1 \text{ atm}}{101.3 \cancel{\text{kPa}}} = 146.3 \text{ atm}$$

$$P(\text{torr}) = 146.3\ \cancel{\text{atm}} \times \frac{760\ \text{torr}}{1\ \cancel{\text{atm}}} = 1.112 \times 10^5\ \text{torr}$$

11. Consider this scenario and answer the following questions: On a mid-August day in the northeastern United States, the following information appeared in the local newspaper: atmospheric pressure at sea level 29.97 in., 1013.9 mbar.
(a) What was the pressure in kPa?
(b) The pressure near the seacoast in the northeastern United States is usually reported near 30.0 in. Hg. During a hurricane, the pressure may fall to near 28.0 in. Hg. Calculate the drop in pressure in torr.

Solution

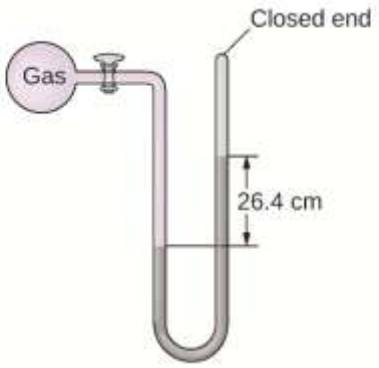
(a) $29.97\ \cancel{\text{in. Hg}} \times \frac{101.325\ \text{kPa}}{29.92\ \cancel{\text{in. Hg}}} = 101.5\ \text{kPa}$; (b) $28.0\ \cancel{\text{in. Hg}} \times \frac{760\ \text{torr}}{29.92\ \cancel{\text{in. Hg}}} = 711\ \text{torr}$;
762 – 711 = 51 torr drop

12. Why is it necessary to use a nonvolatile liquid in a barometer or manometer?

Solution

A volatile liquid evaporates easily, which would produce some gas pressure in enclosed volumes, thus affecting the measurements.

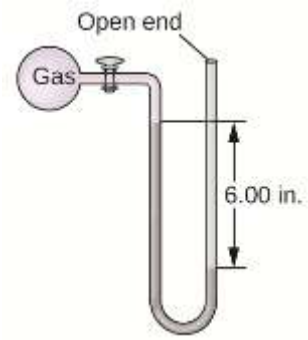
13. The pressure of a sample of gas is measured at sea level with a closed-end manometer. The liquid in the manometer is mercury. Determine the pressure of the gas in:
(a) torr
(b) Pa
(c) bar



Solution

(a) $26.4\ \cancel{\text{cm}} \times \frac{10\ \cancel{\text{mm}}}{1\ \cancel{\text{cm}}} \times \frac{1\ \text{torr}}{1\ \cancel{\text{mm}}} = 264\ \text{torr}$; (b) $264\ \text{torr} \times \frac{101{,}325\ \text{Pa}}{760\ \text{torr}} = 35{,}200\ \text{Pa}$; (c)
$264\ \cancel{\text{torr}} \times \frac{1.01325\ \text{bar}}{760\ \cancel{\text{torr}}} = 0.352\ \text{bar}$

14. The pressure of a sample of gas is measured with anopen-end manometer, partially shown to the right. The liquid in the manometer is mercury. Assuming atmospheric pressure is 29.92 in. Hg, determine the pressure of the gas in:
(a) torr
(b) Pa
(c) bar

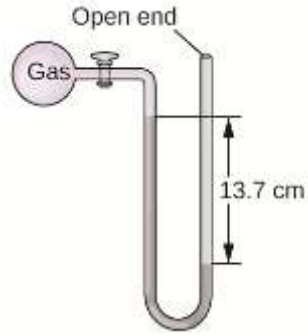


Solution
Since the mercury level is lower in the open arm of the manometer tube, atmospheric pressure is greater than the trapped gas pressure. The pressure of the gas is therefore calculated by subtracting the hydrostatic pressure corresponding to a 6 in. column of mercury from atmospheric pressure. (a) In in. Hg, this is: 29.92 in. Hg – 6.00 in. Hg = 23.92 in. Hg,

$$23.92 \text{ in. Hg} \times \frac{760 \text{ torr}}{29.92 \text{ in. Hg}} = 608 \text{ torr}$$; (b) $$608 \text{ torr} \times \frac{101325 \text{ Pa}}{760 \text{ torr}} = 81100 \text{ Pa}$$; (c)

$$608 \ \cancel{\text{torr}} \times \frac{1.01325 \text{ bar}}{760 \ \cancel{\text{torr}}} = 0.811 \text{ bar}$$

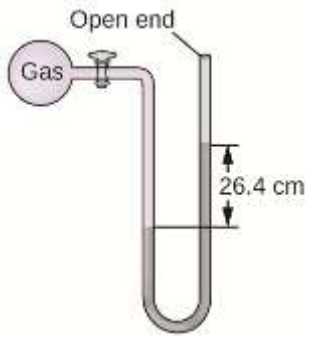
15. The pressure of a sample of gas is measured at sea level with an open-end mercury manometer. Assuming atmospheric pressure is 760.0 mm Hg, determine the pressure of the gas in:
(a) mm Hg
(b) atm
(c) kPa



Solution
The pressure of the gas equals the hydrostatic pressure due to the pressure of the atmosphere at sea level minus a column of mercury of height 13.7 cm. The pressure on the left is due to the gas and the pressure on the right is due to the atmospheric pressure minus 13.7 cm Hg).(a) In mm Hg, this is: 760 mm Hg – 137 mmHg = 623 mm Hg; (b)

$$623 \text{ mm Hg} \times \frac{1 \text{ atm}}{760 \text{ mm Hg}} = 0.820 \text{ atm}$$; (c) $$0.820 \text{ atm} \times \frac{101.325 \text{ kPa}}{1 \text{ atm}} = 83.1 \text{ kPa}$$

16. The pressure of a sample of gas is measured at sea level with an open-end mercury manometer. Assuming atmospheric pressure is 760 mm Hg, determine the pressure of the gas in:
(a) mm Hg
(b) atm
(c) kPa



Solution
(a) In mm Hg, this is: 760 mm Hg + 264 mm Hg = 1024 mm Hg; (b)
$1024 \text{ mm Hg} \times \frac{1 \text{ atm}}{760 \text{ mm Hg}} = 1.34 \text{ atm}$; (c) $1024 \text{ mm Hg} \times \frac{101.325 \text{ kPa}}{760 \text{ mm Hg}} = 136 \text{ kPa}$

17. How would the use of a volatile liquid affect the measurement of a gas using open-ended manometers vs. closed-end manometers?

Solution
With a closed-end manometer, no change would be observed, since the vaporized liquid would contribute equal, opposing pressures in both arms of the manometer tube. However, with an open-ended manometer, a higher pressure reading of the gas would be obtained than expected, since $P_{gas} = P_{atm} + P_{vol\ liquid}$.

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Chemistry: Atoms First 2e
8: Gases
8.2: Relating Pressure, Volume, Amount, and Temperature: The Ideal Gas Law

18. Sometimes leaving a bicycle in the sun on a hot day will cause a blowout. Why?

Solution
The temperature of the air in the tire increases, which causes the pressure and/or volume to increase. The volume cannot increase substantially, and high enough pressure can cause the tire to burst.

19. Explain how the volume of the bubbles exhausted by a scuba diver (Figure 8.16) change as they rise to the surface, assuming that they remain intact.

Solution
As the bubbles rise, the pressure decreases, so their volume increases as suggested by Boyle's law.

20. One way to state Boyle's law is "All other things being equal, the pressure of a gas is inversely proportional to its volume."
(a) What is the meaning of the term "inversely proportional?"
(b) What are the "other things" that must be equal?

Solution

(a) The pressure increases as the volume decreases and vice-versa. Mathematically, this can be expressed $P \times V$ = a constant, or P = constant $\times \frac{1}{V}$. (b) amount of gas and temperature; the temperature and the amount (number of moles) of gas must not change

21. An alternate way to state Avogadro's law is "All other things being equal, the number of molecules in a gas is directly proportional to the volume of the gas."
(a) What is the meaning of the term "directly proportional?"
(b) What are the "other things" that must be equal?

Solution
(a) The number of particles in the gas increases as the volume increases. This relationship may be written as n = constant × V. It is a direct relationship. (b) The temperature and pressure must be kept constant.

22. How would the graph in Figure 8.12 change if the number of moles of gas in the sample used to determine the curve were doubled?

Solution
The slope of the line would increase by a factor of 2.

23. How would the graph in Figure 8.13 change if the number of moles of gas in the sample used to determine the curve were doubled?

Solution
The curve would be farther to the right and higher up, but the same basic shape.

24. In addition to the data found in Figure 8.13, what other information do we need to find the mass of the sample of air used to determine the graph?

Solution
The temperature and the (average) molar mass of air.

25. Determine the volume of 1 mol of CH_4 gas at 150 K and 1 atm, using Figure 8.12.

Solution
The figure shows the change in volume for 1 mol of CH_4 gas as a function of temperature. The graph shows that the volume is about 12.5 L.

26. Determine the pressure of the gas in the syringe shown in Figure 8.13 when its volume is 12.5 mL, using:
(a) the appropriate graph
(b) Boyle's law

Solution
(a) The graphical approach requires interpolating a value of pressure, and so the linear plot is preferred. The volume of 12.5 mL corresponds to an approximate value of 0.065 psi^{-1} for $\frac{1}{P}$, and so the pressure is approximately $(0.065\ psi^{-1})^{-1}$ = 15 psi. (b) Any of the pressure-volume data pairs provided in the graph may be used to compute the requested pressure via Boyle's law. For example, using the (15.0 mL, 13.0 psi) data point yields $P_1V_1 = P_2V_2$

$$P_2 = \frac{13.0\ \text{psi} \times 15.0\ \cancel{\text{mL}}}{12.5\ \cancel{\text{mL}}} = 15.6\ \text{psi}$$

27. A spray can is used until it is empty except for the propellant gas, which has a pressure of 1344 torr at 23 °C. If the can is thrown into a fire (T = 475 °C), what will be the pressure in the hot can?

Solution

The first thing to recognize about this problem is that the volume and moles of gas remain constant. Thus, we can use the combined gas law equation in the form:

$$\frac{P_2}{T_2} = \frac{P_1}{T_1}$$

$$P_2 = \frac{P_1 T_2}{T_1} = 1344 \text{ torr} \times \frac{475 + 273.15}{23 + 273.15} = 3.40 \times 10^3 \text{ torr}$$

28. What is the temperature of an 11.2-L sample of carbon monoxide, CO, at 744 torr if it occupies 13.3 L at 55 °C and 744 torr?

Solution

This scenario involves a constant amount of gas (unspecified) undergoing a temperature induced change in volume at a constant pressure (744 torr). Charles law may therefore be used.

$V_1 = 13.3$ L

$T_1 = 55$ °C = 328 K

$V_2 = 11.2$ L

$T_2 = ?$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$T_2 = \frac{V_2 T_1}{V_1} = \frac{11.2 \text{ L} \times 328 \text{ K}}{13.3 \text{ L}} = 276 \text{ K}$$

29. A 2.50-L volume of hydrogen measured at –196 °C is warmed to 100 °C. Calculate the volume of the gas at the higher temperature, assuming no change in pressure.

Solution

Apply Charles's law to compute the volume of gas at the higher temperature:

$V_1 = 2.50$ L

$T_1 = –196$ °C = 77.15 K

$V_2 = ?$

$T_2 = 100$ °C = 373.15 K

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V_2 = \frac{V_1 T_2}{T_1} = \frac{2.50 \text{ L} \times 373.15 \cancel{\text{K}}}{77.15 \cancel{\text{K}}} = 12.1 \text{ L}$$

30. A balloon inflated with three breaths of air has a volume of 1.7 L. At the same temperature and pressure, what is the volume of the balloon if five more same-sized breaths are added to the balloon?

Solution

Use Avogadro's law to compute the requested volume. The gas volume added with each breath is 0.567 L, $\left(\frac{1.7\text{ L}}{3\text{ breaths}} = \frac{0.567\text{ L}}{1\text{ breath}}\right)$, keeping a nonsignificant "guard digit" to avoid a rounding error. If a total of eight breaths are in the balloon, the total volume of gas is:

$$\left(8\ \cancel{\text{breaths}} \times \frac{0.567\text{ L}}{1\ \cancel{\text{breath}}}\right) = 4.5\text{ L}.$$

31. A weather balloon contains 8.80 moles of helium at a pressure of 0.992 atm and a temperature of 25° C at ground level. What is the volume of the balloon under these conditions?



Solution

$PV = nRT$

$$V = \frac{nRT}{P} = \frac{8.80\ \cancel{\text{mol}} \times 0.08206\text{ L}\ \cancel{\text{atm}}\ \cancel{\text{mol}^{-1}}\ \cancel{\text{K}^{-1}} \times 298.15\ \cancel{\text{K}}}{0.992\ \cancel{\text{atm}}} = 217\text{ L}$$

32. The volume of an automobile air bag was 66.8 L when inflated at 25 °C with 77.8 g of nitrogen gas. What was the pressure in the bag in kPa?

Solution

$$P = \frac{nRT}{V} = \frac{\left(\frac{77.8\text{ g}}{28.0135\text{ g mol}^{-1}}\right)\left(0.08206\text{ L atm mol}^{-1}\text{ K}^{-1}\right)\left(298.1\text{ K}\right)}{66.8\text{ L}} = 1.02\text{ atm}$$

$$P = 1.02\ \cancel{\text{atm}} \times \frac{101.325\text{ kPa}}{1\ \cancel{\text{atm}}} = 103\text{ kPa}$$

33. How many moles of gaseous boron trifluoride, BF_3, are contained in a 4.3410-L bulb at 788.0 K if the pressure is 1.220 atm? How many grams of BF_3?

Solution

$$n = \frac{PV}{RT} = \frac{1.220\ \cancel{\text{atm}}\ (4.3410\text{ L})}{(0.08206\text{ L}\ \cancel{\text{atm}}\ \text{mol}^{-1}\ \cancel{\text{K}^{-1}})(788.0\ \cancel{\text{K}})} = 0.08190\text{ mol} = 8.190 \times 10^{-2}\text{ mol}$$

$$n \times \text{molar mass} = 8.190 \times 10^{-2}\ \cancel{\text{mol}} \times 67.8052\text{ g}\ \cancel{\text{mol}^{-1}} = 5.553\text{ g}$$

34. Iodine, I_2, is a solid at room temperature but sublimes (converts from a solid into a gas) when warmed. What is the temperature in a 73.3-mL bulb that contains 0.292 g of I_2 vapor at a pressure of 0.462 atm?

Solution

The molar mass of I_2 is $2 \times 126.90447 = 253.8089$ g/mol;

$$T = \frac{PV}{nR} = \frac{0.462\text{ atm}(0.0733\text{ L})}{\left(\frac{0.292\text{ g}}{253.8\text{ g mol}^{-1}}\right)(0.08206\text{ L atm mol}^{-1}\text{ K}^{-1}} = 359\text{ K}$$

35. How many grams of gas are present in each of the following cases?

(a) 0.100 L of CO_2 at 307 torr and 26 °C

(b) 8.75 L of C_2H_4, at 378.3 kPa and 483 K
(c) 221 mL of Ar at 0.23 torr and –54 °C

Solution
In each of these problems, we are given a volume, pressure, and temperature. We can obtain moles from this information using the molar mass, $m = nM$, where M is the molar mass:

$$P,V,T \xrightarrow{n=PV/RT} n, \xrightarrow{m=n\ (\text{molar mass})} \text{grams}$$

or we can combine these equations to obtain:

$$\text{mass} = m = \frac{PV}{RT} \times M$$

(a)

$$307\ \cancel{\text{torr}} \times \frac{1\ \text{atm}}{760\ \cancel{\text{torr}}} = 0.4039\ \text{atm} \qquad 26\ ^\circ\text{C} = 299.1\ \text{K}$$

$$\text{Mass} = m = \frac{0.4039\ \cancel{\text{atm}}\ (0.100\ \cancel{\text{L}})}{0.08206\ \cancel{\text{L}}\ \cancel{\text{atm}}\ \text{mol}^{-1}\ \cancel{\text{K}^{-1}}\ (299.1\ \cancel{\text{K}})} \times 44.01\ \text{g mol}^{-1} = 7.24 \times 10^{-2}\ \text{g};$$

(b)

$$\text{Mass} = m = \frac{378.3\ \cancel{\text{kPa}}\ (8.75\ \cancel{\text{L}})}{8.314\ \cancel{\text{L}}\ \cancel{\text{kPa}}\ \text{mol}^{-1}\ \cancel{\text{K}^{-1}}\ (483\ \cancel{\text{K}})} \times 28.05376\ \text{g mol}^{-1} = 23.1\ \text{g};$$

(c)

$$221\ \cancel{\text{mL}} \times \frac{1\ \text{L}}{1000\ \cancel{\text{mL}}} = 0.221\ \text{L} \qquad -54\ ^\circ\text{C} + 273.15 = 219.15\ \text{K}$$

$$0.23\ \cancel{\text{torr}} \times \frac{1\ \text{atm}}{760\ \cancel{\text{torr}}} = 3.03 \times 10^{-4}\ \text{atm}$$

$$\text{Mass} = m = \frac{3.03 \times 10^{-4}\ \cancel{\text{atm}}\ (0.221\ \cancel{\text{L}})}{0.08206\ \cancel{\text{L}}\ \cancel{\text{atm}}\ \text{mol}^{-1}\ \cancel{\text{K}^{-1}}\ (219.15\ \cancel{\text{K}})} \times 39.948\ \text{g mol}^{-1} = 1.5 \times 10^{-4}\ \text{g}$$

36. A high-altitude balloon is filled with 1.41×10^4 L of hydrogen at a temperature of 21 °C and a pressure of 745 torr. What is the volume of the balloon at a height of 20 km, where the temperature is –48 °C and the pressure is 63.1 torr?

Solution
Write the two sets of conditions in tabular form:
P_1: 745 torr
P_2: 63.1 torr
T_1: 21 °C (294.15 K)
T_2: –48 °C (225.15 K)
V_1: 1.41×10^4 L
V_2: ?
Writing the data given in this way makes it easy to find the unknown. We can use the ideal gas law with the moles of gas (n) held constant:

$$PV = nRT$$

$$\frac{P_1V_1}{T_1} = nR = \frac{P_2V_2}{T_2}$$

$$V_2 = \frac{P_1V_1T_2}{T_1P_2} = \frac{75\ \text{torr}\ (1.41 \times 10^2\ \text{L})(225.15\ \text{K})}{(294.15\ \text{K})(63.1\ \text{torr})} = 1.27 \times 10^5\ \text{L}$$

Note that since R is not required to work the problem, the pressure can be in any pressure unit. The temperature must be in kelvin.

37. A cylinder of medical oxygen has a volume of 35.4 L, and contains O_2 at a pressure of 151 atm and a temperature of 25 °C. What volume of O_2 does this correspond to at normal body conditions, that is, 1 atm and 37 °C?

Solution

$$\frac{P_2}{T_2} = \frac{P_1}{T_1}$$

$T_2 = 49.5 + 273.15 = 322.65$ K

$$P_2 = \frac{P_1 T_2}{T_1} = 149.6 \text{ atm} \times \frac{322.65}{278.15} = 173.5 \text{ atm}$$

38. A large scuba tank with a volume of 18 L is rated for a pressure of 220 bar. The tank is filled at 20 °C and contains enough air to supply 1860 L of air to a diver at a pressure of 2.37 atm (a depth of 45 feet). Was the tank filled to capacity at 20 °C?

Solution

$$\frac{2.37 \cancel{\text{ atm}}}{1} \times \frac{1.01325 \text{ bar}}{1 \cancel{\text{ atm}}} = 2.40 \text{ bar}$$

$P_1V_1 = P_2V_2$

$$P_1 = \frac{P_2V_2}{V_1}$$

$$P_1 = \frac{(2.40 \text{ bar})(1860 \cancel{\text{ L}})}{(18 \cancel{\text{ L}})} = 248 \text{ bar}$$

The pressure when the tank was filled is 248 bar, which exceeds the rated pressure of 220 bar, so the tank was actually overfilled.

39. A 20.0-L cylinder containing 11.34 kg of butane, C_4H_{10}, was opened to the atmosphere. Calculate the mass of the gas remaining in the cylinder if it were opened and the gas escaped until the pressure in the cylinder was equal to the atmospheric pressure, 0.983 atm, and a temperature of 27 °C.

Solution

Calculate the amount of butane in 20.0 L at 0.983 atm and 27 °C. The original amount in the container does not matter.

$$n = \frac{PV}{RT} = \frac{0.983 \cancel{\text{ atm}} \times 20.0 \cancel{\text{ L}}}{0.08206 \cancel{\text{ L}} \cancel{\text{ atm}} \text{ mol}^{-1} \cancel{\text{ K}^{-1}} (300.1 \cancel{\text{ K}})} = 0.798 \text{ mol}$$

Mass of butane = 0.798 mol × 58.1234 g/mol = 46.4 g

40. While resting, the average 70-kg human man consumes 14 L of pure O_2 per hour at 25 °C and 100 kPa. How many moles of O_2 are consumed by a 70-kg man while resting for 1.0 h?

Solution

Use the ideal gas law: $PV = nRT$

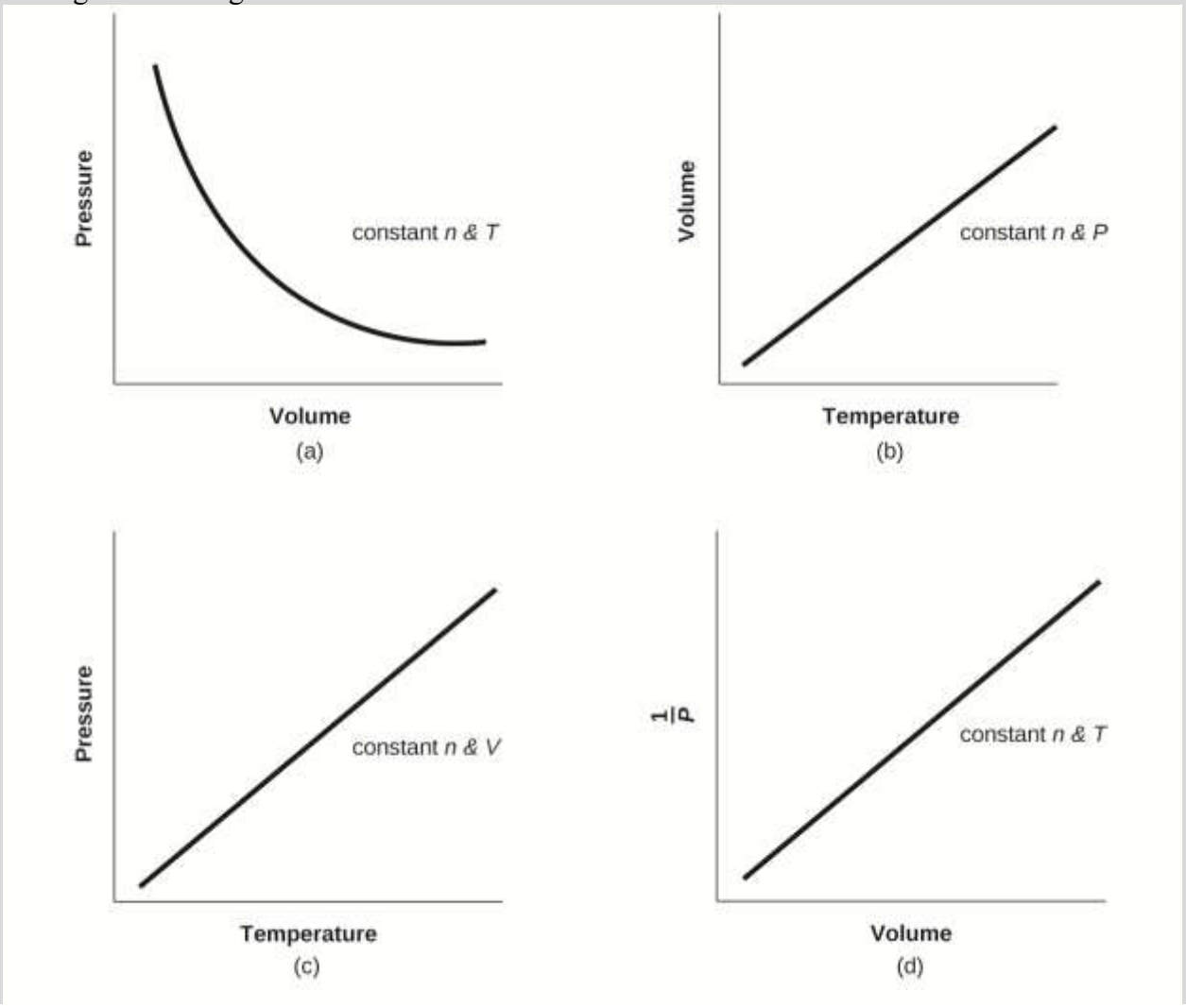
0.99 atm × 14 L = n × 0.08226 atm L/mol K × 298 K

$$n = \frac{(0.99 \text{ atm} \times 14 \text{ L})}{(0.08226 \text{ atm L/mol K} \times 298 \text{ K})} = 0.57 \text{ mol}$$

41. For a given amount of gas showing ideal behavior, draw labeled graphs of:
(a) the variation of P with V

(b) the variation of V with T
(c) the variation of P with T
(d) the variation of $\frac{1}{P}$ with V

Solution
For a gas exhibiting ideal behavior:



42. A liter of methane gas, CH_4, at STP contains more atoms of hydrogen than does a liter of pure hydrogen gas, H_2, at STP. Using Avogadro's law as a starting point, explain why.

Solution
One liter of CH_4 and one liter of H_2 contain the same number of *molecules* at STP (Avogadro's law), but each CH_4 molecule contains four H atoms while each H_2 molecule contains two H atoms.

43. The effect of chlorofluorocarbons (such as CCl_2F_2) on the depletion of the ozone layer is well known. The use of substitutes, such as $CH_3CH_2F(g)$, for the chlorofluorocarbons, has largely corrected the problem. Calculate the volume occupied by 10.0 g of each of these compounds at STP:
(a) $CCl_2F_2(g)$
(b) $CH_3CH_2F(g)$

Solution
(a) Determine the molar mass of CCl_2F_2 then calculate the moles of $CCl_2F_2(g)$ present. Use the ideal gas law $PV = nRT$ to calculate the volume of $CCl_2F_2(g)$:

$$10.0\text{ g } CCl_2F_2 \times \frac{1\text{ mol } CCl_2F_2}{120.91\text{ g } CCl_2F_2} = 0.0827\text{ mol } CCl_2F_2$$

$PV = nRT$, where n = # mol CCl_2F_2

$$1\text{ atm} \times V = 0.0827\text{ mol} \times \frac{0.0821\text{ L atm}}{\text{mol K}} \times 273\text{ K} = 1.85\text{ L } CCl_2F_2;$$

(b) $$10.0\text{ g } CH_3CH_2F \times \frac{1\text{ mol } CH_3CH_2F}{48.07\text{ g } CH_3CH_2F} = 0.208\text{ mol } CH_3CH_2F$$

$PV = nRT$, with n = # mol CH_3CH_2F

$1\text{ atm} \times V = 0.208\text{ mol} \times 0.0821\text{ L atm/mol K} \times 273\text{ K} = 4.66\text{ L } CH_3CH_2F$

44. As 1 g of the radioactive element radium decays over 1 year, it produces 1.16×10^{18} alpha particles (helium nuclei). Each alpha particle becomes an atom of helium gas. What is the pressure in pascal of the helium gas produced if it occupies a volume of 125 mL at a temperature of 25 °C?

Solution
After 1 year, there are:

$$\frac{1.16 \times 10^{18}}{6.022 \times 10^{28}\text{ mol}^{-1}} = 1.926 \times 10^{-6}\text{ mol}$$

From the ideal gas law, $PV = nRT$:

$$P = \frac{nRT}{V} = \frac{1.926 \times 10^{-6}\ \cancel{\text{mol}} \times 8.314\ \cancel{\text{L}}\ \text{kPa}\ \cancel{\text{mol}^{-1}}\ \cancel{\text{K}^{-1}} \times 298\ \cancel{\text{K}}}{0.125\ \cancel{\text{L}}} = 3.82 \times 10^{-2}\text{ kPa}$$

45. A balloon with a volume of 100.21 L at 21 °C and 0.981 atm is released and just barely clears the top of Mount Crumpet in British Columbia. If the final volume of the balloon is 144.53 L at a temperature of 5.24 °C, what is the pressure experienced by the balloon as it clears Mount Crumpet?

Solution
Identify the variables in the problem and determine that the combined gas law $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ is the necessary equation to use to solve the problem. Then solve for P_2:

$$\frac{0.981\text{ atm} \times 100.21\text{ L}}{294\text{ K}} = \frac{P_2 \times 144.53\text{ L}}{278.24\text{ K}}$$

$P_2 = 0.644\text{ atm}$

46. If the temperature of a fixed amount of a gas is doubled at constant volume, what happens to the pressure?

Solution
The pressure is doubled.

47. If the volume of a fixed amount of a gas is tripled at constant temperature, what happens to the pressure?

Solution
The pressure decreases by a factor of 3.

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Chemistry: Atoms First 2e
8: Gases
8.3: Stoichiometry of Gaseous Substances, Mixtures, and Reactions

48. What is the density of laughing gas, dinitrogen monoxide, N_2O, at a temperature of 325 K and a pressure of 113.0 kPa?

Solution

$$\rho = \frac{PM}{RT} = \frac{113.0\ \cancel{\text{kPa}}\ (2 \times 14.00674 + 15.9994)\ \text{g}\ \cancel{\text{mol}^{-1}}}{8.314\ \text{L}\ \cancel{\text{kPa}}\ \cancel{\text{mol}^{-1}}\ \cancel{\text{K}^{-1}} \times 325\ \cancel{\text{K}}} = 1.84\ \text{g L}^{-1}$$

49. Calculate the density of Freon 12, CF_2Cl_2, at 30.0 °C and 0.954 atm.

Solution

$$\rho = \frac{PM}{RT} = \frac{0.954\ \cancel{\text{atm}}\ \left[12.011 + 2(18.9954) + 2(35.453)\right]\ \text{g}\ \cancel{\text{mol}^{-1}}}{0.08206\ \text{L}\ \cancel{\text{atm}}\ \cancel{\text{mol}^{-1}}\ \cancel{\text{K}^{-1}} \times 303.15\ \cancel{\text{K}}} = 4.64\ \text{g L}^{-1}$$

50. Which is denser at the same temperature and pressure, dry air or air saturated with water vapor? Explain.

Solution

Dry air is denser; it has a larger molecular mass. Since density is mass per unit volume, at a given temperature and pressure, *n* is a constant. Thus, a given volume will have the same number of moles of gas. Therefore, if the air becomes moist while the pressure, temperature, and volume remain the same, then some of the O_2 and N_2 molecules will be replaced by H_2O molecules to keep the total number of moles of gas the same. Because the molar mass of H_2O is less than that of O_2 and N_2, the air becomes less dense. Thus, air saturated with water vapor is less dense. Therefore, dry air is denser.

51. A cylinder of $O_2(g)$ used in breathing by patients with emphysema has a volume of 3.00 L at a pressure of 10.0 atm. If the temperature of the cylinder is 28.0 °C, what mass of oxygen is in the cylinder?

Solution

$$\text{mass } O_2 = \frac{(31.9988\ \text{g}\ \cancel{\text{mol}^{-1}})(10.0\ \cancel{\text{atm}})(3.00\ \cancel{\text{L}})}{(0.08206\ \cancel{\text{L}}\ \cancel{\text{atm}}\ \cancel{\text{mol}^{-1}}\ \cancel{\text{K}^{-1}})(301.15\ \cancel{\text{K}})} = 38.8\ \text{g}$$

52. What is the molar mass of a gas if 0.0494 g of the gas occupies a volume of 0.100 L at a temperature 26 °C and a pressure of 307 torr?

Solution

From the ideal gas law, $PV = nRT$, set $n = \frac{\text{mass}}{\text{molar mass}}$ and solve for the molar mass.

$$\text{molar mass} = \frac{(0.0494\ \text{g})(0.08206\ \cancel{\text{L}}\ \cancel{\text{atm}}\ \text{mol}^{-1}\ \cancel{\text{K}^{-1}})(299.15\ \cancel{\text{K}})}{\left(\frac{307\ \cancel{\text{torr}}}{760\ \cancel{\text{torr}}\ \cancel{\text{atm}^{-1}}}\right)(0.1\ \cancel{\text{L}})} = 30.0\ \text{g mol}^{-1}$$

53. What is the molar mass of a gas if 0.281 g of the gas occupies a volume of 125 mL at a temperature 126 °C and a pressure of 777 torr?

Solution

From the ideal gas law, $PV = nRT$, set $n = \frac{\text{mass}}{\text{molar mass}}$ and solve the molar mass.

$$\text{molar mass} = \frac{(0.281\text{ g})(0.08206\text{ L atm mol}^{-1}\text{ K}^{-1})(399.15\text{ K})}{\left(\frac{777\text{ torr}}{760\text{ torr atm}^{-1}}\right)(0.125\text{ L})} = 72.0\text{ g mol}^{-1}$$

54. How could you show experimentally that the molecular formula of propene is C_3H_6, not CH_2?

Solution

A person could measure the mass, volume, and pressure of the gas and calculate the molar mass from the ideal gas equation. C_3H_6 will have three times the molar mass expected for CH_2.

55. The density of a certain gaseous fluoride of phosphorus is 3.93 g/L at STP. Calculate the molar mass of this fluoride and determine its molecular formula.

Solution

$$M = \frac{mRT}{PV} \qquad D = \frac{m}{V} \qquad M = \frac{DRT}{P}$$

$$M = \frac{3.93\text{ g L}^{-1}\ (0.08206\text{ L atm mol}^{-1}\text{ K}^{-1})(273.15\text{ K})}{1.00\text{ atm}} = 88.1\text{ g mol}^{-1}$$

$M_{\text{phosphorous}} = 30.97376$ g/mol

$M_{\text{fluorine}} = 18.998403$ g/mol

molecular formula: phosphorous: 30.97376

fluorine: $\frac{3(18.998403)}{87.968969}$

The molecular formula is PF_3.

To find this answer you can either use trial and error, or you can realize that since phosphorus is in group 5, it can fill its valence shell by forming three bonds. Fluorine, being in group 7, needs to form only one bond to fill its shell. Thus it makes sense to start with PF_3 as a probable formula.

56. Consider this question: What is the molecular formula of a compound that contains 39% C, 45% N, and 16% H if 0.157 g of the compound occupies 125 mL with a pressure of 99.5 kPa at 22 °C?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

Solution

(a) Determine the empirical formula of the compound from the percent composition. Determine the molar mass from the mass of the sample and its volume, temperature, and pressure. Then determine the molecular formula from the molar mass and the empirical formula.

(b) Assume that a 100.0-g sample is present and the percentages translate directly to grams of the sample.

$$\text{C: } 39\text{ g} \times \frac{1\text{ mol C}}{12.011\text{ g mol}^{-1}} = 3.247\text{ mol C}$$

$$\text{H: } 16\text{ g} \times \frac{1\text{ mol H}}{1.00794\text{ g mol}^{-1}} = 15.874\text{ mol H}$$

$$\text{N: } 45\text{ g} \times \frac{1\text{ mol N}}{14.00674\text{ g mol}^{-1}} = 3.213\text{ mol N}$$

Divide each quantity by the smallest value. After rounding, the values are 1C, 5H, and 1N. The empirical formula is CH_5N. The empirical mass is $CH_5N = 31$. The likely arrangement of hydrogen atoms is CH_3NH_2.
Now the molar mass from the ideal gas law:

$$\text{molar mass} = \frac{\text{mass} \times RT}{PV}$$

$$= \frac{(0.157\text{ g})(8.314\ \cancel{\text{L}}\ \cancel{\text{kPa}}\ \text{mol}^{-1}\ \cancel{\text{K}^{-1}})(295.15\ \cancel{\text{K}})}{99.5\ \cancel{\text{kPa}} \times 0.125\ \cancel{\text{L}}}$$

$$= 31.0\text{ g mol}^{-1}$$

The empirical formula is the molar formula, CH_3NH_2.

57. A 36.0–L cylinder of a gas used for calibration of blood gas analyzers in medical laboratories contains 350 g CO_2, 805 g O_2, and 4,880 g N_2. At 25° C, what is the pressure in the cylinder in atmospheres, in torr, and in kilopascals?

Solution
Calculate the moles of each gas present and from that, calculate the pressure from the ideal gas law. Assume 25 °C. The calibration gas contains:

$$\frac{350\ \cancel{\text{g}}\ \text{CO}_2}{44.0098\ \cancel{\text{g}}\ \text{mol}^{-1}\ \text{CO}_2} = 7.953\text{ mol CO}_2$$

$$\frac{805\ \cancel{\text{g}}\ \text{O}_2}{31.9988\ \cancel{\text{g}}\ \text{mol}^{-1}\ \text{O}_2} = 25.157\text{ mol O}_2$$

$$\frac{4880\ \cancel{\text{g}}\ \text{N}_2}{28.01348\ \cancel{\text{g}}\ \text{mol}^{-1}\ \text{N}_2} = 174.202\text{ mol N}_2$$

Total moles = 7.953 + 25.157+ 174.202 = 207.312 mol

$$P = \frac{nRT}{V} = \frac{207.312\ \cancel{\text{mol}} \times 0.08206\ \cancel{\text{L}}\ \text{atm}\ \cancel{\text{mol}^{-1}\ \text{K}^{-1}} \times 298.15\ \cancel{\text{K}}}{36.0\ \cancel{\text{L}}} = 141\text{ atm}$$

P in torr = 107,000 torr
P in kPa = 14,300 kPa

58. A cylinder of a gas mixture used for calibration of blood gas analyzers in medical laboratories contains 5.0% CO_2, 12.0% O_2, and the remainder N_2 at a total pressure of 146 atm. What is the partial pressure of each component of this gas? (The percentages given indicate the percent of the total pressure that is due to each component.)

Solution
The calibration gas contains:
5.0% CO_2
12.0% O_2
100 – (5 + 12) = 83% N_2

Since these are percentages of the total pressure, the partial pressures can be calculated as follows:
CO_2: 5% of 146 atm = 0.05 ×146 = 7.3 atm = 7 atm
O_2: 12% of 146 atm = 0.12 × 146 = 17.5 atm = 18 atm
N_2: 83% of 146 atm = 0.83 × 146 = 121 atm = 1.2×10^2 atm

59. A sample of gas isolated from unrefined petroleum contains 90.0% CH_4, 8.9% C_2H_6, and 1.1% C_3H_8 at a total pressure of 307.2 kPa. What is the partial pressure of each component of this gas? (The percentages given indicate the percent of the total pressure that is due to each component.)

Solution
Since these are percentages of the total pressure, the partial pressure can be calculated as follows:
CH_4: 90% of 307.2 kPa = 0.900 × 307.2 = 276 kPa
C_2H_6: 8.9% of 307.2 kPa = 0.089 × 307.2 = 27 kPa
C_3H_8: 1.1% of 307.2 kPa = 0.011 × 307.2 = 3.4 kPa

60. A mixture of 0.200 g of H_2, 1.00 g of N_2, and 0.820 g of Ar is stored in a closed container at STP. Find the volume of the container, assuming that the gases exhibit ideal behavior.

Solution
First find the number of moles of gases present.

H_2: $\frac{0.200\ \cancel{\text{g}}}{2.016\ \cancel{\text{g}}\ \text{mol}^{-1}} = 0.0992$ mol

N_2: $\frac{1.00\ \cancel{\text{g}}}{28.013\ \cancel{\text{g}}\ \text{mol}^{-1}} = 0.0357$ mol

Ar: $\frac{0.820\ \cancel{\text{g}}}{39.948\ \cancel{\text{g}}\ \text{mol}^{-1}} = 0.0205$ mol

The total amount of substance is 0.1555 mol.

$$V = \frac{nRT}{P} = \frac{0.155\ \cancel{\text{mol}} \times 0.08206\ \text{L}\ \cancel{\text{atm}}\ \cancel{\text{mol}^{-1}}\ \cancel{\text{K}^{-1}} \times 273.15\ \cancel{\text{K}}}{1.00\ \cancel{\text{atm}}} = 3.474\ \text{L}$$

61. Most mixtures of hydrogen gas with oxygen gas are explosive. However, a mixture that contains less than 3.0 % O_2 is not. If enough O_2 is added to a cylinder of H_2 at 33.2 atm to bring the total pressure to 34.5 atm, is the mixture explosive?

Solution
The oxygen increases the pressure within the tank to (34.5 atm – 33.2 atm =) 1.3 atm. The percentage O_2 on a mole basis is $\frac{1.3}{34.5} \times 100\% = 3.77\%$. The mixture is explosive. However, the percentage is given as a weight percent. Converting to a mass basis increases the percentage of oxygen even more, so the mixture is still explosive.

62. A commercial mercury vapor analyzer can detect, in air, concentrations of gaseous Hg atoms (which are poisonous) as low as 2×10^{-6} mg/L of air. At this concentration, what is the partial pressure of gaseous mercury if the atmospheric pressure is 733 torr at 26 °C?

Solution
The total pressure is the pressure of the normal atmospheric components plus that due to mercury. Use the ideal gas equation to calculate the total number of moles of gas required to produce the stated conditions. The pressure of mercury is the mole fraction of mercury times the total pressure:

$$\text{mol (Hg)} = 2 \times 10^{-6}\ \cancel{\text{mg}}\ \text{L}^{-1} \times \frac{1\ \cancel{\text{g}}}{1000\ \cancel{\text{mg}}} \times \frac{1\ \text{mol}}{200.59\ \cancel{\text{g}}} = 9.97 \times 10^{-12}\ \text{mol L}^{-1}$$

$$n_T = \frac{PV}{RT} = \frac{\left(\frac{733}{760\ \cancel{\text{atm}}}\right)(1.0\ \cancel{\text{L}})}{(0.08206\ \cancel{\text{L}}\ \cancel{\text{atm}}\ \text{mol}^{-1}\ \cancel{\text{K}^{-1}})(294.15\ \cancel{\text{K}})} = 0.0400\ \text{mol}$$

$$P(\text{Hg}) = \frac{9.97 \times 10^{-12}\ \cancel{\text{mol}}}{0.0400\ \cancel{\text{mol}}} \times \frac{733\ \cancel{\text{torr}}}{760\ \cancel{\text{torr}}\ \text{atm}^{-1}} = 2.4 \times 10^{-10}\ \text{atm}$$

$$= 2.4 \times 10^{-10}\ \text{atm} \times 760\ \text{torr atm}^{-1}$$

$$= 2 \times 10^{-7}\ \text{torr}$$

63. A sample of carbon monoxide was collected over water at a total pressure of 756 torr and a temperature of 18 °C. What is the pressure of the carbon monoxide? (See Table 8.2 for the vapor pressure of water.)

Solution

The vapor pressure of water at 18 °C is 15.5 torr. Subtract the vapor pressure of water from the total pressure to find the pressure of the carbon monoxide:

$P_T = P_{gas} + P_{water}$

Rearrangement gives:

$P_T - P_{water} = P_{gas}$

756 torr – 15.5 torr = 740 torr

64. In an experiment in a general chemistry laboratory, a student collected a sample of a gas over water. The volume of the gas was 265 mL at a pressure of 753 torr and a temperature of 27 °C. The mass of the gas was 0.472 g. What was the molar mass of the gas?

Solution

First, find the water vapor pressure at 27 °C and subtract it from the measured pressure. From a rearranged form of the ideal gas equation, find the molar mass of the gas:

$$\text{molar mass} = \frac{0.472\ \text{g} \times 0.08206\ \cancel{\text{L}}\ \cancel{\text{atm}}\ \text{mol}^{-1}\ \cancel{\text{K}^{-1}} \times 303.15\ \cancel{\text{K}}}{\frac{726\ \cancel{\text{torr}}}{760\ \cancel{\text{torr}}}\ \cancel{\text{atm}^{-1}} \times 0.265\ \cancel{\text{L}}} = 46.4\ \text{g mol}^{-1}$$

65. Joseph Priestley first prepared pure oxygen by heating mercuric oxide, HgO:

$$2\text{HgO}(s) \longrightarrow 2\text{Hg}(l) + \text{O}_2(g)$$

(a) Outline the steps necessary to answer the following question: What volume of O_2 at 23 °C and 0.975 atm is produced by the decomposition of 5.36 g of HgO?

(b) Answer the question.

Solution

(a) Determine the moles of HgO that decompose; using the chemical equation, determine the moles of O_2 produced by decomposition of this amount of HgO; and determine the volume of O_2 from the moles of O_2, temperature, and pressure.

(b)

$$5.36\ \cancel{\text{g HgO}} \times \frac{1\ \text{mol HgO}}{(200.59 + 15.9994)\ \cancel{\text{g HgO}}} = 0.0247\ \text{mol HgO}$$

$$0.0247\ \cancel{\text{mol HgO}} \times \frac{1\ \text{mol O}_2}{2\ \cancel{\text{mol HgO}}} = 0.01235\ \text{mol O}_2$$

$PV = nRT$

$P = 0.975$ atm
$T = (23.0 + 273.15)$ K

$$V = \frac{nRT}{P} = \frac{0.01235 \cancel{\text{ mol}}\ (0.08206 \text{ L } \cancel{\text{atm}}\ \cancel{\text{mol}^{-1}}\ \cancel{\text{K}^{-1}})(296.15\ \cancel{\text{K}})}{0.975\ \cancel{\text{atm}}} = 0.308 \text{ L}$$

66. Cavendish prepared hydrogen in 1766 by the novel method of passing steam through a red-hot gun barrel:

$$4H_2O(g) + 3Fe(s) \longrightarrow Fe_3O_4(s) + 4H_2(g)$$

(a) Outline the steps necessary to answer the following question: What volume of H_2 at a pressure of 745 torr and a temperature of 20°C can be prepared from the reaction of 15.O g of H_2O?
(b) Answer the question.

Solution
(a) Determine the moles of water in 15.0 g. Using the chemical equation, determine the moles of H_2 produced from this amount of water; then determine the volume of H_2 from the number of moles of H_2, its temperature, and its pressure.
(b)

$$15.0\ \cancel{\text{g } H_2O} \times \frac{1\ \cancel{\text{mol } H_2O}}{18.015\ \cancel{\text{g } H_2O}} \times \frac{4 \text{ mol } H_2}{4\ \cancel{\text{mol } H_2O}} = 0.8326 \text{ mol } H_2$$

$$V = \frac{nRT}{P} = \frac{(0.8326\ \cancel{\text{mol}})\ (0.08206 \text{ L } \cancel{\text{atm}}\ \cancel{\text{mol}^{-1}}\ \cancel{\text{K}^{-1}})(296.15\ \cancel{\text{K}})}{\frac{745\ \cancel{\text{torr}}}{760\ \cancel{\text{torr}}\ \cancel{\text{atm}}}} = 20.4 \text{ L}$$

67. The chlorofluorocarbon CCl_2F_2 can be recycled into a different compound by reaction with hydrogen to produce $CH_2F_2(g)$, a compound useful in chemical manufacturing:

$$CCl_2F_2(g) + 4H_2(g) \longrightarrow CH_2F_2(g) + 2HCl(g).$$

(a) Outline the steps necessary to answer the following question: What volume of hydrogen at 225 atm and 35.5 °C would be required to react with 1 ton (1.000×10^3 kg) of CCl_2F_2?
(b) Answer the question.

Solution
(a) Determine the molar mass of CCl_2F_2. From the balanced equation, calculate the moles of H_2 needed for the complete reaction. From the ideal gas law, convert moles of H_2into volume.
(b) Molar mass of $CCl_2F_2 = 12.011 + 2 \times 18.9984 + 2 \times 35.4527 = 120.913$ g/mol

$$\text{mol } H_2 = 1.000 \times 10^6 \text{ g} \times \frac{1 \text{ mol } CCL_2F_2}{120.913 \text{ g}} \times \frac{4 \text{ mol } H_2}{1 \text{ mol } CCl_2F_2} = 3.308 \times 10^4 \text{ mol}$$

$$V = \frac{nRT}{P} = \frac{(3.308 \times 10^4\ \cancel{\text{mol}})(0.08206 \text{ L } \cancel{\text{atm}}\ \cancel{\text{mol}^{-1}}\ \cancel{\text{K}^{-1}})(308.65\ \cancel{\text{K}})}{225\ \cancel{\text{atm}}} = 3.72 \times 10^3 \text{ L}$$

68. Automobile air bags are inflated with nitrogen gas, which is formed by the decomposition of solid sodium azide (NaN_3). The other product is sodium metal. Calculate the volume of nitrogen gas at 27 °C and 756 torr formed by the decomposition of 125 g of sodium azide.

Solution

$$2NaN_3(s) \longrightarrow 3N_2(g) + 2Na(s)$$

First, find the moles of N_2 produced. Molar mass = NaN_3 = 65.01 g/mol.

$$\text{mol } N_2 = 125 \cancel{\text{ g NaN}_3} \times \frac{1 \cancel{\text{ mol NaN}_3}}{65.01 \cancel{\text{ g NaN}_3}} \times \frac{3 \text{ mol } N_2}{2 \cancel{\text{ mol NaN}_3}} = 2.884 \text{ mol}$$

$$V = \frac{nRT}{P} = \frac{(2.884 \cancel{\text{ mol}})(0.08206 \text{ L } \cancel{\text{atm}}\ \cancel{\text{mol}^{-1}}\ \cancel{\text{K}^{-1}})(300.15 \cancel{\text{ K}})}{\frac{756 \cancel{\text{ torr}}}{760 \cancel{\text{ torr}}\ \text{atm}^{-1}}} = 71.4 \text{ L}$$

69. Lime, CaO, is produced by heating calcium carbonate, $CaCO_3$; carbon dioxide is the other product.
(a) Outline the steps necessary to answer the following question: What volume of carbon dioxide at 875 K and 0.966 atm is produced by the decomposition of 1 ton (1.000×10^3 kg) of calcium carbonate?
(b) Answer the question.

Solution
(a) Balance the equation. Determine the grams of CO_2 produced and the number of moles. From the ideal gas law, determine the volume of gas.
(b) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

$$\text{mass } CO_2 = 1.00 \times 10^6 \text{ g} \times \frac{1 \text{ mol } CaCO_2}{100.087 \text{ g}} \times \frac{44.01 \text{ g } CO_2}{1 \text{ mol } CO_2} \times \frac{1 \text{ mol } CO_2}{1 \text{ mol } CaCO_2} = 4.397 \times 10^5 \text{ g}$$

$$\text{mol } CO_2 = \frac{4.397 \times 10^5 \text{ g}}{44.01 \text{ g mol}^{-1}} = 9991 \text{ mol}$$

$$V = \frac{nRT}{P} = \frac{(9991 \text{ mol})(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(875 \text{ K})}{0.966 \text{ atm}} = 7.43 \times 10^5 \text{ L}$$

70. Before small batteries were available, carbide lamps were used for bicycle lights. Acetylene gas, C_2H_2, and solid calcium hydroxide were formed by the reaction of calcium carbide, CaC_2, with water. The ignition of the acetylene gas provided the light. Currently, the same lamps are used by some cavers, and calcium carbide is used to produce acetylene for carbide cannons.
(a) Outline the steps necessary to answer the following question: What volume of C_2H_2 at 1.005 atm and 12.2 °C is formed by the reaction of 15.48 g of CaC_2 with water?
(b) Answer the question.

Solution
(a) First, write a balanced equation for the reaction. Then determine the moles of CaC_2 in 15.48 g. From the equation, determine the moles of C_2H_2 produced, and, from the ideal gas law, find the volume of the gas.

(b)
$$CaC_2 + 2H_2O \longrightarrow C_2H_2 + Ca(OH)_2$$
Molar mass of $CaC_2 = (40.078 + 2 \times 12.011) = 64.100$ g

$$\text{mol } CaC_2 = \frac{15.48 \text{ g}}{64.100 \text{ g mol}^{-1}} = 0.2415 \text{ mol}$$

From the balanced equation, 1 mol CaC_2 produces 1 mol C_2H_2. Consequently, 0.2415 mol of C_2H_2 is present.

$$V = \frac{nRT}{P} = \frac{(0.2415\ \text{mol})(0.08206\ \text{L atm mol}^{-1}\ \text{K}^{-1})(285.35\ \text{K})}{1.005\ \text{atm}} = 5.627\ \text{L}$$

71. Calculate the volume of oxygen required to burn 12.00 L of ethane gas, C_2H_6, to produce carbon dioxide and water, if the volumes of C_2H_6 and O_2 are measured under the same conditions of temperature and pressure.

Solution

$$2C_2H_6(g) + 7O_2(g) \longrightarrow 4CO_2(g) + 6H_2O(g)$$

From the balanced equation, we see that 2 mol of C_2H_6 requires 7 mol of O_2 to burn completely. Gay-Lussac's law states that gases react in simple proportions by volume. As the number of liters is proportional to the number of moles,

$$\frac{12.00\ \text{L}}{2\ \text{mol}\ C_2H_6} = \frac{V(O_2)}{7\ \text{mol}\ O_2}$$

$$V(O_2) = \frac{12.00\ \text{L} \times 7}{2} = 42.00\ \text{L}$$

72. What volume of O_2 at STP is required to oxidize 8.0 L of NO at STP to NO_2? What volume of NO_2 is produced at STP?

Solution

Write the balanced equation for the reaction:

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

Here, 2 mol of NO requires 1 mol of O_2 and 2 mol of NO_2 is produced. Gay-Lussac's law states that gases react in simple proportions by volume. Therefore, 8.0 L of NO requires 4.0 L of O_2 for reaction to produce 8.0 L of NO_2.

73. Consider the following questions:
(a) What is the total volume of the $CO_2(g)$ and $H_2O(g)$ at 600 °C and 0.888 atm produced by the combustion of 1.00 L of $C_2H_6(g)$ measured at STP?
(b) What is the partial pressure of H_2O in the product gases?

Solution

(a) The scheme to solve this problem is:

$$\text{volume } C_2H_6(g) \xrightarrow{\text{ideal gas equation}} \text{mol } C_2H_6(g) \xrightarrow{\text{reaction stoichiometry}} \text{mol } CO_2 + H_2O \xrightarrow{\text{ideal gas equation}} \text{volume } CO_2 + H_2O$$

$$C_2H_6(g) + 3\frac{1}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(g)$$

$$1.\ n(C_2H_6) = \frac{PV}{RT} = \frac{1.00\ \cancel{\text{atm}} \times 1.00\ \cancel{\text{L}}}{0.08206\ \cancel{\text{L}}\ \cancel{\text{atm}}\ \text{mol}^{-1}\ \cancel{\text{K}^{-1}}(273.15\ \cancel{\text{K}})} = 0.0446\ \text{mol}$$

$$2.\ 0.0446\ \cancel{\text{mol } C_2H_6} \times \frac{5\ \text{mol products}}{1\ \cancel{\text{mol } C_2H_6}} = 0.223\ \text{mol products}$$

$$3.\ V = nRT = \frac{(0.223\ \cancel{\text{mol}})(0.08206\ \text{L}\ \cancel{\text{atm}}\ \cancel{\text{mol}^{-1}}\ \cancel{\text{K}^{-1}})(873.15\ \cancel{\text{K}})}{0.888\ \cancel{\text{atm}}} = 18.0\ \text{L}$$

(b) First, calculate the mol H_2O produced:

$$0.0446 \text{ mol } C_2H_6 \times \frac{3 \text{ mol products}}{1 \text{ mol } C_2H_6} = 0.1338 \text{ mol}$$

Second, calculate the pressure of H_2O:

$$P = \frac{nRT}{V} = \frac{(0.1338 \text{ mol})(0.8206 \text{ L atm mol}^{-1} \text{ K}^{-1})(873.15 \text{ K})}{18.0 \text{ L}} = 0.533 \text{ atm}$$

74. Methanol, CH_3OH, is produced industrially by the following reaction:

$$CO(g) + 2H_2(g) \xrightarrow{\text{copper catalyst, 300 °C, 300 atm}} CH_3OH(g)$$

Assuming that the gases behave as ideal gases, find the ratio of the total volume of the reactants to the final volume.

Solution

In this reaction, 3 mol of gas forms 1 mol of gas.

$$PV = nRT$$

$$\frac{V_1}{n_1} = \frac{RT}{P} = \frac{V_2}{n_2}$$

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

This tells us that the value, at constant P and T, is directly proportional to the moles of gas. The volume ratio of reactants to final volume, V_1/V_2, will be equal to the mole ratio of reactants to products:

$$\frac{n_1}{n_2} = \frac{3}{1}$$

The ratio is 3:1.

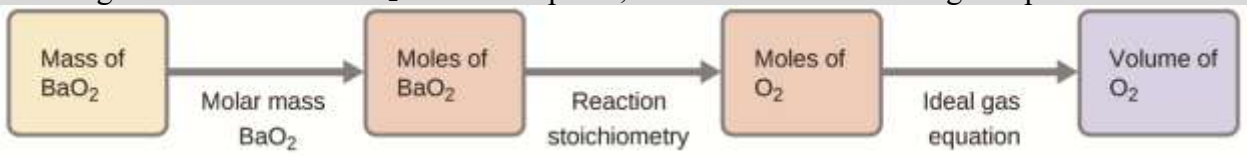
75. What volume of oxygen at 423.0 K and a pressure of 127.4 kPa is produced by the decomposition of 129.7 g of BaO_2 to BaO and O_2?

Solution

First, we must write a balanced equation to establish the stoichiometry of the reaction:

$$2BaO_2 \longrightarrow 2BaO + O_2$$

We are given the mass of BaO_2 that decomposes, so the scheme for solving this problem will be:



Mass (BaO_2) = 137.33 + 2(15.9994) = 169.33 g/mol

$$n(O_2) = 129.7 \text{ g } BaO_2 \times \frac{1 \text{ mol } BaO_2}{169.33 \text{ g } BaO_2} \times \frac{1 \text{ mol } O_2}{2 \text{ mol } BaO_2} = 0.3830 \text{ mol } O_2$$

$$V(O_2) = \frac{nRT}{P} = \frac{0.3830 \text{ mol}(8.314 \text{ L kPa mol}^{-1} \text{ K}^{-1})(423.0 \text{ K})}{127.4 \text{ kPa}} = 10.57 \text{ L } O_2$$

76. A 2.50-L sample of a colorless gas at STP decomposed to give 2.50 L of N_2 and 1.25 L of O_2 at STP. What is the colorless gas?

Solution

Because gas volumes are directly related to the number of moles present, the production of 2.50 L of N_2 indicates that two nitrogen atoms occur in the compound. The formation of 1.25 L of O_2 gives one-half the original volume, indicating that only one oxygen atom occurs in the original compound. The compound is N_2O.

77. Ethanol, C_2H_5OH, is produced industrially from ethylene, C_2H_4, by the following sequence of reactions:

$$3C_2H_4 + 2H_2SO_4 \longrightarrow C_2H_5HSO_4 + \left(C_2H_5\right)_2 SO_4$$

$$C_2H_5HSO_4 + \left(C_2H_5\right)_2 SO_4 + 3H_2O \longrightarrow 3C_2H_5OH + 2H_2SO_4$$

What volume of ethylene at STP is required to produce 1.000 metric ton (1000 kg) of ethanol if the overall yield of ethanol is 90.1%?

Solution

At 90.1% conversion, a 1.000×10^6 g final yield would require a $\left(\frac{1.000 \times 10^6}{0.901}\right) = 1.1099 \times 10^6$ g theoretical yield.

$3C_2H_4$ produces $3C_2H_5OH$, giving a 1:1 ratio:

$$\text{mol } (C_2H_4) = 1.1099 \times 10^6 \ \cancel{\text{g } C_2H_5OH} \times \frac{1 \ \cancel{\text{mol } C_2H_2OH}}{46.069 \ \cancel{\text{g } C_2H_5OH}} \times \frac{1 \text{ mol } C_2H_4}{1 \ \cancel{\text{mol } C_2H_2OH}}$$

$$= 2.409 \times 10^4 \text{ mol}$$

$V(C_2H_4) = 22.4 \text{ L/mol} \times 2.409 \times 10^4 \text{ mol} = 5.40 \times 10^5 \text{ L}$

78. One molecule of hemoglobin will combine with four molecules of oxygen. If 1.0 g of hemoglobin combines with 1.53 mL of oxygen at body temperature (37 °C) and a pressure of 743 torr, what is the molar mass of hemoglobin?

Solution

The oxygen reacts on a 1:4 mol basis. First, find the number of moles of O_2 from the ideal gas law; then, divide by 4.

$$n = \frac{PV}{RT} = \frac{\left(\frac{743 \ \cancel{\text{torr}}}{763 \ \cancel{\text{torr}} \ \cancel{\text{atm}^{-1}}}\right)(1.53 \ \cancel{\text{mL}})\left(\frac{1 \ \cancel{\text{L}}}{1000 \ \cancel{\text{mL}}}\right)}{(0.08206 \ \cancel{\text{L}} \ \cancel{\text{atm}^{-1}} \text{ mol}^{-1} \ \cancel{\text{K}^{-1}})\ (310.15 \ \cancel{\text{K}})} = 5.854 \times 10^{-5} \text{ mol}$$

$$\frac{1}{4}(5.854 \times 10^{-5} \text{ mol}) = 1.464 \times 10^{-5} \text{ mol hemoglobin}$$

Divide 1.0 g by the corresponding number of moles to find the molar mass.

$$\frac{1.0 \text{ g}}{1.464 \times 10^{-5} \text{ mol}} = 6.8 \times 10^4 \text{ g mol}^{-1}$$

79. A sample of a compound of xenon and fluorine was confined in a bulb with a pressure of 18 torr. Hydrogen was added to the bulb until the pressure was 72 torr. Passage of an electric spark through the mixture produced Xe and HF. After the HF was removed by reaction with solid KOH, the final pressure of xenon and unreacted hydrogen in the bulb was 36 torr. What is the empirical formula of the xenon fluoride in the original sample? (Note: Xenon fluorides contain only one xenon atom per molecule.)

Solution

The reaction is:

$$XeF_x + \frac{x}{2}H_2 \longrightarrow Xe + x\text{HF}$$

Immediately after the H_2 is added (before the reaction):

$$P_{Total} = P_{XeF_2} + P_{H_2}$$

$$P_{H_2} = P_{Total} - P_{XeF_2}$$

$$= 72 \text{ torr} - 18 \text{ torr}$$

$$= 54 \text{ torr}$$

After the reaction:

$P_{Xe} = 18$ torr $\quad (1 \text{ mol } XeF_x \longrightarrow 1 \text{ mol Xe})$

And the partial pressure of unreacted H_2 is:

$$P_{H_2} = P_{Total} - P_{Xe}$$

$$= 36 \text{ torr} - 18 \text{ torr}$$

$$= 18 \text{ torr}$$

The pressure of H_2 that reacts is:

54 torr – 18 torr = 36 torr

The number of moles of gas is proportional to the partial pressures. The reaction used 18 torr of XeF_x and 36 torr of H_2 so:

$$\frac{x}{2} = 1 \text{ and } x = 2$$

$$\frac{\text{mol } H_2}{\text{mol } XeF_x} = \frac{x/2}{1} = \frac{x}{2} = \frac{36 \text{ torr}}{18 \text{ torr}} \longrightarrow x = \frac{72 \text{ torr}}{18 \text{ torr}} = 4$$

The empirical formula for the compound is XeF_4.

80. One method of analyzing amino acids is the van Slyke method. The characteristic aminogroups ($–NH_2$) in protein material are allowed to react with nitrous acid, HNO_2, to form N_2 gas. From the volume of the gas, the amount of amino acid can be determined. A 0.0604-g sample of a biological sample containing glycine, $CH_2(NH_2)COOH$, was analyzed by the van Slyke method and yielded 3.70 mL of N_2 collected over water at a pressure of 735 torr and 29 °C. What was the percentage of glycine in the sample?

$$CH_2\left(NH_2\right)CO_2H + HNO_2 \longrightarrow CH_2\left(OH\right)CO_2H + H_2O + N_2$$

Solution

$$\text{volume } N_2 \text{ moist} \xrightarrow[\text{partial pressure}]{\text{(1) law of}} \xrightarrow[\text{gas equation}]{\text{(2) ideal}} \text{mol } N_2 \xrightarrow[\text{stoichiometry}]{\text{(3) reaction}} \text{mol glycine} \xrightarrow{(4)} \text{wt \% glycine in sample}$$

The N_2 was collected over water, so the partial pressure of water at 29 °C, which is 30.0 torr, must be taken into account:

$$P_T = P_{N_2} + P_{H_2O}$$

$$P_{N_2} = P_T - P_{H_2O} = (735 - 30.0) \text{ torr} = 705 \text{ torr}$$

$$2.\ n(N_2) = \frac{PV}{RT} = \frac{\left(\frac{705}{760}\right) \cancel{\text{atm}}\ (0.00370\ \cancel{\text{L}})}{(0.08206\ \cancel{\text{L}}\ \cancel{\text{atm}}\ \text{mol}^{-1}\ \cancel{\text{K}^{-1}})\ (302.15\ \cancel{\text{K}})} = 1.38 \times 10^{-4} \text{ mol}$$

3. $1.38 \times 10^{-4}\ \cancel{\text{mol N}_2} \times \dfrac{1\ \text{mol glycine}}{1\ \cancel{\text{mol N}_2}} = 1.38 \times 10^{-4}\ \text{glycine}$

4. $M_{\text{glycine}} = 2(12.011) + 5(1.00794) + 2(15.9994) + (14.0067)$

$= 75.067\ \text{g mol}^{-1}$

$\text{mass glycine} = 1.38 \times 10^{-4}\ \cancel{\text{mol}} \times \dfrac{75.067\ \text{g}}{\cancel{\text{mol}}} = 1.04 \times 10^{-2}\ \text{g}$

$\text{wt \% glycine} = \dfrac{\text{mass glycine}}{\text{mass sample}} \times 100\% = \dfrac{1.04 \times 10^{-2}\ \cancel{\text{g}}}{0.0604\ \cancel{\text{g}}} \times 100\% = 17.2\%$

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Chemistry: Atoms First 2e
8: Gases
8.4: Effusion and Diffusion of Gases

81. A balloon filled with helium gas takes 6 hours to deflate to 50% of its original volume. How long will it take for an identical balloon filled with the same volume of hydrogen gas (instead of helium) to decrease its volume by 50%?

Solution

Use the rate of effusion equation:

$$\frac{6\ \text{hours}}{t} = \sqrt{\frac{4}{2}}$$

$$t = \frac{6\ \text{hours}}{1.4} = 4.2\ \text{hours}$$

82. Explain why the numbers of molecules are not identical in the left- and right-hand bulbs shown in the center illustration of Figure 8.27.

Solution

When the stopcock is opened, the faster-moving H_2 will effuse through the small opening faster than the slower-moving O_2. Thus, in a unit of time, more hydrogen will effuse through the hole into the oxygen compartment faster than oxygen will move into the hydrogen compartment.

83. Starting with the definition of rate of effusion and Graham's finding relating rate and molar mass, show how to derive the Graham's law equation, relating the relative rates of effusion for two gases to their molecular masses.

Solution

Effusion can be defined as the process by which a gas escapes through a pinhole into a vacuum. Graham's law states that with a mixture of two gases A and B:

$\left(\frac{\text{rate A}}{\text{rate B}}\right) = \left(\frac{\text{molar mass of B}}{\text{molar mass of A}}\right)^{1/2}$. Both A and B are in the same container at the same temperature and, therefore, will have the same kinetic energy:

$KE_A = KE_B$

$KE = \frac{1}{2}mv^2$

Therefore, $\frac{1}{2}m_A v_A^2 = \frac{1}{2}m_B v_B^2$

$\frac{v_A^2}{v_B^2} = \frac{m_B}{m_A}$

$\left(\frac{v_A^2}{v_B^2}\right)^{1/2} = \left(\frac{m_B}{m_A}\right)^{1/2}$

$\frac{v_A}{v_B} = \left(\frac{m_B}{m_A}\right)^{1/2}$

84. Heavy water, D_2O (molar mass = 20.03 g mol^{-1}), can be separated from ordinary water, H_2O (molar mass = 18.01), as a result of the difference in the relative rates of diffusion of the molecules in the gas phase. Calculate the relative rates of diffusion of H_2O and D_2O.

Solution

In this problem, we use Graham's law for rates of diffusion of gases:

$\frac{R_1}{R_2} = \frac{\sqrt{M_2}}{\sqrt{M_1}}$

$\frac{R_{H_2O}}{R_{D_2O}} = \frac{\sqrt{M_{D_2O}}}{\sqrt{M_{H_2O}}} = \frac{\sqrt{20.03}}{\sqrt{18.01}} = 1.055$

Therefore, H_2O diffuses 1.055-times faster than does D_2O.

85. Which of the following gases diffuse more slowly than oxygen? F_2, Ne, N_2O, C_2H_2, NO, Cl_2, H_2S

Solution

Gases with molecular masses greater than that of oxygen (31.9988 g/mol) will diffuse more slowly than O_2. These gases are F_2 (37.9968 g/mol), N_2O (44.0128 g/mol), Cl_2 (70.906 g/mol), and H_2S (34.082 g/mol).

86. During the discussion of gaseous diffusion for enriching uranium, it was claimed that $^{235}UF_6$ diffuses 0.4% faster than $^{238}UF_6$. Show the calculation that supports this value. The molar mass of $^{235}UF_6$ = 235.043930 + 6 × 18.998403 = 349.034348 g/mol, and the molar mass of $^{238}UF_6$ = 238.050788 + 6 × 18.998403 = 352.041206 g/mol.

Solution

The diffusion rate for ^{235}U is proportional to $\frac{1}{\sqrt{349.034348}} = 0.053526139$, whereas the diffusion rate for ^{238}U is proportional to $\frac{1}{\sqrt{352.041206}} = 0.05329706$.

$\frac{\text{diffusion rate for } ^{235}U}{\text{diffusion rate for } ^{238}U} = \frac{0.053526139}{0.05329706} = 1.0043$. Therefore, the rate for ^{235}U is 0.43% faster.

87. Calculate the relative rate of diffusion of $^{1}H_2$ (molar mass 2.0 g/mol) compared with $^{2}H_2$ (molar mass 4.0 g/mol) and the relative rate of diffusion of O_2 (molar mass 32 g/mol) compared to that of O_3 (molar mass 48 g/mol).

Solution

$$\frac{R_{H_2}}{R_{D_2}} = \frac{\sqrt{M_{D_2}}}{\sqrt{M_{H_2}}} = \frac{\sqrt{4.0}}{\sqrt{2.0}} = \frac{2.000}{1.414} = 1.4$$

$$\frac{R_{O_2}}{R_{O_3}} = \frac{\sqrt{M_{O_3}}}{\sqrt{M_{O_2}}} = \frac{\sqrt{48}}{\sqrt{32}} = 1.2$$

88. A gas of unknown identity diffuses at a rate of 83.3 mL/s in a diffusion apparatus in which carbon dioxide diffuses at the rate of 102 mL/s. Calculate the molecular mass of the unknown gas.

Solution

According to Graham's law of effusion, the rate of diffusion is inversely proportional to the square root of its molar mass or molecular mass. Thus,

$$\frac{R_1}{R_2} = \frac{\sqrt{\text{molar mass}_1}}{\sqrt{\text{molar mass}_1}}$$

$$\frac{83.3 \text{ mL/s}}{102 \text{ mL/s}} = \frac{\sqrt{44}}{\sqrt{\text{molar mass}_1}}$$

It is perhaps easiest to square both sides in this case and then solve for molar mass$_1$. Thus,

$$\text{molar mass}_1 = 44.0 \text{ g/mol} \times \frac{(102 \text{ mL s}^{-1})^2}{(83.3 \text{ mL s}^{-1})^2} = 44.0 \times \frac{102^2 \text{ g}}{83.3^2 \text{ g mol}} = 66.0 \text{ g mol}^{-1}$$

89. When two cotton plugs, one moistened with ammonia and the other with hydrochloric acid, are simultaneously inserted into opposite ends of a glass tube that is 87.0 cm long, a white ring of NH_4Cl forms where gaseous NH_3 and gaseous HCl first come into contact. (Hint: Calculate the rates of diffusion for both NH_3 and HCl, and find out how much faster NH_3 diffuses than HCl.) $NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$ At approximately what distance from the ammonia-moistened plug does this occur?

Solution

Rate of diffusion for NH_3 is proportional to $\frac{1}{17.04^{1/2}} = 0.242250792$

Rate of diffusion for HCl is proportional to $\frac{1}{36.46^{1/2}} = 0.165611949$, $\left(\frac{0.242250792}{0.165611949}\right) = 1.4627$.

Set up an algebraic expression, letting x represent the distance travelled by the HCl: $x + 1.4627x = 87$, $x = 35.3$, so the distance travelled by the NH_3 is $(1.4627)x = 51.7$ cm.

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Chemistry: Atoms-First 2e
8: Gases
8.5: The Kinetic-Molecular Theory

90. Using the postulates of the kinetic-molecular theory, explain why a gas uniformly fills a container of any shape.

Solution
From the first postulate, the gas molecules travel in straight lines and change direction only when they collide. With a large sample of gas, many collisions occur with the walls of the container as well as between gas molecules. These events are completely random. Consequently, the direction of motion of the gases becomes completely random.

91. Can the speed of a given molecule in a gas double at constant temperature? Explain your answer.

Solution
Yes. At any given instant, there are a range of values of molecular speeds in a sample of gas. Any single molecule can speed up or slow down as it collides with other molecules. The average speed of all the molecules is constant at constant temperature.

92. Describe what happens to the average kinetic energy of ideal gas molecules when the conditions are changed as follows:
(a) The pressure of the gas is increased by reducing the volume at constant temperature.
(b) The pressure of the gas is increased by increasing the temperature at constant volume.
(c) The average speed of the molecules is increased by a factor of 2.

Solution
(a) The average kinetic energy remains the same at constant temperature. (b) A temperature increase corresponds to an increase in kinetic energy. (c) As the average speed is doubled, a corresponding increase must occur in temperature and, therefore, also in kinetic energy.

93. The distribution of molecular speeds in a sample of helium is shown in Figure 8.34. If the sample is cooled, will the distribution of speeds look more like that of H_2 or of H_2O? Explain your answer.

Solution
H_2O. Cooling slows the speeds of the He atoms, causing them to behave as though they were heavier.

94. What is the ratio of the average kinetic energy of a SO_2 molecule to that of an O_2 molecule in a mixture of two gases? What is the ratio of the root mean square speeds, u_{rms}, of the two gases?

Solution
According to the kinetic-molecular theory, the kinetic energies of the two gases are equal as long as they remain at the same temperature, as in this case. Because their kinetic energies are equal, we can write:

$$\frac{u_{rms}(SO_2)}{u_{rms}(O_2)} = \frac{\sqrt{M_{O_2}}}{\sqrt{M_{SO_2}}}$$

$$\frac{u_{rms}(SO_2)}{u_{rms}(O_2)} = \frac{\sqrt{M_{O_2}}}{\sqrt{M_{SO_2}}} = \frac{\sqrt{31.9988}}{\sqrt{64.0648}} = \frac{5.6567}{8.0040} = 0.70673$$

Thus, the average kinetic energies are equal (1:1 ratio), and the ratio is $\frac{u_{SO_2}}{u_{O_2}} = 0.70673$.

95. A 1-L sample of CO initially at STP is heated to 546 K, and its volume is increased to 2 L.
(a) What effect do these changes have on the pressure exerted by the gas?
(b) What is the effect on the average kinetic energy of the molecules?
(c) What is the effect on the root mean square speed of the molecules?

Solution
Both the temperature and the volume are doubled for this gas (*n* constant), so *P* remains constant. (a) The pressure of the gas remains constant. (b) The average kinetic energy doubles; it is proportional to temperature. (c) The root mean square speed increases to $\sqrt{2}$ times its initial value; u_{rms} is proportional to $\sqrt{KE_{avg}}$.

96. The root mean square speed of H_2 molecules at 25 °C is about 1.6 km/s. What is the root mean square speed of a N_2 molecule at 25 °C?

Solution
As the temperature and, thus, the kinetic energy remain the same,

$$\frac{u_{rms}(H_2)}{u_{rms}(N_2)} = \frac{\sqrt{M_{N_2}}}{\sqrt{M_{H_2}}} = \frac{\sqrt{2.01588}}{\sqrt{28.01348}} = \frac{1.4198169}{5.2927762} = 0.2682556$$

$u_{rms}(N_2) = 1.6 \text{ km/s} \times 0.2683 = 0.43 \text{ km/s}$

97. Answer the following questions:
(a) Is the pressure of the gas in the hot-air balloon shown at the opening of this chapter greater than, less than, or equal to that of the atmosphere outside the balloon?
(b) Is the density of the gas in the hot-air balloon shown at the opening of this chapter greater than, less than, or equal to that of the atmosphere outside the balloon?
(c) At a pressure of 1 atm and a temperature of 20 °C, dry air has a density of 1.2256 g/L. What is the (average) molar mass of dry air?
(d) The average temperature of the gas in a hot-air balloon is 1.30×10^2 °F. Calculate its density, assuming the molar mass equals that of dry air.
(e) The lifting capacity of a hot-air balloon is equal to the difference in the mass of the cool air displaced by the balloon and the mass of the gas in the balloon. What is the difference in the mass of 1.00 L of the cool air in part (c) and the hot air in part (d)?
(f) An average balloon has a diameter of 60 feet and a volume of 1.1×10^5 ft^3. What is the lifting power of such a balloon? If the weight of the balloon and its rigging is 500 pounds, what is its capacity for carrying passengers and cargo?
(g) A balloon carries 40.0 gallons of liquid propane (density 0.5005 g/L). What volume of CO_2 and H_2O gas is produced by the combustion of this propane at STP?
(h) A balloon flight can last about 90 minutes. If all of the fuel is burned during this time, what is the approximate rate of heat loss (in kJ/min) from the hot air in the bag during the flight?

Solution
(a) equal, because the balloon is free to expand until the pressures are equalized; (b) less than the density outside; (c) assume three-place accuracy throughout unless greater accuracy is stated:

$$\text{molar mass} = \frac{DRT}{P} = 1.2256 \text{ g } \cancel{\text{L}^{-1}} \times \frac{0.08206 \cancel{\text{ L}} \cancel{\text{ atm}} \text{ mol}^{-1} \cancel{\text{ K}^{-1}} \times 293.15 \cancel{\text{ K}}}{1.00 \cancel{\text{ atm}}};$$

$$= 29.48 \text{ g mol}^{-1}$$

(d) convert the temperature to °C; then use the ideal gas law:

$$°\text{C} = \frac{5}{9}(\text{F} - 32) = \frac{5}{9}(130 - 32) = 54.44 \ ^{\circ}\text{C} = 327.6 \text{ K}$$

$$D = \frac{MP}{RT} = 29.48 \text{ g } \cancel{\text{mol}^{-1}} \times \frac{1.00 \cancel{\text{ atm}}}{0.08206 \text{ L } \cancel{\text{atm}} \cancel{\text{ mol}^{-1}} \cancel{\text{ K}^{-1}} \times 327.6 \cancel{\text{ K}}} = 1.0966 \text{ g L}^{-1};$$

(e) 1.2256 g/L – 1.09966 g/L = 0.129 g/L; (f) calculate the volume in liters, multiply the volume by the density difference to find the lifting capacity of the balloon, subtract the weight of the balloon after converting to pounds:

$$1.1 \times 105 \text{ ft}^3 \times \left(\frac{12\text{in}}{91\text{ft}}\right)^3 \times \left(\frac{2.54\text{cm}}{\text{in}}\right)^3 \times \frac{1 \text{ L}}{1000 \text{ cm}^3} = 3.11 \times 10^6 \text{ L}$$

$$3.11 \times 106 \text{ L} \times 0.129 \text{ g/L} = 4.01 \times 10^5 \text{ g}$$

$$\frac{4.01\,10^5 \text{g}}{453.59 \text{ g lb}^{-1}} = 884 \text{ lb}; 884 \text{ lb} - 500 \text{ lb} = 384 \text{ lb}$$

net lifting capacity = 384 lb; (g) First, find the mass of propane contained in 40.0 gal. Then calculate the moles of $CO_2(g)$ and $H_2O(g)$ produced from the balanced equation.

$$40.0 \cancel{\text{ gal}} \times \frac{4(0.9463 \text{ L})}{1 \cancel{\text{ gal}}} = 151.4 \text{ L}$$

$$151.4 \text{ L} \times 0.5005 \text{ g L}^{-1} = 75.8\text{g}$$

Molar mass of propane = 3(12.011) + 8(1.00794) = 36.033 + 8.064 = 44.097 g mol^{-1}

$$\frac{75.8 \cancel{\text{ g}}}{44.097 \cancel{\text{ g}} \text{ mol}^{-1}} = 1.72 \text{ mol}$$

The reaction is $C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(g)$

For each 1.72 mol propane, there are 3 × 1.72 mol = 5.15 mol of CO_2 and 4 × 1.72 mol = 6.88 mol H_2O. The total volume at STP = 22.4 L × 12.04 = 270 L; (h) The total heat released is determined from the heat of combustion of the propane. Using the equation in part (g),

$$\Delta H^{\circ}_{\text{combustion}} = 3\Delta H^{\circ}_{CO_2(g)} + 4\Delta H^{\circ}_{H_2O(g)} - \Delta H^{\circ}_{\text{propane}}$$

$$= 3(-393.51) + 4(-241.82) - (-103.85)$$

$$= -1180.52 - 967.28 + 103.85 = -2043.96 \text{ kJ mol}^{-1}$$

Since there is 1.72 mol propane, 1.72 × 2043.96 kJ mol^{-1} = 3.52 × 10^3 kJ is used for heating.

This heat is used over 90 minutes, so $\frac{3.52 \times 10^3 \text{ kJ}}{90 \text{ min}} = 39.1 \text{ kJ min}^{-1}$ is released.

98. Show that the ratio of the rate of diffusion of Gas 1 to the rate of diffusion of Gas 2, $\frac{R_1}{R_2}$, is the same at 0 °C and 100 °C.

Solution

The rate at which a gas will diffuse, *R,* is proportional to u_{rms}, the root mean square speed of its molecules. The square of this value, in turn, is proportional to the average kinetic energy. The average kinetic energy is:

$\overline{KE}_{avg} = kT$.

For two different gases, 1 and 2, the constant of proportionality can be represented as k_1 and k_2, respectively. Thus,

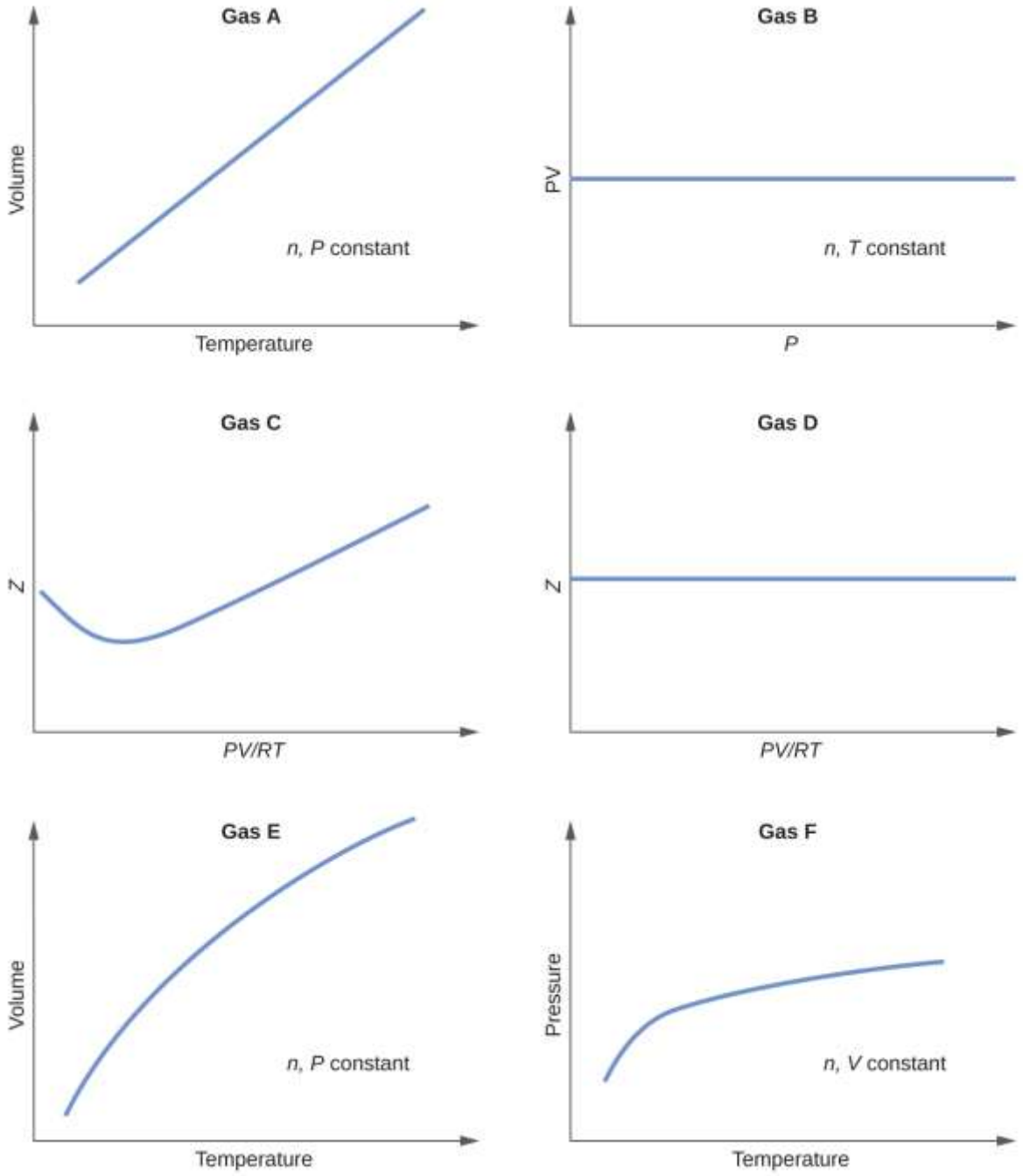
$$\frac{R_1}{R_2} = \frac{k_1\sqrt{T}}{k_2\sqrt{T}} .$$

As a result of this relationship, no matter at which temperature diffusion occurs, the temperature term will cancel out of the equation and the ratio of rates will be the same.

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Chemistry: Atoms First 2e
8: Gases
8.6: Non-Ideal Gas Behavior

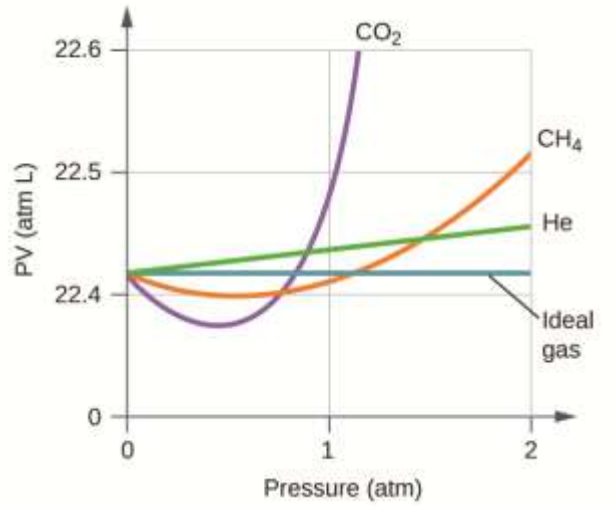
99. Graphs showing the behavior of several different gases follow. Which of these gases exhibit behavior significantly different from that expected for ideal gases?



Solution
Gas A: volume increases linearly as temperature increases with moles and pressure held constant, as expected by the ideal gas law $V = (\boldsymbol{nR}/\boldsymbol{P})T$; Gas B: PV stays constant as pressure increases with moles and temperature held constant, as expected by the ideal gas law $PV = \boldsymbol{nRT}$; Gas C: compressibility factor (Z) varies as PV/RT increases, as expected of a real gas; Gas D: compressibility factor (Z) stays constant as PV/RT increases with moles and pressure held constant, as expected of an ideal gas; Gas E: as temperature increases, volume increases, but not linearly with moles and pressure held constant, as would *not* be expected by the ideal gas law $V = (\boldsymbol{nR}/\boldsymbol{P})T$, as seen in Gas A; Gas F: as temperature increases, pressure increases with moles and volume held constant, but not linearly, as would *not* be expected by the ideal gas law $P =$

(***nR*/*V***)*T*, as seen in Gas A; Gases C, E, and F exhibit behavior significantly different from that expected for an ideal gas.

100. Explain why the plot of *PV* for CO_2 differs from that of an ideal gas.



Solution
All real gases have finite volume, which shows itself as larger than ideal volume (and consequently *PV* value) at high pressures. The gases that are capable of van der Waals forces (CO_2, CH_4) also show a smaller than ideal volume at some pressures due to the attraction between molecules.

101. Under which of the following sets of conditions does a real gas behave most like an ideal gas, and for which conditions is a real gas expected to deviate from ideal behavior? Explain.

(a) high pressure, small volume

(b) high temperature, low pressure

(c) low temperature, high pressure

Solution
The gas behavior most like an ideal gas will occur under the conditions that minimize the chances of significant interactions between the gaseous atoms/molecules, namely, low pressures (fewer atoms/molecules per unit volume) and high temperatures (greater kinetic energies of atoms/molecules make them less susceptible to attractive forces). The conditions described in (b), high temperature and low pressure, are therefore most likely to yield ideal gas behavior.

102. Describe the factors responsible for the deviation of the behavior of real gases from that of an ideal gas.

Solution
Anything that causes the gas particles to move close together, or have attractions, will cause deviations. Lowering the temperature will enhance this deviant behavior. In addition, the larger the molecules, the larger the volume occupied by the gas, which, in turn, causes deviations.

103. For which of the following gases should the correction for the molecular volume be largest: CO, CO_2, H_2, He, NH_3, SF_6?

Solution
We would expect the molecule with the largest volume to need the largest correction. SF_6 would need the largest correction.

104. A 0.245-L flask contains 0.467 mol CO_2 at 159 °C. Calculate the pressure:

(a) using the ideal gas law
(b) using the van der Waals equation
(c) Explain the reason for the difference.
(d) Identify which correction (that for P or V) is dominant and why.

Solution
(a) $PV = nRT$
$P \times 0.245\ \text{L} = 0.467\ \text{mol} \times 0.0821\ \text{atm L/mol K} \times 432\ \text{K}$

$$P = \frac{(0.467\ \cancel{\text{mol}} \times 0.0821\ \text{atm}\ \cancel{\text{L}}/\cancel{\text{mol}}\ \cancel{\text{K}} \times 432\ \cancel{\text{K}})}{0.245\ \cancel{\text{L}}} = 67.6\ \text{atm}$$

; (b) For CO_2, a = 3.59 L^2 atm mol^2 and b = 0.427 L/mol. The rearranged equation for P is:

$$P = \frac{nRT}{(V - nb)} - \frac{n^2 a}{V^2}$$

$$= \frac{0.467\ \cancel{\text{mol}} \times 0.0821\ \text{atm}\ \cancel{\text{L}}/\cancel{\text{mol}^{-1}}\ \cancel{\text{K}^{-1}} \times 432\ \cancel{\text{K}}}{0.245\ \cancel{\text{L}} - 0.467\ \cancel{\text{mol}} \times 0.0427\ \cancel{\text{L}}/\cancel{\text{mol}^{-1}}} ;$$

$$- \frac{(0.467\ \cancel{\text{mol}})^2 \times 3.59\ \cancel{\text{L}^2}\ \text{atm}\ \cancel{\text{mol}^{-2}}}{(0.245\ \cancel{\text{L}})^2}$$

$$= 60.5\ \text{atm}$$

(c) Differences are due to the intermolecular attractions between gas molecules and the volume of the gas molecules themselves. (d) The pressure correction factor due to intermolecular attractions is dominant, which is usually the case at relatively low pressures; the volume correction would result in a higher pressure than expected, but a lower pressure than the value obtained with $PV = nRT$.

105. Answer the following questions:
(a) If XX behaved as an ideal gas, what would its graph of Z vs. P look like?
(b) For most of this chapter, we performed calculations treating gases as ideal. Was this justified?
(c) What is the effect of the volume of gas molecules on Z? Under what conditions is this effect small? When is it large? Explain using an appropriate diagram.
(d) What is the effect of intermolecular attractions on the value of Z? Under what conditions is this effect small? When is it large? Explain using an appropriate diagram.
(e) In general, under what temperature conditions would you expect Z to have the largest deviations from the Z for an ideal gas?

Solution
Answer: (a) A straight horizontal line at 1.0 (see Figure 8.35) for the line representing an ideal gas. (b) When real gases are at low pressures and high temperatures they behave close enough to ideal gases that they are approximated as such; however, in some cases, we see that at a high pressure and temperature, the ideal gas approximation breaks down and is significantly different from the pressure calculated by the van der Waals equation. (c) The greater the compressibility, the more the volume matters. At low pressures, the correction factor for intermolecular attractions is more significant, and the effect of the volume of the gas molecules on Z would be a small lowering compressibility. At higher pressures, the effect of the volume of the gas molecules themselves on Z would increase compressibility (see Figure 8.35). (d) Once again, at low pressures, the effect of intermolecular attractions on Z would be more important than the correction factor for the volume of the gas molecules themselves, though perhaps still small. At

higher pressures and low temperatures, the effect of intermolecular attractions would be larger. See Figure 8.35. (e) Low temperatures

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Chemistry: Atoms First 2e
9: Thermochemistry
9.1: Energy Basics

1. A burning match and a bonfire may have the same temperature, yet you would not sit around a burning match on a fall evening to stay warm. Why not?

Solution

The temperature of 1 gram of burning wood is approximately the same for both a match and a bonfire. This is an intensive property and depends on the material (wood). However, the overall

amount of produced heat depends on the amount of material; this is an extensive property. The amount of wood in a bonfire is much greater than that in a match; the total amount of produced heat is also much greater, which is why we can sit around a bonfire to stay warm, but a match would not provide enough heat to keep us from getting cold.

2. Prepare a table identifying several energy transitions that take place during the typical operation of an automobile.

Solution

Chemical (potential) energy of the car battery is converted into mechanical (kinetic) energy of the engine starter when the ignition switch is turned or pressed; chemical (potential) energy in the gasoline is converted into heat and mechanical energy through its combustion in the auto's engine; kinetic energy of the automobile is converted into heat created by friction of the brake pads during braking.

3. Explain the difference between heat capacity and specific heat of a substance.

Solution

Heat capacity refers to the heat required to raise the temperature of the mass of the substance 1 degree; specific heat refers to the heat required to raise the temperature of 1 gram of the substance 1 degree. Thus, heat capacity is an extensive property, and specific heat is an intensive one.

4. Calculate the heat capacity, in joules and in calories per degree, of the following:
(a) 28.4 g of water
(b) 1.00 oz of lead

Solution

(a) $28.4\ \text{g} \times 4.184\ \text{J/g °C} = 119\ \text{J/°C}$; $28.4\ \text{g} \times 1.000\ \text{cal/g °C} = 28.4\ \text{cal/°C}$; (b) $28.4\ \text{g} \times 0.129\ \text{J/g °C} = 3.66\ \text{J/°C}$; $28.4\ \text{g} \times 0.129\ \text{J g}^{-1}\ \text{°C}^{-1} \times \frac{(1\ \text{cal})}{4.184\ \text{J}} = 0.882\ \text{cal °C}^{-1}$

5. Calculate the heat capacity, in joules and in calories per degree, of the following:
(a) 45.8 g of nitrogen gas
(b) 1.00 pound of aluminum metal

Solution

(a) $45.8\ \cancel{\text{g}} \times 1.04\ \text{J/}\cancel{\text{g}}\text{°C} = 47.6\ \text{J/°C}$; $45.8\ \cancel{\text{g}} \times 1.04\ \text{J}\ \cancel{\text{g}^{-1}}\ \text{°C}^{-1} \times \frac{1\ \text{cal}}{4.184\ \text{J}} = 11.38\ \text{J °C}^{-1}$; (b) $454\ \text{g} \times 0.897\ \text{J/g °C} = 407\ \text{J/°C}$; $454\ \cancel{\text{g}} \times 0.897\ \text{J}\ \cancel{\text{g}^{-1}}\ \text{°C}^{-1} \times \frac{1\ \text{cal}}{4.184\ \text{J}} = 97.3\ \text{cal °C}^{-1}$

6. How much heat, in joules and in calories, must be added to a 75.0-g iron block with a specific heat of 0.449 J/g °C to increase its temperature from 25 °C to its melting temperature of 1535 °C?

Solution

$q = cm\Delta T$; $q = 0.449\ \text{J/g °C} \times 75.0\ \text{g} \times (1535 - 25)\ \text{°C} = 5.08 \times 10^4\ \text{J}$; the conversion is $4.184\ \text{J} = 1\ \text{cal}$; $5.08 \times 10^4\ \text{J} \times \frac{1\ \text{cal}}{4.184\ \text{J}} = 1.21 \times 10^4\ \text{cal}$

7. How much heat, in joules and in calories, is required to heat a 28.4-g (1-oz) ice cube from –23.0 °C to –1.0 °C?

Solution

$q = cm\Delta T$; q = 2.093 J/g °C × 28.4 g × [–1 – (–23)] °C = 1308 J (or 1310 J with the correct number of significant digits); the conversion factor is 4.184 J = 1 cal; 1308 J × 1 cal / 4.184 J = 312.6 cal (313 calories with the correct number of significant digits)

8. How much would the temperature of 275 g of water increase if 36.5 kJ of heat were added?

Solution

$q = cm\Delta T$

$36{,}500\ \text{J} = 4.184\ \text{J g}^{-1}\ \text{°C}^{-1} \times 2.75 \times 10^2\ \text{g} \times \Delta T$

$$\Delta T = \frac{36{,}500\ \text{°C}}{4.184 \times 2.75 \times 10^2} = 31.7\ \text{°C}$$

9. If 14.5 kJ of heat were added to 485 g of liquid water, how much would its temperature increase?

Solution

$q = cm\Delta T$

$14{,}500\ \text{J} = 4.184\ \text{J g}^{-1}\ \text{°C} \times 4.85 \times 10^2\ \text{g} \times \Delta T$

$$\Delta T = \frac{14{,}500\ \text{°C}}{4.184 \times 4.85 \times 10^2} = 7.15\ \text{°C}$$

10. A piece of unknown substance weighs 44.7 g and requires 2110 J to increase its temperature from 23.2 °C to 89.6 °C.
(a) What is the specific heat of the substance?
(b) If it is one of the substances found in Table 9.1, what is its likely identity?

Solution

(a) $q = cm\Delta T$, $c = q/(m\Delta T)$ = 2110 J / [44.7 g (89.6 – 23.2] °C) = 0.711 J/g °C; (b) According to the data in the table, silicon seems to be a likely candidate.

11. A piece of unknown solid substance weighs 437.2 g, and requires 8460 J to increase its temperature from 19.3 °C to 68.9 °C.
(a) What is the specific heat of the substance?
(b) If it is one of the substances found in Table 9.1, what is its likely identity?

Solution

(a) $q = cm\Delta T$, $c = q/(m\Delta T)$ = 8460 J / [437.2 g (68.9 – 19.3) °C] = 0.390 J/g °C; (b) Copper is a likely candidate.

12. An aluminum kettle weighs 1.05 kg.
(a) What is the heat capacity of the kettle?
(b) How much heat is required to increase the temperature of this kettle from 23.0 °C to 99.0 °C?
(c) How much heat is required to heat this kettle from 23.0 °C to 99.0 °C if it contains 1.25 L of water (density of 0.997 g/mL and a specific heat of 4.184 J/g °C)?

Solution

(a) Heat capacity can be used in several ways. The molar heat capacity is the amount of heat necessary to raise 1 molar mass of the substance 1 ºC. If the term *heat capacity* is used without qualifiers, it means the heat necessary to raise the temperature of the body 1 ºC:
Heat capacity = mc = 1050 g × 0.897 J/g °C = 942 J/°C = 9.42×10^2 J/°C; (b) use $q = mc\Delta T$, where mc is known from part (a):
q = 942 J/°C($T_f - T_i$)
= 942 J/°C(99.0 °C – 23.0 °C) = 7.2×10^4 J;
(c) Two items of different heat capacity must be heated, so the heat required for each must be added. Use the density to determine the mass of the water being heated:

1.25 L × 1000 mL/L × 0.997 g/mL = 1246 g
$q_{kettle} = mc(T_f - T_i)$
= 1050 g × 0.897 J/g °C(99.0 °C – 23.0 °C) = 71,600 J
$q_{water} = mc(T_f - T_i)$
= 1246 g × 4.184 J/g °C(99.0 °C – 23.0 °C) = 396.2 J
$q_{kettle} + q_{water} = 7.16 \times 10^4$ J + 3.962×10^5J = 4.68×10^5J.

13. Most people find waterbeds uncomfortable unless the water temperature is maintained at about 85 °F. Unless it is heated, a waterbed that contains 892 L of water cools from 85 °F to 72 °F in 24 hours. Estimate the amount of electrical energy required over 24 hours, in kWh, to keep the bed from cooling. Note that 1 kilowatt-hour (kWh) = 3.6×10^6 J, and assume that the density of water is 1.0 g/mL (independent of temperature). What other assumptions did you make? How did they affect your calculated result (i.e., were they likely to yield 'positive' or 'negative' errors)?

Solution
We assume that the density of water is 1.0 g/cm^3(1 g/mL) and that it takes as much energy to keep the water at 85 °F as to heat it from 72 °F to 85 °F. We also assume that only the water is going to be heated. First, find the mass of water in the bed. The volume is 72 in. × 84 in. × 9 in.

$$= 54,432 \text{ in.}^3 \left(\frac{2.54 \text{ cm}}{1 \text{ in.}} \right)^3 = 8.9 \times 10^5 \text{ cm}^3 \longrightarrow 8.9 \times 10^5 \text{ g};$$

second, convert the change of 13 °F to °C:
$q = mc\Delta T$ = 4.184 J/g °C(8.92×10^5 g) × 7.22 °C

$$°C = \frac{5}{9} °F = \frac{5}{9} \times 13 = 7.22 °C$$

= 2.69×10^7 J

$$\text{Energy required} = \frac{2.689 \times 10^7 \text{ J}}{3.6 \times 10^6 \text{ kWh}^{-1}} = 7.47 \text{ kWh}$$

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Chemistry: Atoms First 2e
9: Thermochemistry
9.2: Calorimetry

14. A 500-mL bottle of water at room temperature and a 2-L bottle of water at the same temperature were placed in a refrigerator. After 30 minutes, the 500-mL bottle of water had cooled to the temperature of the refrigerator. An hour later, the 2-L of water had cooled to the same temperature. When asked which sample of water lost the most heat, one student replied that both bottles lost the same amount of heat because they started at the same temperature and finished at the same temperature. A second student thought that the 2-L bottle of water lost more heat because there was more water. A third student believed that the 500-mL bottle of water lost more heat because it cooled more quickly. A fourth student thought that it was not possible to tell because we do not know the initial temperature and the final temperature of the water. Indicate which of these answers is correct and describe the error in each of the other answers.

Solution

The 2-L bottle of water lost more heat than the 500-mL bottle; the other statements are incorrect. The first student did not realize that the heat lost depends on the mass of the two objects, as it is an extensive property. The intensive property would be heat lost per unit mass of water, and it should be the same for both objects. The third student did not understand that, regardless of the rate of heat exchange, only the mass of water and the temperature change matter. The fourth student did not realize that once the initial and final temperatures are set for a specific substance, only the mass of the two bodies determines how much heat is transferred. Also, the fourth student is wrong because the problem states that the temperatures would be the same.

15. Would the amount of heat measured for the reaction in Example 9.5 be greater, lesser, or remain the same if we used a calorimeter that was a poorer insulator than a coffee cup calorimeter? Explain your answer.

Solution
lesser; more heat would be lost to the coffee cup and the environment and so ΔT for the water would be lesser and the calculated q would be lesser

16. Would the amount of heat absorbed by the dissolution in Example 9.6 appear greater, lesser, or remain the same if the experimenter used a calorimeter that was a poorer insulator than a coffee cup calorimeter? Explain your answer.

Solution
lesser; more heat would enter the reaction solution from the environment and ΔT would be lesser

17. Would the amount of heat absorbed by the dissolution in Example 9.6 appear greater, lesser, or remain the same if the heat capacity of the calorimeter were taken into account? Explain your answer.

Solution
greater, since taking the calorimeter's heat capacity into account will compensate for the thermal energy transferred to the solution from the calorimeter; this approach includes the calorimeter itself, along with the solution, as "surroundings:" $q_{rxn} = -(q_{solution} + q_{calorimeter})$; since both $q_{solution}$ and $q_{calorimeter}$ are negative, including the latter term (q_{rxn}) will yield a greater value for the heat of the dissolution

18. How many milliliters of water at 23 °C with a density of 1.00 g/mL must be mixed with 180 mL (about 6 oz) of coffee at 95 °C so that the resulting combination will have a temperature of 60 °C? Assume that coffee and water have the same density and the same specific heat.

Solution
From the law of conservation of energy:
$q_{water} + q_{coffee} = 0$
$q_{water} = -q_{coffee}$
$cm_{water}\Delta T = -cm_{coffee}\Delta T$.
Since the specific heats are the same, they cancel on both sides of the equation. Also, 1.00 g = 1.00 mL:
$m_{water}\,(60 - 23) = -180(60 - 95)$

$$m_{water} = \frac{180(35)}{37} = 170\text{ g} \times \frac{1.00\text{ mL}}{1.00\text{ g}} = 170\text{ mL} = 1.7 \times 10^2\text{ mL}.$$

19. How much will the temperature of a cup (180 g) of coffee at 95 °C be reduced when a 45-g silver spoon (specific heat 0.24 J/g °C) at 25 °C is placed in the coffee and the two are allowed to reach the same temperature? Assume that the coffee has the same density and specific heat as water.

Solution

Because of the law of conservation of energy, we write:
$q_{spoon} + q_{coffee} = 0$; $q_{spoon} = -q_{coffee}$
$c_{spoon} \times m_{spoon} \times \Delta T = -c_{coffee} \times m_{coffee} \times \Delta T$
0.24 J/g °C × 45 g × (T_f – 25 °C) = 4.184 J/g °C × 180 g × (T_f – 95 °C)
$10.8T_f - 270 = -753.1T_f + 71546.4$
$763.9\ T_f = 71816.4$
T_f = 94 °C.
The temperature of the coffee will drop 1 degree.

20. A 45-g aluminum spoon (specific heat 0.88 J/g °C) at 24 °C is placed in 180 mL (180 g) of coffee at 85 °C and the temperature of the two become equal.
(a) What is the final temperature when the two become equal? Assume that coffee has the same specific heat as water.
(b) The first time a student solved this problem she got an answer of 88 °C. Explain why this is clearly an incorrect answer.

Solution
(a) because of the law of conservation of energy, we write:
$q_{spoon} + q_{coffee} = 0$
$q_{spoon} = -q_{coffee}$
$c_{spoon} \times m_{spoon} \times \Delta T = c_{coffee} \times m_{coffee} \times \Delta T$
0.88 J/g °C × 45 g × (T_f – 24 °C)
= –4.184 J/g °C × 180 g × (T_f – 85 °C)
$39.6T_f - 950.4 = -753.12T_f + 64{,}015$
$753.12T_f + 39.6T_f = 64{,}015 + 950.4$
$792.7T_f = 64{,}965.4$
T_f = 82 °C; (b) The temperature of the coffee cannot increase when a colder spoon is placed in it.

21. The temperature of the cooling water as it leaves the hot engine of an automobile is 240 °F. After it passes through the radiator it has a temperature of 175 °F. Calculate the amount of heat transferred from the engine to the surroundings by one gallon of water with a specific heat of 4.184 J/g °C.

Solution
First, find the change in temperature of the water in °C:
240 °F – 175 °F = 65 °F.
We are concerned here only with the difference between temperatures and not the conversion from one temperature to the corresponding temperature.

$$°C = \frac{5}{9}(°F) = \frac{5}{9}(65) = 36.1\ °C$$

Assuming 1 mL of water has a mass of 1 g, 1.0 gal of water has a mass of:

$$1.0\ gal \times \frac{4\ qt}{1\ gal} \times \frac{0.9463\ L}{1\ qt} \times 1000\ g = 3785\ g$$

$q = cm\Delta T$ = 4.184 J/g °C × 3758 g × 36.1 °C
= 5.7×10^2 kJ.

22. A 70.0-g piece of metal at 80.0 °C is placed in 100 g of water at 22.0 °C contained in a calorimeter like that shown in Figure 9.12. The metal and water come to the same temperature at 24.6 °C. How much heat did the metal give up to the water? What is the specific heat of the metal?

Solution

$q_{water} = 4.184\ J/g\ °C \times 100\ g \times (24.6 - 22.0)\ °C = 1.1\ kJ$

$$c_{metal} = \frac{1.1\ kJ \times 1000\ J\ kJ^{-1}}{70.0\ g\ (80.0 - 24.6)\ °C}$$

$= 0.28\ J/g\ °C$

23. If a reaction produces 1.506 kJ of heat, which is trapped in 30.0 g of water initially at 26.5 °C in a calorimeter like that in Figure 9.12, what is the resulting temperature of the water?

Solution

$q = cm\Delta T = 4.184\ J/g\ °C \times 30.0\ g \times (T_f - 26.5\ °C) = 1506\ J$

$T_f - 26.5\ °C = 1506\ J / (4.184\ J/g°\ C \times 30.0\ g) = 12.0\ °C$

$T_f = 26.5\ °C + 12.0\ °C = 38.5\ °C$

24. A 0.500-g sample of KCl is added to 50.0 g of water in a calorimeter (Figure 9.12). If the temperature decreases by 1.05 °C, what is the approximate amount of heat involved in the dissolution of the KCl, assuming the heat capacity of the resulting solution is 4.18 J/g °C? Is the reaction exothermic or endothermic?

Solution

Assume that both the KCl and the water are at the same temperature. The entire temperature change can then be attributed to the heat of dissolution:

$q = cm\Delta T = 4.18\ J/g\ °C \times (50.0\ g + 0.500\ g) \times (-1.05\ °C)$

$= -222\ J.$

The reaction is endothermic, which means that 222 J has been absorbed from the water and the KCl in order for the KCl to dissolve.

25. Dissolving 3.0 g of $CaCl_2(s)$ in 150.0 g of water in a calorimeter (Figure 9.12) at 22.4 °C causes the temperature to rise to 25.8 °C. What is the approximate amount of heat involved in the dissolution, assuming the heat capacity of the resulting solution is 4.18 J/g °C? Is the reaction exothermic or endothermic?

Solution

Assume that the mass of the added $CaCl_2$ in solution must be added to the mass of the water:

$q_{reaction} + q_{solution} = 0$

$q_{reaction} = q_{solution}$

$q_{solution} = cm\Delta T$

$= 4.18\ J/g\ °C \times 153.0\ g \times (25.8 - 22.4)\ °C = 2200\ J$

$= -2.2\ kJ.$

The heat produced shows that the reaction is exothermic.

26. When 50.0 g of 0.200 M NaCl(*aq*) at 24.1 °C is added to 100.0 g of 0.100 M $AgNO_3(aq)$ at 24.1 °C in a calorimeter, the temperature increases to 25.2 °C as AgCl(*s*) forms. Assuming the specific heat of the solution and products is 4.20 J/g °C, calculate the approximate amount of heat in joules produced.

Solution

$q = cm\Delta T$

$= 4.20\ J/g\ °C \times 150\ g \times (25.2 - 24.1)\ °C = 693\ J$

27. The addition of 3.15 g of $Ba(OH)_2 \cdot 8H_2O$ to a solution of 1.52 g of NH_4SCN in 100 g of water in a calorimeter caused the temperature to fall by 3.1 °C. Assuming the specific heat of the solution and products is 4.20 J/g°C, calculate the approximate amount of heat absorbed by the reaction, which can be represented by the following equation:

$$Ba(OH)_2 \cdot 8H_2O(s) + 2NH_4SCN(aq) \longrightarrow Ba(SCN)_2(aq) + 2NH_3(aq) + 10H_2O(l)$$

Solution
$q = cm\Delta T$
= 4.20 J/g °C × (3.15 + 1.52 + 100) g × 3.1 °C
= 1362.8 J = 1.4 kJ (two significant figures)

28. The reaction of 50 mL of acid and 50 mL of base described in Example 9.5 increased the temperature of the solution by 6.9 degrees. How much would the temperature have increased if 100 mL of acid and 100 mL of base had been used in the same calorimeter starting at the same temperature of 22.0 °C? Explain your answer.

Solution
The answer is still 6.9 °C. Twice as much heat would be produced, but it would be absorbed by twice as much solution.

29. If the 3.21 g of NH_4NO_3 in Example 9.6 were dissolved in 100.0 g of water under the same conditions, how much would the temperature change? Explain your answer.

Solution
The heat of the reaction would be approximately the same as before or 1.0×10^3 J. The reaction is endothermic, and the temperature would decrease:
$q_{rxn} = -q_{soln} = -(c \times m \times \Delta T)_{soln}$
$-(4.18 \text{ J/g° C}) \times (103.2 \text{ g}) \times (T_f - 24.9 \text{ °C}) = 1000 \text{ J}$
$T_f - 24.9 \text{ °C} = -2.3 \text{ °C}$
$T_f = 22.6$. Since the mass and the heat capacity of the solution is approximately equal to that of the water, the two-fold increase in the amount of water leads to a two-fold decrease of the temperature change.

30. When 1.0 g of fructose, $C_6H_{12}O_6(s)$, a sugar commonly found in fruits, is burned in oxygen in a bomb calorimeter, the temperature of the calorimeter increases by 1.58 °C. If the heat capacity of the calorimeter and its contents is 9.90 kJ/°C, what is q for this combustion?

Solution
$q_{comb} + q_{cal} = 0$
$q_{comb} = -q_{cal}$
= –9.90 kJ/°C (1.58 °C) = –15.6 kJ
The negative sign indicates that this was reaction exothermic, as expected. The mass did not directly enter into the calculation because the heat capacity of the system is calculated on a kJ/°C basis. The mass of the calorimeter is constant.

31. When a 0.740-g sample of trinitrotoluene (TNT), $C_7H_5N_2O_6$, is burned in a bomb calorimeter, the temperature increases from 23.4 °C to 26.9 °C. The heat capacity of the calorimeter is 534 J/°C, and it contains 675 mL of water. How much heat was produced by the combustion of the TNT sample?

Solution
The heat absorbed by the calorimeter is $q_1 = 534 \text{ J/°C} \times (26.9 \text{ °C} - 23.4 \text{ °C}) = 1869$ J. The heat absorbed by water is $q_1 = 675 \text{ mL} \times 0.997 \text{ g/mL} \times 4.184 \text{ J/g °C} \times (26.9 \text{ °C} - 23.4 \text{ °C}) = 9855$ J. The overall amount of heat $q = q_1 + q_1 = 11{,}724$ J or 11.7 kJ with three significant digits.

32. One method of generating electricity is by burning coal to heat water, which produces steam that drives an electric generator. To determine the rate at which coal is to be fed into the burner in this type of plant, the heat of combustion per ton of coal must be determined using a bomb calorimeter. When 1.00 g of coal is burned in a bomb calorimeter (Figure 9.17), the temperature increases by 1.48 °C. If the heat capacity of the calorimeter is 21.6 kJ/°C, determine the heat produced by combustion of a ton of coal (2.000×10^3 pounds).

Solution
$q = mc\Delta T = 21.6\ \text{kJ/°C} \times 1.48\ \text{°C} = 32.0\ \text{kJ}$
This is the heat released by burning 1 g of coal.
Find the mass in kilograms of one ton:
$2.000 \times 10^3\ \text{lb} \times 453.6\ \text{g/lb} = 907.2\ \text{kg}$
Total heat = heat per g × mass of coal
$= 32.0\ \text{kJ/g} \times 1000\ \text{J/kJ} \times 907{,}200\ \text{g} = 2.90 \times 10^{10}\ \text{J}.$

33. The amount of fat recommended for someone with a daily diet of 2000 Calories is 65 g. What percent of the calories in this diet would be supplied by this amount of fat if the average number of Calories for fat is 9.1 Calories/g?

Solution
Energy released by burning fat is:
$65\ \text{g} \times 9.1\ \text{Calories/g} = 5.9 \times 10^2\ \text{Calories}$
% Calories from fat = 5.9×10^2 Calories/2000 Calories × 100%
= 30% (one significant figure).

34. A teaspoon of the carbohydrate sucrose (common sugar) contains 16 Calories (16 kcal). What is the mass of one teaspoon of sucrose if the average number of Calories for carbohydrates is 4.1 Calories/g?

Solution
$$\frac{16\ \text{kcal teaspoon}^{-1}}{4.1\ \text{kcal g}^{-1}} = 3.9\ \text{g teaspoon}^{-1}$$

35. What is the maximum mass of carbohydrate in a 6-oz serving of diet soda that contains less than 1 Calorie per can if the average number of Calories for carbohydrates is 4.1 Calories/g?

Solution
The average energy from carbohydrates is 4.1 kcal/g (4.1 Calories/g). The drink cannot contain more than $\frac{1\ \text{Calorie}}{4.1\ \text{Calorie g}^{-1}} = 0.24\ \text{g}$.

36. A pint of premium ice cream can contain 1100 Calories. What mass of fat, in grams and pounds, must be produced in the body to store an extra 1.1×10^3 Calories if the average number of Calories for fat is 9.1 Calories/g?

Solution
The average heat of combustion of fats is –9.1 kcal/g = –9.1 Calories/g:
$$\text{Mass} = 1100\ \text{Calories} \times \frac{1.0\ \text{g}}{9.1\ \text{Calories}} = 121\ \text{g} = 1.2 \times 10^2$$
$$\text{Mass} = 121\ \text{g} \times \frac{10\ \text{lb}}{453.6\ \text{g}} = 0.27\ \text{lb}.$$

37. A serving of a breakfast cereal contains 3 g of protein, 18 g of carbohydrates, and 6 g of fat. What is the Calorie content of a serving of this cereal if the average number of Calories for fat is 9.1 Calories/g, for carbohydrates is 4.1 Calories/g, and for protein is 4.1 Calories/g?

Solution

Protein: 3 g × 4.1 Calories/g	12.3 Calories
Carbohydrates: 18 g × 4.1 Calories/g	73.8 Calories
Fat: 6 g × 9.1 Calories/g	54.6 Calories
	140.7 Calories

Total = 1.4×10^2 Calories

38. Which is the least expensive source of energy in kilojoules per dollar: a box of breakfast cereal that weighs 32 ounces and costs $4.23, or a liter of isooctane (density, 0.6919 g/mL) that costs $0.45? Compare the nutritional value of the cereal with the heat produced by combustion of the isooctane under standard conditions. A 1.0-ounce serving of the cereal provides 130 Calories.

Solution

Convert ounces to grams and liters to grams, and then find the cost per gram. Determine the heat of combustion of isooctane on a per gram basis, and compare it with the cost of the heat produced by cereal.

For isooctane:

1 L = 1000 mL

Mass = 1000 mL × 0.6919 g/mL = 691.9 g

$$\frac{\$0.45}{691.9\ \text{g}} = \$0.000650\ \text{g}^{-1}$$

On a heat-released basis, we must calculate the heat of combustion of isooctane. This value is: 5460 kJ/mol for C_8H_{18} (M.W. = 114.23 g/mol). Division gives $\frac{5460\ \text{kJ mol}^{-1}}{114.23\ \text{g mol}^{-1}} = 47.80\ \text{kJ g}^{-1}$ and from the previous calculation:

$$\frac{47.80\ \text{kJ g}^{-1}}{\$0.000650\ \text{g}^{-1}} = 7.35 \times 10^4\ \text{kJ/\$}.$$

For cereal:

32 oz × 28.35 g/oz = 907.2 g

$$\frac{\$4.23}{907.2\ \text{g}} = \$0.00466\ \text{g}^{-1}$$

For 1.0 oz or 28.35 g, 130 Calories or 130,000 cal are produced. For 1.0 g of cereal:

$$1.30 \times 10^3\ \text{calories} \times \frac{4.184\ \text{J cal}^{-1}}{28.35\ \text{g}} = 19.2\ \text{kJ g}^{-1}.$$

The cost of cereal heat is then:

$$\frac{19.2\ \text{kJ g}^{-1}}{\$0.00466\ \text{g}^{-1}} = 4.12 \times 10^3\ \text{kJ/\$}.$$

Isooctane is the least expensive source.

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9.3: Enthalpy

39. Explain how the heat measured in Example 9.5 differs from the enthalpy change for the exothermic reaction described by the following equation:

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$$

Solution

The enthalpy change of the indicated reaction is for exactly 1 mol HCL and 1 mol NaOH; the heat in the example is produced by 0.0500 mol HCl and 0.0500 mol NaOH.

40. Using the data in the check your learning section of Example 9.5, calculate ΔH in kJ/mol of $AgNO_3(aq)$ for the reaction: $NaCl(aq) + AgNO_3(aq) \longrightarrow AgCl(s) + NaNO_3(aq)$.

Solution

$q_{soln} = cm\Delta T = 4.184 \text{ J/g °C} \times 200 \text{ g} \times (23.5 - 21.9) \text{ °C} = 1.3 \times 10^3 \text{ J}$

$q_{soln} = -q_{rxn}$

Therefore, $q_{rxn} = -1.3 \times 10^3$ J. At constant pressure, $\Delta H = q_{rxn}$ so $\Delta H = -1.3 \times 10^3$ J or –1.3 kJ

$$0.100 \cancel{\text{L}} \times \frac{0.200 \text{ mol}}{1 \cancel{\text{L}}} = 0.02 \text{ mol } AgNO_3$$

ΔH in kJ/mol AgNO3 would be $\dfrac{-1.3 \text{ kJ}}{0.0200 \text{ mol } AgNO_3} = -65 \text{ kJ/mol } AgNO_3$

41. Calculate the enthalpy of solution (ΔH for the dissolution) per mole of NH_4NO_3 under the conditions described in Example 9.6.

Solution

The molar mass of NH_4NO_3 is 80.0423 g/mol. From the example, 1000 J is required to dissolve 3.21 g of NH_4NO_3. One mole under the same conditions would require

$$\frac{80.0432 \cancel{\text{g}} \text{ mol}^{-1}}{3.21 \cancel{\text{g}}} \times 1000 \text{ J} = 25 \text{ kJ mol}^{-1}.$$

(The heat of solution is positive because the process is endothermic.)

42. Calculate ΔH for the reaction described by the equation. (Hint: Use the value for the approximate amount of heat absorbed by the reaction that you calculated in a previous exercise.)

$$Ba(OH)_2 \cdot 8H_2O(s) + 2NH_4SCN(aq) \longrightarrow Ba(SCN)_2(aq) + 2NH_3(aq) + 10H_2O(l)$$

Solution

$Ba(OH)_2 \cdot 8H_2O$: Ba $1 \times 137.327 = 137.327$

O $10 \times 15.9994 = 159.994$

H $18 \times 1.00794 = \underline{18.143}$

$315.464 \text{ g mol}^{-1}$

$2NH_4SCN$: N $4 \times 14.00674 = 56.02696$

S $2 \times 32.066 = 64.132$

C $2 \times 12.011 = 24.022$

H $8 \times 1.0079 = \underline{8.0632}$

$152.244 \text{ or } 76.122 \text{ g mol}^{-1}$

3.15 g of $Ba(OH)_2 \cdot 8H_2O$ is 0.01 mol and 1.52 g of NH_4SCN is 0.02 mol. Assume that a solution of these substances is 100 g and still gives 100 mL of solution, with their concentrations being 0.1 *M* and 0.2 *M*, respectively. This relation is the ratio needed to make 0.01 *M* $Ba(SCN)_2$. Since

1.4 kJ is released for these quantities, 1 mol of $Ba(OH)_2 \cdot 8H_2O$ should release 100 × 1.4 kJ = 140 kJ mol^{-1}.

43. Calculate the enthalpy of solution (ΔH for the dissolution) per mole of $CaCl_2$ (refer to Exercise 25).

Solution
The molar mass of $CaCl_2$ is 40.078 + 2(35.4572) = 110.992 g/mol. In Exercise 25, 3.0 g of $CaCl_2$ dissolved in water releases a heat of 2.2 kJ. Therefore,

$$\frac{3.0\ \cancel{g}}{110.992\ \cancel{g}\ mol^{-1}} = 0.027\ mol$$

$$\frac{2.2\ kJ}{0.027\ mol} = 81\ kJ\ mol^{-1}.$$

44. Although the gas used in an oxyacetylene torch (Figure 9.7) is essentially pure acetylene, the heat produced by combustion of one mole of acetylene in such a torch is likely not equal to the enthalpy of combustion of acetylene listed in Table 9.2. Considering the conditions for which the tabulated data are reported, suggest an explanation.

Solution
The tabulated enthalpy changes are reported for standard state conditions (1 bar pressure, and a specified temperature of 25 °C). The combustion of acetylene in the torch is clearly taking place at a much higher temperature. Also, since the acetylene and oxygen are usually supplied from compressed gas cylinders, the pressures of these gases in the torch combustion zone is very likely greater than 1 bar. Since the conditions for the combustion are far from standard state conditions, it stands to reason the molar enthalpy change will be different from the standard value.

45. How much heat is produced by burning 4.00 moles of acetylene under standard state conditions?

Solution
The heat of combustion is –1301.1 as given in Table 9.2.
Heat released = 4.00 mol × (–1301.1 kJ/mol) = 5204.4 kJ

46. How much heat is produced by combustion of 125 g of methanol under standard state conditions?

Solution
The molar mass of methanol = 32.04 g/mol.

$$\frac{125\ g}{32.01\ g/mol} = 3.90\ mol$$

The heat of combustion is –726.1 as given in Table 9.2. $\Delta H = -726.1 \times 3.90 = 2833$ kJ or 2.83×10^3 kJ.

47. How many moles of isooctane must be burned to produce 100 kJ of heat under standard state conditions?

Solution
The value of $\Delta H_{comb} = -5461$ kJ/mol. To produce 100 kJ requires:

$$\frac{100\ kJ}{5461\ kJ\ mol^{-1}} = 1.83 \times 10^{-2}\ mol.$$

48. What mass of carbon monoxide must be burned to produce 175 kJ of heat under standard state conditions?

Solution

Find the heat generated from burning 1 mol of carbon monoxide. The reaction is:

$$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$$

ΔH_f°/kJ mol^{-1} = -110.52 0 -393.51

$\Delta H_{comb} = -393.51 - (-110.52) = -282.99$ kJ mol^{-1}

Moles of CO required = $\frac{175 \cancel{\text{kJ}}}{282.99 \cancel{\text{kJ}}\ \text{mol}^{-1}} = 0.618$ mol

The molar mass of CO is 28.01 g/mol, the total mass of CO required is 0.618 mol × 28.01 g/mol = 17.3 g.

49. When 2.50 g of methane burns in oxygen, 125 kJ of heat is produced. What is the enthalpy of combustion per mole of methane under these conditions?

Solution

The molar mass of CH_4 is 16.04 g/mol.

Find the mole of CH_4 present: $\frac{2.50 \cancel{\text{g}}}{16.04 \cancel{\text{g}}\ \text{mol}^{-1}} = 0.15586$ mol

$\Delta H_{comb} = \frac{125 \text{ kJ}}{0.15586 \text{ mol}} = 802$ kJ mol^{-1}.

50. How much heat is produced when 100 mL of 0.250 *M* HCl (density, 1.00 g/mL) and 200 mL of 0.150 *M* NaOH (density, 1.00 g/mL) are mixed?

$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l) \qquad \Delta H_{298}^\circ = -58$ kJ

If both solutions are at the same temperature and the specific heat of the products is 4.19 J/g °C, how much will the temperature increase? What assumption did you make in your calculation?

Solution

for HCl: 0.100 L × 0.250 *M* = 0.0250 mol;
for NaOH, 0.200 L × 0.150 *M* = 0.0300 mol;
Only a total of 0.0250 mol of NaCl can be produced. To find the heat produced, multiply the moles of product times the heat produced per mole:
0.0250 mol × 58 kJ/mol = 1.5 kJ.
This solution assumes that $\Delta H°$ is not different from ΔH under the conditions of the reaction (1 °C temperature increase and assuming volumes are additive).
Assuming the overall mass of the final system is approximately 300 g, the increase of temperature will be $\frac{1500 \cancel{\text{J}}}{(300 \cancel{\text{g}} \times 4.19 \cancel{\text{J}}\ \cancel{\text{g}}^{-1}\ °\text{C}^{-1})} = 1.2$ °C.

51. A sample of 0.562 g of carbon is burned in oxygen in a bomb calorimeter, producing carbon dioxide. Assume both the reactants and products are under standard state conditions, and that the heat released is directly proportional to the enthalpy of combustion of graphite. The temperature of the calorimeter increases from 26.74 °C to 27.93 °C. What is the heat capacity of the calorimeter and its contents?

Solution

The heat produced is found from the enthalpy of combustion:

$\frac{0.562 \cancel{\text{g}}\ \cancel{°\text{C}}}{12.011 \cancel{\text{g}}\ \text{mol}^{-1}\ \cancel{°\text{C}}} \times -393.5 \text{ kJ mol}^{-1} = -18.4$ kJ.

This is the heat released.

q = heat capacity × ΔT
18.4 kJ = heat capacity × (27.93 ºC – 26.74 ºC) = specific heat × 1.19 ºC
specific heat = 15.5 kJ/ºC

52. Before the introduction of chlorofluorocarbons, sulfur dioxide (enthalpy of vaporization, 6.00 kcal/mol) was used in household refrigerators. What mass of SO_2 must be evaporated to remove as much heat as evaporation of 1.00 kg of CCl_2F_2 (enthalpy of vaporization is 17.4 kJ/mol)?
The vaporization reactions for SO_2 and CCl_2F_2 are $SO_2(l) \longrightarrow SO_2(g)$ and $CCl_2F_2(l) \longrightarrow CCl_2F_2(g)$, respectively.

Solution
Convert enthalpy of vaporization in kilocalories to kilojoules:
6.00 kcal/mol × 4.18 kJ/kcal = 25.1 kJ/mol.
Convert 1.00 kg CCl_2F_2 into moles of CCl_2F_2. Let the change in temperature be 1.0 °C.
Molar mass: For CCl_2F_2, 12.011 + 2(35.4527) + 2(18.9984) = 120.913 g/mol;
for SO_2, 32.066 + 2(15.9994) = 64.065 g/mol

$$\frac{1.00 \times 10^3 \text{ g}}{120.913 \text{ g mol}^{-1}} = 8.27 \text{ mol}$$

g SO_2 = mol SO_2 × 25.1 kJ/mol = mol CCl_2F_2 × 17.4 kJ/mol

$$\text{mol } SO_2 = \frac{8.27 \text{ mol} \times 17.4}{25.1} = 5.73 \text{ mol}$$

g SO_2 = 5.73 mol × 64.065 g/mol = 367 g

53. Homes may be heated by pumping hot water through radiators. What mass of water will provide the same amount of heat when cooled from 95.0 to 35.0 °C, as the heat provided when 100 g of steam is cooled from 110 °C to 100 °C.

Solution
$q = mc\Delta T$. The amount of heat transferred from steam is:
q_{steam} = 100 g × 1.864 J/(g °C) × (110 – 100) °C = 1864 J
$q_{water} = m_{water}$× 4.184 J/(g °C) × (95 – 35) °C = m_{water}× 251.04 J/g = q_{steam} = 1864 J

$$m_{water} = \frac{1864 \text{ J}}{251.04 \text{ J/g}} = 7.43 \text{ g}.$$

54. Which of the enthalpies of combustion in Table 9.2 the table are also standard enthalpies of formation?

Solution

Substance	Combustion/Formation Reaction
carbon	$C(s) + \frac{1}{2}O_2(s) \longrightarrow CO(g)$ $C(s) + O_2(g) \longrightarrow CO_2(g)$
hydrogen	$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$
magnesium	$Mg(s) + \frac{1}{2}O_2(g) \longrightarrow MgO(s)$
sulfur	$S(s) + O_2(g) \longrightarrow SO_2(g)$

55. Does the standard enthalpy of formation of $H_2O(g)$ differ from $\Delta H°$ for the reaction $2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$?

Solution
Yes. The heat of this reaction is defined for 2 moles of $H_2O(g)$, thus the heat of formation is half of the heat of the reaction.

56. Joseph Priestly prepared oxygen in 1774 by heating red mercury(II) oxide with sunlight focused through a lens. How much heat is required to decompose exactly 1 mole of red $HgO(s)$ to $Hg(l)$ and $O_2(g)$ under standard conditions?

Solution
The reaction $HgO(s) \longrightarrow Hg(l) + \frac{1}{2}O_2(g)$ under standard state conditions is the reverse of the reaction that forms 1 mol $HgO(s)$ from the elements in their most stable states under standard state conditions. Thus, $\Delta H^{o}_{298} = -\Delta H^{o}_{f_{HgO(s)}} = -(-90.83\text{ kJ}) = 90.83\text{ kJ}$.

57. How many kilojoules of heat will be released when exactly 1 mole of manganese, Mn, is burned to form $Mn_3O_4(s)$ at standard state conditions?

Solution
This process requires 3 mol of Mn. For 1 mol, $\frac{1}{3}(-1378.83\text{ kJ}) = 459.6\text{ kJ}$.

58. How many kilojoules of heat will be released when exactly 1 mole of iron, Fe, is burned to form $Fe_2O_3(s)$ at standard state conditions?

Solution
$2Fe(s) + 3O_2(g) \longrightarrow Fe_2O_3(s) \qquad \Delta H^{o}_{f} = -1388\text{ kJ mol}^{-1}$

$\Delta H^{o}_{f} = -824.2\text{ kJ/mol}$

This process requires 2 mol of Fe. For 1 mol, $\frac{1}{2}(-1388\text{ kJ}) = 462.7\text{ kJ}$. $\frac{1}{2}(-8.24.2) = 412.1\text{ kJ}$ of heat will be released.

59. The following sequence of reactions occurs in the commercial production of aqueous nitric acid:

$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(l) \qquad \Delta H = -907\text{ kJ}$

$2NO(g) + O_2(g) \longrightarrow 2NO_2(g) \qquad \Delta H = -113\text{ kJ}$

$3NO_2 + H_2O(l) \longrightarrow 2HNO_3(aq) + NO(g) \qquad \Delta H = -139\text{ kJ}$

Determine the total enthalpy change for the production of one mole of aqueous nitric acid by this process. Coproducts of the net reaction include water and nitrogen monoxide.

Solution
First, appropriately sum these three equations to yield a balanced equation for the overall reaction. Although fractional coefficients may be used in thermochemical calculations such as this, the approach shown here uses the smallest possible integer coefficients:

$3 \times [4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(l)]$ $\Delta H = (3)(-907\ \text{kJ}) = -2721\ \text{kJ}$

$6 \times [2NO(g) + O_2(g) \longrightarrow 2NO_2(g)]$ $\Delta H = (6)(-113\ \text{kJ}) = -678\ \text{kJ}$

$4 \times [3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(aq) + NO(g)$ $\Delta H = (4)(-139\ \text{kJ}) = -556\ \text{kJ}$

$12NH_3(g) + 21O_2(g) \longrightarrow 8HNO_3(aq) + 14H_2O(l) + 4NO(g)$ $\Delta H = -3955\ \text{kJ}$

The energy change shown is for production of 8 moles of aqueous nitric acid; therefore, production of 1 mole is
$(1/8)(-3995\ \text{kJ}) = -494\ \text{kJ}$.

60. Both graphite and diamond burn.

$C(s, \text{diamond}) + O_2(g) \longrightarrow CO_2(g)$

For the conversion of graphite to diamond:

$C(s, \text{graphite}) \longrightarrow C(s, \text{diamond})$ $\Delta H^\circ_{298} = 1.90\ \text{kJ}$

Which produces more heat, the combustion of graphite or the combustion of diamond?

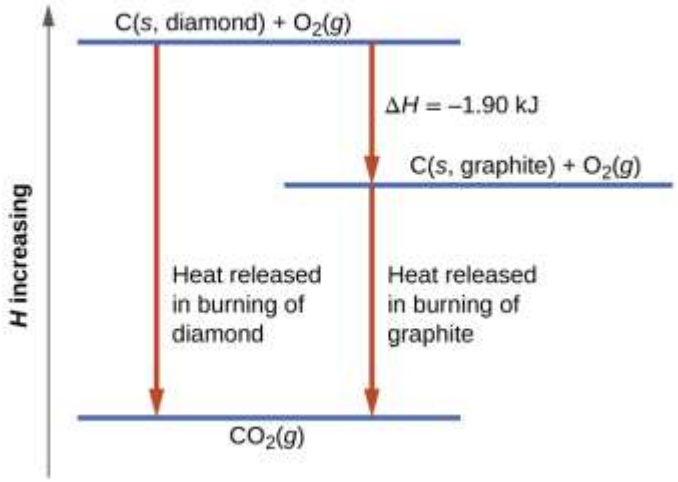
Solution

Heat is consumed by graphite as it is converted into diamond. Therefore, the enthalpy of diamond is higher than that of graphite. The heat of formation of C(*s*, graphite) is 0, the heat of formation of C(*s*, diamond) is 1.90 kJ/mol. The combustion reaction is:

$C(s) + O_2(g) \longrightarrow CO_2(g)$,

and the heat of combustion may be calculated using heats of formation as:

$\Delta H^\circ = \Delta H^\circ_f(\text{CO2}) - \Delta H^\circ_f(C(s))$. Since $\Delta H^\circ_f(C(s))$ is higher for diamond than for graphite, the heat of this reaction will be lower (more negative) for diamond, thus more heat will be released in burning of diamond than in burning of graphite.



61. From the molar heats of formation in Appendix G, determine how much heat is required to evaporate one mole of water: $H_2O(l) \longrightarrow H_2O(g)$

Solution

The heat of formation of $H_2O(l)$ is –285.83 kJ/mol. The heat of formation of $H_2O(g)$ is –241.82 kJ/mol. For the reaction:

$H_2O(l) \longrightarrow H_2O(g)$,

the enthalpy of the reaction is the difference of heats of formation of the reactant and the product; thus, it is –241.82 – (–285.83) = 44.01 kJ/mol.

62. Which produces more heat?

$$Os(s) + 2O_2(g) \longrightarrow OsO_4(s)$$

or

$$Os(s) + 2O_2(g) \longrightarrow OsO_4(g)$$

for the phase change $OsO_4(s) \longrightarrow OsO_4(g)$ $\Delta H = 56.4$ kJ

Solution

Heat must be added to make the transition to the gas phase. Therefore, the formation of the solid produces more heat.

63. Calculate ΔH°_{298} for the process

$$Sb(s) + \frac{5}{2}Cl_2(g) \longrightarrow SbCl_5(g)$$

from the following information:

$$Sb(s) + \frac{3}{2}Cl_2(g) \longrightarrow SbCl_3(s) \qquad \Delta H^\circ_{298} = -314 \text{ kJ}$$

$$SbCl_3(s) + Cl_2(g) \longrightarrow SbCl_5(g) \qquad \Delta H^\circ_{298} = -80 \text{ kJ}$$

Solution

Add the two equations and their heat together.

$$Sb(s) + \frac{3}{2}Cl_2(g) \longrightarrow SbCl_3(s) \qquad \Delta H^\circ_{298} = -314 \text{ kJ}$$

$$\underline{SbCl_3(s) + Cl_2(g) \longrightarrow SbCl_5(g)} \qquad \underline{\Delta H^\circ_{298} = -80 \text{ kJ}}$$

$$Sb(s) + \frac{5}{2}Cl_2(g) \longrightarrow SbCl_5(g) \qquad \Delta H^\circ_{298} = -394 \text{ kJ}$$

64. Calculate ΔH°_{298} for the process $Zn(s) + S(s) + 2O_2(g) \longrightarrow ZnSO_4(s)$ from the following information:

$$Zn(s) + S(s) \longrightarrow ZnS(s) \qquad \Delta H^\circ_{298} = -206.0 \text{ kJ}$$

$$ZnS(s) + 2O_2(g) \longrightarrow ZnSO_4(s) \qquad \Delta H^\circ_{298} = -776.8 \text{ kJ}$$

Solution

Addition of the two reaction equations as though they were mathematical equation gives:

$$Zn(s) + S(s) + 2O_2(g) \longrightarrow ZnSO_4(s) \qquad \Delta H^\circ = -206.0 \text{ kJ} + (-776.8 \text{ kJ}) = -982.8 \text{ kJ}$$

.

65. Calculate ΔH for the process $Hg_2Cl_2(s) \longrightarrow 2Hg(l) + Cl_2(g)$

from the following information:

$$Hg(l) + Cl_2(g) \longrightarrow HgCl_2(s) \qquad \Delta H = -224 \text{ kJ}$$

$$Hg(l) + HgCl_2(s) \longrightarrow Hg_2Cl_2(s) \qquad \Delta H = -41.2 \text{ kJ}$$

Solution

Reverse the direction of both equations and add the new equations and enthalpies.

$$HgCl_2(s) \longrightarrow Hg(l) + Cl_2(l) \qquad \Delta H = 224 \text{ kJ}$$

$$\underline{Hg_2Cl_2(s) \longrightarrow Hg(l) + HgCl_2(s)} \qquad \underline{\Delta H = 41.2 \text{ kJ}}$$

$$Hg_2Cl_2(s) \longrightarrow 2Hg(l) + Cl_2(g) \qquad \Delta H = 265 \text{ kJ}$$

66. Calculate ΔH°_{298} for the process $Co_3O_4(s) \longrightarrow 3Co(s) + 2O_2(g)$ from the following information:

$Co(s) + \frac{1}{2}O_2(g) \longrightarrow CoO(s) \qquad \Delta H^{\circ}_{298} = -237.9 \text{ kJ}$

$3CoO(s) + O_2(g) \longrightarrow Co_3O_4(s) \qquad \Delta H^{\circ}_{298} = -177.5 \text{ kJ}$

Solution
Reverse the directions of the two equations so that $Co_3O_4(s)$ will be on the left-hand side and multiply the first equation by 3:

$3\left[CoO(s) \longrightarrow Co(s) + \frac{1}{2}O_2(g)\right] \qquad 3[\Delta H^{\circ}_{298} = 237.9 \text{ kJ}] = 713.7 \text{ kJ}$;

$Co_3O_4(s) \longrightarrow 3CoO(s) + \frac{1}{2}O_2(g) \qquad \Delta H^{\circ}_{298} = 177.5 \text{ kJ}$

addition of the two resulting equation gives:

$Co_3O_4(s) \longrightarrow 3Co(s) + 2O_2(g) \qquad \Delta H^{\circ}_{298} = 891.2 \text{ kJ}$.

67. Calculate the standard molar enthalpy of formation of $NO(g)$ from the following data:

$N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g) \qquad \Delta H^{\circ}_{298} = 66.4 \text{ kJ}$

$2NO(g) + O_2(g) \longrightarrow 2NO_2(g) \qquad \Delta H^{\circ}_{298} = -114.1 \text{ kJ}$

Solution
Hess's law can be applied to the two equations by reversing the direction of the second equation. The first equation is a formation reaction and is so indicated by writing ΔH°_{298}.

$N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g) \qquad \Delta H^{\circ}_{298} = 66.4 \text{ kJ}$

$2NO_2(g) \longrightarrow 2NO(g) + O_2(g) \qquad \Delta H^{\circ} = 114.1 \text{ kJ}$

Adding the equations yields: $N_2(g) + O_2(g) \longrightarrow 2NO(g) \qquad \Delta H^{\circ} = 180.5 \text{ kJ}$.

This is the heat of formation of 2 mol of NO. For 1 mol,

$\Delta H^{\circ}_{298} = \frac{180.5 \text{ kJ}}{2} = 90.3 \text{ kJ/mol of NO}$.

68. Using the data in Appendix G, calculate the standard enthalpy change for each of the following reactions:

(a) $N_2(g) + O_2(g) \longrightarrow 2NO(g)$

(b) $Si(s) + 2Cl_2(g) \longrightarrow SiCl_4(g)$

(c) $Fe_2O(s) + 3H_2(g) \longrightarrow 2Fe(s) + 3H_2O(l)$

(d) $2LiOH(s) + CO_2(g) \longrightarrow Li_2CO_3(s) + H_2O(g)$

Solution
(a) $N_2(g) + O_2(g) \longrightarrow 2NO(g) \qquad \Delta H^{\circ} = 2(90.25 \text{ kJ}) = 180.50 \text{ kJ}$, the reaction is twice the reaction of formation of $NO(g)$. (b) This reaction is simply the reaction of formation of SiCl4(g); thus, its enthalpy is the enthalpy of formation of SiCl4(g), which is –662.75 (from Appendix G). (c)

$3H_2(g) + \frac{3}{2}O_2(g) \longrightarrow 3H_2O(l)$ $\Delta H_1^o = 3(-285.83\ \text{kJ}) = -857.49\ \text{kJ}$

$Fe_2O_3(s) \longrightarrow 3Fe(s) + \frac{3}{2}O_2(g)$ $\Delta H_1^o = -(-824.2\ \text{kJ})$;

$Fe_2O_3(s) + 3H_2(g) \longrightarrow 2Fe(s) + 3H_2O(l)$ $\Delta H_1^o = -33.3\ \text{kJ}$

(d)

$2LiOH(s) \longrightarrow 2Li(s) + O_2(g)$ $\Delta H_1^o = -2(-487.23\ \text{kJ}) = 975\ \text{kJ}$

$CO_2(g) \longrightarrow C(s) + O_2(g)$ $\Delta H_2^o = -(-393.51\ \text{kJ})$

$2Li(s) + C(s) + \frac{3}{2}O_2(g) \longrightarrow LiCO_3(s)$ $\Delta H_3^o = -1216.04\ \text{kJ}$

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$ $\Delta H_4^o = -241.82\ \text{kJ}$

$2LiOH(s) + CO_2(g) \longrightarrow Li_2CO_3(g) + H_2O(g)$ $\Delta H^o = -89.4\ \text{kJ}$

69. Using the data in Appendix G, calculate the standard enthalpy change for each of the following reactions:

(a) $Si(s) + 2F_2(g) \longrightarrow SiF_4(g)$

(b) $2C(s) + 2H_2(g) + O_2(g) \longrightarrow CH_3CO_2H(l)$

(c) $CH_4(g) + N_2(g) \longrightarrow HCN(g) + NH_3(g)$

(d) $Cs_2(g) + 3Cl_2(g) \longrightarrow CCl_4(g) + S_2Cl_2(g)$

Solution

(a)

$Si(s) + 2F_2(g) \longrightarrow SiF_4(g)$

$\Delta H^o_{\text{reaction}} = \Delta H^o_{\text{products}} - \Delta H^o_{\text{reactants}}$;

$= \Delta H^o_{SiF_4(g)} - \Delta H^o_{Si(s)} - 2\Delta H^o_{F_2(g)}$

$= -1614.9 - (0) - 2(0) = -1615.0\ \text{kJ mol}^{-1}$

(b) $2C(s) + 2H_2(g) + O_2(g) \longrightarrow CH_3CO_2H(l)$

$\Delta H^o_{\text{reaction}} = \Delta H^o_{\text{products}} - \Delta H^o_{\text{reactants}}$

$= \Delta H^o_{CH_3CO_2H(l)} - 2\Delta H^o_{C(s)} - 2\Delta H^o_{H_2(g)} - \Delta H^o_{O_2(g)}$;

$= -484.5 - 2(0) - 2(0) - (0) = -484.3\ \text{kJ mol}^{-1}$

(c) $CH_4(g) \longrightarrow C(s) + 2H_2(g)$ $\Delta H_1^o = -(-74.6\ \text{kJ})$

$\frac{1}{2}H_2(g) + C(s) + \frac{1}{2}N_2(g) \longrightarrow HCN(g)$ $\Delta H_2^o = 135.5\ \text{kJ}$

$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g)$ $\Delta H_3^o = -45.9\ \text{kJ}$;

$CH_4(g) + N_2(g) \longrightarrow HCN(g) + NH_3(g)$ $\Delta H^o = 164.2\ \text{kJ}$

(d)
$$CS_2(g) \longrightarrow C(s) + 2S(s) \qquad \Delta H_1^\circ = -(116.9\text{ kJ})$$
$$C(s) + 2Cl_2(g) \longrightarrow CCl_4(g) \qquad \Delta H_2^\circ = -95.7\text{ kJ}$$
$$2S(s) + Cl_2(g) \longrightarrow S_2Cl_2(g) \qquad \Delta H_3^\circ = -19.50\text{ kJ}$$
$$CS_2(g) + 3Cl_2(g) \longrightarrow CCl_4(g) + S_2Cl_2(g) \qquad \Delta H^\circ = -232.1\text{ kJ}$$

70. The following reactions can be used to prepare samples of metals. Determine the enthalpy change under standard state conditions for each.

(a) $2Ag_2O(s) \longrightarrow 4Ag(s) + O_2(g)$

(b) $SnO(s) + CO(g) \longrightarrow Sn(s) + CO_2(g)$

(c) $Cr_2O_3(s) + 3H_2(g) \longrightarrow 2Cr(s) + 3H_2O(l)$

(d) $2Al(s) + Fe_2O_3(s) \longrightarrow Al_2O_3(s) + 2Fe(s)$

Solution

(a) $\Delta H^\circ = -2\Delta H^\circ_{f(Ag_2O(s))} = -2(-31.5\text{ kJ}) = 63.0\text{ kJ}$; (b)

$\Delta H^\circ = \Delta H^\circ_{(CO_2(g))} - \Delta H^\circ_{(SnO(s))} - \Delta H^\circ_{(CO(g))} = -393.51\text{ kJ} - (-285.8\text{ kJ}) - (-110.52\text{ kJ}) = 2.8\text{ kJ}$

; (c) $\Delta H^\circ = 3\Delta H^\circ_{(H_2O(l))} - \Delta H^\circ_{(Cr_2O_3(s))} = 3(-285.83) - (-1139.7) = 282.2\text{ kJ}$; (d)

$\Delta H^\circ = \Delta H^\circ_{(Al_2O_4(s))} - \Delta H^\circ_{(Fe_2O_3(s))} = -1676 - (-824.2) = -852\text{ kJ}$

71. The decomposition of hydrogen peroxide, H_2O_2, has been used to provide thrust in the control jets of various space vehicles. Using the data in Appendix G, determine how much heat is produced by the decomposition of exactly 1 mole of H_2O_2 under standard conditions.

$2H_2O_2(l) \longrightarrow 2H_2O(g) + O_2(g)$

Solution

$$\Delta H^\circ_{reaction} = \Delta H^\circ_{products} - \Delta H^\circ_{reactants}$$
$$= 2\Delta H^\circ_{H_2O(g)} + \Delta H^\circ_{O_2(g)} - 2\Delta H^\circ_{H_2O_2(l)}$$
$$= 2(-241.82) + 0 - 2(-187.78) = -108.08\text{ kJ}$$

The value relates to the decomposition of 2 mol of hydrogen peroxide. For 1 mol, $\frac{-108.0}{2} = -54.04\text{ kJ mol}^{-1}$.

72. Calculate the enthalpy of combustion of propane, $C_3H_8(g)$, for the formation of $H_2O(g)$ and $CO_2(g)$. The enthalpy of formation of propane is –104 kJ/mol.

Solution

The equation for the combustion of $C_3H_8(g)$ is: $C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(g)$

Thus, in order to work this problem, we have to have three equations with known ΔH_f°:

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H_f^\circ = -394\text{ kJ mol}^{-1}$$
$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g) \qquad \Delta H_f^\circ = -242\text{ kJ mol}^{-1};$$
$$3C(s) + 4H_2(g) \longrightarrow C_3H_8(g) \qquad \Delta H_f^\circ = -104\text{ kJ mol}^{-1}$$

We want C_3H_8 as a reactant, so we will reverse the third reaction (along with making the ΔH positive). The other two reactions will have to be multiplied appropriate factors. The answers are shown to four significant figures.

Step 1: $3[C(s) + O_2(g) \longrightarrow CO_2(g)]$ $\Delta H^\circ = 3(-394\ \text{kJ mol}^{-1})$

Step 2: $4[H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)]$ $\Delta H^\circ = 4(-242\ \text{kJ mol}^{-1})$

Step 3: $C_3H_8 \longrightarrow 3C(s) + 4H_2(g)$ $\Delta H^\circ = +104\ \text{kJ mol}^{-1}$

Sum: $C_3H_8 + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$ $\Delta H^\circ_{298} = -2046\ \text{kJ mol}^{-1}$

73. Calculate the enthalpy of combustion of butane, $C_4H_{10}(g)$ for the formation of $H_2O(g)$ and $CO_2(g)$. The enthalpy of formation of butane is –126 kJ/mol.

Solution

Step 1: $4[C(s) + O_2(g) \longrightarrow CO_2(g)]$ $\Delta H^\circ = 4(-394\ \text{kJ mol}^{-1})$

Step 2: $5[H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)]$ $\Delta H^\circ = 5(-242\ \text{kJ mol}^{-1})$

Step 3: $C_4H_{10} \longrightarrow 4C(s) + 5H_2(g)$ $\Delta H^v = +126\ \text{kJ mol}^{-1}$

Sum: $C_4H_{10} + \frac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(l)$ $\Delta H^\circ_{298} = -2660\ \text{kJ mol}^{-1}$

74. Both propane and butane are used as gaseous fuels. Which compound produces more heat per gram when burned?

Solution

The molar masses of the two compounds are C_3H_8 = 44.1 g/mol and C_4H_{10} = 58.1 g/mol. The kilojoules per gram for each compound is:

$$C_3H_8: \frac{-2046\ \text{kJ}}{\cancel{\text{mol}}} \times \frac{1\ \cancel{\text{mol}}}{44.1\ \text{g}} = -46.4\ \text{kJ g}^{-1}$$

$$C_4H_{10}: \frac{-2660\ \text{kJ}}{\cancel{\text{mol}}} \times \frac{1\ \cancel{\text{mol}}}{58.1\ \text{g}} = -45.8\ \text{kJ g}^{-1}$$

Therefore, propane, C_3H_8, gives more heat per gram when combusted.

75. The white pigment TiO_2 is prepared by the reaction of titanium tetrachloride, $TiCl_4$, with water vapor in the gas phase: $TiCl_4(g) + 2H_2O(g) \longrightarrow TiO_2(s) + 4HCl(g)$.

How much heat is evolved in the production of exactly 1 mole of $TiO_2(s)$ under standard state conditions?

Solution

$TiCl_4(g) \longrightarrow Ti(s) + 2Cl_2(g)$ $\Delta H^\circ_1 = -(-763.2\ \text{kJ})$

$2H_2O(g) \longrightarrow 2H_2(g) + O_2(g)$ $\Delta H^\circ_2 = -2(-241.82\ \text{kJ}) = 483.6\ \text{kJ}$

$Ti(s) + O_2(g) \longrightarrow TiO_2(s)$ $\Delta H^\circ_3 = -944.0\ \text{kJ}$

$2H_2(g) \longrightarrow 2Cl_2(g) + 4HCl(g)$ $\Delta H^\circ_4 = 4(-92.3\ \text{kJ}) = -369.2\ \text{kJ}$

$TiCl_4(g) + 2H_2O(g) \longrightarrow TiO_2(s) + 4HCl(g)$ $\Delta H^\circ_{rx} = -66.4\ \text{kJ}$

Thus, 66.4 kJ of heat is evolved.

76. Water gas, a mixture of H_2 and CO, is an important industrial fuel produced by the reaction of steam with red hot coke, essentially pure carbon: $C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)$.

(a) Assuming that coke has the same enthalpy of formation as graphite, calculate ΔH°_{298} for this reaction.

(b) Methanol, a liquid fuel that could possibly replace gasoline, can be prepared from water gas and additional hydrogen at high temperature and pressure in the presence of a suitable catalyst: $2H_2(g) + CO(g) \longrightarrow CH_3OH(g)$.

Under the conditions of the reaction, methanol forms as a gas. Calculate ΔH°_{298} for this reaction and for the condensation of gaseous methanol to liquid methanol.

(c) Calculate the heat of combustion of 1 mole of liquid methanol to $H_2O(g)$ and $CO_2(g)$.

Solution

(a) $\Delta H^\circ = \Delta H^\circ_f(CO(g)) - \Delta H^\circ_f(H_2O(g)) = -110.52 - (-241.82) = 131.30$ kJ;

(b) $\Delta H^\circ = \Delta H^\circ_f(CH_3OH(g)) - \Delta H^\circ_f(CO(g)) = -201.0 - (-110.52) = -90.5$ kJ;

For the condensation,

$CH_3OH(g) \longrightarrow CH_3OH(l)$

$\Delta H^\circ = \Delta H^\circ_f(CO_2(g)) - \Delta H^\circ = \Delta H^\circ_f(CH_3OH(g)) = -239.2 - (-201.0) = -38.2$ kJ;

$$CH_3OH(l) + \frac{3}{2}O_2 \longrightarrow CO_2(g) + 2H_2O(g)$$

(c) $\Delta H^\circ = \Delta H^\circ_f(CO_2(g)) + 2\Delta H^\circ_f(H_2O(g)) - \Delta H^\circ_f(CH_3OH(l))$

$= -393.51 + 2(-241.82) - (-239.2) = -638.0$ kJ

77. In the early days of automobiles, illumination at night was provided by burning acetylene, C_2H_2. Though no longer used as auto headlamps, acetylene is still used as a source of light by some cave explorers. The acetylene is (was) prepared in the lamp by the reaction of water with calcium carbide, CaC_2:

$CaC_2(s) + H_2O(l) \longrightarrow Ca(OH)_2(s) + C_2H_2(g)$.

Calculate the standard enthalpy of the reaction. The ΔH°_f of CaC_2 is –15.14 kcal/mol.

Solution

convert –15.14 kcal to kJ:

–15.14 kcal × 4.184 kJ/kcal = 63.35 kJ/mol

$$\Delta H^\circ_{reaction} = \Delta H^\circ_{products} - \Delta H^\circ_{reactants}$$

$$= \Delta H^\circ_{Ca(OH)_2(s)} + \Delta H^\circ_{C_2H_2(g)} - \Delta H^\circ_{CaC_2(s)} - 2\Delta H^\circ_{H_2O_2(l)}$$

$$= -985.2 + 227.4 - (-63.35) - 2(-285.83) = -122.8 \text{ kJ}$$

78. From the data in Table 9.2, determine which of the following fuels produces the greatest amount of heat per gram when burned under standard conditions: $CO(g)$, $CH_4(g)$, or $C_2H_2(g)$.

Solution

$$CO(g): \frac{-285.8 \text{ kJ}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{28.01 \text{ g}} = -10.20 \text{ kJ/g}$$

$$CH_4(g): \frac{-809.8 \text{ kJ}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{16.04 \text{ g}} = -55.54 \text{ kJ/g}$$

$$C_2H_2(g): \frac{-1301.1 \text{ kJ}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{26.04 \text{ g}} = -49.97 \text{ kJ/g}$$

$CH_4(g)$ produces the greatest heat per gram.

79. The enthalpy of combustion of hard coal averages –35 kJ/g, that of gasoline, -1.28×10^5 kJ/gal. How many kilograms of hard coal provide the same amount of heat as is available from

1.0 gallon of gasoline? Assume that the density of gasoline is 0.692 g/mL (the same as the density of isooctane).

Solution

the amount of heat produced by burning of 1.0 gallon of gasoline is:

q = 1.0 gallon × (–1.28 × 10^5 kJ/gal) = –1.28 × 10^5 kJ

Mass × (–35 kJ/g) = –1.28 × 10^5 kJ

Mass = 3657 g or 3.7 kg

80. Ethanol, C_2H_5OH, is used as a fuel for motor vehicles, particularly in Brazil.

(a) Write the balanced equation for the combustion of ethanol to $CO_2(g)$ and $H_2O(g)$, and, using the data in Appendix G, calculate the enthalpy of combustion of 1 mole of ethanol.

(b) The density of ethanol is 0.7893 g/mL. Calculate the enthalpy of combustion of exactly 1 L of ethanol.

(c) Assuming that an automobile's mileage is directly proportional to the heat of combustion of the fuel, calculate how much farther an automobile could be expected to travel on 1 L of gasoline than on 1 L of ethanol. Assume that gasoline has the heat of combustion and the density of n–octane, C_8H_{18} (ΔH_f^o = –208.4 kJ/mol; density = 0.7025 g/mL).

Solution

(a) $C_2H_5OH(l) + 3O_2 \longrightarrow 3H_2O(g) + 2CO_2(g)$;

(b) the molecular weight of ethanol is 46.077 g/mol, then:

$$\frac{46.07\ \cancel{\text{g}}\ \text{mol}^{-1}}{0.7839\ \cancel{\text{g}}\ \text{mL}^{-1}} = 58.37\ \text{mL mol}^{-1}$$

$$\Delta H_{\text{comb}} = \frac{-1234.9\ \cancel{\text{g}}\ \text{mol}^{-1}}{58.37\cancel{\text{g}}\ \text{mL}^{-1}} = \frac{-21.17\ \text{kJ}}{\cancel{\text{mL}}} \times \frac{1000\ \cancel{\text{mL}}}{1\ \text{L}} = -2.17 \times 10^4\ \text{kJ/L}$$;

(c) the heat of combustion expression is

$$C_8H_{18}(l) + \frac{25}{2}O_2(g) \longrightarrow 8CO_2(g) + 9H_2O(g)$$

$$\Delta H^o = 8\Delta H_f^o(CO_2(g)) + 9\Delta H_f^o(H_2O(g)) - \Delta H_f^o(C_8H_{18}(l))$$

$$= 8(-393.51) + 9(-241.82) - (-208.4) = -5116.1\ \text{kJ/mol}$$ and the

molar mass of C_8H_{18} is 114.23 g/mol; $\frac{114.23\ \cancel{\text{g}}/\text{mol}}{0.7025\ \cancel{\text{g}}/\text{mL}} = 162.6\ \text{mL/mol}$

$$\frac{-5116.1\ \text{kJ/mol}}{162.6\ \text{mL/mol}} = 31.46\ \text{kJ/mol} = -3.146 \times 10^4\text{kJ/L}$$

$$\frac{-3.146 \times 10^4\ \cancel{\text{kJ/L}}}{-2.17 \times 10^4\ \cancel{\text{kJ/L}}} = 1.45\ ;$$

gasoline will make the automobile travel 1.45 times farther than ethanol; from the heats of formation we have:

$C_8H_{18}(l) \longrightarrow 8C(s) + 9H_2(g) \qquad -[\Delta H_f^\circ = -208.4 \text{ kJ mol}^{-1}]$

$8[C(s) + O_2(g) \longrightarrow CO_2(g)] \qquad 8[\Delta H_f^\circ = -393.5 \text{ kJ mol}^{-1}]$

$9[H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)] \qquad 9[\Delta H_f^\circ = -241.82 \text{ kJ mol}^{-1}]$

$$\Delta H_{comb} = \frac{-5116.0 \text{ kJ } \cancel{\text{mol}^{-1}}}{162.49 \text{ mL } \cancel{\text{mol}^{-1}}} = -31.485 \text{ kJ mL}$$

$$\frac{\Delta H_{comb}(\text{octane})}{\Delta H_{comb}(\text{ethanol})} = \frac{-31.485 \ \cancel{\text{kJ/mL}}}{-21.15 \ \cancel{\text{kJ/mL}}} = 1.489 \text{ times farther}$$

81. Among the substances that react with oxygen and that have been considered as potential rocket fuels are diborane [B_2H_6, produces $B_2O_3(s)$ and $H_2O(g)$], methane [CH_4, produces $CO_2(g)$ and $H_2O(g)$], and hydrazine [N_2H_4, produces $N_2(g)$ and $H_2O(g)$]. On the basis of the heat released by 1.00 g of each substance in its reaction with oxygen, which of these compounds offers the best possibility as a rocket fuel? The ΔH_f° of $B_2H_6(g)$, $CH_4(g)$, and $N_2H_4(l)$ may be found in Appendix G.

Solution

Write the balanced equation for each reaction.

$B_2H_6(g) + 3O_2(g) \longrightarrow B_2O_3(s) + 3H_2O(g)$

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$

$N_2H_4(l) + O_2(g) \longrightarrow N_2(g) + 2H_2O(g)$

Calculate the heat released per mole; then, calculate the heat per gram.

$\Delta H_{rxn}^\circ = \Delta H_P^\circ - \Delta H_R^\circ$

$\Delta H_{comb}^\circ = -1273.5 + 3(-241.82) + 36.4 = -1962.6 \text{ kJ mol}^{-1}$

$\Delta H_{comb}^\circ = -393.51 + 2(-241.82) - (-74.6) = -802.6 \text{ kJ mol}^{-1}$

$\Delta H_{comb}^\circ = 2(-241.82) - (50.63) = -534.27 \text{ kJ mol}^{-1}$

Calculate the heat per mole released per gram.

For B_2H_6: $\frac{-1912.26 \text{ kJ}}{27.610 \text{ g}} = -69.26 \text{ kJ g}^{-1} - \frac{1962.6}{27.67} = -70.93$

For CH_4: $\frac{-802.34 \text{ kJ}}{16.043 \text{ g}} = -50.012 \text{ kJ g}^{-1} - \frac{802.6}{16.043} = -50.03$

For N_2H_4: $\frac{-534.27}{32.0452} = 16.67$

On the assumption that the best rocket fuel is the one that gives off the most heat, B_2H_6 is the prime candidate. Other things must be considered, however. For example, the moles of gaseous product formed are related to the specific impulse of the fuel, toxicity of products, cost, and ability to contain original fuel (stability and corrosiveness).

82. How much heat is produced when 1.25 g of chromium metal reacts with oxygen gas under standard conditions?

Solution

The heat of formation of Cr_2O_3 is –1139.7 kJ/mol. Then, the heat released is 0.0120 $\cancel{\text{mol}}$ × –1140 kJ/$\cancel{\text{mol}}$ = –13.7 kJ.

83. Ethylene, C_2H_4, a byproduct from the fractional distillation of petroleum, is fourth among the 50 chemical compounds produced commercially in the largest quantities. About 80% of synthetic ethanol is manufactured from ethylene by its reaction with water in the presence of a suitable catalyst. $C_2H_4(g) + H_2O(g) \longrightarrow C_2H_5OH(l)$
Using the data in the table in Appendix G, calculate $\Delta H°$ for the reaction.

Solution

$$\Delta H^{o}_{rxn} = \Delta H^{o}_{C_2H_5OH(l)} - \Delta H^{o}_{H_2O(g)} - \Delta H^{o}_{C_2H_4(g)}$$
$$= -277.7 - (-241.82) - (52.4)$$
$$= -88.2 \text{ kJ}$$

84. The oxidation of the sugar glucose, $C_6H_{12}O_6$, is described by the following equation:
$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l) \qquad \Delta H = -2816 \text{ kJ}$
The metabolism of glucose gives the same products, although the glucose reacts with oxygen in a series of steps in the body.
(a) How much heat in kilojoules can be produced by the metabolism of 1.0 g of glucose?
(b) How many Calories can be produced by the metabolism of 1.0 g of glucose?

Solution

(a) The molar mass of glucose is 180.158 g/mol

$$\frac{\Delta H_{comb}}{g} = \frac{-2816 \text{ kJ } \cancel{\text{mol}^{-1}}}{180.16 \text{ g } \cancel{\text{mol}}} = -15.63 \text{ kJ g}^{-1} \text{ or } -16 \text{ kJ g}^{-1}$$

to the correct number of significant figures. Thus, 16 kJ of heat are released.

(b) $\frac{-15.63 \cancel{\text{kJ}}}{1 \text{ g}} \times \frac{1000 \cancel{\text{J}}}{1 \cancel{\text{kJ}}} \times \frac{1 \cancel{\text{cal}}}{4.184 \cancel{\text{J}}} \times \frac{1 \text{ Cal}}{1000 \cancel{\text{cal}}} = 3.7 \text{ Calories g}^{-1}$.]

85. Propane, C_3H_8, is a hydrocarbon that is commonly used as a fuel.
(a) Write a balanced equation for the complete combustion of propane gas.
(b) Calculate the volume of air at 25 °C and 1.00 atmosphere that is needed to completely combust 25.0 grams of propane. Assume that air is 21.0 percent O_2 by volume. (Hint: We will see how to do this calculation in a later chapter on gases—for now use the information that 1.00 L of air at 25 °C and 1.00 atm contains 0.275 g of O_2.)
(c) The heat of combustion of propane is –2219.2 kJ/mol. Calculate the heat of formation, ΔH^{o}_{f}, of propane given that ΔH^{o}_{f} of $H_2O(l)$ = –285.8kJ/mol and ΔH^{o}_{f} of $CO_2(g)$ = –393.5 kJ/mol.
(d) Assuming that all of the heat released in burning 25.0 grams of propane is transferred to 4.00 kilograms of water, calculate the increase in temperature of the water.

Solution

(a) $C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$
(b) Determine the number of moles of O_2 required and from that the number of grams. Then use the density to find the volume.

$$\text{Mass } O_2 = 25.0 \cancel{\text{ g } C_3H_8} \times \frac{1 \cancel{\text{ mol } C_3H_8}}{44.097 \cancel{\text{ g}}} \times \frac{5 \cancel{\text{ mol } O_2}}{1 \cancel{\text{ mol } C_3H_8(g)}} \times \frac{31.999 \text{ g}}{1 \cancel{\text{ mol } O_2}} = 90.7 \text{ g};$$

$$\text{Volume air} = \frac{90.7 \cancel{\text{ g}}}{0.275 \cancel{\text{ g}} \text{ L}^{-1}} = 330 \text{ L}$$

(c)

$$\Delta H^\circ_{comb}(C_3H_6(g) = -2219.2 \text{ kJ mol}^{-1} = 3\Delta H^\circ_f(CO_2(g)) + 4\Delta H^\circ_f(H_2O(l)) - \Delta H^\circ_f(C_3H_6(g))$$

$$\Delta H^\circ_f(C_3H_6(g)) = [2220.1 + 3(-393.5) + 4(-285.8)] \text{ kJ mol}^{-1} \quad ;$$

$$= -104.5 \text{ kJ mol}^{-1}$$

$$\frac{25.0 \text{ g}}{44.097 \text{ g mol}^{-1}} \times 2219.2 \text{ kJ mol}^{-1} = 1258 \text{ kJ} = 1.26 \times 10^6 \text{ J}$$

(d) Heat = 1.26×10^6 J = 4.18 J g^{-1} $°C^{-1}$ $\times$ 4.00×10^3 $\times$ ΔT

ΔT = 75.4 °C

86. During a recent winter month in Sheboygan, Wisconsin, it was necessary to obtain 3500 kWh of heat provided by a natural gas furnace with 89% efficiency to keep a small house warm (the efficiency of a gas furnace is the percent of the heat produced by combustion that is transferred into the house).
(a) Assume that natural gas is pure methane and determine the volume of natural gas in cubic feet that was required to heat the house. The average temperature of the natural gas was 56 °F; at this temperature and a pressure of 1 atm, natural gas has a density of 0.681 g/L.
(b) How many gallons of LPG (liquefied petroleum gas) would be required to replace the natural gas used? Assume the LPG is liquid propane [C_3H_8: density, 0.5318 g/mL; enthalpy of combustion, 2219 kJ/mol for the formation of $CO_2(g)$ and $H_2O(l)$] and the furnace used to burn the LPG has the same efficiency as the gas furnace.
(c) What mass of carbon dioxide is produced by combustion of the methane used to heat the house?
(d) What mass of water is produced by combustion of the methane used to heat the house?
(e) What volume of air is required to provide the oxygen for the combustion of the methane used to heat the house? Air contains 23% oxygen by mass. The average density of air during the month was 1.22 g/L.
(f) How many kilowatt-hours (1 kWh = 3.6×10^6 J) of electricity would be required to provide the heat necessary to heat the house? Note electricity is 100% efficient in producing heat inside a house.
(g) Although electricity is 100% efficient in producing heat inside a house, production and distribution of electricity is not 100% efficient. The efficiency of production and distribution of electricity produced in a coal-fired power plant is about 40%. A certain type of coal provides 2.26 kWh per pound upon combustion. What mass of this coal in kilograms will be required to produce the electrical energy necessary to heat the house if the efficiency of generation and distribution is 40%?

Solution
(a) The total heat that has to be obtained from combustion of methane is

$$q = 3500 \text{ kWh} \times 1000 \text{ W/kW} \times \frac{3600 \text{ J/Wh}}{0.89} = \frac{1.26 \times 10^{10} \text{ kJ}}{0.89} = 1.42 \times 10^7 \text{ kJ}.$$

Methane's heat of combustion is –890.8 kJ/mol as given in Table 9.2. The number of moles of methane that have to be burned is $\frac{1.42 \times 10^7 \text{ kJ}}{890.8 \text{ kJ/mol}} = 15{,}940 \text{ mol}$. The molar mass of methane is 16.04 g/mol, so the total mass of methane needed is 15940 mol × 16.04 g/mol = 255,700 g. The volume of this mass of methane is

$\frac{255700\ \cancel{g}}{0.681\ \cancel{g}/\text{L}} = 375500\ \text{L}$. $\frac{375500\ \cancel{\text{L}}}{28.316\ \cancel{\text{L}}/\text{cubic foot}} = 13{,}260$ cubic feet (the conversion factor is taken from Appendix C). (b) We found in (a) that the total amount of heat to be obtained is $q = 1.42 \times 10^7$ kJ. The number of moles of propane required is $\frac{1.42 \times 10^7\ \cancel{\text{kJ}}}{2219\ \cancel{\text{kJ}}/\text{mol}} = 6399$ mol. Given the molar mass of propane, 44.1 g/mol, the mass of propane needed is 6399 mol × 44.1 g/mol = 282,200 g. The volume of LPG is $\frac{28220\ \cancel{g}}{0.5318\ \cancel{g}/\text{mL}} = 530700$ mL or 530.7 L or

$530.7\ \text{L} \times \frac{1\ \text{gallon}}{(4 \times 0.9463\ \text{L})} = 140.2$ gallons of LPG. With three significant figures, the answer is 140 gallons of LPG. (c) The reaction is $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$. We have determined in part (a) that 15,940 mol of methane are needed. According to the reaction equation, this leads to production of the same amount of CO_2. Given that the molar mass of CO_2 is 44.01 g/mol, the mass of produced CO_2 is 15940 mol × 44.01 g/mol = 701,500 g or 701.5 kg. Leaving only three significant digits, the resulting mass of CO_2 is 702 kg. (d) The reaction equation is given in part (c). 15,940 mol of methane are needed. According to the reaction equation, this leads to the production of twice the amount of H_2O or 31,880 mol of H_2O. Given that the molar mass of H_2O is 18.015 g/mol, the mass of produced H_2O is 31880 mol × 18.015 g/mol = 574,300 g or 574.3 kg. Leaving only three significant digits, the resulting mass of H_2O is 574 kg. (e) Two moles of oxygen are consumed in combustion of each mole of methane. Thus, the overall amount of oxygen needed is 2 × 15,940 mol = 31,880 mol. The molar mass of oxygen is 32.0 g/mol; thus, the mass of oxygen required is 31,880 mol × 32.0 g/mol = 1,020,000 g. Given that only 23% of air is oxygen, the overall mass of air is $\frac{1020000\ \text{g}}{0.23} = 4435000$ g. The volume of air required is $\frac{4435000\ \cancel{g}}{1.22\ \cancel{g}/\text{L}} = 3635000$ L or 3635 m^3. Keeping only three significant figures, we obtain a result of 3640 m^3 of air. (f) Since the efficiency is 100% in this case, the amount of energy is the same as specified in the problem or 3500 kWh. (g) The overall amount of heat to be obtained from the burning of coal is $\frac{3500\ \text{kWh}}{0.4} = 8750$ kWh. The mass of coal required for this process is $\frac{8750\ \cancel{\text{kWh}}}{2.26\ \cancel{\text{kWh}}/\text{lb}} = 3872$ lb. The mass of coal in kilograms is 3872 lb × 0.4536 kg/lb = 1620 kg.

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Chemistry: Atoms First 2e
9: Thermochemistry
9.4: Strengths of Ionic and Covalent Bonds

87. Which bond in each of the following pairs of bonds is the strongest?
(a) C–C or C = C

(b) C–N or $C \equiv N$
(c) $C \equiv O$ or C = O
(d) H–F or H–Cl
(e) C–H or O–H
(f) C–N or C–O

Solution
In general, a multiple bond between the same two elements is stronger than a single bond. The greater the electronegativity difference between two similar elements, the greater the bond energy.
(a) $C = C$; (b) $C \equiv N$; (c) $C \equiv O$; (d) H–F; (e) O–H; (f) C–O

88. Using the bond energies in Table 9.3, determine the approximate enthalpy change for each of the following reactions:

(a) $H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$

(b) $CH_4(g) + I_2(g) \longrightarrow CH_3I(g) + HI(g)$

(c) $C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(g)$

Solution

(a)
$$\Delta H^\circ_{298} = \sum D_{\text{bonds broken}} - \sum D_{\text{bonds formed}}$$
$$= D_{H-H} + D_{Br-Br} - 2D_{H-Br} \quad ;$$
$$= 436 + 190 - 2(370) = -114 \text{ kJ}$$

(b)
$$\Delta H^\circ_{298} = \sum D_{\text{bonds broken}} - \sum D_{\text{bonds formed}}$$
$$= 4D_{C-H} + D_{I-I} - 3D_{C-H} - D_{C-I} - D_{H-I} \quad ;$$
$$= 4(415) + 150 - 3(415) - 240 - 295 = 30 \text{ kJ}$$

(c)
$$\Delta H^\circ_{298} = \sum D_{\text{bonds broken}} - \sum D_{\text{bonds formed}}$$
$$= D_{C=C} + 4D_{C-H} + 3D_{O=O} - 4D_{C=O} - 4D_{O-H}$$
$$= 611 + 4(415) + 3(498) - 4(741) - 4(464)$$
$$= -1055 \text{ kJ}$$

89. Using the bond energies in Table 9.3, determine the approximate enthalpy change for each of the following reactions:

(a) $Cl_2(g) + 3F_2(g) \longrightarrow 2ClF_3(g)$

(b) $H_2C = CH_2(g) + H_2(g) \longrightarrow H_3CCH_3(g)$

(c) $2C_2H_6(g) + 7O_2(g) \longrightarrow 4CO_2(g) + 6H_2O(g)$

Solution

(a)
$$DH^\circ = \sum D_{\text{bonds broken}} - \sum D_{\text{bonds formed}}$$
$$= 2D_{Cl-Cl} + 3D_{F-F} - 6D_{Cl-F} \quad ;$$
$$= -564 \text{ kJ}$$

(b)
$$DH^\circ = \sum D_{\text{bonds broken}} - \sum D_{\text{bonds formed}}$$
$$= D_{C-C} + 4D_{C-H} + D_{H-H} - D_{C-C} - 6D_{C-H} \; ;$$
$$= 611 + 4(415) + 436 - 345 - 6(415)$$
$$= -128 \text{ kJ}$$

(c)
$$\begin{aligned} DH^\circ &= \sum D_{\text{bonds broken}} - \sum D_{\text{bonds formed}} \\ &= 2D_{C-C} + 12D_{C-H} + 7D_{O-O} - 8D_{C-O} - 12D_{O-H} \\ &= 2(345) + 12(415) + 7(496) - 8(741) - 12(464) \\ &= -2354 \text{ kJ} \end{aligned}$$

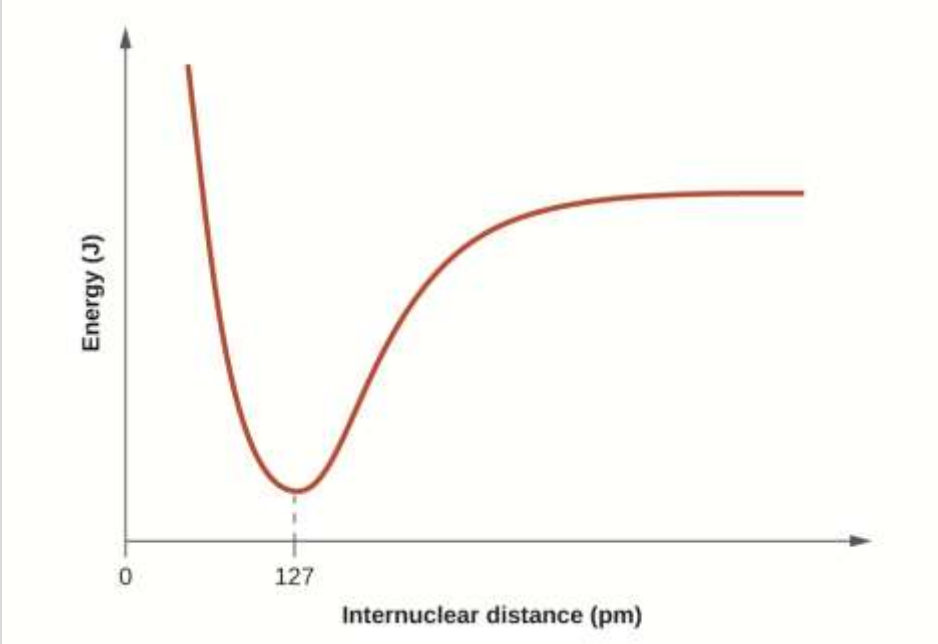
90. Draw a curve that describes the energy of a system with H and Cl atoms at varying distances. Then, find the minimum energy of this curve two ways.

(a) Use the bond energy found in Table 9.3 and Table 9.4 to calculate the energy for one single HCl bond. (Hint: How many bonds are in a mole?)

(b) Use the enthalpy of reaction and the bond energies for H_2 and Cl_2 to solve for the energy of one mole of HCl bonds.

$$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g) \qquad \Delta H^\circ_{\text{rxn}} = -184.7 \text{ kJ/mol}$$

Solution



When H and Cl are separate (the *x* axis) the energy is at a particular value. As they approach, it decreases to a minimum at 127 pm (the bond distance), and then it increases sharply as you get closer.

(a) $\text{H–Cl}\,\dfrac{431\,\cancel{\text{kJ}}}{\cancel{\text{mol}}} \times \dfrac{\cancel{\text{mol}}}{6.022\times10^{23}\text{ bonds}} \times \dfrac{1000\,\text{J}}{\cancel{\text{kJ}}} = 7.16 \times 10^{-19}$

(b) We know Hess's law related to bond energies:

$$\Delta H^\circ = \sum \Delta H^\circ_{\text{BDE}}(\text{broken}) - \sum \Delta H^\circ_{\text{BDE}}(\text{formed})$$

We are given the enthalpy of reaction

$$-184.7 \text{ kJ/mol} = \left(\Delta H^\circ_{\text{BDE(H–H)}} + \Delta H^\circ_{\text{BDE(Cl–Cl)}}\right) - \left(2\Delta H^\circ_{\text{BDE(H–Cl)}}\right)$$

H–H is 436 kJ/mol and Cl–Cl is 243

$-184.7 \text{ kJ/mol} = (436 + 243) - 2x = 679 - 2x$

$2x = 863.7 \text{ kJ/mol}$

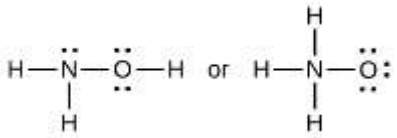
$x = 432 \text{ kJ/mol}$, which is very close to the value we looked up in part (a).

91. Explain why bonds occur at specific average bond distances instead of the atoms approaching each other infinitely close.

Solution

The specific average bond distance is the distance with the lowest energy. At distances less than the bond distance, the positive charges on the two nuclei repel each other, and the overall energy increases.

92. When a molecule can form two different structures, the structure with the stronger bonds is usually the more stable form. Use bond energies to predict the correct structure of the hydroxylamine molecule:



Solution

(a) $\begin{array}{l} 2\text{ N}-\text{H bonds} = 2(390) \\ 1\text{ N}-\text{O bond} = \quad 200 \\ 1\text{ O}-\text{H bond} = \underline{\quad 464} \\ \qquad\qquad\quad 1444\text{ kJ} \end{array}$; (b) $\begin{array}{l} 3\text{ N}-\text{H bonds} = 3(390) \\ 1\text{ N}-\text{O bond} = \underline{\quad 200} \\ \qquad\qquad\quad 1370\text{ kJ} \end{array}$; the greater bond energy is for (a), and it is more stable

93. How does the bond energy of HCl(g) differ from the standard enthalpy of formation of HCl(g)?

Solution

The bond energy involves breaking HCl into H and Cl atoms. The enthalpy of formation involves making HCl from H_2 and Cl_2 molecules.

94. Using the standard enthalpy of formation data in Appendix G, show how can the standard enthalpy of formation of HCl(g) can be used to determine the bond energy.

Solution

$$\text{HCl}(g) \longrightarrow \frac{1}{2}\text{H}_2(g) + \frac{1}{2}\text{Cl}_2(g) \qquad \Delta H_1^\circ = -\Delta H_{\text{f [HCl}(g)]}^\circ$$

$$\frac{1}{2}\text{H}_2(g) \longrightarrow \text{H}(g) \qquad \Delta H_2^\circ = \Delta H_{\text{f [H}(g)]}^\circ$$

$$\frac{1}{2}\text{Cl}_2(g) \longrightarrow \text{Cl}(g) \qquad \Delta H_3^\circ = \Delta H_{\text{f [Cl}(g)]}^\circ$$

$$\text{HCl}(g) \longrightarrow \text{H}(g) + \text{Cl}(g) \qquad \Delta H_{298}^\circ = \Delta H_1^\circ + \Delta H_2^\circ + \Delta H_3^\circ$$

$$\begin{aligned} D_{\text{HCl}} = \Delta H_{298}^\circ &= -\Delta H_{\text{f [HCl}(g)]}^\circ + \Delta H_{\text{f [H}(g)]}^\circ + \Delta H_{\text{f [Cl}(g)]}^\circ \\ &= -(-92.307\text{ kJ}) + 217.97\text{ kJ} + 121.3\text{ kJ} \\ &= 431.6\text{ kJ} \end{aligned}$$

95. Using the standard enthalpy of formation data in Appendix G, calculate the bond energy of the carbon-sulfur double bond in CS_2.

Solution

$$\text{CS}_2(g) \longrightarrow \text{C(graphite)} + 2\text{S}(s) \qquad \Delta H_1^\circ = \Delta H_{\text{f[(CS}_2(g)]}^\circ$$

$$\text{C(graphite)} \longrightarrow \text{C}(g) \qquad \Delta H_2^\circ = \Delta H_{\text{f C}(g)}^\circ$$

$2S(s) \longrightarrow 2S(g) \qquad 2\Delta H_3^\circ = 2\Delta H_{f\,S(g)}^\circ$

$D_{CS_2} = \Delta H^\circ = -\Delta H_{f[(CS_2(g)]}^\circ + \Delta H_{f\,C(g)}^\circ + 2\Delta H_{f\,S(g)}^\circ$

$= -116.9 + 716.681 + 2(278.81)$

$= 1157.4 \text{ kJ mol}^{-1}$

$D_{C=S} = \dfrac{1157.4}{2} = 578.7 \text{ kJ mol}^{-1} \text{ of C} = \text{S bonds}$

96. Using the standard enthalpy of formation data in Appendix G, determine which bond is stronger: the S–F bond in $SF_4(g)$ or in $SF_6(g)$?

Solution

$SF_4(g) \longrightarrow \dfrac{1}{8}S_8(s) + 2F_2(g) \qquad \Delta H_1^\circ = -\Delta H_{f[SF_4(g)]}$

$\dfrac{1}{8}S_8(s) \longrightarrow S(g) \qquad \Delta H_2^\circ = \Delta H_{f\,S(g)}^\circ$

$2F_2(g) \longrightarrow 4F(g) \qquad 4\Delta H_3^\circ = 4\Delta H_{f\,F(g)}^\circ$

$D_{SF_4} = \Delta H_{298}^\circ = -\Delta H_{f[SF_4(g)]} + \Delta H_{f\,S(g)}^\circ + 4\Delta H_{f\,F(g)}^\circ$

$= 728.43 + 278.81 + 4(79.4) = 1369.7 \text{ kJ}$

$D_{S-F} = \dfrac{1324.84 \text{ kJ}}{4 \text{ S} - \text{F}} = 331.21 \text{ kJ}$

Proceeding in the same manner, $-\Delta H_{f[SF_6(g)]} = 1220.5 \text{ kJ mol}^{-1}$. The $6F(g)$ and $S(g)$ contribute 755.21 kJ; then $DF_{SF_6} = 1962.7 \text{ kJ}$ and $D_{S-F} = \dfrac{1975.71}{6} = 392.3 \text{ kJ mol}^{-1}$ per mole of bonds. The S–F bond in SF_4 is stronger.

97. Using the standard enthalpy of formation data in Appendix G, determine which bond is stronger: the P–Cl bond in $PCl_3(g)$ or in $PCl_5(g)$?

Solution

$PCl_3(g) \longrightarrow \dfrac{1}{4}P_4(s) + \dfrac{3}{2}Cl_2(g) \qquad \Delta H_1^\circ = -\Delta H_{f[(PCl_3(g)]}^\circ$

$\dfrac{1}{4}P_4(s) \longrightarrow P(g) \qquad \Delta H_2^\circ = \Delta H_{f\,P(g)}^\circ$

$\dfrac{3}{2}Cl_2(g) \longrightarrow 3Cl(g) \qquad 3\Delta H_3^\circ = 3\Delta H_{f\,Cl(g)}^\circ$

$D_{PCl_3} = \Delta H^\circ = -\Delta H_{f[(PCl_3(g)]}^\circ + \Delta H_{f\,P(g)}^\circ + 3\Delta H_{f\,Cl(g)}^\circ$

$= 287.0 + 314.64 + 3(121.3) = 965.54 \text{ kJ mol}^{-1}$

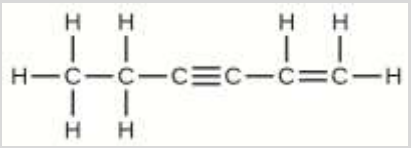
$D_{PCl_3} = \dfrac{965.54 \text{ kJ}}{3} = 321.8 \text{ kJ per mol}^{-1} \text{ of bonds}$

Proceeding in the same manners, $-\Delta H_{f[PCl_5(g)]} = 374.9$ kJ mol^{-1}. The P(g) and the 5Cl(g) contribute 921.14 kJ; then $DF_{PCl_5} = 1296.04$ kJ and $D_{P-Cl} = \frac{1296.04 \text{ kJ/mol}}{5} = 259.2$ kJ/mol of bonds. The P–Cl bond in PCl_3 is stronger.

98. Complete the following Lewis structure by adding bonds (not atoms), and then indicate the longest bond:

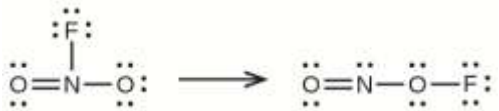


Solution



The C–C single bonds are longest.

99. Use the bond energy to calculate an approximate value of ΔH for the following reaction. Which is the more stable form of FNO_2?



Solution

the left hand arrangement: O = N not listed, N–F 270, N–O 200; the right hand arrangement: O = N not listed, N–O 200, O–F 185; the bond energy of O = N does not matter because it must be the same in both cases, the form on the right has a bond energy of $X + 470$; that on the right, $X + 385$; the form on the left is more stable.

100. Use principles of atomic structure to answer each of the following:[1]

(a) The radius of the Ca atom is 197 pm; the radius of the Ca^{2+} ion is 99 pm. Account for the difference.

(b) The lattice energy of CaO(s) is –3460 kJ/mol; the lattice energy of K_2O is –2240 kJ/mol. Account for the difference.

(c) Given these ionization values, explain the difference between Ca and K with regard to their first and second ionization energies.

Element	First Ionization Energy (kJ/mol)	Second Ionization Energy (kJ/mol)
K	419	3050
Ca	590	1140

(d) The first ionization energy of Mg is 738 kJ/mol and that of Al is 578 kJ/mol. Account for this difference.

Solution

(a) When two electrons are removed from the valence shell, the Ca radius loses the outermost energy level and reverts to the lower $n = 3$ level, which is much smaller in radius.

1 This question is taken from the Chemistry Advanced Placement Examination and is used with the permission of the Educational Testing Service.

(b) The +2 charge on calcium pulls the oxygen much closer compared with K, thereby increasing the lattice energy relative to a less charged ion.
(c) Removal of the 4*s* electron in Ca requires more energy than removal of the 4*s* electron in K, because of the stronger attraction of the nucleus and the extra energy required to break the pairing of the electrons. The second ionization energy for K requires that an electron be removed from a lower energy level, where the attraction is much stronger from the nucleus for the electron. In addition, energy is required to unpair two electrons in a full orbital. For Ca, the second ionization potential requires removing only a lone electron in the exposed outer energy level.
(d) In Al, the removed electron is relatively unprotected and unpaired in a *p* orbital. The higher energy for Mg mainly reflects the unpairing of the 2*s* electron.

101. The lattice energy of LiF is 1023 kJ/mol, and the Li–F distance is 200.8 pm. NaF crystallizes in the same structure as LiF but with a Na–F distance of 231 pm. Which of the following values most closely approximates the lattice energy of NaF: 510, 890, 1023, 1175, or 4090 kJ/mol? Explain your choice.

Solution

The lattice energy is given by $U = C\left(\frac{Z^+Z^-}{R_o}\right)$, where R_o is the interatomic distance. The charges are the same in both LiF and NaF. The major difference is expected to be the interatomic distance 2.008 Å versus 2.31 Å. From the data for LiF, with $Z^+Z^- = -1$,

$$C = \frac{UR_o}{Z^+Z^-} = \frac{1023 \times 2.008}{-1} = -2054 \text{ kJ Å mol}^{-1}.$$

Then,

$$U_{NaF} = \frac{-2054 \text{ kJ Å mol}^{-1}\ (-1)}{2.31 \text{ Å}} = 889 \text{ kJ mol}^{-1} \text{ or } 890 \text{ kJ mol}^{-1}.$$

102. For which of the following substances is the least energy required to convert one mole of the solid into separate ions?
(a) MgO
(b) SrO
(c) KF
(d) CsF
(e) MgF_2

Solution

The lattice energy, *U*, is the energy required to convert the solid into separate ions. *U* may be calculated from the Born-Haber cycle.
The values in kJ/mol are approximately (a) 3791; (b) 3223; (c) 821; (d) 740; and (e) 2957.
The answer is (d), which requires about 740 kJ/mol.

103. The reaction of a metal, M, with a halogen, X_2, proceeds by an exothermic reaction as indicated by this equation: $M(s) + X_2(g) \longrightarrow MX_2(s)$. For each of the following, indicate which option will make the reaction more exothermic. Explain your answers.
(a) a large radius vs. a small radius for M^{+2}
(b) a high ionization energy vs. a low ionization energy for M
(c) an increasing bond energy for the halogen
(d) a decreasing electron affinity for the halogen
(e) an increasing size of the anion formed by the halogen

Solution
In each case, think about how it would affect the Born-Haber cycle. Recall that the more negative the overall value, the more exothermic the reaction is. (a) The smaller the radius of the cation, the shorter the interionic distance and the greater the lattice energy would be. Since the lattice energy is negative in the Born-Haber cycle, this would lead to a more exothermic reaction. (b) A lower ionization energy is a lower positive energy in the Born-Haber cycle. This would make the reaction more exothermic, as a smaller positive value is "more exothermic." (c) As in part (b), the bond energy is a positive energy. The lower it is, the more exothermic the reaction will be. (d) A higher electron affinity is more negative. In the Born-Haber cycle, the more negative the electron affinity, the more exothermic the overall reaction. (e) The smaller the radius of the anion, the shorter the interionic distance and the greater the lattice energy would be. Since the lattice energy is negative in the Born-Haber cycle, this would lead to a more exothermic reaction.

104. The lattice energy of LiF is 1023 kJ/mol, and the Li–F distance is 201 pm. MgO crystallizes in the same structure as LiF but with a Mg–O distance of 205 pm. Which of the following values most closely approximates the lattice energy of MgO: 256 kJ/mol, 512 kJ/mol, 1023 kJ/mol, 2046 kJ/mol, or 4090 kJ/mol? Explain your choice.

Solution
4008 kJ/mol; both ions in MgO have twice the charge of the ions in LiF; the bond length is very similar and both have the same structure; a quadrupling of the energy is expected based on the equation for lattice energy

105. Which compound in each of the following pairs has the larger lattice energy? Note: Mg^{2+} and Li^{+} have similar radii; O^{2-} and F^{-} have similar radii. Explain your choices.
(a) MgO or MgSe
(b) LiF or MgO
(c) Li_2O or LiCl
(d) Li_2Se or MgO

Solution
(a) MgO; selenium has larger radius than oxygen and, therefore, a larger interionic distance and thus, a larger smaller lattice energy than MgO;
(b) MgO; the higher charges on Mg and O, given the similar radii of the ions, leads to a larger lattice energy;
(c) Li_2O; the higher charge on O^{2-} leads to a larger energy; additionally, Cl^{-} is larger than O^{2-}; this leads to a larger interionic distance in LiCl and a lower lattice energy;
(d) MgO; the higher charge on Mg leads to a larger lattice energy

106. Which compound in each of the following pairs has the larger lattice energy? Note: Ba^{2+} and
K^{+} have similar radii; S^{2-} and Cl^{-} have similar radii. Explain your choices.
(a) K_2O or Na_2O
(b) K_2S or BaS
(c) KCl or BaS
(d) BaS or $BaCl_2$

Solution
(a) Na_2O; Na^{+} has a smaller radius than K^{+}; (b) BaS; Ba has a larger charge than K; (c) BaS; Ba and S have larger charges; (d) BaS; S has a larger charge

107. Which of the following compounds requires the most energy to convert one mole of the solid into separate ions?
(a) MgO
(b) SrO
(c) KF
(d) CsF
(e) MgF_2

Solution
MgO

108. Which of the following compounds requires the most energy to convert one mole of the solid into separate ions?
(a) K_2S
(b) K_2O
(c) CaS
(d) Cs_2S
(e) CaO

Solution
CaO

109. The lattice energy of KF is 794 kJ/mol, and the interionic distance is 269 pm. The Na–F distance in NaF, which has the same structure as KF, is 231 pm. Which of the following values is the closest approximation of the lattice energy of NaF: 682 kJ/mol, 794 kJ/mol,924 kJ/mol, 1588 kJ/mol, or 3175 kJ/mol? Explain your answer.

Solution
924 kJ/mol

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1. In terms of their bulk properties, how do liquids and solids differ? How are they similar?

Solution
Liquids and solids are similar in that they are matter composed of atoms, ions, or molecules. They are incompressible and have similar densities that are both much larger than those of gases. They are different in that liquids have no fixed shape, and solids are rigid.

2. In terms of the kinetic molecular theory, in what ways are liquids similar to solids? In what ways are liquids different from solids?

Solution
Similarities: Both are composed of atoms, ions, or molecules; there is little empty space between these particles; the motion of the particles changes with changing temperature. Differences: Particles in the solid are fixed in a regular arrangement; although they vibrate, they do not move about; particles in the liquid have no regular arrangement and are free to move past each other.

3. In terms of the kinetic molecular theory, in what ways are liquids similar to gases? In what ways are liquids different from gases?

Solution
They are similar in that the atoms or molecules are free to move from one position to another. They differ in that the particles of a liquid are confined to the shape of the vessel in which they are placed. In contrast, a gas will expand without limit to fill the space into which it is placed.

4. Explain why liquids assume the shape of any container into which they are poured, whereas solids are rigid and retain their shape.

Solution
Molecules in a liquid are free to move past each other, whereas molecules in a solid are held in fixed positions.

5. What is the evidence that all neutral atoms and molecules exert attractive forces on each other?

Solution
All atoms and molecules will condense into a liquid or solid in which the attractive forces exceed the kinetic energy of the molecules, at sufficiently low temperature.

6. Open the PhET States of Matter Simulation (http://phet.colorado.edu/en/simulation/states-of-matter) to answer the following questions:
(a) Select the Solid, Liquid, Gas tab. Explore by selecting different substances, heating and cooling the systems, and changing the state. What similarities do you notice between the four substances for each phase (solid, liquid, gas)? What differences do you notice?
(b) For each substance, select each of the states and record the given temperatures. How do the given temperatures for each state correlate with the strengths of their intermolecular attractions? Explain.
(c) Select the Interaction Potential tab, and use the default neon atoms. Move the Ne atom on the right and observe how the potential energy changes. Select the Total Force button, and move the Ne atom as before. When is the total force on each atom attractive and large enough to matter? Then select the Component Forces button, and move the Ne atom. When do the attractive (van der Waals) and repulsive (electron overlap) forces balance? How does this relate to the potential energy versus the distance between atoms graph? Explain.

Solution
(a) The common general trend is that the substances retain both volume and shape in the solid state, generally retain the volume but change shape in the liquid state (and also produce more vapor/gas phase as the systems transition from solids to liquids), and the shape is not retained in the gas phase while the substances can expand to occupy the whole available volume. The

difference is that water molecules have highly directional interactions resulting in a hydrogen-bonded structured network in the solid state, and the oxygen molecules have ordered packing in the solid state because of their nonsymmetric molecule shape, while argon and neon atoms show no directionality in their interactions. (b) Neon – solid at 13 K, liquid at 26 K, gas at 55 K. Argon – solid at 43 K, liquid at 86 K, gas at 189 K. Oxygen – solid at 31 K, liquid at 69 K, gas at 194 K. Water – solid at 157 K, liquid at 328 K, gas at 809 K. Water molecules have the strongest intermolecular interactions (hydrogen bonds, electrostatic forces), and so the transitions from solid to liquid and from liquid to gas occur at higher temperatures. The other three compounds experience weaker van der Waals (nonpolar) interactions only, and thus they turn to less ordered phases (liquid and gas) at lower temperatures. (c) The total forces are attractive and large enough to matter when the distance between the atoms is larger than at the equilibrium point, but still not too large so that the interactions are still not too weak. The attractive and repulsive components balance each other at the equilibrium point. At the point the interaction energy has a minimum, and so its derivative is equal to zero. Forces are derivatives of the energy multiplied by –1.

7. Define the following and give an example of each:
(a) dispersion force
(b) dipole-dipole attraction
(c) hydrogen bond

Solution
(a) Dispersion forces occur as an atom develops a temporary dipole moment when its electrons are distributed asymmetrically about the nucleus. This structure is more prevalent in large atoms such as argon or radon. A second atom can then be distorted by the appearance of the dipole in the first atom. The electrons of the second atom are attracted toward the positive end of the first atom, which sets up a dipole in the second atom. The net result is rapidly fluctuating, temporary dipoles that attract one another (e.g., Ar).
(b) A dipole-dipole attraction is a force that results from an electrostatic attraction of the positive end of one polar molecule for the negative end of another polar molecule (e.g., ICI molecules attract one another by dipole-dipole interaction).
(c) Hydrogen bonds form whenever a hydrogen atom is bonded to one of the more electronegative atoms, such as a fluorine, oxygen, nitrogen, or chlorine atom. The electrostatic attraction between the partially positive hydrogen atom in one molecule and the partially negative atom in another molecule gives rise to a strong dipole-dipole interaction called a hydrogen bond (e.g., $HF\cdots HF$).

8. The types of intermolecular forces in a substance are identical whether it is a solid, a liquid, or a gas. Why then does a substance change phase from a gas to a liquid or to a solid?

Solution
At some point, the amount of available heat decreases to a level such that the kinetic energy is just equal to or less than the attractive forces that are present in the gas, allowing it to condense into a liquid. A similar situation exists when the kinetic energy falls below the level required to exceed the attractive forces of the solid; in this case the liquid will solidify.

9. Why do the boiling points of the noble gases increase in the order He < Ne < Ar < Kr < Xe?

Solution
The London forces typically increase as the number of electrons increase.

10. Neon and HF have approximately the same molecular masses.
(a) Explain why the boiling points of Neon and HF differ.

(b) Compare the change in the boiling points of Ne, Ar, Kr, and Xe with the change of the boiling points of HF, HCl, HBr, and HI, and explain the difference between the changes with increasing atomic or molecular mass.

Solution

(a) The boiling point of Ne is –245.9 °C, whereas that of HF is –83.1 °C. As their molecular masses are similar, the higher boiling point of HF can be explained on the basis of its hydrogen bonds preventing the escape of molecules from the liquid surface. (b) In each case (HF and Ne; HCl and Ar; HBr and Kr; HI and Xe), the corresponding pairs have similar molecular or atomic masses. The much higher boiling point of HF compared with Ne is due to hydrogen bonding in HF. HCl has a much higher (about 100 °C) boiling point than Ar because of dipole-dipole interactions. In HBr and HI, where hydrogen bonding is impossible, dipole-dipole interactions make the boiling points of HBr and HI approximately 60 °C to 40 °C higher than those of the corresponding atomic species.

11. Arrange each of the following sets of compounds in order of increasing boiling point temperature:

(a) HCl, H_2O, SiH_4

(b) F_2, Cl_2, Br_2

(c) CH_4, C_2H_6, C_3H_8

(d) O_2, NO, N_2

Solution

(a) $SiH_4 < HCl < H_2O$; (b) $F_2 < Cl_2 < Br_2$; (c) $CH_4 < C_2H_6 < C_3H_8$; (d) $N_2 < O_2 < NO$

12. The molecular mass of butanol, C_4H_9OH, is 74.14; that of ethylene glycol, $CH_2(OH)CH_2OH$, is 62.08, yet their boiling points are 117.2 °C and 174 °C, respectively. Explain the reason for the difference.

Solution

The two hydroxyl groups in ethylene glycol provide more locations for the formation of hydrogen bonds. The existence of more hydrogen bonds considerably increases the boiling point.

13. On the basis of intermolecular attractions, explain the differences in the boiling points of *n*–butane (–1 °C) and chloroethane (12 °C), which have similar molar masses.

Solution

Only rather small dipole-dipole interactions from C-H bonds are available to hold *n*-butane in the liquid state. Chloroethane, however, has rather large dipole interactions because of the Cl-C bond; the interaction, therefore, is stronger, leading to a higher boiling point.

14. On the basis of dipole moments and/or hydrogen bonding, explain in a qualitative way the differences in the boiling points of acetone (56.2 °C) and 1-propanol (97.4 °C), which have similar molar masses.

Solution

Both have approximately equal London dispersion forces, but because it contains an –OH group, 1-propanol forms hydrogen bonds, which are stronger intermolecular forces than the dipole-dipole attractions in acetone that result from the C = O bond.

15. The melting point of $H_2O(s)$ is 0 °C. Would you expect the melting point of $H_2S(s)$ to be –85 °C, 0 °C, or 185 °C? Explain your answer.

Solution

–85 °C. Water has stronger hydrogen bonds, so it melts at a higher temperature.

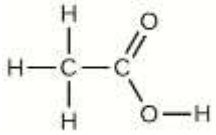
16. Silane (SiH_4), phosphine (PH_3), and hydrogen sulfide (H_2S) melt at –185 °C, –133 °C, and –85 °C, respectively. What does this suggest about the polar character and intermolecular attractions of the three compounds?

Solution
The molecules become more polar and the intermolecular forces increase as the melting temperatures increase from –185 °C to –85 °C.

17. Explain why a hydrogen bond between two water molecules is weaker than a hydrogen bond between two hydrogen fluoride molecules.

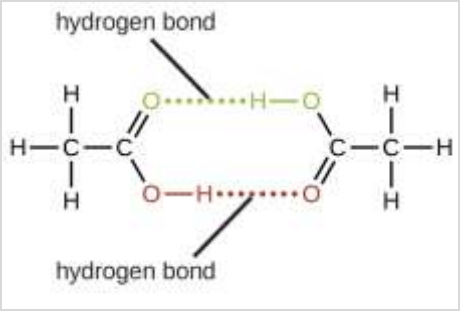
Solution
The hydrogen bond between two hydrogen fluoride molecules is stronger than that between two water molecules because the electronegativity of F is greater than that of O. Consequently, the partial negative charge on F is greater than that on O. The hydrogen bond between the partially positive H and the larger partially negative F will be stronger than that formed between H and O.

18. Under certain conditions, molecules of acetic acid, CH_3COOH, form "dimers," pairs of acetic acid molecules held together by strong intermolecular attractions:



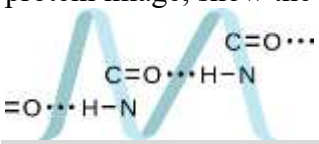
Draw a dimer of acetic acid, showing how two CH_3COOH molecules are held together, and stating the type of IMF that is responsible.

Solution



A dimer of acetic acid is displayed by showing two acetic acid molecules. The molecules combine by H-bonding between the H and O. Two H-bonds per dimer are thus established.

19. Proteins are chains of amino acids that can form in a variety of arrangements, one of which is a helix. What kind of IMF is responsible for holding the protein strand in this shape? On the protein image, show the locations of the IMFs that hold the protein together:



Solution
H-bonding is the principle IMF holding the protein strands together. The H-bonding is between the $N-H$ and $C=O$.

20. The density of liquid NH_3 is 0.64 g/mL; the density of gaseous NH_3 at STP is 0.0007 g/mL. Explain the difference between the densities of these two phases.

Solution

Molecules of gases are widely separated, whereas molecules in a liquid touch. Thus, a given volume of a gas contains a much smaller number of molecules and a much smaller mass than the same volume of a liquid.

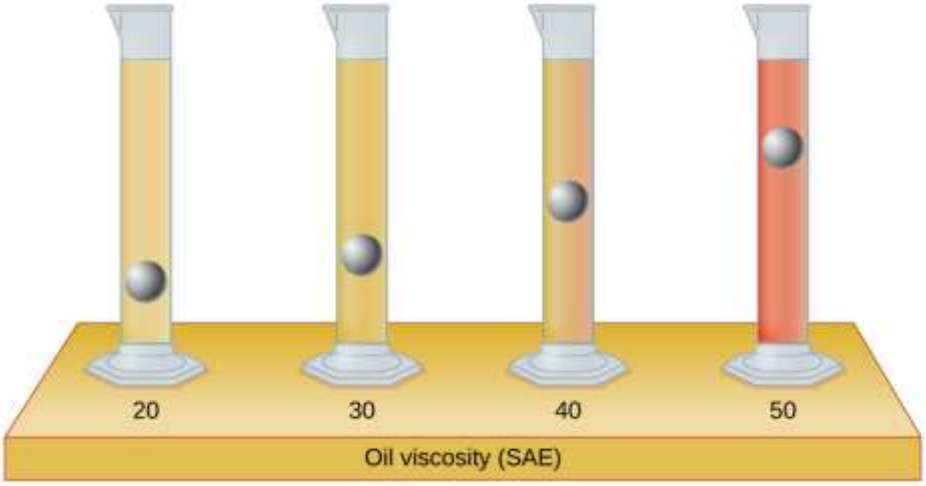
21. Identify the intermolecular forces present in the following solids:
(a) CH_3CH_2OH
(b) $CH_3CH_2CH_3$
(c) CH_3CH_2Cl

Solution
(a) hydrogen bonding, dipole-dipole attraction, and dispersion forces; (b) dispersion forces; (c) dipole-dipole attraction and dispersion forces

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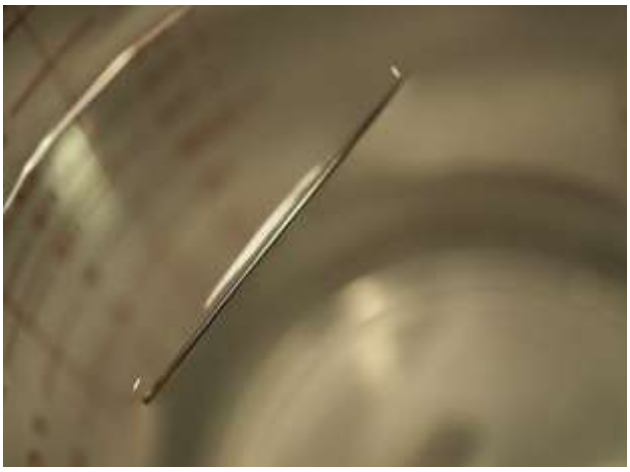
Chemistry: Atoms First 2e
10: Liquids and Solids
10.2: Properties of Liquids

22. The test tubes shown here contain equal amounts of the specified motor oils. Identical metal spheres were dropped at the same time into each of the tubes, and a brief moment later, the spheres had fallen to the heights indicated in the illustration.
Rank the motor oils in order of increasing viscosity, and explain your reasoning:



Solution
The more viscous the oil, the more slowly the sphere will descend. The depth to which the metal sphere has descended at any given time is therefore inversely related to the viscosity of the oil. The relative viscosities of these oil samples is then SAE 20 < SAE 30 < SAE 40 < SAE 50.

23. Although steel is denser than water, a steel needle or paper clip placed carefully lengthwise on the surface of still water can be made to float. Explain at a molecular level how this is possible.

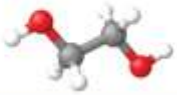


(credit: Cory Zanker)

Solution

The water molecules have strong intermolecular forces of hydrogen bonding. The water molecules are thus attracted strongly to one another and exhibit a relatively large surface tension, forming a type of "skin" at its surface. This skin can support a bug or paper clip if gently placed on the water.

24. The surface tension and viscosity values for diethyl ether, acetone, ethanol, and ethylene glycol are shown here.

Compound	Molecule	Surface Tension (mN/m)	Viscosity (mPa s)
diethyl ether $C_2H_5OC_2H_5$		17	0.22
acetone CH_3COCH_3		23	0.31
ethanol C_2H_5OH		22	1.07
ethylene glycol $CH_2(OH)CH_2(OH)$		48	16.1

(a) Explain their differences in viscosity in terms of the size and shape of their molecules and their IMFs.

(b) Explain their differences in surface tension in terms of the size and shape of their molecules and their IMFs:

Solution

(a) The higher the viscosity, the stronger the intermolecular forces are. Ethylene glycol and ethanol both exhibit hydrogen bonding, but ethylene glycol molecules contain twice as many –OH groups as ethanol molecules, and so its viscosity is higher. Acetone has a lower viscosity than ethanol since its dipole-dipole force is weaker than hydrogen bonding. Ether has a lower viscosity than acetone, since it is less polar than acetone. (b) The higher the surface tension, the stronger the intermolecular forces are. Ethylene glycol has a higher surface tension than ethanol, since it can hydrogen bond more with its two –OH groups per molecule. Surprisingly, the surface

tension of ethanol and acetone are roughly the same. The acetone molecules are planar, and so are able to orient themselves in a planar manner so as to create a tight skin at the surface to match the hydrogen bonding of ethanol. Ether is nonplanar, and it displays a weaker dipole and so its surface tension is lowest.

25. You may have heard someone use the figure of speech "slower than molasses in winter" to describe a process that occurs slowly. Explain why this is an apt idiom, using concepts of molecular size and shape, molecular interactions, and the effect of changing temperature.

Solution

Temperature has an effect on intermolecular forces: The higher the temperature, the greater the kinetic energies of the molecules and the greater the extent to which their intermolecular forces are overcome, and so the more fluid (less viscous) the liquid. The lower the temperature, the less the intermolecular forces are overcome, and so the less viscous the liquid.

26. It is often recommended that you let your car engine run idle to warm up before driving, especially on cold winter days. While the benefit of prolonged idling is dubious, it is certainly true that a warm engine is more fuel efficient than a cold one. Explain the reason for this.

Solution

A warm engine's oil is less viscous, and so it flows more freely and thus more effectively lubricates the engines internal parts (primarily its pistons). This permits the engine to run with less friction and, subsequently, more fuel efficiently.

27. The surface tension and viscosity of water at several different temperatures are given in this table.

Water	Surface Tension (mN/m)	Viscosity (mPa s)
0 °C	75.6	1.79
20 °C	72.8	1.00
60 °C	66.2	0.47
100 °C	58.9	0.28

(a) As temperature increases, what happens to the surface tension of water? Explain why this occurs, in terms of molecular interactions and the effect of changing temperature.
(b) As temperature increases, what happens to the viscosity of water? Explain why this occurs, in terms of molecular interactions and the effect of changing temperature.

Solution

(a) As the water reaches higher temperatures, the increased kinetic energies of its molecules are more effective in overcoming hydrogen bonding, and so its surface tension decreases. Surface tension and intermolecular forces are directly related. (b) The same trend in viscosity is seen as in surface tension, and for the same reason.

28. At 25 °C, how high will water rise in a glass capillary tube with an inner diameter of 0.63 mm? Refer to Example 10.4 for the required information.

Solution

The liquid will rise to a height h given by: $h = \frac{2T\cos\theta}{r\rho g}$.

$$h = \frac{2(0.0799\ \text{kg/s}^2)}{(0.00063\ \text{m})(1000\ \text{kg/m}^2)(9.8\ \text{m/s}^2)} = 0.025\ \text{m} = 2.5\ \text{cm}$$

29. Water rises in a glass capillary tube to a height of 17 cm. What is the diameter of the capillary tube?

Solution

This time we will solve for r, as we are given h = 17 cm = 0.17 m.

$$0.17 \text{ m} = \frac{2(0.0799 \text{ kg/s}^2)}{r(1000 \text{ kg/m}^2)(9.8 \text{ m/s}^2)}$$

$$r = 9.5 \times 10^{-5} \text{ m}$$

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Chemistry: Atoms First 2e
10: Liquids and Solids
10.3: Phase Transitions

30. Heat is added to boiling water. Explain why the temperature of the boiling water does not change. What does change?

Solution

The heat increases the kinetic energy of a limited number of molecules in the liquid water so that they have enough energy to escape into the gas phase. The escape of these molecules requires the additional energy be used to overcome intermolecular attractive forces in the liquid, and so the temperature of the remaining liquid does not increase. The amount of liquid water changes (decreases) as the additional heat causes some to change to a gas.

31. Heat is added to ice at 0 °C. Explain why the temperature of the ice does not change. What does change?

Solution

The heat is absorbed by the ice, providing the energy required to partially overcome intermolecular attractive forces in the solid and causing a phase transition to liquid water. The solution remains at 0 °C until all the ice is melted. Only the amount of water existing as ice changes until the ice disappears. Then the temperature of the water can rise.

32. What feature characterizes the dynamic equilibrium between a liquid and its vapor in a closed container?

Solution

Molecules are continually exchanged between the liquid and the vapor. This exchange of position and energy maintains a constant vapor pressure and a constant temperature.

33. Identify two common observations indicating some liquids have sufficient vapor pressures to noticeably evaporate?

Solution

We can see the amount of liquid in an open container decrease and we can smell the vapor of some liquids.

34. Identify two common observations indicating some solids, such as dry ice and mothballs, have vapor pressures sufficient to sublime?

Solution

We can see solid ice disappear outside even when the temperature is below freezing and no liquid water is formed. The other substances disappear without forming the respective liquids, and an aroma can be detected for mothballs, attesting to the sublimation of the substance.

35. What is the relationship between the intermolecular forces in a liquid and its vapor pressure?

Solution

The vapor pressure of a liquid decreases as the strength of its intermolecular forces increases.

36. What is the relationship between the intermolecular forces in a solid and its melting temperature?

Solution
The melting point of a substance increases as the strength of its intermolecular increases.

37. Why does spilled gasoline evaporate more rapidly on a hot day than on a cold day?

Solution
As the temperature increases, the average kinetic energy of the molecules of gasoline increases and so a greater fraction of molecules have sufficient energy to escape from the liquid than at lower temperatures.

38. Carbon tetrachloride, CCl_4, was once used as a dry cleaning solvent, but is no longer used because it is carcinogenic. At 57.8 °C, the vapor pressure of CCl_4 is 54.0 kPa, and its enthalpy of vaporization is 33.05 kJ/mol. Use this information to estimate the normal boiling point for CCl_4.

Solution
Normal boiling point corresponds to pressure of 1 atm. Using Clausius Clapeyron equation,

$$\ln\left(\frac{P_1}{P_2}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

54 kPa = 0.53 atm

$$\ln\left(\frac{0.53\text{ atm}}{1\text{ atm}}\right) = \left(\frac{33050\text{ J/mol}}{8.31\text{ J/mol K}}\right)\left(\frac{1}{T_2} - \frac{1}{331.0\text{ K}}\right)$$

Solving for $\frac{1}{T_2} = 0.00286$ and so, $T_2 = 349$ K or, 76 °C

39. When is the boiling point of a liquid equal to its normal boiling point?

Solution
They are equal when the pressure of gas above the liquid is exactly 1 atm.

40. How does the boiling of a liquid differ from its evaporation?

Solution
At the boiling point, the vapor pressure of the liquid is the same as the atmospheric pressure. During evaporation, the vapor pressure of the liquid is less than atmospheric pressure. Evaporation is the term used to describe a relatively slow vaporization process that can occur at temperatures below the boiling point.

41. Use the information in Figure 10.24 to estimate the boiling point of water in Denver when the atmospheric pressure is 83.3 kPa.

Solution
Follow an imaginary horizontal line at 83.3 kPa to the curve representing the vapor pressure of water. Then drop a vertical line to the temperature axis. The intersection is at approximately 95 °C.

42. A syringe at a temperature of 20 °C is filled with liquid ether in such a way that there is no space for any vapor. If the temperature is kept constant and the plunger is withdrawn to create a volume that can be occupied by vapor, what would be the approximate pressure of the vapor produced?

Solution
(a) about 450 torr; ether boils at approximately 36 °C; at 20 °C, the vapor pressure will be relatively high

43. Explain the following observations:
(a) It takes longer to cook an egg in Ft. Davis, Texas (altitude, 5000 feet above sea level) than it does in Boston (at sea level).
(b) Perspiring is a mechanism for cooling the body.

Solution
(a) At 5000 feet, the atmospheric pressure is lower than at sea level, and water will therefore boil at a lower temperature. This lower temperature will cause the physical and chemical changes involved in cooking the egg to proceed more slowly, and a longer time is required to fully cook the egg. (b) As long as the air surrounding the body contains less water vapor than the maximum that air can hold at that temperature, perspiration will evaporate, thereby cooling the body by removing the heat of vaporization required to vaporize the water.

44. The enthalpy of vaporization of water is larger than its enthalpy of fusion. Explain why.

Solution
When water melts, the hydrogen bonding in the solid is only partially overcome to yield the liquid. When water evaporates, intermolecular attractions between its molecules must be completely overcome, requiring a greater amount of energy.

45. Explain why the molar enthalpies of vaporization of the following substances increase in the order $CH_4 < C_2H_6 < C_3H_8$, even though all three substances experience the same dispersion forces when in the liquid state.

Solution
Dispersion forces increase with molecular mass or size. As the number of atoms composing the molecules in this homologous series increases, so does the extent of intermolecular attraction via dispersion forces and, consequently, the energy required to overcome these forces and vaporize the liquids.

46. Explain why the enthalpies of vaporization of the following substances increase in the order $CH_4 < NH_3 < H_2O$, even though all three substances have approximately the same molar mass.

Solution
Methane, CH_4, is a nonpolar molecule and thus experiences only relatively weak dispersion forces in the liquid state. Ammonia and water are both polar molecules and, furthermore, are capable of hydrogen bonding. The greater IMFs associated with hydrogen bonding result in higher enthalpies of vaporization for these two substances. Because the electronegativity of O is greater than that for N, it is reasonable to predict that the O-H bond moments are greater than the N-H bond moments, and that hydrogen bonding is more extensive in water than in ammonia, supporting the reported trend in vaporization enthalpies.

47. The enthalpy of vaporization of $CO_2(l)$ is 9.8 kJ/mol. Would you expect the enthalpy of vaporization of $CS_2(l)$ to be 28 kJ/mol, 9.8 kJ/mol, or –8.4 kJ/mol? Discuss the plausibility of each of these answers.

Solution
The boiling point of CS_2 is higher than that of CO_2 partially because of the higher molecular weight of CS_2; consequently, the attractive forces are stronger in CS_2. It would be expected, therefore, that the heat of vaporization would be greater than that of 9.8 kJ/mol for CO_2. A value of 28 kJ/mol would seem reasonable. A value of –8.4 kJ/mol would indicate a release of energy upon vaporization, which is clearly implausible.

48. The hydrogen fluoride molecule, HF, is more polar than a water molecule, H_2O (for example, has a greater dipole moment), yet the molar enthalpy of vaporization for liquid hydrogen fluoride is lesser than that for water. Explain.

Solution
Each water molecule has two H atoms that may participate in hydrogen bonding with other water molecules, while a hydrogen fluoride molecule has only one. Less heat is therefore required to overcome hydrogen bonding in liquid HF than in liquid H_2O.

49. Ethyl chloride (boiling point, 13 °C) is used as a local anesthetic. When the liquid is sprayed on the skin, it cools the skin enough to freeze and numb it. Explain the cooling effect of liquid ethyl chloride.

Solution
The thermal energy (heat) needed to evaporate the liquid is removed from the skin.

50. Which contains the compounds listed correctly in order of increasing boiling points?
(a) $N_2 < CS_2 < H_2O < KCl$
(b) $H_2O < N_2 < CS_2 < KCl$
(c) $N_2 < KCl < CS_2 < H_2O$
(d) $CS_2 < N_2 < KCl < H_2O$
(e) $KCl < H_2O < CS_2 < N_2$

Solution
The trend in boiling points should follow the trend in forces holding the substances (atoms/molecules) together. KCl is an ionic compound, and so the ionic bonding (electrostatic attraction between the potassium cations and chloride anions) is expected to be far stronger than any intermolecular forces within the other covalent compounds. KCl is, therefore, expected to exhibit the greatest boiling point. Of the remaining compounds, only H_2O is polar (and, indeed, it exhibits strong hydrogen bonding), and so its IMFs are predicted to be greater than the other covalent compounds listed. Comparing the remaining nonpolar compounds, CS_2 molecules are larger/more massive than N_2 molecules, and so carbon disulfide will experience greater dispersion forces, and a greater boiling point.

51. How much heat is required to convert 422 g of liquid H_2O at 23.5 °C into steam at 150 °C?

Solution

$$422 \text{ g } H_2O \times \frac{1 \text{ mol}}{18.02 \text{ g } H_2O} = 23.4 \text{ mol } H_2O$$

Heat needed to bring this amount of water to the normal boiling point: $\Delta H_1 = mC_s\Delta T = (422 \text{ g})(4.184 \text{ J/g °C})(100.0 – 23.5) = 135{,}000 \text{ J}$
Heat needed to vaporize this amount of water: $\Delta H_2 = n\Delta H_{vap} = (23.4 \text{ mol})(40{,}650 \text{ J/mol}) = 951{,}000 \text{ J}$
Heat to needed to increase the temperature of the steam: $\Delta H_3 = mC_s\Delta T = (422 \text{ g})(1.86 \text{ J/g °C})(150 – 100) = 39{,}000 \text{ J}$.
Adding ΔH_1, ΔH_2, and ΔH_3: 135,000 J + 951,000 J + 39,000 J = 1,125,000 J = 1125 kJ.

52. Evaporation of sweat requires energy and thus take excess heat away from the body. Some of the water that you drink may eventually be converted into sweat and evaporate. If you drink a 20-ounce bottle of water that had been in the refrigerator at 3.8 °C, how much heat is needed to convert all of that water into sweat and then to vapor? (Note: Your body temperature is 36.6 °C. For the purpose of solving this problem, assume that the thermal properties of sweat are the same as for water.

Solution

$$20 \text{ oz } H_2O \times \frac{29.6 \text{ g}}{1 \text{ oz}} = 590 \text{ mL } H_2O$$

$590 \text{ mL } H_2O \times 1.00 \text{ g/mL} = 590 \text{ g } H_2O$

$590\ \text{g}\ H_2O \times \frac{1\ \text{mol}}{18.02\ \text{g}\ H_2O} = 32.7\ \text{mol}\ H_2O$ or 33 mol H_2O using the correct number of significant figures. The amount of heat needed to increase the temperature of water from 3.8 °C to 36.6 °C is $\Delta H_1 = mC_s\Delta T = (590\ \text{g})(4.184\ \text{J/g °C})(36.6 - 3.8) = 81{,}000$ J. Heat needed to vaporize this amount of water: $\Delta H_2 = n\Delta H_{vap} = (33\ \text{mol})(40{,}650\ \text{J/mol}) = 1{,}340{,}000$ J. The total heat required for the process is 81,000 J + 1,340,000 J = 1,420,000 J = 1420 kJ.

53. Titanium tetrachloride, $TiCl_4$, has a melting point of –23.2 °C and has a $\Delta H_{fusion} = 9.37$ kJ/mol.
(a) How much energy is required to melt 263.1 g $TiCl_4$?
(b) For $TiCl_4$, which will likely have the larger magnitude: ΔH_{fusion} or $\Delta H_{vaporization}$? Explain your reasoning.

Solution

(a) $263.1\ \text{g}\ TiCl_4 \times \frac{1\ \text{mol}}{189.9\ \text{g}} = 1.385\ \text{mol}\ TiCl_4$. Heat required to melt this amount of $TiCl_4$ is $n\Delta H_{fusion} = 1.385\ \text{mol} \times 9.37\ \text{kJ/mol} = 13.0\text{kJ}$. (b) It is likely that the heat of vaporization will have a larger magnitude since in the case of vaporization the intermolecular interactions have to be completely overcome, while melting weakens or destroys only some of them.

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Chemistry: Atoms First 2e
10: Liquids and Solids
10.4: Phase Diagrams

54. From the phase diagram for water (Figure 10.31), determine the state of water at:
(a) 35 °C and 85 kPa
(b) –15 °C and 40 kPa
(c) –15 °C and 0.1 kPa
(d) 75 °C and 3 kPa
(e) 40 °C and 0.1 kPa
(f) 60 °C and 50 kPa

Solution

(a) liquid; (b) solid; (c) gas; (d) gas; (e) gas; (f) liquid

55. What phase changes will take place when water is subjected to varying pressure at a constant temperature of 0.005 °C? At 40 °C? At –40 °C?

Solution

At low pressures and 0.005 °C, the water is a gas. As the pressure increases to 4.6 torr, the water becomes a solid; as the pressure increases still more, it becomes a liquid. At 40 °C, water at low pressure is a vapor; at pressures higher than about 75 torr, it converts into a liquid. At –40 °C, water goes from a gas to a solid as the pressure increases above very low values.

56. Pressure cookers allow food to cook faster because the higher pressure inside the pressure cooker increases the boiling temperature of water. A particular pressure cooker has a safety valve that is set to vent steam if the pressure exceeds 3.4 atm. What is the approximate maximum temperature that can be reached inside this pressure cooker? Explain your reasoning.

Solution
From looking at a phase diagram for water, the maximum temperature would be around 150 °C. Increased pressure from the pressure cooker allows water to boil at higher temperatures.

57. From the phase diagram for carbon dioxide in Figure 10.34, determine the state of CO_2 at:
(a) 20 °C and 1000 kPa
(b) 10 °C and 2000 kPa
(c) 10 °C and 100 kPa
(d) –40 °C and 500 kPa
(e) –80 °C and 1500 kPa
(f) –80 °C and 10 kPa

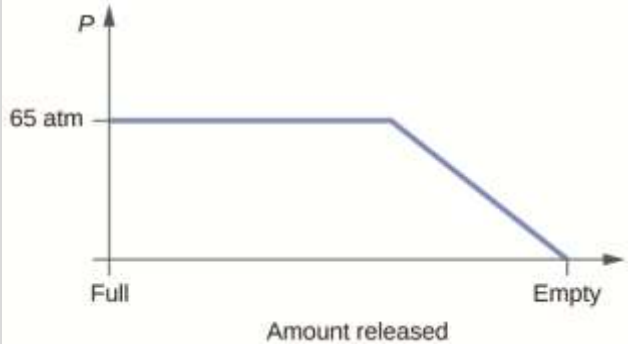
Solution
(a) gas; (b) gas; (c) gas; (d) gas; (e) solid; (f) gas

58. Determine the phase changes that carbon dioxide undergoes as pressure is increased at a constant temperature of (a) –50 °C and (b) 50 °C? (See the phase diagram in Figure 10.34.)

Solution
(a) At –50 °C and low pressures, carbon dioxide is gaseous. Increasing the pressure at this temperature will result in condensation (gas-to-liquid phase transition) at ~700 kPa and freezing (liquid-to-solid phase transition) at ~10,000 kPa.
(b) Since 50 °C is above the critical temperature for carbon dioxide (31 °C), increasing the pressure cannot cause condensation, but instead a transition to the supercritical fluid state occurs at ~7000 kPa.

59. Consider a cylinder containing a mixture of liquid carbon dioxide in equilibrium with gaseous carbon dioxide at an initial pressure of 65 atm and a temperature of 20 °C. Sketch a plot depicting the change in the cylinder pressure with time as gaseous carbon dioxide is released at constant temperature.

Solution
The carbon dioxide pressure will remain roughly constant at 65 atm (the equilibrium vapor pressure of CO_2 at 20 °C) as long as liquid CO_2 remains in the cylinder. The gas released from the cylinder will be replaced by vaporization of the liquid. When all the liquid has vaporized, the tank pressure will drop as the cylinder continues to release gas:



60. Dry ice, $CO_2(s)$, does not melt at atmospheric pressure. It sublimes at a temperature of –78 °C. What is the lowest pressure at which $CO_2(s)$ will melt to give $CO_2(l)$? At approximately what temperature will this occur? (See Figure 10.34 for the phase diagram.)

Solution
The lowest pressure at which a solid may melt is that corresponding to its triple point. Dry ice, $CO_2(s)$, will melt to give $CO_2(l)$ at ~500 kPa and –60°C.

61. If a severe storm results in the loss of electricity, it may be necessary to use a clothesline to dry laundry. In many parts of the country in the dead of winter, the clothes will quickly freeze when they are hung on the line. If it does not snow, will they dry anyway? Explain your answer.

Solution

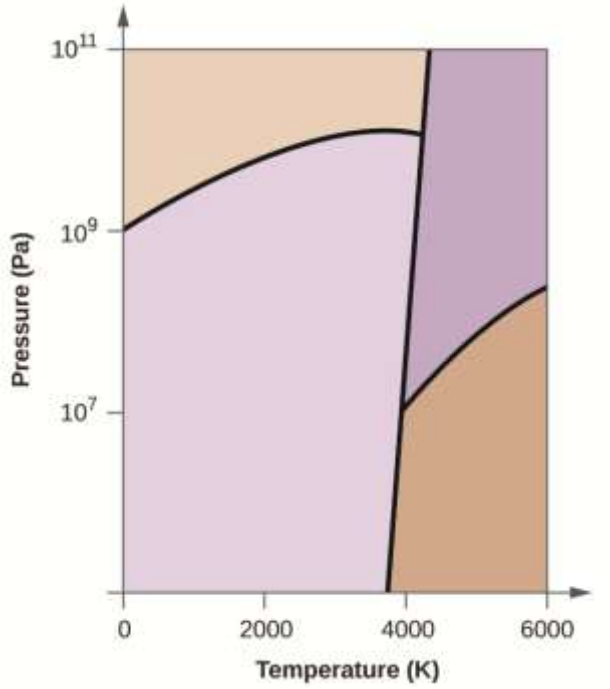
Yes, ice will sublime, although it may take it several days. Ice has a small vapor pressure, and some ice molecules form gas and escape from the ice crystals. As time passes, more and more solid converts to gas until eventually the clothes are dry.

62. Is it possible to liquefy nitrogen at room temperature (about 25 °C)? Is it possible to liquefy sulfur dioxide at room temperature? Explain your answers.

Solution

From Table 10.3, the critical temperature of nitrogen is 126.0 K. Since this value is below room temperature, nitrogen cannot be liquefied at room temperature. The critical temperature is 430.5 K for sulfur dioxide, which is above room temperature. It can be liquefied at room temperature.

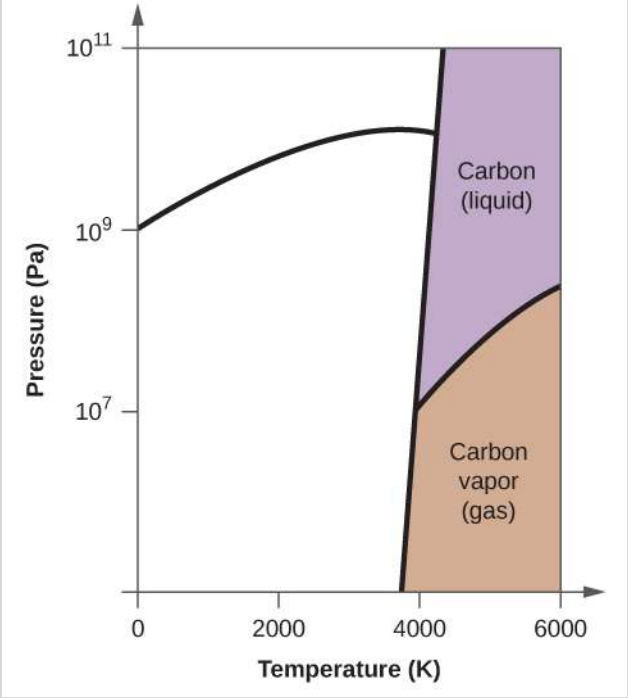
63. Elemental carbon has one gas phase, one liquid phase, and three different solid phases, as shown in the phase diagram:



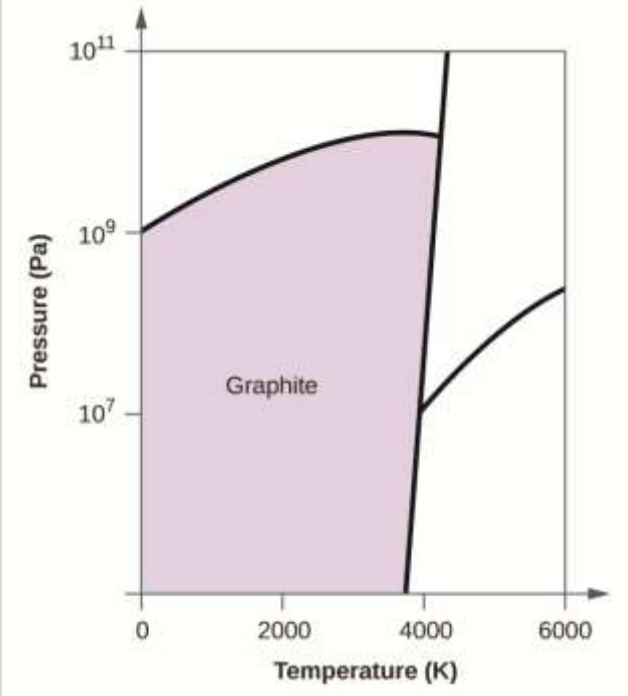
(a) On the phase diagram, label the gas and liquid regions.
(b) Graphite is the most stable phase of carbon at normal conditions. On the phase diagram, label the graphite phase.
(c) If graphite at normal conditions is heated to 2500 K while the pressure is increased to 10^{10} Pa, it is converted into diamond. Label the diamond phase.
(d) Circle each triple point on the phase diagram.
(e) In what phase does carbon exist at 5000 K and 10^{8} Pa?
(f) If the temperature of a sample of carbon increases from 3000 K to 5000 K at a constant pressure of 10^{6} Pa, which phase transition occurs, if any?

Solution

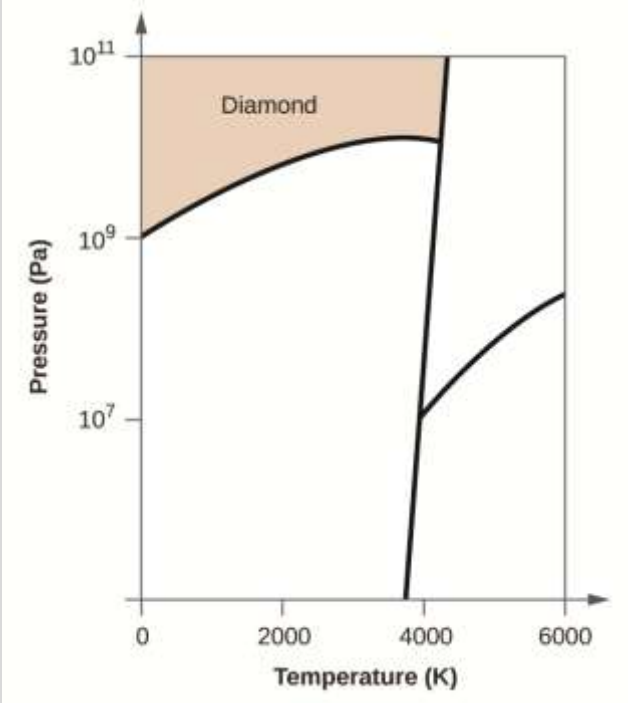
(a)


10^{11}
10^{9}
10^{7}
Pressure (Pa)
Carbon
(liquid)
Carbon
vapor
(gas)
0
2000
4000
6000
Temperature (K)

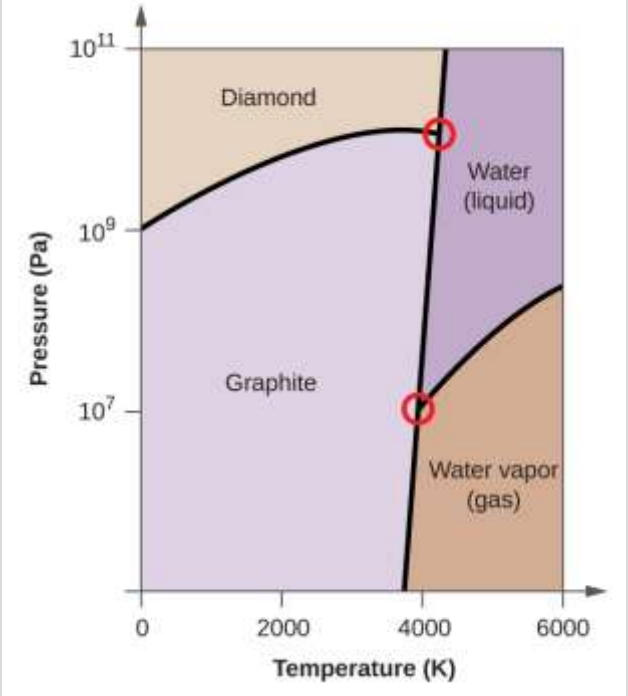
(b)


10^{11}
10^{9}
10^{7}
Pressure (Pa)
Graphite
0
2000
4000
6000
Temperature (K)

(c)



(d)



(e) Carbon exists in the liquid phase under these conditions. (f) The phase transition would be one of sublimation. Carbon would convert from graphite to vapor.

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Chemistry: Atoms First 2e
10: Liquids and Solids
10.5: The Solid State of Matter

64. What types of liquids typically form amorphous solids?

Solution
Amorphous solids lack an ordered internal structure. Liquid materials that contain large, cumbersome molecules that cannot move readily into ordered positions generally form such solids.

65. At very low temperatures oxygen, O_2, freezes and forms a crystalline solid. Which best describes these crystals?
(a) ionic
(b) covalent network
(c) metallic
(d) amorphous
(e) molecular crystals

Solution
(e) molecular crystals

66. As it cools, olive oil slowly solidifies and forms a solid over a range of temperatures. Which best describes the solid?
(a) ionic
(b) covalent network
(c) metallic
(d) amorphous
(e) molecular crystals

Solution
(d) amorphous

67. Explain why ice, which is a crystalline solid, has a melting temperature of 0 °C, whereas butter, which is an amorphous solid, softens over a range of temperatures.

Solution
Ice has a crystalline structure stabilized by hydrogen bonding. These intermolecular forces are of comparable strength and thus require the same amount of energy to overcome. As a result, ice melts at a single temperature and not over a range of temperatures. The various, very large molecules that compose butter experience varied van der Waals attractions of various strengths that are overcome at various temperatures, and so the melting process occurs over a wide temperature range.

68. Identify the type of crystalline solid (metallic, network covalent, ionic, or molecular) formed by each of the following substances:
(a) SiO_2
(b) KCl
(c) Cu
(d) CO_2
(e) C (diamond)
(f) $BaSO_4$
(g) NH_3
(h) NH_4F
(i) C_2H_5OH

Solution
(a) SiO_2, covalent network; (b) KCl, ionic; (c) Cu, metallic; (d) CO, molecular; (e) C (diamond), covalent network; (f) $BaSO_4$, ionic; (g) NH_3, molecular; (h) NH_4F, ionic; (i) C_2H_5OH, molecular

69. Identify the type of crystalline solid (metallic, network covalent, ionic, or molecular) formed by each of the following substances:
(a) $CaCl_2$
(b) SiC
(c) N_2
(d) Fe
(e) C (graphite)
(f) $CH_3CH_2CH_2CH_3$
(g) HCl
(h) NH_4NO_3
(i) K_3PO_4

Solution
(a) $CaCl_2$, ionic; (b) SiC, covalent network; (c) N_2, molecular; (d) Fe, metallic; (e) C (graphite), covalent network; (f) $CH_3CH_2CH_2CH_3$, molecular; (g) HCl, molecular; (h) NH_4NO_3, ionic; (i) K_3PO_4, ionic

70. Classify each substance in the table as either a metallic, ionic, molecular, or covalent network solid:

Substance	Appearance	Melting Point	Electrical Conductivity	Solubility in Water
X	lustrous, malleable	1500 °C	high	insoluble
Y	soft, yellow	113 °C	none	insoluble
Z	hard, white	800 °C	only if melted/dissolved	soluble

Solution
X = metallic; Y = covalent network; Z = ionic

71. Classify each substance in the table as either a metallic, ionic, molecular, or covalent network solid:

Substance	Appearance	Melting Point	Electrical Conductivity	Solubility in Water
X	brittle, white	800 °C	only if melted/dissolved	soluble
Y	shiny, malleable	1100 °C	high	insoluble
Z	hard, colorless	3550 °C	none	insoluble

Solution
X = ionic; Y = metallic; Z = covalent network

72. Identify the following substances as ionic, metallic, covalent network, or molecular solids: Substance A is malleable, ductile, conducts electricity well, and has a melting point of 1135 °C. Substance B is brittle, does not conduct electricity as a solid but does when molten, and has a melting point of 2072 °C. Substance C is very hard, does not conduct electricity, and has a melting point of 3440 °C. Substance D is soft, does not conduct electricity, and has a melting point of 185 °C.

Solution
A = metallic; B = ionic; C = covalent network; D = molecular

73. Substance A is shiny, conducts electricity well, and melts at 975 °C. Substance A is likely a(n):
(a) ionic solid
(b) metallic solid
(c) molecular solid
(d) covalent network solid

Solution
(b) metallic solid

74. Substance B is hard, does not conduct electricity, and melts at 1200 °C. Substance B is likely a(n):
(a) ionic solid
(b) metallic solid
(c) molecular solid
(d) covalent network solid

Solution
(d) covalent network solid

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Chemistry: Atoms First 2e
10: Liquids and Solids
10.6: Lattice Structures in Crystalline Solids

75. Describe the crystal structure of iron, which crystallizes with two equivalent metal atoms in a cubic unit cell.

Solution
The structure of this low-temperature form of iron (below 910 °C) is body-centered cubic. There is one-eighth atom at each of the eight corners of the cube and one atom in the center of the cube.

76. Describe the crystal structure of Pt, which crystallizes with four equivalent metal atoms in a cubic unit cell.

Solution
Each of the eight corners of a cube has $\frac{1}{8}$ Pt atom contributing to the cube. In addition, each of the six faces includes $\frac{1}{2}$ Pt atom. The total is $8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$. The structure is, therefore, is face-centered cubic, or cubic closest packed.

77. What is the coordination number of a chromium atom in the body-centered cubic structure of chromium?

Solution

Coordination number refers to the number of nearest neighbors. A chromium atom lies at the center of a body-centered cube and has eight nearest neighbors (at the corners of the cube): four in one plane above and four in one plane below. The coordination number, therefore, is eight.

78. What is the coordination number of an aluminum atom in the face-centered cubic structure of aluminum?

Solution

Face-centered cubic structures occur with cubic closest packing in which each atom touches 12 nearest neighbors: six in its own layer and three in each adjacent layer. The coordination number, therefore, is 12.

79. Cobalt metal crystallizes in a hexagonal closest packed structure. What is the coordination number of a cobalt atom?

Solution

Hexagonal closest packing occurs in such a way that each atom touches 12 nearest neighbors: six in its own layer and three in each adjacent layer. The coordination number is therefore 12.

80. Nickel metal crystallizes in a cubic closest packed structure. What is the coordination number of a nickel atom?

Solution

Cubic closest packed structures are packed with each atom touching 12 nearest neighbors: six in its own layer, and three in each adjacent layer. The coordination number, therefore, is 12.

81. Tungsten crystallizes in a body-centered cubic unit cell with an edge length of 3.165 Å.
(a) What is the atomic radius of tungsten in this structure?
(b) Calculate the density of tungsten.

Solution

(a) In a body-centered cubic unit cell, the metal atoms are in contact along the interior diagonal of the cube. The interior diagonal forms a right triangle with the unit cell edge and the diagonal of the face. Use the Pythagorean theorem to determine the length of the diagonal, d, on the face of the cube in terms of the edge, *e*. See the figure in Example 10.14:

$d^2 = e^2 + e^2 = 2e^2$

$d = \sqrt{2}\, e$

The interior diagonal of the cube is the length of four atomic radii and can be calculated again by using the Pythagorean theorem and the face diagonal and edge.

$(\text{diagonal})^2 = d^2 + e^2$

$= (\sqrt{2}\, e) + e^2$

$= 2e^2 + e^2$

$= 3e^2$

$\text{diagonal} = \sqrt{3}\, e = 4r$

$$\text{radius of tungsten} = \frac{\text{diagonal}}{4} = \frac{\sqrt{3}e}{4} = \frac{\sqrt{3}}{4}(3.165\ \text{Å}) = 1.370\ \text{Å};$$

(b) Given the body-centered cubic structure, each unit cell contains two atoms. Use the unit cell edge length to calculate the unit cell volume and the volume occupied by each atom. Multiply to obtain the molar volume and divide the atomic mass by this value to obtain density (e = edge length):

$V(\text{cell}) = e^3 = (3.165 \times 10^{-8}\ \text{cm})^3 = 3.170 \times 10^{-23}\ \text{cm}^3$

$$V(\text{atom}) = \frac{3.170 \times 10^{-23}\ \text{cm}^3}{2\ \text{atoms}} = 1.585 \times 10^{-23}\ \text{cm}^3\ \text{atom}^{-1}$$

$V(\text{mol}) = 1.585 \times 10^{-23}\ \text{cm}^3/\text{atom} \times 6.022 \times 10^{23}\ \text{atoms/mol}$
$= 9.546\ \text{cm}^3/\text{mol}$

$$\text{density} = \frac{183.85\ \text{g mol}^{-1}}{9.546\ \text{cm}^3\ \text{mol}^{-1}}$$

$= 19.26\ \text{g/cm}$

82. Platinum (atomic radius = 1.38 Å) crystallizes in a cubic closely packed structure. Calculate the edge length of the face-centered cubic unit cell and the density of platinum.

Solution

In a face-centered cube containing identical atoms or radius, *r*, the edge length it $2r\sqrt{2}$. For platinum, *r* =1.38 Å

edge length = $2(1.38)\sqrt{2} = 3.90$

The volume of a unit cell is:

$$V\ (\text{unit cell}) = \left(3.90\ \text{Å} \times \frac{10^{-8}\ \text{cm}}{\text{Å}}\right)^3 \text{Å}$$

$$= 5.93 \times 10^{-23}\ \text{cm}^3$$

One unit cell contains four atoms, so 1 mol of Pt contains:

$$\frac{6.022 \times 10^{23}\ \text{atoms}}{1\ \text{mol}} \times \frac{1\ \text{unit cell}}{4\ \text{atoms}} = 1.506 \times 10^{23}\ \text{unit cells mol}^{-1}$$

The mass of 1 mol of Pt is 195.09 g. The density is:

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{195.09\ \text{g mol}^{-1}}{(1.506 \times 10^{23}\ \text{cells mol}^{-1})\ (5.93 \times 10^{-23}\ \text{cm}^3)} = 21.8\ \text{g cm}^{-3}$$

83. Barium crystallizes in a body-centered cubic unit cell with an edge length of 5.025 Å
(a) What is the atomic radius of barium in this structure?
(b) Calculate the density of barium.

Solution

(a) In a body-centered cubic unit cell, the metal atoms are in contact along the diagonal of the cube. The diagonal of the cube forms a right triangle with the unit cell edge and the diagonal of a face. Use the Pythagorean theorem to determine the length of the diagonal, d, on the face of the cube in terms of e.

$d^2 = e^2 + e^2 = 2e^2$

$d = \sqrt{2}\ e$

The diagonal of the cube is the length of four atomic radii and can be calculated by again using the Pythagorean theorem:

$(\text{diagonal})^2 = (4r)^2 = (2e)^2 + e^2 = 16r^2 = 3e^2$

$\text{diagonal} = 4r = \sqrt{3e}$

$$r = \frac{\sqrt{3}}{4}e = \frac{\sqrt{3}}{4}(5.025\ \text{Å}) = 2.176\ \text{Å};$$

(b) Given a body-centered cubic structure, each unit cell contains two atoms. Use the unit cell edge length to calculate the unit cell volume and the volume occupied by each atom. Multiply to obtain the molar volume and divide the gram atomic weight by this value to obtain density (e = edge length):

$V\ (\text{cell}) = e^3 = (5.025 \times 10^{-8}\ \text{cm})^3 = 1.26884 \times 10^{-22}\ \text{cm}^3$

$V\text{ (atom)} = 1.26884 \times \dfrac{10^{-22}\text{ cm}^3\text{ atom}^{-1}}{2\text{ atoms}} = 6.3442 \times 10^{-23}\text{ cm}^3$

$V\text{ (mole)} = 6.3442 \times 10^{-23}\text{ cm}^3 \times 6.022 \times 10^{23}\text{ atoms/mol} = 38.205\text{ cm}^3$

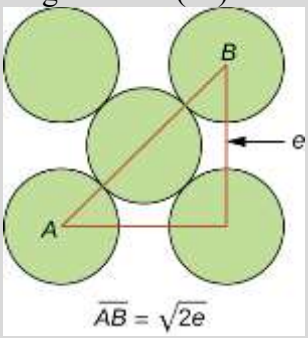
$d(\text{Ba}) = \dfrac{137.33\text{ g}}{38.204\text{ cm}^3} = 3.595\text{ g/cm}^3$

84. Aluminum (atomic radius = 1.43 Å) crystallizes in a cubic closely packed structure. Calculate the edge length of the face-centered cubic unit cell and the density of aluminum.

Solution

Aluminum atoms are in contact along the diagonal of the cube face:

diagonal = 4*r*(Al):



The diagonal $\overline{AB}$ or d is given by 4*r* or 4 × 1.43Å. The edge length is found from the Pythagorean theorem where $d = \sqrt{2}e$.

$e = \dfrac{d}{\sqrt{2}} = \dfrac{5.72\text{ Å}}{\sqrt{2}} = 4.05\text{ Å}$

$V(\text{cell}) = e^3 = (4.05 \times 10^{-8}\text{ cm})^3 = 6.643 \times 10^{-23}\text{ cm}^3$

$V(\text{mol}) = 6.643 \times 10^{-23}\dfrac{\text{cm}^3}{\text{cell}} \times \dfrac{1\text{ cell}}{4\text{ atoms}} \times 6.022 \times 10^{23}\dfrac{\text{atoms}}{\text{mol}}$

$= 10.001\text{ cm}^3/\text{mol}$

$d(\text{Al}) = 26.9815\dfrac{\text{g}}{\text{mol}} \times \dfrac{1\text{ mol}}{10.001\text{ cm}^3} = 2.70\text{ g cm}^{-3}$

85. The density of aluminum is 2.7 g/cm^3; that of silicon is 2.3 g/cm^3. Explain why Si has the lower density even though it has heavier atoms.

Solution

The crystal structure of Si shows that it is less tightly packed (coordination number 4) in the solid than Al (coordination number 12).

86. The free space in a metal may be found by subtracting the volume of the atoms in a unit cell from the volume of the cell. Calculate the percentage of free space in each of the three cubic lattices if all atoms in each are of equal size and touch their nearest neighbors. Which of these structures represents the most efficient packing? That is, which packs with the least amount of unused space?

Solution

A simple cubic crystal lattice of side 2*r* contains one atom of radius *r*:

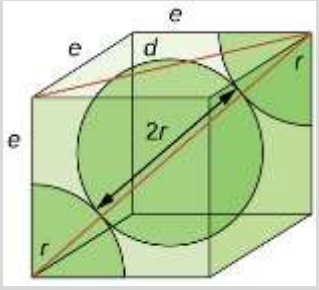
free space = volume of cube – volume of atom

$= (2r)^3 - \dfrac{4}{3}\pi r^3$

$= 8r^3 - 4.1888\ r^3$
$= 3.8112\ r^3$

percent free space = $\frac{3.8112r^3}{8r^3} \times 100 = 47.64\%$

A body-centered cube contains two atoms of radius *r* in the unit cell. The length of the edge of the cube is calculated using the Pythagorean theorem:

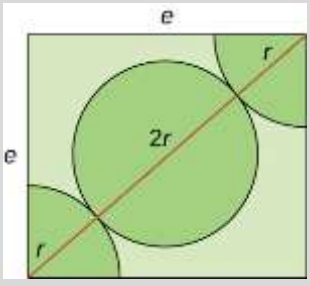


The diagonal of the cube is 4*r*.
$(4r)^2 = d^2 + e^2$
but $d^2 = e^2 + e^2$
so $(4r)^2 = 3e^2$
$e = 4r/\sqrt{3}$ (length of edge)

free space = $(4r/\sqrt{3})^3 - 2\left(\frac{4}{3}\pi r^3\right)$
$= 12.3168r^3 - 8.3776r^3$
$= 3.9392r^3$

percent free space = $\frac{3.9392r^3}{12.3168r^3} \times 100 = 31.98\%$

A face-centered cube contains four atoms of radius *r* in the unit cell. The length of the edge of the cube is calculated using the Pythagorean theorem:
$(4r)^2 = e^2 + e^2 = 2e^2$
$e = 2r\sqrt{2}$:



free space = $(2r\sqrt{2})^3 - 4\left(\frac{4}{3}\pi r^3\right)$
$= 22.624r^3 - 16.7552r^3$
$= 5.8722r^3$

percent free space = $\frac{5.8722r^3}{22.6274r^3} \times 100 = 25.95\%$

The face-centered cube has the least amount of unused space.

87. Cadmium sulfide, sometimes used as a yellow pigment by artists, crystallizes with cadmium, occupying one-half of the tetrahedral holes in a closest packed array of sulfide ions. What is the formula of cadmium sulfide? Explain your answer.

Solution
In a closest-packed array, two tetrahedral holes exist for each anion. If only half the tetrahedral holes are occupied, the numbers of anions and cations are equal. The formula for cadmium sulfide is CdS.

88. A compound of cadmium, tin, and phosphorus is used in the fabrication of some semiconductors. It crystallizes with cadmium occupying one-fourth of the tetrahedral holes and tin occupying one-fourth of the tetrahedral holes in a closest packed array of phosphide ions. What is the formula of the compound? Explain your answer.

Solution
In a closest-packed array, two tetrahedral holes exist for each anion. If only half the tetrahedral holes are occupied, the numbers of anions and cations are equal. When one-fourth of the holes are occupied, there is one cation for two phosphide ions. Therefore, there is one cadmium and one tin for every two phosphide ions. The formula for the compound is $CdSnP_2$.

89. What is the formula of the magnetic oxide of cobalt, used in recording tapes, that crystallizes with cobalt atoms occupying one-eighth of the tetrahedral holes and one-half of the octahedral holes in a closely packed array of oxide ions?

Solution
In a closest-packed array of oxide ions, one octahedral hole and two tetrahedral holes exist for each oxide ion. If one-half of the octahedral holes are filled, there is one Co ion for every two oxide ions. If one-eighth of the tetrahedral holes are filled, there is one Co ion for each four oxide ions. For every four oxide ions, there are two Co ions in octahedral holes and one Co in a tetrahedral hole; thus the formula is Co_3O_4.

90. A compound containing zinc, aluminum, and sulfur crystallizes with a closest-packed array of sulfide ions. Zinc ions are found in one-eighth of the tetrahedral holes and aluminum ions in one-half of the octahedral holes. What is the empirical formula of the compound?

Solution
The ratio of Zn:Al:S is determined from the ratio of holes to the sulfur anions. In this case, two tetrahedral:one octahedral: 1 S. Given the filling order $\frac{1}{8}:\frac{1}{2}:1$, the empirical formula is

$$\mathrm{Zn}\frac{1}{8}\times 2:\mathrm{Al}\frac{1}{2}\times 1:\mathrm{S};\ \text{or}\ \mathrm{Zn}\frac{1}{4}:\mathrm{Al}\frac{1}{2}:\mathrm{S}$$

After multiplying through by 4, the equation is $ZnAl_2S_4$

91. A compound of thallium and iodine crystallizes in a simple cubic array of iodide ions with thallium ions in all of the cubic holes. What is the formula of this iodide? Explain your answer.

Solution
In a simple cubic array, only one cubic hole can be occupied be a cation for each anion in the array. The ratio of thallium to iodide must be 1:1; therefore, the formula for thallium is TlI.

92. Which of the following elements reacts with sulfur to form a solid in which the sulfur atoms form a closest-packed array with all of the octahedral holes occupied: Li, Na, Be, Ca, or Al?

Solution
There is one octahedral hole for each anion in a closest-packed array. If all of the octahedral holes are occupied, the substance contains one sulfur ion for each other ion. Only the elements

Be and Ca are expected to form a compound with the formula ES, where E is a doubly charged cation and S is the anion. The radius ratios are:
Be^{2+}: r^+/r^- = 0.31/1.84 = 0.17
Ca^{2+}: r^+/r^- = 0.99/1.84 = 0.54
Only Ca^{2+} has a ratio within the 0.414 to 0.732 range expected for a coordination number of six. The answer is Ca.

93. What is the percent by mass of titanium in rutile, a mineral that contains titanium and oxygen, if structure can be described as a closest packed array of oxide ions with titanium ions in one-half of the octahedral holes? What is the oxidation number of titanium?

Solution
The ration of octahedral holes to oxygen anions is 1:1 in a closest-packed array. Only one-half of the octahedral holes are occupied. Thus, the titanium to oxygen ratio is 1:2 and the formula is TiO_2. The percentage by mass of Ti in the structure is:

$$\text{percent Ti} = \frac{47.90}{47.90 + 2(15.9994)} \times 100\% = 59.95\%$$

The oxidation number of titanium is +4 because there are two O^{2-} ions for each Ti ion.

94. Explain why the chemically similar alkali metal chlorides NaCl and CsCl have different structures, whereas the chemically different NaCl and MnS have the same structure.

Solution
Structures are determined from charge and size and are not directly related to chemical similarity. In this case, the r^+/r^- value for CsCl is sufficiently greater than that of NaCl so that a different structure is required.

95. As minerals were formed from the molten magma, different ions occupied the same cites in the crystals. Lithium often occurs along with magnesium in minerals despite the difference in the charge on their ions. Suggest an explanation.

Solution
Both ions are close in size: Mg, 0.65; Li, 0.60. This similarity allows the two to interchange rather easily. The difference in charge is generally compensated by the switch of Si^{4+} for Al^{3+}.

96. Rubidium iodide crystallizes with a cubic unit cell that contains iodide ions at the corners and a rubidium ion in the center. What is the formula of the compound?

Solution
Because an iodide ion is located at each corner, the unit cell contains one-eighth of each of the eight anions, or one iodide ion. Because one rubidium ion appears at the center of the cell, the ratio of ions contained in the cell is 1:1. The formula is RbI.

97. One of the various manganese oxides crystallizes with a cubic unit cell that contains manganese ions at the corners and in the center. Oxide ions are located at the center of each edge of the unit cell. What is the formula of the compound?

Solution
The total number of Mn ions is determined by adding the contributions from the corners and center. Mn (corners): $8 \times \frac{1}{8}$; Mn (center) = 1. Total Mn contribution to the unit cell = 2.
For O, there are a total of 12 edges in the cube and each ion in the edge contributes one-fourth to the unit cell. Consequently, there are $12 \times \frac{1}{4} = 3$ O atoms. The ratio is Mn:O = 2:3, and the formula is Mn_2O_3.

98. NaH crystallizes with the same crystal structure as NaCl. The edge length of the cubic unit cell of NaH is 4.880 Å.
(a) Calculate the ionic radius of H^-. (The ionic radius of Li^+ is 0.0.95 Å.)
(b) Calculate the density of NaH.

Solution
(a) Assume a face-centered arrangement with the hydride ions in contact along the diagonal face. Sodium ions fill the space along the edge, giving an edge length of $2r_{Na^+} + 2r_{H^-}$. The radius of the hydride is computed from the edge length and the reported radius of Na^+:

$$e = 4.880\ \text{Å} = 2(0.95\ \text{Å}) + 2r_{H^-}$$

$$r_{H^-} = \frac{4.880\ \text{Å} - 1.90\ \text{Å}}{2} = 1.49\ \text{Å};$$

(b) To find the density of NaH, consider that the system is face-centered cubic; there are four NaH units per cell.

V (cell) = $(4.880 \times 10^{-8}\ \text{cm})^3 = 1.162 \times 10^{-22}\ \text{cm}^3$

$$V\ (\text{NaH unit cell}) = \frac{1.162 \times 10^{-22}\ \text{cm}^3}{4} = 2.905 \times 10^{-23}\ \text{cm}^3$$

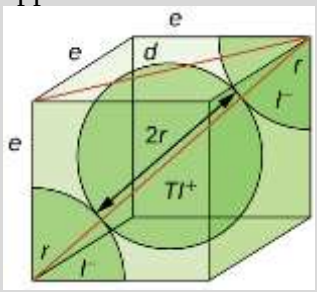
V (mol) = $2.905 \times 10^{-23}\ \text{cm}^3 \times 6.022 \times 10^{23}$ units/mol = $17.496\ \text{cm}^3/\text{mol}$

The formula weight of NaH is 24.00 g/mol.

$$d(\text{NaH}) = \frac{24.00\ \text{g mol}^{-1}}{17.496\ \text{cm}^3\ \text{mol}^{-1}} = 1.372\ \text{g cm}^{-3}$$

99. At temperatures above ~175 °C, thallium(I) iodide crystallizes with the same structure as CsCl. The edge length of the unit cell of TlI is 4.20 Å. Assuming contact between the body-centered Tl^+ ion and the cube-corner I^- ions of a unit cell, calculate the ionic radius of TI^+. (The ionic radius of I^- is 2.16 Å.)

Solution
Though the TlI unit cell is not truly a BCC structure (the body-centered and corner atoms/ions are not identical), the geometry of this structure is appropriate here and may be used to calculate approximate values for ionic radii.



The diagonal of the cube is $2r_{I^-} + 2r_{Tl^+}$. The Pythagorean theorem gives

$(2r_{I^-} + 2r_{Tl^+})^2 = d^2 + e^2$.

Since $d^2 = e^2 + e^2$,

$(2r_{I^-} + 2r_{Tl^+})^2 = 3e^2$

$2r_{I^-} + 2r_{Tl^+} = \sqrt{3e}$

Substituting the provided cell edge length and I^- radius values yields:

$$(2)(2.16\,\text{Å}) + 2r_{Tl+} = \sqrt{3}(4.20\,\text{Å})$$

$$r_{Tl+} = \frac{\sqrt{3}(4.20\ \text{Å}) - 2(2.16)\,\text{Å}}{2} = 1.48\,\text{Å}$$

100. A cubic unit cell contains manganese ions at the corners and fluoride ions at the center of each edge.
(a) What is the empirical formula of this compound? Explain your answer.
(b) What is the coordination number of the Mn^{3+} ion?
(c) Calculate the edge length of the unit cell if the radius of a Mn^{3+} ion is 0.65 A.
(d) Calculate the density of the compound.

Solution

(a) Mn (corners) $8 \times \frac{1}{8} = 1$

F (edges) $12 \times \frac{1}{4} = 3$

The formula is MnF_3.

(b) There are six edges radiating from each Mn^{3+}. Each edge contains a nearest-neighbor F^- ion, so the coordination number of the Mn^{3+} ion is 6.

(c) The edge length is:

$$\begin{aligned} r_{Mn} + 2r_F + r_{Mn} &= 2(r_{Mn} + r_F) \\ &= 2(0.65 + 1.36) \\ &= 4.02\ \text{Å} \end{aligned}$$

(d) Each unit cell contains one Mn^{3+} ion, so 1 mol of MnF_3 contains 6.022×10^{23} unit cells:

$$V\,(\text{unit cell}) = \left(4.02\ \text{Å} \times \frac{10^{-8}\ \text{cm}}{1\ \text{Å}}\right)^3$$

$= 6.50 \times 10^{-23}\ \text{cm}^3/\text{cell}$

The mass of 1 mol of MnF_3 is 111.9375 g/mol.

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{111.9375\ \text{g mol}^{-1}}{(6.022 \times 10^{23}\ \text{cell mol}^{-1})\left(\frac{6.50 \times 10^{-23}\ \text{cm}^3}{\text{cell}}\right)}$$

$$= 2.68\ \text{g cm}^{-3}$$

101. What is the spacing between crystal planes that diffract X-rays with a wavelength of 1.541 Å at an angle θ of 15.55° (first order diffraction)?

Solution

The Bragg equation is:

$n\lambda = 2d \sin\theta$

where d is the spacing between planes.

$$d = \frac{n\lambda}{2 \sin\theta} = \frac{1\,(1.541\text{Å})}{2 \sin 15.55°} = \frac{1.541\text{Å}}{2(0.2681)}$$

$= 2.874$ Å

102. A diffractometer using X-rays with a wavelength of 0.2287 nm produced first order diffraction peak for a crystal angle $\theta = 16.21°$. Determine the spacing between the diffracting planes in this crystal.

Solution

$$d = \frac{n\lambda}{2\sin\theta} = \frac{(1)(0.2287\text{ nm})}{(2)(\sin 16.21)} = 0.41\text{ nm}$$

103. A metal with spacing between planes equal to 0.4164 nm diffracts X-rays with a wavelength of 0.2879 nm. What is the diffraction angle for the first order diffraction peak?

Solution

$$\sin\theta = \frac{n\lambda}{2d} = \frac{(1)(0.2879\text{ nm})}{(2)(0.4164)} = 0.3457\text{, so } \theta = \sin^{-1}(0.3457) = 20.2°$$

104. Gold crystallizes in a face-centered cubic unit cell. The second-order reflection (n = 2) of X-rays for the planes that make up the tops and bottoms of the unit cells is at $\theta = 22.20°$. The wavelength of the X-rays is 1.54 Å. What is the density of metallic gold?

Solution

The unit cell edge is d (from the Bragg equation), the spacing between planes. Calculate d and use it to compute unit cell volumes. Given that the face-centered cell contains four atoms, calculate the molar volume and then the density.

$$\text{e} = d = \frac{n\lambda}{2\sin\theta} = \frac{2(1.54 \times 10^{-8}\text{ cm})}{2\sin 22.20°} = 4.0758 \times 10^{-8}\text{ cm}$$

$$V\text{ (cell)} = (4.0758 \times 10^{-8}\text{ cm})^3 = 6.7707 \times 10^{-23}\text{ cm}$$

$$V\text{ (atom)} = \frac{V\text{(cell)}}{4} = 1.6927 \times 10^{-23}\text{ cm}^3$$

$$V\text{ (mol)} = \frac{1.692710^{-23}\text{ cm}^3}{\text{atom}} \times 6.022 \times 10^{23}\text{ atom/mol}$$

$$= 10.1933\text{ cm}^3\text{ mol}^{-1}$$

$$\text{density (Au)} = \frac{196.9665\text{ g}}{10.1933\text{ cm}^3} = 19.3\text{ g cm}^{-3}$$

105. When an electron in an excited molybdenum atom falls from the L to the K shell, an X-ray is emitted. These X-rays are diffracted at an angle of 7.75° by planes with a separation of 2.64 Å. What is the difference in energy between the K shell and the L shell in molybdenum assuming a first order diffraction?

Solution

Use the Bragg equation, where $n = 1$,

$$\lambda = 2d\sin\theta = 2(2.64\text{ Å})\sin 7.75 = 0.712\text{ Å}$$

Then

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34}\text{ J s})(2.998 \times 10^{8}\text{ m s}^{-1})}{0.712 \times 10^{-10}\text{ m}}$$

$$= 2.79 \times 10^{-15}\text{ J} = 1.74 \times 10^{4}\text{ eV}$$

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Chemistry: Atoms First 2e
11: Solutions and Colloids
11.1: The Dissolution Process

1. How do solutions differ from compounds? From other mixtures?

Solution
A solution can vary in composition, while a compound cannot vary in composition. Solutions are homogeneous at the molecular level, while other mixtures are heterogeneous.

2. Which of the principal characteristics of solutions are evident in the solutions of $K_2Cr_2O_7$ shown in Figure 11.2?

Solution
The solutions are the same throughout (the color is constant throughout), and the composition of a solution of $K_2Cr_2O_7$ in water can vary.

3. When KNO_3 is dissolved in water, the resulting solution is significantly colder than the water was originally.
(a) Is the dissolution of KNO_3 an endothermic or an exothermic process?
(b) What conclusions can you draw about the intermolecular attractions involved in the process?
(c) Is the resulting solution an ideal solution?

Solution
(a) The process is endothermic as the solution is consuming heat. (b) Attraction between the K^+ and NO_3^- ions is stronger than between the ions and water molecules (the ion-ion interactions have a lower, more negative energy). Therefore, the dissolution process increases the energy of the molecular interactions, and it consumes the thermal energy of the solution to make up for the difference. (c) No, an ideal solution is formed with no appreciable heat release or consumption.

4. Give an example of each of the following types of solutions:
(a) a gas in a liquid
(b) a gas in a gas
(c) a solid in a solid

Solution
(a) CO_2 in water; (b) O_2 in N_2 (air); (c) bronze (solution of tin or other metals in copper)

5. Indicate the most important types of intermolecular attractions in each of the following solutions:
(a) The solution in Figure 11.2
(b) NO(g) in CO(l)
(c) Cl_2(g) in Br_2(l)
(d) HCl(g) in benzene C_6H_6(l)
(e) Methanol CH_3OH(l) in H_2O(l)

Solution
(a) ion-dipole forces; (b) dipole-dipole forces; (c) dispersion forces; (d) dispersion forces; (e) hydrogen bonding

6. Predict whether each of the following substances would be more soluble in water (polar solvent) or in a hydrocarbon such as heptane (C_7H_{16}, nonpolar solvent):
(a) vegetable oil (nonpolar)
(b) isopropyl alcohol (polar)
(c) potassium bromide (ionic)

Solution
(a) heptane; (b) water; (c) water

7. Heat is released when some solutions form; heat is absorbed when other solutions form. Provide a molecular explanation for the difference between these two types of spontaneous processes.

Solution

Heat is released when the total intermolecular forces (IMFs) between the solute and solvent molecules are stronger than the total IMFs in the pure solute and in the pure solvent: Breaking weaker IMFs and forming stronger IMFs releases heat. Heat is absorbed when the total IMFs in the solution are weaker than the total of those in the pure solute and in the pure solvent: Breaking stronger IMFs and forming weaker IMFs absorbs heat.

8. Solutions of hydrogen in palladium may be formed by exposing Pd metal to H_2 gas. The concentration of hydrogen in the palladium depends on the pressure of H_2 gas applied, but in a more complex fashion than can be described by Henry's law. Under certain conditions, 0.94 g of hydrogen gas is dissolved in 215 g of palladium metal (solution density = 10.8 g/cm^3).
(a) Determine the molarity of this solution.
(b) Determine the molality of this solution.
(c) Determine the percent by mass of hydrogen atoms in this solution.

Solution

(a) $\text{mol H} = \dfrac{0.94\ \text{g}}{1.00794\ \text{g mol}^{-1}} = 0.9326\ \text{mol}$

$\text{liters of solution} = \dfrac{(215 + 0.94)\ \text{g}}{10.8\ \text{g cm}^{-3}} = \dfrac{215.94}{10.8\ \text{cm}^{-3}} = 20\ \text{cm}^3$

$M = \dfrac{0.9326\ \text{mol}}{0.020\ \text{L}} = 47\ M$

(b) $m = \dfrac{0.9326\ \text{mol}}{0.215\ \text{kg}} = 4.3\ m$

(c) $\%\text{H} = \dfrac{0.94\ \text{g}}{(215 + 0.94)\ \text{g}} \times 100 = 0.44\%$

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Chemistry: Atoms First 2e
11: Solutions and Colloids
11.2: Electrolytes

9. Explain why the ions Na^+ and Cl^- are strongly solvated in water but not in hexane, a solvent composed of nonpolar molecules.

Solution

Crystals of NaCl dissolve in water, a polar liquid with a very large dipole moment, and the individual ions become strongly solvated. Hexane is a nonpolar liquid with a dipole moment of zero and, therefore, does not significantly interact with the ions of the NaCl crystals.

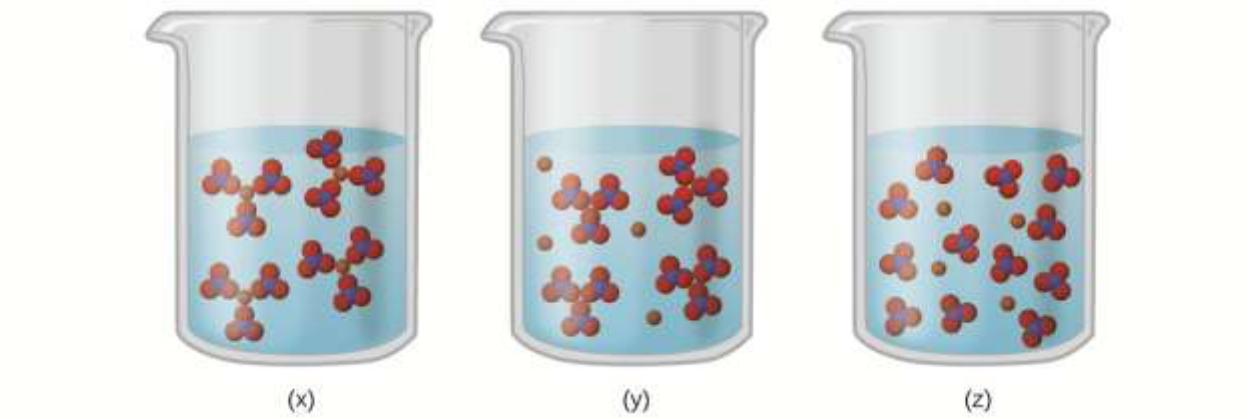
10. Explain why solutions of HBr in benzene (a nonpolar solvent) are nonconductive, while solutions in water (a polar solvent) are conductive.

Solution

HBr is an acid and so its molecules react with water molecules to form H_3O^+ and Br^- ions that provide conductivity to the solution. Though HBr is soluble in benzene, it does not react chemically but remains dissolved as neutral HBr molecules. With no ions present in the benzene solution, it is electrically nonconductive.

11. Consider the solutions presented:

(a) Which of the following sketches best represents the ions in a solution of $Fe(NO_3)_3(aq)$?



(b) Write a balanced chemical equation showing the products of the dissolution of $Fe(NO_3)_3$.

Solution

(a) $Fe(NO_3)_3$ is a strong electrolyte, thus it should completely dissociate into Fe^{3+} and NO_3^- ions. Therefore, (z) best represents the solution. (b)

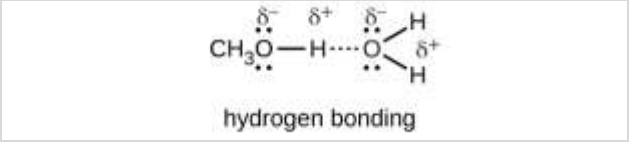
$$Fe(NO_3)_3(s) \longrightarrow Fe^{3+}(aq) + 3NO_3^-(aq)$$

12. Compare the processes that occur when methanol (CH_3OH), hydrogen chloride (HCl), and sodium hydroxide (NaOH) dissolve in water. Write equations and prepare sketches showing the form in which each of these compounds is present in its respective solution.

Solution

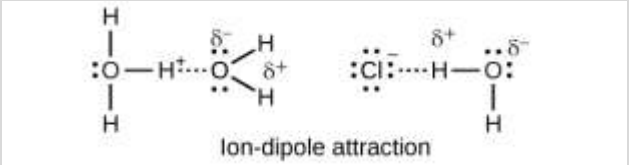
Methanol, CH_3OH, dissolves in water in all proportions, interacting via hydrogen bonding.

Methanol: $CH_3OH(l) + H_2O(l) \longrightarrow CH_3OH(aq)$



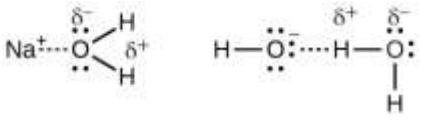
Hydrogen chloride, HCl, dissolves in and reacts with water to yield hydronium cations and chloride anions that are solvated by strong ion-dipole interactions.

Hydrogen chloride: $HCl(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$



Sodium hydroxide, NaOH, dissolves in water and dissociates to yield sodium cations and hydroxide anions that are strongly solvated by ion-dipole interactions and hydrogen bonding, respectively.

Sodium hydroxide: $NaOH(s) \longrightarrow Na^+(aq) + OH^-(aq)$



13. What is the expected electrical conductivity of the following solutions?
(a) NaOH(*aq*)
(b) HCl(*aq*)
(c) $C_6H_{12}O_6$(*aq*) (glucose)
(d) NH_3(*aq*)

Solution
(a) high conductivity (solute is an ionic compound that will dissociate when dissolved); (b) high conductivity (solute is a strong acid and will ionize completely when dissolved); (c) nonconductive (solute is a covalent compound, neither acid nor base, unreactive towards water); (d) low conductivity (solute is a weak base and will partially ionize when dissolved)

14. Why are most *solid* ionic compounds electrically nonconductive, whereas aqueous solutions of ionic compounds are good conductors? Would you expect a *liquid* (molten) ionic compound to be electrically conductive or nonconductive? Explain.

Solution
A medium must contain freely mobile, charged entities to be electrically conductive. The ions present in a typical ionic solid are immobilized in a crystalline lattice and so the solid is not able to support an electrical current. When the ions are mobilized, either by melting the solid or dissolving it in water to dissociate the ions, current may flow and these forms of the ionic compound are conductive.

15. Indicate the most important type of intermolecular attraction responsible for solvation in each of the following solutions:
(a) the solutions in Figure 11.7
(b) methanol, CH_3OH, dissolved in ethanol, C_2H_5OH
(c) methane, CH_4, dissolved in benzene, C_6H_6
(d) the polar halocarbon CF_2Cl_2 dissolved in the polar halocarbon $CF_2ClCFCl_2$
(e) O_2(*l*) in N_2(*l*)

Solution
(a) ion-dipole; (b) hydrogen bonds; (c) dispersion forces; (d) dipole-dipole attractions; (e) dispersion forces

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Chemistry: Atoms First 2e
11: Solutions and Colloids
11.3: Solubility

16. Suppose you are presented with a clear solution of sodium thiosulfate, $Na_2S_2O_3$. How could you determine whether the solution is unsaturated, saturated, or supersaturated?

Solution

Add a small crystal of $Na_2S_2O_3$. It will dissolve in an unsaturated solution, remain apparently unchanged in a saturated solution, or initiate precipitation in a supersaturated solution.

17. Supersaturated solutions of most solids in water are prepared by cooling saturated solutions. Supersaturated solutions of most gases in water are prepared by heating saturated solutions. Explain the reasons for the difference in the two procedures.

Solution

The solubility of solids usually decreases upon cooling a solution, while the solubility of gases usually decreases upon heating.

18. Suggest an explanation for the observations that ethanol, C_2H_5OH, is completely miscible with water and that ethanethiol, C_2H_5SH, is soluble only to the extent of 1.5 g per 100 mL of water.

Solution

The hydrogen bonds between water and C_2H_5OH are much stronger than the intermolecular attractions between water and C_2H_5SH.

19. Calculate the percent by mass of KBr in a saturated solution of KBr in water at 10 °C. See Figure 11.16 for useful data, and report the computed percentage to one significant digit.

Solution

At 10 °C, the solubility of KBr in water is approximately 60 g per 100 g of water.

$$\%\ \text{KBr} = \frac{60\ \text{g KBr}}{(60 + 100)\ \text{g solution}} = 40\%$$

20. Which of the following gases is expected to be most soluble in water? Explain your reasoning.

(a) CH_4

(b) CCl_4

(c) $CHCl_3$

Solution

(c) $CHCl_3$ is expected to be most soluble in water. Of the three gases, only this one is polar and thus capable of experiencing relatively strong dipole-dipole attraction to water molecules.

21. At 0 °C and 1.00 atm, as much as 0.70 g of O_2 can dissolve in 1 L of water. At 0 °C and 4.00 atm, how many grams of O_2 dissolve in 1 L of water?

Solution

This problem requires the application of Henry's law. The governing equation is $C_g = kP_g$.

$$k = \frac{C_g}{P_g} = \frac{0.70\ \text{g}}{1.00\ \text{atm}} = 0.70\ \text{g atm}^{-1}$$

Under the new conditions, $C_g = 0.70\ \text{g atm}^{-1} \times 4.00\ \text{atm} = 2.80\ \text{g}$.

22. Refer to Figure 11.10.
(a) How did the concentration of dissolved CO_2 in the beverage change when the bottle was opened?
(b) What caused this change?
(c) Is the beverage unsaturated, saturated, or supersaturated with CO_2?

Solution
(a) It decreased as some of the CO_2 gas left the solution (evidenced by effervescence). (b) Opening the bottle released the high-pressure CO_2 gas above the beverage. The reduced CO_2 gas pressure, per Henry's law, lowers the solubility for CO_2. (c) The dissolved CO_2 concentration will continue to slowly decrease until equilibrium is reestablished between the beverage and the very low CO_2 gas pressure in the opened bottle. Immediately after opening, the beverage, therefore, contains dissolved CO_2 at a concentration greater than its solubility, a nonequilibrium condition, and is said to be supersaturated.

23. The Henry's law constant for CO_2 is 3.4×10^{-2} *M*/atm at 25 °C. Assuming ideal solution behavior, what pressure of carbon dioxide is needed to maintain a CO_2 concentration of 0.10 *M* in a can of lemon-lime soda?

Solution

$$P_g = \frac{C_g}{k} = \frac{0.10\ M}{3.4 \times 10^{-2}\ M/\text{atm}} = 2.9\ \text{atm}$$

24. The Henry's law constant for O_2 is 1.3×10^{-3} *M*/atm at 25 °C. Assuming ideal solution behavior, what mass of oxygen would be dissolved in a 40-L aquarium at 25 °C, assuming an atmospheric pressure of 1.00 atm, and that the partial pressure of O_2 is 0.21 atm?

Solution
$C_g = kP_g$. $C(O_2) = 1.3 \times 10^{-3}\ M/\text{atm} \times 0.21\ \text{atm} = 2.7 \times 10^{-4}$ mol/L. The total amount is 2.7×10^{-4} mol/L × 40 L = 1.08×10^{-2} mol. The mass of oxygen is 1.08×10^{-2} mol × 32.0 g/mol = 0.346 g or, using two significant figures, 0.35 g.

25. Assuming ideal solution behavior, how many liters of HCl gas, measured at 30.0 °C and 745 torr, are required to prepare 1.25 L of a 3.20-*M* solution of hydrochloric acid?

Solution
First, calculate the moles of HCl needed. Then use the ideal gas law to find the volume required.
$M = \text{mol L}^{-1}$

$$3.20\ M = \frac{x\ \text{mol}}{1.25\ \text{L}}$$

$x = 4.00$ mol HCl
Before using the ideal gas law, change pressure to atmospheres and convert temperature from °C to kelvins.

$$\frac{1\ \text{atm}}{x} = \frac{760\ \text{torr}}{745\ \text{torr}}$$

$x = 0.9803$ atm

$$V = \frac{nRT}{P} = \frac{(4.000\ \cancel{\text{mol}}\ \text{HCl})(0.08206\ \text{L}\ \cancel{\text{atm}}\ \cancel{\text{K}^{-1}}\ \cancel{\text{mol}^{-1}})(303.15\ \cancel{\text{K}})}{0.9803\ \cancel{\text{atm}}} = 102\ \text{L HCl}$$

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Chemistry: Atoms First 2e
11: Solutions and Colloids
11.4: Colligative Properties

26. Which is/are part of the macroscopic domain of solutions and which is/are part of the microscopic domain: boiling point elevation, Henry's law, hydrogen bond, ion-dipole attraction, molarity, nonelectrolyte, nonstoichiometric compound, osmosis, solvated ion?

Solution

Macroscopic: boiling point elevation, Henry's law, molarity, nonelectrolyte, nonstoichiometric compound, osmosis. Microscopic: hydrogen bond, ion-dipole attraction, solvated ion

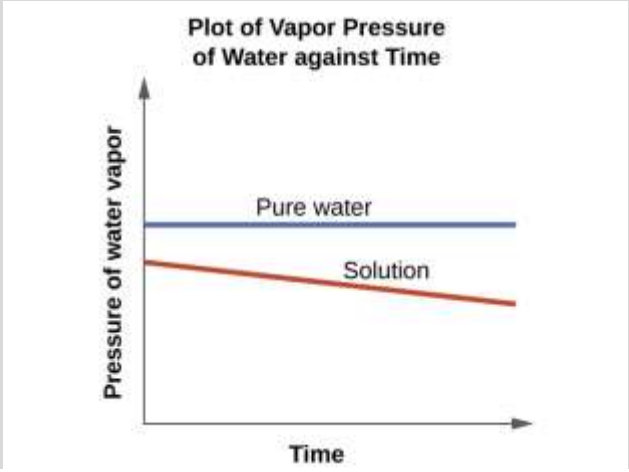
27. What is the microscopic explanation for the macroscopic behavior illustrated in Figure 11.14?

Solution

The strength of the bonds between like molecules is stronger than the strength between unlike molecules. Therefore, some regions will exist in which the water molecules will exclude oil molecules and other regions will exist in which oil molecules will exclude water molecules, forming a heterogeneous region.

28. Sketch a qualitative graph of the pressure versus time for water vapor above a sample of pure water and a sugar solution, as the liquids evaporate to half their original volume.

Solution



29. A solution of potassium nitrate, an electrolyte, and a solution of glycerin ($C_3H_5(OH)3$), a nonelectrolyte, both boil at 100.3 °C. What other physical properties of the two solutions are identical?

Solution

Both form homogeneous solutions; their boiling point elevations are the same, as are their lowering of vapor pressures. Osmotic pressure and the lowering of the freezing point are also the same for both solutions.

30. What are the mole fractions of H_3PO_4 and water in a solution of 14.5 g of H_3PO_4 in 125 g of water?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

Solution

(a) Determine the number of moles of each component. Then add the number of moles of components and divide that number into the moles of the component whose percentage is desired. (b)

$$\text{mol } H_3PO_4 = \frac{14.5 \text{ g}}{97.9952 \text{ g mol}^{-1}} = 0.148 \text{ mol}$$

$$\text{mol } H_2O = \frac{125 \text{ g}}{18.0153 \text{ g mol}^{-1}} = 6.939 \text{ mol}$$

Total number of moles = 0.148 mol + 6.939 mol = 7.087 mol

$$X_{H_3PO_4} = \frac{0.148 \text{ mol}}{7.087 \text{ mol}} = 0.0209$$

$$X_{H_2O} = \frac{6.939 \text{ mol}}{7.087 \text{ mol}} = 0.979$$

31. What are the mole fractions of HNO_3 and water in a concentrated solution of nitric acid (68.0% HNO_3 by mass)?
(a) Outline the steps necessary to answer the question.
(b) Answer the question.

Solution
(a) Find number of moles of HNO_3 and H_2O in 100 g of the solution. Find the mole fractions for the components.
(b) The number of moles of HNO_3 is $\frac{68 \text{ g}}{63.01 \text{ g/mol}} = 1.079 \text{ mol}$. The number of moles of water is $\frac{32 \text{ g}}{18.015 \text{ g/mol}} = 1.776 \text{ mol}$. The mole fraction of HNO_3 is $\frac{1.079}{(1.079 + 1.776)} = 0.378$. The mole fraction of H_2O is $1 - 0.378 = 0.622$.

32. Calculate the mole fraction of each solute and solvent:
(a) 583 g of H_2SO_4 in 1.50 kg of water—the acid solution used in an automobile battery
(b) 0.86 g of NaCl in 1.00×10^2 g of water—a solution of sodium chloride for intravenous injection
(c) 46.85 g of codeine, $C_{18}H_{21}NO_3$, in 125.5 g of ethanol, C_2H_5OH
(d) 25 g of I_2 in 125 g of ethanol, C_2H_5OH

Solution
(a)

$$\text{mol } H_2SO_4 = \frac{583 \text{ g}}{98.079 \text{ g mol}^{-1}} = 5.94 \text{ mol}$$

$$\text{mol } H_2O = \frac{1.5 \times 10^3 \text{ g}}{18.0153 \text{ g mol}^{-1}} = 83.3 \text{ mol}$$

Total number of moles = 5.94 mol + 83.3 mol = 89.24 mol

$$X_{H_2SO_4} = \frac{83.3 \text{ mol}}{89.24 \text{ mol}} = 0.933$$

$$X_{H_2O} = \frac{5.94 \text{ mol}}{89.24 \text{ mol}} = 0.0666$$

(b)

$$\text{mol NaCl} = \frac{0.86\ \text{g}}{58.44\ \text{g/mol}} = 0.015\ \text{mol}$$

$$\text{mol } H_2O = \frac{100\ \text{g}}{18.0153\ \text{g mol}^{-1}} = 5.551\ \text{mol}$$

Total number of moles = 0.015 mol + 5.551 mol = 5.566 mol

$$X_{\text{NaCl}} = \frac{0.015\ \text{mol}}{5.566\ \text{mol}} = 0.0027$$

$$X_{H_2O} = \frac{5.551\ \text{mol}}{5.566\ \text{mol}} = 0.997$$

If the mole fraction of water is calculated by subtraction of the mole fraction of NaCl from 1, the answer is 0.9973. This procedure points out the importance in maintaining the correct number of significant figures and shows that slightly different answers may be obtained by different methods.

(c)

$$\text{mol } C_{18}H_{21}NO_3 = \frac{46.85\ \text{g}}{299.364\ \text{g mol}^{-1}} = 0.156\ \text{mol}$$

$$\text{mol } C_2H_5OH = \frac{125\ \text{g}}{46.068\ \text{g mol}^{-1}} = 2.724\ \text{mol}$$

Total number of moles = 0.156 mol + 2.724 mol = 2.880 mol

$$X_{C_{15}H_{21}NO_3} = \frac{0.156\ \text{mol}}{2.880\ \text{mol}} = 0.0542$$

$$X_{C_2H_5OH} = \frac{2.724\ \text{mol}}{2.880\ \text{mol}} = 0.9458$$

(d)

$$\text{mol } I_2 = \frac{25\ \text{g}}{253.809\ \text{g mol}^{-1}} = 0.0985\ \text{mol}$$

$$\text{mol } C_2H_5OH = \frac{125\ \text{g}}{46.068\ \text{g mol}^{-1}} = 2.713\ \text{mol}$$

Total number of moles = 0.0985 mol + 2.713 mol = 2.812 mol

$$X_{I_2} = \frac{0.0985\ \text{mol}}{2.812\ \text{mol}} = 0.035$$

$$X_{C_2H_5OH} = \frac{2.713\ \text{mol}}{2.812\ \text{mol}} = 0.965$$

33. Calculate the mole fraction of each solute and solvent:

(a) 0.710 kg of sodium carbonate (washing soda), Na_2CO_3, in 10.0 kg of water—a saturated solution at 0 °C

(b) 125 g of NH_4NO_3 in 275 g of water—a mixture used to make an instant ice pack

(c) 25 g of Cl_2 in 125 g of dichloromethane, CH_2Cl_2

(d) 0.372 g of tetrahydropyridine, C_5H_9N, in 125 g of chloroform, $CHCl_3$

Solution

(a)

$$\text{mol } Na_2CO_3 = 710 \text{ g } Na_2CO_3 \times \frac{1 \text{ mol}}{105.9886 \text{ g } Na_2CO_3} = 6.70 \text{ mol}$$

$$\text{mol } H_2O = \frac{10{,}000 \text{ g}}{18.0153 \text{ g/mol}} = 555.08 \text{ mol}$$

Total number of moles = 555.08 mol + 6.70 mol = 561.78 mol

$$X_{Na_2CO_3} = \frac{6.70 \text{ mol}}{561.78 \text{ mol}} = 0.0119$$

$$X_{H_2O} = \frac{555.08 \text{ mol}}{561.78 \text{ mol}} = 0.988$$

(b)

$$\text{mol } NH_4NO_3 = 125 \text{ g } NH_4NO_3 \times \frac{1 \text{ mol}}{80.0434 \text{ g } NH_4NO_3} = 1.56 \text{ mol}$$

$$\text{mol } H_2O = \frac{275 \text{ g}}{18.0153 \text{ g/mol}} = 15.26 \text{ mol}$$

Total number of moles = 15.26 mol + 1.56 mol = 16.82 mol

$$X_{NH_4NO_3} = \frac{1.56 \text{ mol}}{16.82 \text{ mol}} = 0.9927$$

$$X_{H_2O} = \frac{15.26 \text{ mol}}{16.82 \text{ mol}} = 0.907$$

(c)

$$\text{mol } Cl_2 = 25 \text{ g } Cl_2 \times \frac{1 \text{ mol}}{70.9054 \text{ g } Cl_2} = 0.35 \text{ mol}$$

$$\text{mol } CH_2Cl_2 = \frac{125 \text{ g}}{84.93 \text{ g/mol}} = 1.47 \text{ mol}$$

Total number of moles = 1.47 mol + 0.35 mol = 1.82 mol

$$X_{Cl_2} = \frac{0.35 \text{ mol}}{1.82 \text{ mol}} = 0.192$$

$$X_{CH_2Cl_2} = \frac{1.47 \text{ mol}}{1.82 \text{ mol}} = 0.808$$

(d)

$$\text{mol } C_5H_9N = 0.372 \text{ g } C_5H_9N \times \frac{1 \text{ mol}}{83.1332 \text{ g } C_5H_9N} = 4.47 \times 10^{-3} \text{ mol}$$

$$\text{mol } CHCl_3 = \frac{125 \text{ g}}{119.38 \text{ g/mol}} = 1.047 \text{ mol}$$

Total number of moles = 1.047 mol + 0.00447 mol = 1.05 mol

$$X_{C_5H_9N} = \frac{0.00447 \text{ mol}}{1.05 \text{ mol}} = 0.00426$$

$$X_{CHCl_3} = \frac{1.047 \text{ mol}}{1.05 \text{ mol}} = 0.997$$

34. Calculate the mole fractions of methanol, CH_3OH; ethanol, C_2H_5OH; and water in a solution that is 40% methanol, 40% ethanol, and 20% water by mass. (Assume the data are good to two significant figures.)

Solution
Assume that the total solution mass is 100 g. Calculate the mass and the number of moles of each component. Then calculate the respective mole fractions.

$$\text{mol } CH_3OH = 0.40 \times 100 \text{ g} \times \frac{1 \text{ mol}}{32.042 \text{ g}} = 1.24836 \text{ mol}$$

$$\text{mol } C_2H_5OH = 0.40 \times 100 \text{ g} \times \frac{1 \text{ mol}}{46.069 \text{ g}} = 0.86827 \text{ mol}$$

$$\text{mol } H_2O = 0.20 \times 100 \text{ g} \times \frac{1 \text{ mol}}{18.0152 \text{ g}} = 1.1101736 \text{ mol}$$

Total number of moles = 1.24836 mol + 0.84827 mol + 1.1101736 mol = 3.22680 mol

$$X_{CH_3OH} = \frac{1.24836}{3.22680} = 0.39$$

$$X_{C_2H_5OH} = \frac{0.86827}{3.22680} = 0.27$$

$$X_{H_2O} = \frac{1.1101736}{3.22680} = 0.34$$

35. What is the difference between a 1 *M* solution and a 1 *m* solution?

Solution
In a 1 *M* solution, the mole is contained in exactly 1 L of solution. In a 1 *m* solution, the mole is contained in exactly 1 kg of solvent.

36. What is the molality of phosphoric acid, H_3PO_4, in a solution of 14.5 g of H_3PO_4 in 125 g of water?
(a) Outline the steps necessary to answer the question.
(b) Answer the question.

Solution
(a) Determine the molar mass of H_3PO_4; determine the number of moles of acid in the solution; from the number of moles and the mass of solvent, determine the molality. (b) 1.18 *m*

37. What is the molality of nitric acid in a concentrated solution of nitric acid (68.0% HNO_3 by mass)?
(a) Outline the steps necessary to answer the question.
(b) Answer the question.

Solution
(a) Determine the molar mass of HNO_3. Determine the number of moles of acid in the solution. From the number of moles and the mass of solvent, determine the molality.
(b) Molar mass $HNO_3 = 63.01288 \text{ g mol}^{-1}$
If we assume 100 g of solution, then 68.0 g is HNO_3 and 32.0 g is water.

$$\text{mol } HNO_3 = 68.0 \cancel{\text{ g HNO}_3} \times \frac{1 \text{ mol}}{63.02188 \cancel{\text{ g HNO}_3}} = 1.08 \text{ mol}$$

$$m \text{ } HNO_3 = \frac{1.08 \text{ mol}}{0.0320 \text{ g}} = 33.7 \text{ } m$$

38. Calculate the molality of each of the following solutions:
(a) 583 g of H_2SO_4 in 1.50 kg of water—the acid solution used in an automobile battery
(b) 0.86 g of NaCl in 1.00×10^2 g of water—a solution of sodium chloride for intravenous injection
(c) 46.85 g of codeine, $C_{18}H_{21}NO_3$, in 125.5 g of ethanol, C_2H_5OH
(d) 25 g of I_2 in 125 g of ethanol, C_2H_5OH

Solution
(a) 3.96 *m*; (b) 0.15 *m*; (c) 1.247 *m*; (d) 0.79 *m*

39. Calculate the molality of each of the following solutions:
(a) 0.710 kg of sodium carbonate (washing soda), Na_2CO_3, in 10.0 kg of water—a saturated solution at 0 °C
(b) 125 g of NH_4NO_3 in 275 g of water—a mixture used to make an instant ice pack
(c) 25 g of Cl_2 in 125 g of dichloromethane, CH_2Cl_2
(d) 0.372 g of tetrahydropyridine, C_5H_9N, in 125 g of chloroform, $CHCl_3$

Solution
(a)

$$\text{mol } Na_2CO_3 = 710 \text{ g } Na_2CO_3 \times \frac{1 \text{ mol}}{105.9886 \text{ g } Na_2CO_3}$$

$$\text{molality of } Na_2CO_3 = \frac{6.70 \text{ mol}}{10.0 \text{ kg}} = 6.70 \times 10^{-1} \ m$$

(b)

$$\text{mol } NH_4NO_3 = 125 \cancel{\text{ g } NH_4NO_3} \times \frac{1 \text{ mol}}{80.0434 \cancel{\text{ g } NH_4NO_3}} = 1.56 \text{ mol}$$

$$\text{molality of } NH_4NO_3 = \frac{1.56 \text{ mol}}{0.275 \text{ kg}} = 5.67 \ m$$

(c)

$$\text{mol } Cl_2 = 25 \cancel{\text{ g } Cl_2} \times \frac{1 \text{ mol}}{70.9054 \cancel{\text{ g } Cl_2}} = 0.35 \text{ mol}$$

$$m \text{ } Cl_2 = \frac{0.35 \text{ mol}}{0.125 \text{ kg}} = 2.8 \ m$$

(d)

$$\text{mol } C_5H_9N = 0.372 \cancel{\text{ g } C_5H_9N} \times \frac{1 \text{ mol}}{83.1332 \cancel{\text{ g } C_5H_9N}} = 4.47 \times 10^{-3} \text{ mol}$$

$$\text{molality of } C_5H_9N = \frac{4.47 \times 10^{-3} \text{ mol}}{0.125 \text{ kg}} = 0.0358 \ m$$

40. The concentration of glucose, $C_6H_{12}O_6$, in normal spinal fluid is $\frac{75 \text{ mg}}{100 \text{ g}}$. What is the molality of the solution?

Solution
$4.2 \times 10^{-3} \ m$

41. A 13.0% solution of K_2CO_3 by mass has a density of 1.09 g/cm^3. Calculate the molality of the solution.

Solution
Find the mass of K_2CO_3 and the mass of water in solution. Assume 100.0 mL of solution and that the density of water is 1.00 g cm^{-3}. Then find the moles of K_2CO_3 and the molality.

$$\text{Mass (solution)} = 100.0 \cancel{\text{mL}} \times \frac{1 \cancel{\text{cm}^3}}{1 \cancel{\text{mL}}} \times 1.09 \text{ g } \cancel{\text{cm}^3} = 109.0 \text{ g}$$

$$\text{Mass } (K_2CO_3) = \frac{13.0\%}{100\%} \times 109 \text{ g} = 14.2 \text{ g}$$

$$\text{Mass } (H_2O) = 109.0 \text{ g} - 14.2 \text{ g} = 94.8 \text{ g}$$

$$m \ (K_2CO_3) = \frac{0.1027 \text{ mol}}{0.0948 \text{ kg}} = 1.08 \ m$$

42. Why does 1 mol of sodium chloride depress the freezing point of 1 kg of water almost twice as much as 1 mol of glycerin?

Solution
The presence of two ions for each NaCl molecule in a solution of NaCl compared with only one molecule for each glycerin in a solution of glycerin doubles the freezing point depression. This relationship is accounted for by the van't Hoff factor in the expression $\Delta T_f = K_f m$.

43. Assuming ideal solution behavior, what is the boiling point of a solution of 115.0 g of nonvolatile sucrose, $C_{12}H_{22}O_{11}$, in 350.0 g of water?
(a) Outline the steps necessary to answer the question
(b) Answer the question

Solution
(a) Determine the molar mass of sucrose; determine the number of moles of sucrose in the solution; convert the mass of solvent to units of kilograms; from the number of moles and the mass of solvent, determine the molality; determine the difference between the boiling point of water and the boiling point of the solution; determine the new boiling point.

(b) $$\text{mol sucrose} = \frac{115.0 \text{ g}}{342.300 \text{ g mol}^{-1}} = 0.3360 \text{ mol}$$

$$\text{molality} = \frac{0.3360 \text{ mol } C_{12}H_{22}O_{11}}{0.3500 \text{ kg } H_2O} = 0.9599 \ m$$

$\Delta T_b = K_b m = (0.512 \text{ °C } m^{-1})(0.9599 \ m) = 0.491 \text{ °C}$
The boiling point of pure water at 100.0 °C increases 0.491 °C to 100.491 °C, or 100.5 °C.

44. Assuming ideal solution behavior, what is the boiling point of a solution of 9.04 g of I_2 in 75.5 g of benzene, assuming the I_2 is nonvolatile?
(a) Outline the steps necessary to answer the question.
(b) Answer the question.

Solution
(a) Determine the molar mass of I_2. Determine the number of moles of I_2 in the solution. From the number of moles and the mass of solvent, determine the molality. Then determine the difference between the boiling point of benzene and the boiling point of the solution. Finally, determine the new boiling point.
(b)
$\Delta T_b = K_b m = (2.53 \text{ °C m}^{-1})(0.472 \text{ m}) = 1.19 \text{ °C}$
The boiling point of pure benzene is 80.1 °C. Since the temperature increase is 1.19 °C, the new temperature is (80.1 + 1.19) = 81.3 °C.

45. Assuming ideal solution behavior, what is the freezing temperature of a solution of 115.0 g of sucrose, $C_{12}H_{22}O_{11}$, in 350.0 g of water?
(a) Outline the steps necessary to answer the question.
(b) Answer the question.

Solution
(a) Determine the molar mass of sucrose; determine the number of moles of sucrose in the solution; convert the mass of solvent to units of kilograms; from the number of moles and the mass of solvent, determine the molality; determine the difference between the freezing temperature of water and the freezing temperature of the solution; determine the new freezing temperature.

(b) $\text{mol sucrose} = \dfrac{115.0\text{ g}}{342.300\text{ g mol}^{-1}} = 0.336\text{ mol}$

$m\text{ sucrose} = \dfrac{0.336\text{ mol}}{0.350\text{ kg}} = 0.960\ m$

$\Delta T_b = K_b m = (1.86\text{ °C } m^{-1})(0.960\ m) = 1.78\text{ °C}$
The freezing temperature is 0.0 °C − 1.78 °C = –1.8 °C.

46. Assuming ideal solution behavior, what is the freezing point of a solution of 9.04 g of I_2 in 75.5 g of benzene?
(a) Outline the steps necessary to answer the following question.
(b) Answer the question.

Solution
(a) Determine the molar mass of I_2. Determine the number of moles of I_2 in the solution. From the number of moles and the mass of solvent, determine the molality. Then determine the difference between the freezing temperature of pure benzene and the freezing temperature of the solution. Finally, determine the new freezing temperature.

(b) $\text{mol } I_2 = \dfrac{9.04\text{ g}}{\left(253.80894\text{ g mol}^{-1}\right)} = 0.0356\text{ mol}$

$m\ I_2 = \dfrac{0.0356\text{ mol}}{0.0755\text{ kg}} = 0.472\ m$

$\Delta T_b = K_b m = (5.12\text{ °C } m^{-1})(0.472\ m) = 2.42\text{ °C}$
Benzene freezes at 5.5 °C. The freezing temperature is 5.5 °C – 2.42 °C = 3.1 °C.

47. Assuming ideal solution behavior, what is the osmotic pressure of an aqueous solution of 1.64 g of $Ca(NO_3)_2$ in water at 25 °C? The volume of the solution is 275 mL.
(a) Outline the steps necessary to answer the question.
(b) Answer the question.

Solution
(a) Determine the molar mass of $Ca(NO_3)_2$; determine the number of moles of $Ca(NO_3)_2$ in the solution; determine the number of moles of ions in the solution; determine the molarity of ions, then the osmotic pressure.

(b) $M\ \text{Ca}\left(\text{NO}_3\right)_2 = \dfrac{1.64\text{ g Ca}\left(\text{NO}_3\right)_2 \times 1\text{ mol}/164.088\text{ g Ca}(\text{NO}_3)_2}{0.275\text{ L}} = 0.0363\ M$

The molarity of the ions is three times the molarity of $Ca(NO_3)_2$. Therefore, multiply the molarity of $Ca(NO_3)_2$ by 3: $\Pi = MRT = 3 \times 0.0363\text{ mol L}^{-1} \times 0.08206\text{ L atm mol}^{-1}\text{ K}^{-1} \times 298.15\text{ K} = 2.67$ atm.

48. Assuming ideal solution behavior, what is osmotic pressure of a solution of bovine insulin (molar mass, 5700 g mol^{-1}) at 18 °C if 100.0 mL of the solution contains 0.103 g of the insulin?
(a) Outline the steps necessary to answer the question.
(b) Answer the question.

Solution
(a) From the molar mass of bovine insulin, determine the number of moles of insulin in the solution. Determine the molarity of insulin, and then determine the osmotic pressure.

(b) M insulin $= \dfrac{\dfrac{0.103\ \cancel{\text{g}}}{5700\ \cancel{\text{g}}\ \text{mol}^{-1}}}{0.100\ \text{L}} = 1.807 \times 10^{-4}\ M$

$\Pi = MRT = 1.804 \times 10^{-4}\ \text{mol L}^{-1} \times 0.0826\ \text{L atm mol}^{-1}\ \text{K}^{-1} \times (273.15 + 18)\ \text{K} = 4.3 \times 10^{-3}\ \text{atm}$

49. A solution containing 5.00 g of a compound dissolved in 25.00 g of carbon tetrachloride (bp 76.8 °C; K_b = 5.02 °C/m) exhibits a normal boiling point of 81.5 °C. Assuming ideal solution behavior, what is the molar mass of the compound?
(a) Outline the steps necessary to answer the question.
(b) Solve the problem.

Solution
(a) Determine the molal concentration from the change in boiling point and K_b; determine the moles of solute in the solution from the molal concentration and mass of solvent; determine the molar mass from the number of moles and the mass of solute. (b) $\Delta T_b = 81.5 - 76.8 = 4.7$ °C,

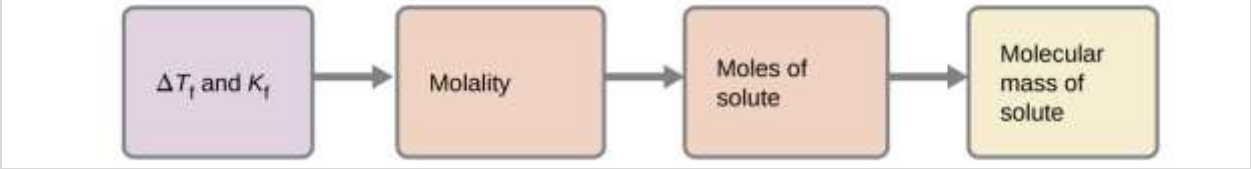
$\Delta T_b = K_b m$, so $m = \dfrac{\Delta T_b}{K_b} = \dfrac{4.7\ ^\circ\text{C}}{5.02\ ^\circ\text{C}/m} = 0.94\ m$. Moles of solute = molality × kg of solvent = $0.94\ m \times 0.02500\ \text{kg} = 0.024\ \text{mol}$;

$\text{molar mass} = \dfrac{\text{mass}}{\text{moles}} = \dfrac{5.00\ \text{g}}{0.024\ \text{mol}} = 2.1 \times 10^2\ \text{g mol}^{-1}$

Molecular mass = 2.1×10^2 amu

50. A sample of an organic compound (a nonelectrolyte) weighing 1.35 g lowered the freezing point of 10.0 g of benzene by 3.66 °C. Assuming ideal solution behavior, calculate the molar mass of the compound.

Solution
The freezing point lowering (ΔT_f) is known to be 3.66 °C. Also, K_f for benzene can be obtained from Table 11.2 (K_f = 5.12 °C/m). Therefore, the equation $\Delta T_f = K_f m$ can be used to find the molality of the solution. The definition of molality is moles of solute per kilogram of solvent. By using the mass of the solvent, benzene, the number of moles of solute may be found. Using this information with the grams of solute, the molar mass of the organic solute may be found.



$\Delta T_f = K_f m$
3.66 °C = (5.12 °C/m) × m

$$m = \frac{\text{mol of solute}}{\text{kg solvent}} = 0.715$$

$$\text{molality} = \frac{0.715 \text{ mol solute}}{\text{kg solvent}} = 0.715\ m$$

$$0.715\ m = \frac{x}{0.010 \text{ kg benzene}}$$

$x\text{mol} = 0.715 \times 0.010 = 7.15 \times 10^{-3}\text{mol solute}$

$$\text{mol} = \frac{\text{g}}{\text{molar mass}}$$

$$7.15 \times 10^{-3} \text{ mol solute} = \frac{1.350 \text{ g}}{\text{molar mass}}$$

Molar mass = 189 g mol^{-1}

51. A 1.0 *m* solution of HCl in benzene has a freezing point of 0.4 °C. Is HCl an electrolyte in benzene? Explain.

Solution

No. Pure benzene freezes at 5.5 °C, and so the observed freezing point of this solution is depressed by $\Delta T_f = 5.5 - 0.4 = 5.1$ °C. The value computed, assuming no ionization of HCl, is $\Delta T_f = (1.0 \text{ m})(5.14 \text{ °C}/m) = 5.1$ °C. Agreement of these values supports the assumption that HCl is not ionized.

52. A solution contains 5.00 g of urea, $CO(NH_2)_2$, a nonvolatile compound, dissolved in 0.100 kg of water. If the vapor pressure of pure water at 25 °C is 23.7 torr, what is the vapor pressure of the solution (assuming ideal solution behavior)?

Solution

The vapor pressure of the pure solvent is known; therefore, Raoult's law can be used along with the mole fraction to calculate the vapor pressure of the solution. First, calculate the molar amounts of urea and water, then compute the mole fraction of water, then use Raoult's law to compute the solution's vapor pressure:

$$P_{\text{solution}} = X_{\text{solvent}} P^{\circ}_{\text{solvent}}$$

$$X_{H_2O} = \frac{5.55}{0.833 + 5.55} = 0.9852$$

$$P_{\text{solution}} = (0.9852)(23.7 \text{ torr}) = 23.3 \text{ torr}$$

53. A 12.0-g sample of a nonelectrolyte is dissolved in 80.0 g of water. The solution freezes at –1.94 °C. Assuming ideal solution behavior, calculate the molar mass of the substance.

Solution

$\Delta T_f = 1.94$ °C

$$m = \frac{\Delta T_f}{K_f} = \frac{1.94 \text{ °C}}{1.86 \text{ °C}/m} = 1.04\ m$$

Moles of solute = 1.04 $m \times$ 0.0800 kg = 0.0834 mol

$$\text{Molar mass} = \frac{12.0 \text{ g}}{0.0834 \text{ mol}} = 144 \text{ g mol}^{-1}$$

Molecular mass = 144 amu

54. Arrange the following solutions in order by their decreasing freezing points: 0.1 *m* Na_3PO_4, 0.1 *m* C_2H_5OH, 0.01 *m* CO_2, 0.15 *m* NaCl, and 0.2 *m* $CaCl_2$.

Solution
The number of particles (ions or molecules) per mole is Na_3PO_4, 4; C_2H_5OH, 1; CO_2, 1; NaCl, 2; and $CaCl_2$, 3. For a 1.00-L solution, the number of moles of particles is:
Na_3PO_4: 0.1 mol × 4 = 0.4 mol
C_2H_5OH: 0.1 mol × 1 = 0.1 mol
CO_2: 0.01 mol × 1 = 0.01 mol
NaCl: 0.15 mol × 2 = 0.30 mol
$CaCl_2$: 0.2 mol × 3 = 0.6 mol
From the highest freezing point to lowest freezing point:
0.01 mol CO_2 > 0.1 mol C_2H_5OH > 0.15 mol NaCl > 0.1 mol Na_3PO_4 > 0.2 mol $CaCl_2$.

55. Calculate the boiling point elevation of 0.100 kg of water containing 0.010 mol of NaCl, 0.020 mol of Na_2SO_4, and 0.030 mol of $MgCl_2$, assuming complete dissociation of these electrolytes and ideal solution behavior.

Solution
0.010 mol NaCl contains 0.010 mol Na^+ + 0.010 mol Cl^-
0.020 mol Na_2SO_4 contains 0.040 mol Na^+ + 0.020 mol SO_4^{2-}
0.030 mol $MgCl_2$ contains 0.030 mol Mg^{2+} + 0.060 mol Cl^-
Total numbers of moles = 0.020 mol + 0.060 mol + 0.090 mol = 0.170 mol

$$\Delta T_b = K_b m = 0.512\ ^\circ\text{C}/m \times \frac{0.170\ \text{mol}}{0.100\ \text{kg}} = 0.870\ ^\circ\text{C}$$

56. How could you prepare a 3.08 *m* aqueous solution of glycerin, $C_3H_8O_3$? Assuming ideal solution behavior, what is the freezing point of this solution?

Solution
First, find the molar mass of glycerin. The molar mass of glycerin is 92.095 g mol^{-1}. A 3.08 *m* aqueous solution requires 3.08 mol × 92.095 g mol^{-1} = 284 g
To prepare the solution, dissolve 284 g of glycerin in 1.00 kg of water. Glycerin is nonelectrolyte.
ΔT_f = 1.86 °C/*m* × 3.08 m = 5.73
The freezing point is –5.73 °C.

57. A sample of sulfur weighing 0.210 g was dissolved in 17.8 g of carbon disulfide, CS_2 (K_b = 2.34 °C/*m*). If the boiling point elevation was 0.107 °C, what is the formula of a sulfur molecule in carbon disulfide (assuming ideal solution behavior)?

Solution
The molality is

$$m = \frac{0.107\,^\circ\text{C}}{2.34\,^\circ\text{C}/m} = 0.0457\,m$$

mol S = 0.0457 *m* × 0.0178 kg = 8.13×10^{-4} mol

$$\text{Molecular mass} = \frac{0.210\ \text{g}}{8.13\times10^{-4}\ \text{mol}} = 258\ \text{g mol}^{-1}$$

The atomic mass of sulfur is 32.066.

$$\frac{258}{32.066} = 8.05$$

The formula for the sulfur molecule is S_8.

58. In a significant experiment performed many years ago, 5.6977 g of cadmium iodide in 44.69 g of water raised the boiling point 0.181 °C. What does this suggest about the nature of a solution of CdI_2?

Solution

Determine the number of moles of CdI_2 and then the molarity.
From the elevation of the boiling point, determine the molarity expected to produce that increase. Compare that value with the calculated value. If a difference exists, the ratio of the actual value to the calculated value gives the number of ions.

$$\text{mol } CdI_2 = \frac{5.6977 \text{ g}}{366.220 \text{ g mol}^{-1}} = 0.015558 \text{ mol}$$

$$m \text{ } CdI_2 = \frac{0.015558 \text{ mol}}{0.04469 \text{ kg}} = 0.3481 \text{ } m$$

The boiling point elevation expected if no ionization occurs is:
$\Delta T_b = K_b m = 0.512 \text{ °C } m^{-1} \times 0.3481 \text{ } m = 0.178 \text{ °C}$.
The actual boiling point increase is 0.181°C. Therefore, since the ratio is almost 1, only a very slight amount of CdI_2 actually dissociated in solution.

59. Lysozyme is an enzyme that cleaves cell walls. A 0.100-L sample of a solution of lysozyme that contains 0.0750 g of the enzyme exhibits an osmotic pressure of 1.32×10^{-3} atm at 25 °C. Assuming ideal solution behavior, what is the molar mass of lysozyme?

Solution

The molarity of the solution is:

$$M = \frac{\Pi}{RT} = \frac{1.32 \times 10^{-3} \text{ atm}}{(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(298 \text{ K})} = 5.40 \times 10^{-5} \text{ mol L}^{-1}$$

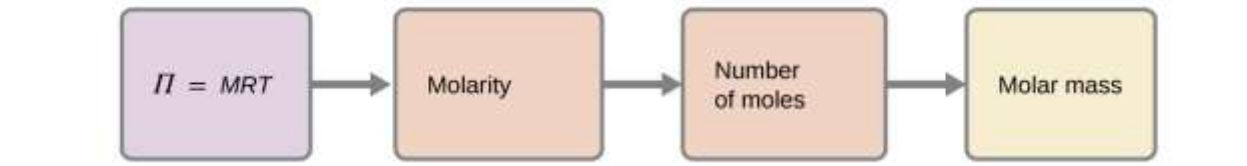
Number of moles = 5.40×10^{-5} mol $L^{-1} \times 0.100$ L = 5.40×10^{-6} mol

$$\text{molar mass} = \frac{0.0750 \text{ g}}{5.40 \times 10^{-6} \text{ mol}} = 1.39 \times 10^{4} \text{ g mol}^{-1}$$

Molecular mass = 1.39×10^4 amu.

60. The osmotic pressure of a solution containing 7.0 g of insulin per liter is 23 torr at 25 °C. Assuming ideal solution behavior, what is the molar mass of insulin?

Solution



First, since the ideal gas constant is in units of (L atm $mol^{-1} \cdot K^{-1}$), convert the osmotic pressure to atmospheres. For the same reasons, convert the temperature from °C to kelvin.
1 atm = 760 torr

$$23 \text{ ~~torr~~} \times \frac{1 \text{ atm}}{760 \text{ ~~torr~~}} = 0.030 \text{ atm}$$

$$M = \frac{\Pi}{RT} = \frac{0.030 \text{ ~~atm~~}}{(0.08206 \text{ L ~~atm~~ mol}^{-1} \text{ ~~K}^{-1}~~)(298.15 \text{ K})} = 1.23 \times 10^{-3} \text{ } M$$

Number of moles = MV (in liters) = $(1.23 \times 10^{-3} M)(1 \text{ L}) = 1.23 \times 10^{-3} M$

$$\text{Number of moles} = \frac{\text{g}}{\text{molar mass}}$$

$$1.23 \times 10^{-3}\ \text{mol} = \frac{7.0\ \text{g insulin}}{\text{molar mass}}$$

Molar mass = 5.7×10^{3} g mol^{-1}

61. The osmotic pressure of human blood is 7.6 atm at 37 °C. What mass of glucose, $C_6H_{12}O_6$, is required to make 1.00 L of aqueous solution for intravenous feeding if the solution must have the same osmotic pressure as blood at body temperature, 37 °C (assuming ideal solution behavior)?

Solution

The molarity of the solution is

$$M = \frac{\Pi}{RT} = \frac{7.6\ \text{atm}}{\left(0.08206\ \text{L atm mol}^{-1}\ \text{K}^{-1}\right)\left(310\ \text{K}\right)} = 0.30\ \text{mol/L}$$

Number of moles = 0.30 mol/L × 1.00 L = 0.30 mol

Mass (glucose) = 180.157 g mol^{-1} × 0.30 mol = 54 g

62. Assuming ideal solution behavior, what is the freezing point of a solution of dibromobenzene, $C_6H_4Br_2$, in 0.250 kg of benzene, if the solution boils at 83.5 °C?

Solution

Find the molality of the solution from the boiling point elevation. Using that value, determine the freezing point depression and then the freezing point. Find the values for the constants needed in Table 11.2.

ΔT = 83.5 °C – 80.1 °C = 3.4 °C = $K_b m$ = 2.53 °C m^{-1} × m

$$m\ \text{dibromobenzene} = \frac{3.4\ ^\circ\text{C}}{2.53\ ^\circ\text{C}\ m^{-1}} = 1.34\ m$$

$\Delta T = K_f m$ = 5.12 °C m^{-1} × 1.34 m = 6.86 °C

The freezing point of pure benzene is 5.5 °C. Subtraction gives 5.5 °C − 6.86 °C = –1.4 °C.

63. Assuming ideal solution behavior, what is the boiling point of a solution of NaCl in water if the solution freezes at –0.93 °C?

Solution

Find the molality of the solution from the freezing point depression. Using that value, determine the boiling point elevation and then the boiling point.

$$\Delta T_f = \left|0.0\ ^\circ\text{C} - 0.93\ ^\circ\text{C}\right| = 0.93\,^\circ\text{C} = K_f m = 1.86\ ^\circ\text{C}\ m^{-1} \times m$$

$$m\ \text{NaCl} = \frac{0.93\ ^\circ\text{C}}{1.86\ ^\circ\text{C}\ m^{-1}} = 0.50\ m$$

$\Delta T_b = K_b m$ = 0.512 °C m^{-1} × 0.50 m = 0.256 °C

The boiling point of pure water is 100.00 °C. Addition gives 100.00 °C + 0.26 °C = 100.26 °C.

64. The sugar fructose contains 40.0% C, 6.7% H, and 53.3% O by mass. A solution of 11.7 g of fructose in 325 g of ethanol has a boiling point of 78.59 °C. The boiling point of ethanol is 78.35 °C, and K_b for ethanol is 1.20 °C/m. Assuming ideal solution behavior, what is the molecular formula of fructose?

Solution

Δbp = $K_b m$ and molecular mass = $(K_b)\dfrac{\text{(mass fructose)}}{\text{(mass ethanol)}}$

$$\text{molecular mass} = \frac{1.20\ ^\circ\text{C}/m \times 11.7\ \text{g}}{(0.24\ ^\circ\text{C})(0.325\ \text{kg})} = 180\ \text{g mol}^{-1}$$

Empirical formula:

$$\text{C: } \frac{40.0\ \text{g}}{12.011\ \text{g mol}^{-1}} = 3.330\ \text{mol} \qquad \frac{3.330}{3.33} = 1$$

$$\text{H: } \frac{6.7\ \text{g}}{1.00794\ \text{g mol}^{-1}} = 6.647\ \text{mol} \qquad \frac{6.647}{3.33} = 2$$

$$\text{O: } \frac{53.3\ \text{g}}{15.9994\ \text{g mol}^{-1}} = 3.331\ \text{mol} \qquad \frac{3.331}{3.33} = 1$$

The molar mass of CH_2O is 30 g/mol.

$$\text{C: } \frac{40.0\ \text{g}}{12.011\ \text{g mol}^{-1}} = 3.330\ \text{mol} \qquad \frac{3.330}{3.33} = 1$$

$$\text{H: } \frac{6.7\ \text{g}}{1.00794\ \text{g mol} - 1} = 6.647\ \text{mol} \qquad \frac{6.647}{3.33} = 2$$

$$\text{O: } \frac{53.3\ \text{g}}{15.9994\ \text{g mol}^{-1}} = 3.331\ \text{mol} \qquad \frac{3.331}{3.33} = 1$$

Given the molecular mass (180), the molecular formula is $C_6H_{12}O_6$.

65. The vapor pressure of methanol, CH_3OH, is 94 torr at 20 °C. The vapor pressure of ethanol, C_2H_5OH, is 44 torr at the same temperature.
(a) Calculate the mole fraction of methanol and of ethanol in a solution of 50.0 g of methanol and 50.0 g of ethanol.
(b) Ethanol and methanol form a solution that behaves like an ideal solution. Calculate the vapor pressure of methanol and of ethanol above the solution at 20 °C.
(c) Calculate the mole fraction of methanol and of ethanol in the vapor above the solution.

Solution



(a)

$$X_A = \frac{X_A}{X_A + X_B}$$

$CH_3OH = 32.04246\ \text{g mol}^{-1}$
$C_2H_5OH = 46.063\ \text{g mol}^{-1}$

$$\text{mol } CH_3OH = \frac{50.0 \text{ g}}{32.04216 \text{ g mol}^{-1}} = 1.5604 \text{ mol}$$

$$\text{mol } C_2H_5OH = \frac{50.0 \text{ g}}{46.069 \text{ g mol}^{-1}} = 1.0853 \text{ mol}$$

$$X_{CH_3OH} = \frac{1.5604}{1.5604 + 1.0853} = 0.590$$

$$X_{C_2H_5OH} = \frac{1.0853}{1.5604 + 1.0853} = 0.410$$

(b) Vapor pressures are:
CH_3OH: 0.590×94 torr = 55 torr
C_2H_5OH: 0.410×44 torr = 18 torr
(c) The number of moles of each substance is proportional to the pressure, so the mole fraction of each component in the vapor can be calculated as follows:

$$CH_3OH: \frac{55}{(55 + 18)} = 0.75$$

$$C_2H_5OH: \frac{18}{(55 + 18)} = 0.25$$

66. The triple point of air-free water is defined as 273.16 K. Why is it important that the water be free of air?

Solution
As a solute, dissolved air will change the vapor pressure and, hence, the freezing point of the solution.

67. Meat can be classified as fresh (not frozen) even though it is stored at –1 °C. Why wouldn't meat freeze at this temperature?

Solution
The ions and compounds present in the water in the beef lower the freezing point of the beef below –1 °C.

68. An organic compound has a composition of 93.46% C and 6.54% H by mass. A solution of 0.090 g of this compound in 1.10 g of camphor melts at 158.4 °C. The melting point of pure camphor is 178.4 °C. K_f for camphor is 37.7 °C/*m*. Assuming ideal solution behavior, what is the molecular formula of the solute? Show your calculations.

Solution
Calculate the molecular mass of the substance. Then, using methods for calculating the empirical formula of the compound, compare the empirical formula mass to the calculated molecular mass to determine the formula of the compound.

$$\Delta fp = K_f m = K_f \left[\frac{\text{mass solute/molar mass}}{\text{mass camphor (kg)}} \right]$$

$$\text{Molar mass} = \frac{K_f (\text{mass solute})}{(\Delta fp)(\text{kg camphor})} = \frac{(37.7 \text{ °C}/m)(0.045 \text{ g})}{(20.0 \text{ °C})(0.000550 \text{ kg})} = 154.2 \text{ g mol}^{-1}$$

Empirical formula:

$$C: \frac{93.46 \text{ g}}{12.011 \text{ g mol}^{-1}} = 7.781 \text{ mol} \qquad \frac{7.781}{6.4885} = 1.199 \text{ or } 1.2$$

H: $\frac{6.5\text{ g}}{1.00794\text{ g mol}^{-1}} = 6.4885\text{ mol}$ $\frac{6.4887}{6.4885} = 1$

Ratio: $C_{1.2}H_1$ or $C_{12}H_{10}$

The formula mass of $C_{12}H_{10}$ agrees with the calculated formula mass.

69. A sample of $HgCl_2$ weighing 9.41 g is dissolved in 32.75 g of ethanol, C_2H_5OH (K_b = 1.20 °C/*m*). The boiling point elevation of the solution is 1.27 °C. Is $HgCl_2$ an electrolyte in ethanol? Show your calculations.

Solution

$$\Delta\text{bp} = K_b m = (1.20\text{ °C}/m)\left(\frac{9.41\text{ g} \times \frac{1\text{ mol HgCl}_2}{271.496\text{ g}}}{0.03275\text{ kg}}\right) = 1.27\text{ °C}$$

The observed change equals the theoretical change; therefore, no dissociation occurs.

70. A salt is known to be an alkali metal fluoride. A quick approximate determination of freezing point indicates that 4 g of the salt dissolved in 100 g of water produces a solution that freezes at about –1.4 °C. Assuming ideal solution behavior, what is the formula of the salt? Show your calculations.

Solution

Assuming complete dissociation of the alkali metal fluoride, $i = 2$.

$$m = \frac{\Delta T_f}{2 \times K_f} = \frac{1.4\text{ °C}}{2 \times 1.86\text{ °C}/m} = 0.38\ m$$

Moles of fluoride = 0.100 kg × 0.38 *m* = 0.038 mol

$$\text{Molar mass} = \frac{4\text{ g}}{0.038\text{ mol}} = 105\text{ g mol}^{-1}$$

The alkali metal fluoride with the nearest molecular mass is RbF (molar mass = 104.4662 g mol^{-1}).

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Chemistry: Atoms First 2e
11: Solutions and Colloids
11.5: Colloids

71. Identify the dispersed phase and the dispersion medium in each of the following colloidal systems: starch dispersion, smoke, fog, pearl, whipped cream, floating soap, jelly, milk, and ruby.

Solution

Colloidal System	Dispersed Phase	Dispersion Medium
starch dispersion	starch	water
smoke	solid particles	air
fog	water	air
pearl	water	calcium carbonate ($CaCO_3$)
whipped cream	air	cream
floating soap	air	soap

jelly	fruit juice	pectin gel
milk	butterfat	water
ruby	chromium(III) oxide (Cr_2O_3)	aluminum oxide (Al_2O_3)

72. Distinguish between dispersion methods and condensation methods for preparing colloidal systems.

Solution
Dispersion methods use a grinding device or some other means to bring about the subdivision of larger particles. Condensation methods bring smaller units together to form a larger unit. For example, water molecules in the vapor state come together to form very small droplets that we see as clouds.

73. How do colloids differ from solutions with regard to dispersed particle size and homogeneity?

Solution
Colloidal dispersions consist of particles that are much bigger than the solutes of typical solutions. Colloidal particles are either very large molecules or aggregates of smaller species that usually are big enough to scatter light. Colloids are homogeneous on a macroscopic (visual) scale, while solutions are homogeneous on a microscopic (molecular) scale.

74. Explain the cleansing action of soap.

Solution
Soap molecules have both a hydrophobic and a hydrophilic end. The charged (hydrophilic) end, which is usually associated with an alkali metal ion, ensures water solubility. The hydrophobic end permits attraction to oil, grease, and other similar nonpolar substances that normally do not dissolve in water but are pulled into the solution by the soap molecules.

75. How can it be demonstrated that colloidal particles are electrically charged?

Solution
If they are placed in an electrolytic cell, dispersed particles will move toward the electrode that carries a charge opposite to their own charge. At this electrode, the charged particles will be neutralized and will coagulate as a precipitate.

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Chemistry: Atoms First 2e
12: Thermodynamics
12.1: Spontaneity

1. What is a spontaneous reaction?

Solution
A reaction has a natural tendency to occur and takes place without the continual input of energy from an external source.

2. What is a nonspontaneous reaction?

Solution
A reaction that has no natural tendency to occur and takes place only with the continual input of energy from an external source.

3. Indicate whether the following processes are spontaneous or nonspontaneous.
(a) Liquid water freezing at a temperature below its freezing point
(b) Liquid water freezing at a temperature above its freezing point
(c) The combustion of gasoline
(d) A ball thrown into the air
(e) A raindrop falling to the ground
(f) Iron rusting in a moist atmosphere

Solution
(a) spontaneous; (b) nonspontaneous; (c) spontaneous; (d) nonspontaneous; (e) spontaneous; (f) spontaneous

4. A helium-filled balloon spontaneously deflates overnight as He atoms diffuse through the wall of the balloon. Describe the redistribution of matter and/or energy that accompanies this process.

Solution
The process involves a greater dispersal of matter as the He atoms transfer from a relatively small initial volume (the balloon) to a much larger final volume (the room, or house, or ultimately earth's atmosphere).

5. Many plastic materials are organic polymers that contain carbon and hydrogen. The oxidation of these plastics in air to form carbon dioxide and water is a spontaneous process; however, plastic materials tend to persist in the environment. Explain.

Solution
Although the oxidation of plastics is spontaneous, the rate of oxidation is very slow. Plastics are therefore kinetically stable and do not decompose appreciably even over relatively long periods of time.

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Chemistry: Atoms First 2e
12: Thermodynamics
12.2: Entropy

6. In Figure 12.8 all possible distributions and microstates are shown for four different particles shared between two boxes. Determine the entropy change, ΔS, if the particles are initially evenly distributed between the two boxes, but upon redistribution all end up in Box (b).

Solution

There are six initial microstates and one final microstate.

$$\Delta S = k \ln \frac{w_f}{w_i} = 1.38 \times 10^{-23} \text{ J/K} \times \ln \frac{1}{6} = -2.47 \times 10^{-23} \text{ J/K}$$

7. In Figure 12.8, all of the possible distributions and microstates are shown for four different particles shared between two boxes. Determine the entropy change, ΔS, for the system when it is converted from distribution (b) to distribution (d).

Solution
There are four initial microstates and four final microstates.

$$\Delta S = k \ln \frac{w_f}{w_i} = 1.38 \times 10^{-23} \text{ J/K} \times \ln \frac{4}{4} = 0$$

8. How does the process described in the previous item relate to the system shown in Figure 12.4?

Solution
The process described represents to the reverse (right-to-left) change shown in the figure. This would correspond to an expanded gas contracting to occupy just one of the two available flasks, which is a nonspontaneous process.

9. Consider a system similar to the one in Figure 12.8, except that it contains six particles instead of four. What is the probability of having all the particles in only one of the two boxes in the case? Compare this with the similar probability for the system of four particles that we have derived to be equal to $\frac{1}{8}$. What does this comparison tell us about even larger systems?

Solution
A system of N particles will have 2^N microstates, since each of the particles can be in one of the two states (on the left or on the right), and its probability to be in one of them is independent of positions of the other particles. Therefore, there are $2^6 = 64$ possible microstates for six particles. Only two of them correspond to all the particles being in one box (one for the right box and one for the left box). Thus, the probability for all the particles to be on one side is $\frac{2}{64} = \frac{1}{32}$. This probability is noticeably lower than the $\frac{1}{8}$ result for the four-particle system. The conclusion we can make is that the probability for all the particles to stay in only one part of the system will decrease rapidly as the number of particles increases, and, for instance, the probability for all molecules of gas to gather in only one side of a room at room temperature and pressure is negligible since the number of gas molecules in the room is very large.

10. Consider the system shown in Figure 12.9. What is the change in entropy for the process where the energy is initially associated only with particle A, but in the final state the energy is distributed between two different particles?

Solution
The figure shows a total of ten microstates. In only one of these is the energy associated with only A. It is found distributed between two different particles in six microstates.

$$\Delta S = k \ln \frac{w_f}{w_i} = 1.38 \times 10^{-23} \text{ J/K} \times \ln \frac{6}{1} = 2.47 \times 10^{-23} \text{ J/K}$$

11. Consider the system shown in Figure 12.9. What is the change in entropy for the process where the energy is initially associated with particles A and B, and the energy is distributed between two particles in different boxes (one in A-B, the other in C-D)?

Solution

There is only one initial state. For the final state, the energy can be contained in pairs A-C, A-D, B-C, or B-D. Thus, there are four final possible states.

$$\Delta S = k \ln\left(\frac{W_\text{f}}{W_\text{i}}\right) = 1.38 \times 10^{-23}\ \text{J/K} \times \ln\left(\frac{4}{1}\right) = 1.91 \times 10^{-23}\ \text{J/K}$$

12. Arrange the following sets of systems in order of increasing entropy. Assume one mole of each substance and the same temperature for each member of a set.

(a) $H_2(g)$, $HBrO_4(g)$, $HBr(g)$

(b) $H_2O(l)$, $H_2O(g)$, $H_2O(s)$

(c) $He(g)$, $Cl_2(g)$, $P_4(g)$

Solution

(a) $H_2(g) < HBr(g) < HBrO_4(g)$, due to increasing complexity and mass of molecules; (b) $H_2O(s) < H_2O(l) < H_2O(g)$ due to increasing dispersal of matter; (c) $He(g) < Cl_2(g) < P_4(g)$ due to increasing complexity and mass of species

13. At room temperature, the entropy of the halogens increases from I_2 to Br_2 to Cl_2. Explain.

Solution

The masses of these molecules would suggest the opposite trend in their entropies. The observed trend is a result of the more significant variation of entropy with a physical state. At room temperature, I_2 is a solid, Br_2 is a liquid, and Cl_2 is a gas.

14. Consider two processes: sublimation of $I_2(s)$ and melting of $I_2(s)$ (Note: the latter process can occur at the same temperature but somewhat higher pressure).

$I_2(s) \rightarrow I_2(g)$

$I_2(s) \rightarrow I_2(l)$

Is ΔS positive or negative in the processes? In which of the processes will the magnitude of the entropy change be greater?

Solution

The change of entropy will be positive in the both cases, as a relatively ordered solid is converted into less ordered liquid or gas. The sublimation will lead to a greater change in S since the final state (gas) is more disordered and dispersed than liquid.

15. Indicate which substance in the given pairs has the higher entropy value. Explain your choices.

(a) $C_2H_5OH(l)$ or $C_3H_7OH(l)$

(b) $C_2H_5OH(l)$ or $C_2H_5OH(g)$

(c) $2H(g)$ or $H(g)$

Solution

(a) $C_3H_7OH(l)$ as it is a larger molecule (more complex and more massive), and so more microstates describing its motions are available at any given temperature. (b) $C_2H_5OH(g)$ as it is in the gaseous state. (c) $2H(g)$, since entropy is an extensive property, and so two H atoms (or two moles of H atoms) possess twice as much entropy as one atom (or one mole of atoms).

16. Predict the sign of the entropy change for the following processes.

(a) An ice cube is warmed to near its melting point.

(b) Exhaled breath forms fog on a cold morning.

(c) Snow melts.

Solution
(a) $\Delta S > 0$; entropy increases since water molecules in the solid possess greater freedom of motion at the higher temperature. (b) $\Delta S < 0$; the fog is comprised of tiny water droplets formed by condensation of water vapor in the exhaled breath, and entropy decreases as the water first cools from body temperature to colder ambient temperature and then transitions from the gaseous to the liquid state. (c) $\Delta S > 0$; entropy increases as the water molecules in the solid snowflakes gain greater freedom of motion upon melting to yield liquid water.

17. Predict the sign of the enthalpy change for the following processes. Give a reason for your prediction.

(a) $Na^+(aq) + Cl^-(aq) \longrightarrow NaCl(s)$

(b) $2Fe + \frac{3}{2}O_2 \rightarrow Fe_2O_2$

(c) $2C_6H_{14}(l) + 19O_2(g) \longrightarrow 14H_2O(g) + 12CO_2(g)$

Solution
(a) Negative. The relatively ordered solid precipitating decreases the number of mobile ions in solution. (b) Negative. There is a net loss of three moles of gas from reactants to products. (c) Positive. There is a net increase of seven moles of gas from reactants to products.

18. Write the balanced chemical equation for the combustion of methane, $CH_4(g)$, to give carbon dioxide and water vapor. Explain why it is difficult to predict whether ΔS is positive or negative for this chemical reaction.

Solution
$CH_4(g) + 2O(g) \longrightarrow 2H_2O(g) + CO_2(g)$
With three moles of gaseous reactants and three moles of gaseous products, it is not clear if the products or reactants have the greater entropy.

19. Write the balanced chemical equation for the combustion of benzene, $C_6H_6(l)$, to give carbon dioxide and water vapor. Would you expect ΔS to be positive or negative in this process?

Solution
$C_6H_6(l) + 7.5O_2(g) \longrightarrow 3H_2O(g) + 6CO_2(g)$
There are 7.5 moles of gas initially, and 3 + 6 = 9 moles of gas in the end. Therefore, it is likely that the entropy increases as a result of this reaction, and ΔS is positive.

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Chemistry: Atoms First 2e
12: Thermodynamics
12.3: The Second and Third Laws of Thermodynamics

20. What is the difference between ΔS and $\Delta S°$ for a chemical change?

Solution
ΔS: any change in entropy under any set of conditions. $\Delta S°$: any change in entropy with products and reactants at standard conditions (1 bar or 1 atm for gases, 1 *M* for solutions); if no temperature information is provided, assume the temperature is 298.15 K.

21. Calculate ΔS°_{298} for the following changes.

(a) $SnCl_4(l) \longrightarrow SnCl_4(g)$

(b) $CS_2(g) \longrightarrow CS_2(l)$

(c) $Cu(s) \longrightarrow Cu(g)$

(d) $H_2O(l) \longrightarrow H_2O(g)$

(e) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

(f) $2HCl(g) + Pb(s) \longrightarrow PbCl_2(s) + H_2(g)$

(g) $Zn(s) + CuSO_4(s) \longrightarrow Cu(s) + ZnSO_4(s)$

Solution

(a)

$$\Delta S^{o}_{298} = \sum \nu \Delta S^{o}_{298}(\text{products}) - \sum \nu \Delta S^{o}_{298}(\text{reactants})$$

$$= 1\Delta S^{\circ}_{298}SnCl_4(g) - 1\Delta S^{\circ}_{298}SnCl_4(l)$$

$$= \left[1\text{ mol}\left(366\ \frac{\text{J}}{\text{mol K}}\right)\right] - \left[1\text{ mol}\left(259\ \frac{\text{J}}{\text{mol K}}\right)\right] = 107\text{ J/K}$$

(b)

$$\Delta S^{o}_{298} = \sum \nu \Delta S^{o}_{298}(\text{products}) - \sum \nu \Delta S^{o}_{298}(\text{reactants})$$

$$= 1\Delta S^{\circ}_{298}Cs_2(l) - 1\Delta S^{\circ}_{298}Cs_2(g)$$

$$= \left[1\text{ mol}\left(151.3\ \frac{\text{J}}{\text{mol K}}\right)\right] - \left[1\text{ mol}\left(238.0\ \frac{\text{J}}{\text{mol K}}\right)\right] = -86.7\text{ J/K}$$

(c)

$$\Delta S^{o}_{298} = \sum \nu \Delta S^{o}_{298}(\text{products}) - \sum \nu \Delta S^{o}_{298}(\text{reactants})$$

$$= 1\Delta S^{\circ}_{298}Cu(g) - 1\Delta S^{\circ}_{298}Cu(s)$$

$$= \left[1\text{ mol}\left(166.3\ \frac{\text{J}}{\text{mol K}}\right)\right] - \left[1\text{ mol}\left(33.15\ \frac{\text{J}}{\text{mol K}}\right)\right] = 133.2\text{ J/K}$$

(d)

$$\Delta S^{o}_{298} = \sum \nu \Delta S^{o}_{298}(\text{products}) - \sum \nu \Delta S^{o}_{298}(\text{reactants})$$

$$= 1\Delta S^{\circ}_{298}H_2O(g) - 1\Delta S^{\circ}_{298}H_2O(l)$$

$$= \left[1\text{ mol}\left(188.8\ \frac{\text{J}}{\text{mol K}}\right)\right] - \left[1\text{ mol}\left(70.0\ \frac{\text{J}}{\text{mol K}}\right)\right] = 118.8\text{ J/K}$$

(e)

$$\Delta S^{o}_{298} = \sum \nu \Delta S^{o}_{298}(\text{products}) - \sum \nu \Delta S^{o}_{298}(\text{reactants})$$

$$= 2\Delta S^{\circ}_{298}H_2O(l) - \left[1\Delta S^{\circ}_{298}O_2(g) + 2\Delta S^{\circ}_{298}H_2(g)\right]$$

$$= \left[2\text{ mol}\left(70.0\ \frac{\text{J}}{\text{mol K}}\right)\right] - \left[1\text{ mol}\left(205.2\ \frac{\text{J}}{\text{mol K}}\right) + 2\text{ mol}\left(130.7\ \frac{\text{J}}{\text{mol K}}\right)\right] = -326.6\text{ J/K};$$

(f)

$$\Delta S^{o}_{298} = \sum \nu \Delta S^{o}_{298}(\text{products}) - \sum \nu \Delta S^{o}_{298}(\text{reactants})$$

$$= \left[1\Delta S^{\circ}_{298}PbCl_2(s) + 1\Delta S^{\circ}_{298}H_2(g)\right] - \left[1\Delta S^{\circ}_{298}Pb(s) + 2\Delta S^{\circ}_{298}HCl(g)\right]$$

$$= \left[1\text{ mol}\left(136.0\ \frac{\text{J}}{\text{mol K}}\right) + 1\text{ mol}\left(130.7\ \frac{\text{J}}{\text{mol K}}\right)\right] -$$

$$\left[1\text{ mol}\left(64.81\ \frac{\text{J}}{\text{mol K}}\right) + 2\text{ mol}\left(186.9\ \frac{\text{J}}{\text{mol K}}\right)\right] = -171.9\text{ J/K}$$

(g)

$$\Delta S^{o}_{298} = \sum \nu \Delta S^{o}_{298}(\text{products}) - \sum \nu \Delta S^{o}_{298}(\text{reactants})$$

$$= \left[1\Delta S^{\circ}_{298}Cu(s) + 1\Delta S^{\circ}_{298}ZnSO_4(s)\right] - \left[1\Delta S^{\circ}_{298}Zn(s) + 1\Delta S^{\circ}_{298}CuSO_4(s)\right]$$

$$= \left[1\text{ mol}\left(33.15\ \frac{\text{J}}{\text{mol K}}\right) + 1\text{ mol}\left(110.5\ \frac{\text{J}}{\text{mol K}}\right)\right] -$$

$$\left[1\text{ mol}\left(41.6\ \frac{\text{J}}{\text{mol K}}\right) + 1\text{ mol}\left(109.2\ \frac{\text{J}}{\text{mol K}}\right)\right] = -7.2\text{ J/K}$$

22. Determine the entropy change for the combustion of liquid ethanol, C_2H_5OH, under the standard conditions to give gaseous carbon dioxide and liquid water.

Solution

The reaction is $C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$.

$$\Delta S^{o}_{298} = \sum \nu \Delta S^{o}_{298}(\text{products}) - \sum \nu \Delta S^{o}_{298}(\text{reactants})$$

$$= \left[2\Delta S^{\circ}_{298}CO_2(g) + 3\Delta S^{\circ}_{298}H_2O(l)\right] - \left[1\Delta S^{\circ}_{298}C_2H_5OH(l) + 3\Delta S^{\circ}_{298}O_2(g)\right]$$

$$= \left[2\text{ mol}\left(213.6\ \frac{\text{J}}{\text{mol K}}\right) + 3\text{ mol}\left(69.91\ \frac{\text{J}}{\text{mol K}}\right)\right] -$$

$$\left[1\text{ mol}\left(161\ \frac{\text{J}}{\text{mol K}}\right) + 3\text{ mol}\left(205.03\ \frac{\text{J}}{\text{mol K}}\right)\right] = -139\text{ J/K}$$

23. Determine the entropy change for the combustion of gaseous propane, C_3H_8, under the standard conditions to give gaseous carbon dioxide and water.

Solution

The reaction is $C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(g)$.

$$\Delta S^{o} = \sum \nu \Delta S^{o}(\text{products}) - \sum \nu \Delta S^{o}(\text{reactants})$$

$$= \left[3\Delta S^{\circ}CO_2(g) + 4\Delta S^{\circ}H_2O(g)\right] - \left[1\Delta S^{\circ}C_3H_8(g) + 5\Delta S^{\circ}O_2(g)\right]$$

$$= \left[3\text{ mol}\left(213.8\ \frac{\text{J}}{\text{mol K}}\right) + 4\text{ mol}\left(188.8\ \frac{\text{J}}{\text{mol K}}\right)\right] -$$

$$\left[1\text{ mol}\left(270.3\ \frac{\text{J}}{\text{mol K}}\right) + 5\text{ mol}\left(205.02\ \frac{\text{J}}{\text{mol K}}\right)\right] = 100.3\text{ J/K}$$

24. “Thermite” reactions have been used for welding metal parts such as railway rails and in metal refining. One such thermite reaction is $Fe_2O_3(s) + 2Al(s) \longrightarrow Al_2O_3(s) + 2Fe(s)$. Is

the reaction spontaneous at room temperature under standard conditions? During the reaction, the surroundings absorb 851.8 kJ/mol of heat.

Solution

Calculating ΔS_{univ} is necessary to answer the question:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T}$$

$$\Delta S^\circ_{\text{sys}} = \sum \nu \Delta S^\circ_{298}(\text{products}) - \sum \nu \Delta S^\circ_{298}(\text{reactants})$$

$$\Delta S^\circ_{\text{sys}} = \left(\Delta S^\circ_{298}\text{Fe} + \Delta S^\circ_{298}\text{Al}_2\text{O}_3\right) - \left(1\Delta S^\circ_{298}\text{Fe}_2\text{O}_3 + 2\Delta S^\circ_{298}\text{Al}\right)$$

$$\Delta S^\circ_{\text{sys}} = \left[2\text{ mol}\left(27.3\frac{\text{J}}{\text{mol K}}\right) + 1\text{ mol}\left(50.92\frac{\text{J}}{\text{mol K}}\right)\right] - \left[1\text{ mol}\left(87.40\frac{\text{J}}{\text{mol K}}\right) + 2\text{ mol}\left(28.3\frac{\text{J}}{\text{mol K}}\right)\right] = -38.48\text{ J/K}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} - \frac{q_{\text{sys}}}{T} = -38.48\frac{\text{J}}{\text{mol•K}} - \frac{-851.8\frac{\text{kJ}}{\text{mol}}\left(\frac{1000\text{ J}}{1\text{ kJ}}\right)}{298.15} = 2820\text{ J/K}$$

As $\Delta S_{\text{univ}} > 0$, the reaction is spontaneous.

25. Using the relevant S°_{298} values listed in Appendix G, calculate ΔS°_{298} for the following changes:

(a) $\text{N}_2(g) + 3\text{H}_2(g) \longrightarrow 2\text{NH}_3(g)$

(b) $\text{N}_2(g) + \frac{5}{2}\text{O}_2(g) \longrightarrow \text{N}_2\text{O}_5(g)$

Solution

(a) $\Delta S^\circ_{\text{sys}} = \sum \nu \Delta S^\circ_{298}(\text{products}) - \sum \nu \Delta S^\circ_{298}(\text{reactants})$

$$\Delta S^\circ_{\text{sys}} = \left(2\Delta S^\circ_{298}\text{NH}_3\right) - \left(1\Delta S^\circ_{298}\text{N}_2 + 3\Delta S^\circ_{298}\text{H}_2\right)$$

$$\Delta S^\circ_{\text{sys}} = \left[2\text{ mol}\left(192.8\frac{\text{J}}{\text{mol K}}\right)\right] - \left[1\text{ mol}\left(191.6\frac{\text{J}}{\text{mol K}}\right) + 3\text{ mol}\left(130.7\frac{\text{J}}{\text{mol K}}\right)\right];$$

$$= -198.1\text{ J/K}$$

(b) $\Delta S^\circ_{\text{sys}} = \sum \nu \Delta S^\circ_{298}(\text{products}) - \sum \nu \Delta S^\circ_{298}(\text{reactants})$

$$\Delta S^\circ_{\text{sys}} = \left(2\Delta S^\circ_{298}\text{N}_2\text{O}_5\right) - \left(1\Delta S^\circ_{298}\text{N}_2 + \frac{5}{2} \times \Delta S^\circ_{298}\text{O}_2\right)$$

$$\Delta S^\circ_{\text{sys}} = \left[1\text{ mol}\left(355.7\frac{\text{J}}{\text{mol K}}\right)\right] - \left[1\text{ mol}\left(191.6\frac{\text{J}}{\text{mol K}}\right) + \frac{5}{2}\text{ mol}\left(205.2\frac{\text{J}}{\text{mol K}}\right)\right]$$

$$= -348.9\text{ J/K}$$

26. From the following information, determine ΔS°_{298} for the following:

$\text{N}(g) + \text{O}(g) \longrightarrow \text{NO}(g) \qquad \Delta S^\circ_{298} = ?$

$N_2(g) + O_2(g) \longrightarrow 2NO(g) \qquad \Delta S^\circ_{298} = 24.8\ \text{J/K}$

$N_2(g) \longrightarrow 2N(g) \qquad \Delta S^\circ_{298} = 115.0\ \text{J/K}$

$O_2(g) \longrightarrow 2O(g) \qquad \Delta S^\circ_{298} = 117.0\ \text{J/K}$

Solution

Reverse the last two reference equations, and change the sign of ΔS°_{298}:

$2N(g) \longrightarrow N_2(g) \qquad \Delta S^\circ_{298} = -115.0\ \text{J/K}$

$2O(g) \longrightarrow O_2(g) \qquad \Delta S^\circ_{298} = -117.0\ \text{J/K}$

Combine these with the other reference equation:

$N_2(g) + O_2(g) \longrightarrow 2NO(g) \qquad \Delta S^\circ_{298} = 24.8\ \text{J/K}$

This generates the following:

$2N(g) + 2O(g) \longrightarrow 2NO(g)$

$\Delta S^\circ_{298} = (-115.0\ \text{J/K}) + (-117.0\ \text{J/K}) + 24.8\ \text{J/K} = -207.2\ \text{J/K}$

As the coefficients are doubled, what is required in the target equation?

$N(g) + O(g) \longrightarrow NO(g) \qquad \Delta S^\circ_{298} = \dfrac{-207.2\ \text{J/K}}{2} = -103.6\ \text{J/K}$

27. By calculating ΔS_{univ} at each temperature, determine if the melting of 1 mole of NaCl(s) is spontaneous at 500 °C and at 700 °C.

$S^\circ_{\text{NaCl}(s)} = 72.11\dfrac{\text{J}}{\text{mol•K}} \qquad S^\circ_{\text{NaCl}(l)} = 95.06\dfrac{\text{J}}{\text{mol•K}} \qquad \Delta H^\circ_{\text{fusion}} = 27.95\ \text{kJ/mol}$

What assumptions are made about the thermodynamic information (entropy and enthalpy values) used to solve this problem?

Solution

The process is $\text{NaCl}(s) \longrightarrow \text{NaCl}(l)$.

At 500 °C, the following is true:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} = (95.06 - 72.11)\frac{\text{J}}{\text{mol•K}} + \frac{-27.95 \times 10^3\ \dfrac{\text{J}}{\text{mol}}}{500 + 273.15} = -13.2\frac{\text{J}}{\text{mol•K}}$$

At 700 °C, the following is true:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} = (95.06 - 72.11)\frac{\text{J}}{\text{mol•K}} + \frac{-27.95 \times 10^3\ \dfrac{\text{J}}{\text{mol}}}{700 + 273.15} = -5.8\frac{\text{J}}{\text{mol•K}}$$

As $\Delta S_{\text{univ}} < 0$ at each of these temperatures, melting is not spontaneous at either of them. The given values for entropy and enthalpy are for NaCl at 298 K. It is assumed that these do not change significantly at the higher temperatures used in the problem.

28. Use the standard entropy data in Appendix G to determine the change in entropy for each of the reactions listed in Exercise 33. All the processes occur at the standard conditions and 25 °C.

Solution

(a) $\Delta S^\circ_{298} = \sum v\Delta S°(\text{products}) - \sum v\Delta S°(\text{reactants})$

$$\Delta S^\circ_{298} = \left[1\ \text{mol}\left(3.20\ \frac{\text{J}}{\text{mol•K}}\right) + 1\ \text{mol}\left(205.2\ \frac{\text{J}}{\text{mol•K}}\right)\right] - \left[1\ \text{mol}\left(53.05\ \frac{\text{J}}{\text{mol•K}}\right)\right] = 184.2\ \text{J/K}$$

(b) $\Delta S^\circ_{298} = \sum v\Delta S^\circ(\text{products}) - \sum v\Delta S^\circ(\text{reactants})$

$$\Delta S^\circ_{298} = \left[2\ \text{mol}\left(198.7\ \frac{\text{J}}{\text{mol•K}}\right)\right] - \left[1\ \text{mol}\left(152.23\ \frac{\text{J}}{\text{mol•K}}\right) + 1\ \text{mol}\left(130.7\ \frac{\text{J}}{\text{mol•K}}\right)\right] = 114.5\ \text{J/K}$$

(c) $\Delta S^\circ_{298} = \sum v\Delta S^\circ(\text{products}) - \sum v\Delta S^\circ(\text{reactants})$

$$\Delta S^\circ_{298} = \left[1\ \text{mol}\left(66.5\ \frac{\text{J}}{\text{mol•K}}\right)\right] - \left[1\ \text{mol}\left(33.15\ \frac{\text{J}}{\text{mol•K}}\right) + 1\ \text{mol}\left(167.82\ \frac{\text{J}}{\text{mol•K}}\right)\right] = -134.5\ \text{J/K}$$

(d) $\Delta S^\circ_{298} = \sum v\Delta S^\circ(\text{products}) - \sum v\Delta S^\circ(\text{reactants})$

$$\Delta S^\circ_{298} = \left[1\ \text{mol}\left(90.71\ \frac{\text{J}}{\text{mol•K}}\right) + 1\ \text{mol}\left(188.8\ \frac{\text{J}}{\text{mol•K}}\right)\right] - \left[2\ \text{mol}\left(42.8\ \frac{\text{J}}{\text{mol•K}}\right) + 1\ \text{mol}\left(213.8\ \frac{\text{J}}{\text{mol•K}}\right)\right] = -20.4\ \text{J/K}$$

(e) $\Delta S^\circ_{298} = \sum v\Delta S^\circ(\text{products}) - \sum v\Delta S^\circ(\text{reactants})$

$$\Delta S^\circ_{298} = \left[1\ \text{mol}\left(5.740\ \frac{\text{J}}{\text{mol•K}}\right) + 2\ \text{mol}\left(188.8\ \frac{\text{J}}{\text{mol•K}}\right)\right] - \left[1\ \text{mol}\left(186.3\ \frac{\text{J}}{\text{mol•K}}\right) + 1\ \text{mol}\left(205.2\ \frac{\text{J}}{\text{mol•K}}\right)\right] = -8.16\ \text{J/K}$$

(f) $\Delta S^\circ_{298} = \sum v\Delta S^\circ(\text{products}) - \sum v\Delta S^\circ(\text{reactants})$

$$\Delta S^\circ_{298} = \left[1\ \text{mol}\left(309.7\ \frac{\text{J}}{\text{mol•K}}\right) + 1\ \text{mol}\left(319.45\ \frac{\text{J}}{\text{mol•K}}\right)\right] - \left[1\ \text{mol}\left(238.0\ \frac{\text{J}}{\text{mol•K}}\right) + 3\ \text{mol}\left(223.1\ \frac{\text{J}}{\text{mol•K}}\right)\right] = -278.2\ \text{J/K}$$

29. Use the standard entropy data in Appendix G to determine the change in entropy for each of the reactions listed in Exercise 34. All the processes occur at the standard conditions and 25 °C.

Solution

(a) $\Delta S^\circ_{298} = \sum v\Delta S^\circ(\text{products}) - \sum v\Delta S^\circ(\text{reactants})$

$$\Delta S^\circ_{298} = \left[1\ \text{mol}\left(213.8\ \frac{\text{J}}{\text{mol•K}}\right)\right] - \left[1\ \text{mol}\left(5.740\ \frac{\text{J}}{\text{mol•K}}\right) + 1\ \text{mol}\left(205.2\ \frac{\text{J}}{\text{mol•K}}\right)\right] = 2.86\ \text{J/K}$$

(b) $\Delta S^\circ_{298} = \sum v\Delta S^\circ(\text{products}) - \sum v\Delta S^\circ(\text{reactants})$

$$\Delta S^\circ_{298} = \left[2\ \text{mol}\left(210.8\ \frac{\text{J}}{\text{mol•K}}\right)\right] - \left[1\ \text{mol}\left(191.6\ \frac{\text{J}}{\text{mol•K}}\right) + 1\ \text{mol}\left(205.2\ \frac{\text{J}}{\text{mol•K}}\right)\right] = 24.8\ \text{J/K}$$

(c) $\Delta S^\circ_{298} = \sum v\Delta S^\circ(\text{products}) - \sum v\Delta S^\circ(\text{reactants})$

$$\Delta S^\circ_{298} = \left[1\ \text{mol}\left(120.9\ \frac{\text{J}}{\text{mol•K}}\right)\right] - \left[2\ \text{mol}\left(33.15\ \frac{\text{J}}{\text{mol•K}}\right) + 1\ \text{mol}\left(167.82\ \frac{\text{J}}{\text{mol•K}}\right)\right]$$

$$= -113.2\ \text{J/K}$$

(d) $\Delta S^\circ_{298} = \sum v\Delta S°(\text{products}) - \sum v\Delta S°(\text{reactants})$

$$\Delta S^\circ_{298} = \left[1\ \text{mol}\left(83.4\ \frac{\text{J}}{\text{mol•K}}\right)\right] - \left[1\ \text{mol}\left(38.1\ \frac{\text{J}}{\text{mol•K}}\right) + 1\ \text{mol}\left(70.0\ \frac{\text{J}}{\text{mol•K}}\right)\right] = -24.7\ \text{J/K}$$

(e) $\Delta S^\circ_{298} = \sum v\Delta S°(\text{products}) - \sum v\Delta S°(\text{reactants})$

$$\Delta S^\circ_{298} = \left[2\ \text{mol}\left(27.3\ \frac{\text{J}}{\text{mol•K}}\right) + 3\ \text{mol}\left(213.8\ \frac{\text{J}}{\text{mol•K}}\right)\right] -$$

$$\left[1\ \text{mol}\left(81.40\ \frac{\text{J}}{\text{mol•K}}\right) + 3\ \text{mol}\left(197.7\ \frac{\text{J}}{\text{mol•K}}\right)\right] = 15.5\ \text{J/K}$$

(f) $\Delta S^\circ_{298} = \sum v\Delta S°(\text{products}) - \sum v\Delta S°(\text{reactants})$

$$\Delta S^\circ_{298} = \left[1\ \text{mol}\left(106.5\ \frac{\text{J}}{\text{mol•K}}\right) + 2\ \text{mol}\left(188.8\ \frac{\text{J}}{\text{mol•K}}\right)\right] - \left[1\ \text{mol}\left(194.14\ \frac{\text{J}}{\text{mol•K}}\right)\right] = 290.0\ \text{J/K}$$

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Chemistry: Atoms First 2e
12: Thermodynamics
12.4: Free Energy

30. What is the difference between ΔG and $\Delta G°$ for a chemical change?

Solution

ΔG: the (Gibbs) free energy change for any reaction under any set of conditions. $\Delta G°$: the (Gibbs) free energy change for a reaction in which the reagents and products are in their standard states (1 bar or 1 atm for gases, 1 *M* for solutions) at a specified temperature.

31. A reactions has $\Delta H^\circ_{298} = 100\ \text{kJ/mol}$ and $\Delta S^\circ_{298} = 250\ \text{J/mol•K}$. Is the reaction spontaneous at room temperature? If not, under what temperature conditions will it become spontaneous?

Solution

$$\Delta G^\circ_{298} = \Delta H^\circ_{298} - T\Delta S^\circ_{298}$$

$$\Delta G^\circ_{298} = 100 - 298.15 \times 250\frac{\text{J}}{\text{mol•K}}\left(\frac{1\ \text{kJ}}{1000\ \text{J}}\right) = 25.5\ \text{kJ/mol}$$

The $\Delta G^\circ_{298} > 0$, so the reaction is nonspontaneous at room temperature.

$\Delta G = \Delta H - T\Delta S$

$$0 = 100 - T\left[250\frac{\text{J}}{\text{mol•K}}\left(\frac{1\ \text{kJ}}{1000\ \text{J}}\right)\right]$$

$T = 400\ \text{K}$

Above 400 K, ΔG will become negative, and the reaction will become spontaneous.

32. Explain what happens as a reaction starts with $\Delta G < 0$ (negative) and reaches the point where $\Delta G = 0$.

Solution

The reaction starts with $Q < K$ as the reaction proceeds, and Q increases until equilibrium is reached (where $Q = K$).

33. Use the standard free energy of formation data in Appendix G to determine the free energy change for each of the following reactions, which are run under standard state conditions and 25 °C. Identify each as either spontaneous or nonspontaneous at these conditions.

(a) $\mathrm{MnO_2}(s) \longrightarrow \mathrm{Mn}(s) + \mathrm{O_2}(g)$

(b) $\mathrm{H_2}(g) + \mathrm{Br_2}(l) \longrightarrow 2\mathrm{HBr}(g)$

(c) $\mathrm{Cu}(s) + \mathrm{S}(g) \longrightarrow \mathrm{CuS}(s)$

(d) $2\mathrm{LiOH}(s) + \mathrm{CO_2}(g) \longrightarrow \mathrm{Li_2CO_3}(s) + \mathrm{H_2O}(g)$

(e) $\mathrm{CH_4}(g) + \mathrm{O_2}(g) \longrightarrow \mathrm{C}(s,\ \text{graphite}) + 2\mathrm{H_2O}(g)$

(f) $\mathrm{CS_2}(g) + 3\mathrm{Cl_2}(g) \longrightarrow \mathrm{CCl_4}(g) + \mathrm{S_2Cl_2}(g)$

Solution

(a) $\Delta G^\circ_{298} = \sum \nu \Delta G^\circ_\mathrm{f}(\text{products}) - \sum \nu \Delta G^\circ_\mathrm{f}(\text{reactants})$

$\Delta G^\circ_{298} = \left[1\ \text{mol}(0\ \text{kJ/mol}) + 1\ \text{mol}(0\ \text{kJ/mol})\right] - \left[1\ \text{mol}(-465.1\ \text{kJ/mol})\right] = 465.1$

nonspontaneous

(b) $\Delta G^\circ_{298} = \sum \nu \Delta G^\circ_\mathrm{f}(\text{products}) - \sum \nu \Delta G^\circ_\mathrm{f}(\text{reactants})$

$\Delta G^\circ_{298} = \left[2\ \text{mol}(-53.43\ \text{kJ/mol})\right] - \left[1\ \text{mol}(0\ \text{kJ/mol}) + 1\ \text{mol}(0\ \text{kJ/mol})\right] = -106.86\ \text{kJ}$

spontaneous

(c) $\Delta G^\circ_{298} = \sum \nu \Delta G^\circ_\mathrm{f}(\text{products}) - \sum \nu \Delta G^\circ_\mathrm{f}(\text{reactants})$

$\Delta G^\circ_{298} = \left[1\ \text{mol}(-53.6\ \text{kJ/mol})\right] - \left[1\ \text{mol}(0\ \text{kJ/mol}) + 1\ \text{mol}(0\ \text{kJ/mol})\right] = -291.9\ \text{kJ}$

spontaneous

(d) $\Delta G^\circ_{298} = \sum \nu \Delta G^\circ_\mathrm{f}(\text{products}) - \sum \nu \Delta G^\circ_\mathrm{f}(\text{reactants})$

$\Delta G^\circ_{298} = \left[1\ \text{mol}(-1132.19\ \text{kJ/mol}) + 1\ \text{mol}(-228.59\ \text{kJ/mol})\right] -$

$\left[2\ \text{mol}(-441.5\ \text{kJ/mol}) + 1\ \text{mol}(-394.36\ \text{kJ/mol})\right] = -83.4\ \text{kJ}$

spontaneous

(e) $\Delta G^\circ_{298} = \sum \nu \Delta G^\circ_\mathrm{f}(\text{products}) - \sum \nu \Delta G^\circ_\mathrm{f}(\text{reactants})$

$\Delta G^\circ_{298} = \left[1\ \text{mol}(0\ \text{kJ/mol}) + 2\ \text{mol}(-228.59\ \text{kJ/mol})\right] -$

$\left[1\ \text{mol}(-50.5\ \text{kJ/mol}) + 1\ \text{mol}(0\ \text{kJ/mol})\right] = -406.7\ \text{kJ}$

spontaneous

(f) $\Delta G^\circ_{298} = \sum \nu \Delta G^\circ_f(\text{products}) - \sum \nu \Delta G^\circ_f(\text{reactants})$

$$\Delta G^\circ_{298} = \left[1\text{ mol}\left(-62.5\text{ kJ/mol}\right) + 1\text{ mol}\left(-29.25\text{ kJ/mol}\right)\right] - \left[1\text{ mol}\left(66.8\text{ kJ/mol}\right) + 3\text{ mol}\left(0\text{ kJ/mol}\right)\right] = -30.0\text{ kJ}$$

spontaneous

34. Use the standard free energy data in Appendix G to determine the free energy change for each of the following reactions, which are run under standard state conditions and 25 °C. Identify each as either spontaneous or nonspontaneous at these conditions.

(a) $C(s, \text{graphite}) + O_2(g) \longrightarrow CO_2(g)$

(b) $O_2(g) + N_2(g) \longrightarrow 2NO(g)$

(c) $2Cu(s) + S(g) \longrightarrow Cu_2S(s)$

(d) $CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(s)$

(e) $Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g)$

(f) $CaSO_4 \cdot 2H_2O(s) \longrightarrow CaSO_4(s) + 2H_2O(g)$

Solution

(a) $\Delta G^\circ_{298} = \sum \nu \Delta G^\circ_f(\text{products}) - \sum \nu \Delta G^\circ_f(\text{reactants})$

$$\Delta G^\circ_{298} = \left[1\text{ mol}\left(-394.36\text{ kJ/mol}\right)\right] - \left[1\text{ mol}\left(0\text{ kJ/mol}\right) + 1\text{ mol}\left(0\text{ kJ/mol}\right)\right] = -394.36\text{ kJ}$$

spontaneous

(b) $\Delta G^\circ_{298} = \sum \nu \Delta G^\circ_f(\text{products}) - \sum \nu \Delta G^\circ_f(\text{reactants})$

$$\Delta G^\circ = \left[2\text{ mol}\left(87.6\text{ kJ/mol}\right)\right] - \left[1\text{ mol}\left(0\text{ kJ/mol}\right) + 1\text{ mol}\left(0\text{ kJ/mol}\right)\right] = 175.2\text{ kJ}$$

nonspontaneous

(c) $\Delta G^\circ_{298} = \sum \nu \Delta G^\circ_f(\text{products}) - \sum \nu \Delta G^\circ_f(\text{reactants})$

$$\Delta G^\circ = \left[1\text{ mol}\left(-86.2\text{ kJ/mol}\right)\right] - \left[2\text{ mol}\left(0\text{ kJ/mol}\right) + 1\text{ mol}\left(238.25\text{ kJ/mol}\right)\right] = -324.4\text{ kJ}$$

spontaneous

(d) $\Delta G^\circ_{298} = \sum \nu \Delta G^\circ_f(\text{products}) - \sum \nu \Delta G^\circ_f(\text{reactants})$

$$\Delta G^\circ = \left[1\text{ mol}\left(-897.5\text{ kJ/mol}\right)\right] - \left[1\text{ mol}\left(-603.3\text{ kJ/mol}\right) + 1\text{ mol}\left(-237.1\text{ kJ/mol}\right)\right] = -57.1\text{ kJ}$$

spontaneous

(e) $\Delta G^\circ_{298} = \sum \nu \Delta G^\circ_f(\text{products}) - \sum \nu \Delta G^\circ_f(\text{reactants})$

$$\Delta G^\circ_{298} = \left[2\text{ mol}\left(0\text{ kJ/mol}\right) + 3\text{ mol}\left(-394.36\text{ kJ/mol}\right)\right] - \left[1\text{ mol}\left(-742.2\text{ kJ/mol}\right) + 3\text{ mol}\left(-137.15\text{ kJ/mol}\right)\right] = -29.4\text{ kJ}$$

spontaneous

(f) $\Delta G^\circ_{298} = \sum \nu \Delta G^\circ_f(\text{products}) - \sum \nu \Delta G^\circ_f(\text{reactants})$

$$\Delta G^\circ = \left[1\text{ mol}\left(-1322.0\text{ kJ/mol}\right) + 2\text{ mol}\left(-228.59\text{ kJ/mol}\right)\right] - \left[1\text{ mol}\left(-1797.45\text{ kJ/mol}\right)\right] = 18.3\text{ kJ}$$

nonspontaneous

35. Given:

$P_4(s) + 5O_2(g) \longrightarrow P_4O_{10}(s) \qquad \Delta G^\circ_{298} = -2697.0\text{ kJ/mol}$

$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g) \qquad \Delta G^\circ_{298} = -457.18\text{ kJ/mol}$

$6H_2O(g) + P_4O_{10}(s) \longrightarrow 4H_3PO_4(l) \qquad \Delta G^\circ_{298} = -428.66\text{ kJ/mol}$

(a) Determine the standard free energy of formation, ΔG°_f, for phosphoric acid.

(b) How does your calculated result compare to the value in Appendix G? Explain.

Solution

(a) The standard free energy of formation is the standard free energy change for $\frac{1}{4}P_4(s) + \frac{3}{2}H_2(g) + 2O_2(g) \longrightarrow H_3PO_4(l)$. We can use a Hess's law-like approach. Note that adding the first reaction plus three times the second reaction plus the third reaction gives, after cancelling terms

$P_4(s) + 6H_2(g) + 8O_2(g) \longrightarrow 4H_3PO_4(l)$

$\Delta G^\circ_{rxn} = \left[\left(-2697.0\right) + 3\left(-457.18\right) + \left(-428.66\right)\right]\text{ kJ/mol} = -4497.2\text{ kJ/mol}$

Dividing this result by four gives the equation of interest. The standard free energy of formation is –1124.3kJ/mol. (b) The calculation agrees with the value in Appendix G because free energy is a state function (just like the enthalpy and entropy), so its change depends only on the initial and final states, not the path between them.

36. Is the formation of ozone ($O_3(g)$) from oxygen ($O_2(g)$) spontaneous at room temperature under standard state conditions?

Solution

$3O_2(g) \longrightarrow 2O_3(g)$

$\Delta G^\circ_{298} = \sum \nu \Delta G^\circ_f(\text{products}) - \sum \nu \Delta G^\circ_f(\text{reactants})$

$\Delta G^\circ_{298} = \left[2\text{ mol}\left(163.2\text{ kJ/mol}\right)\right] - \left[1\text{ mol}\left(0\text{ kJ/mol}\right)\right] = 326.4\text{ kJ};$

nonspontaneous

37. Consider the decomposition of red mercury(II) oxide under standard state conditions.

$2HgO(s,\text{ red}) \longrightarrow 2Hg(l) + O_2(g)$

(a) Is the decomposition spontaneous under standard state conditions?

(b) Above what temperature does the reaction become spontaneous?

Solution

(a) Using the data in Appendix G, determine ΔG°_{298}:

$$\Delta G^\circ_{298} = 2\Delta G^\circ_f\left(\text{Hg}(l)\right) + \Delta G^\circ_f\left(\text{O}_2(g)\right) - 2\Delta G^\circ_f\left(\text{HgO}(s,\text{ red})\right)$$
$$= \left\{2(0) + 0 - 2(-58.5)\right\}\text{ kJ/mol} = 117.0\text{ kJ/mol}$$

From its value at 298.15 K, the reaction is nonspontaneous; (b) requires the ratio of the standard enthalpy change to the standard entropy change:

$$\Delta H^\circ_{298} = 2\Delta H^\circ_f\left(\text{Hg}(l)\right) + \Delta H^\circ_f\left(\text{O}_2(g)\right) - 2\Delta H^\circ_f\left(\text{HgO}(s,\text{ red})\right)$$
$$= [2(0) + 0 - 2(-90.83)]\text{kJ/mol} = 181.66\text{ kJ/mol}$$
$$\Delta S^\circ_{298} = 2S^\circ_{298}\left(\text{Hg}(l)\right) + S^\circ_{298}\left(\text{O}_2(g)\right) - 2S^\circ_{298}\left(\text{HgO}(s,\text{ red})\right)$$
$$= [2(75.9) + 205.0 - 2(70.29)]\text{J/K•mol} = 216.42\text{ J/K•mol}$$
$$T = \frac{\Delta H^\circ_{298}}{\Delta S^\circ_{298}} = \frac{181.66 \times 10^3\text{ J/mol}}{216.42\text{ J/K•mol}} = 839\text{ K} = 566\text{ °C}$$

Above 566 °C the process is spontaneous.

38. Among other things, an ideal fuel for the control thrusters of a space vehicle should decompose in a spontaneous exothermic reaction when exposed to the appropriate catalyst. Evaluate the following substances under standard state conditions as suitable candidates for fuels.

(a) Ammonia: $2\text{NH}_3(g) \longrightarrow \text{N}_2(g) + 3\text{H}_2(g)$

(b) Diborane: $\text{B}_2\text{H}_6(g) \longrightarrow 2\text{B}(g) + 3\text{H}_2(g)$

(c) Hydrazine: $\text{N}_2\text{H}_4(g) \longrightarrow \text{N}_2(g) + 2\text{H}_2(g)$

(d) Hydrogen peroxide: $\text{H}_2\text{O}_2(l) \longrightarrow \text{H}_2\text{O}(g) + \frac{1}{2}\text{O}_2(g)$

Solution

In each case, determine ΔG°_{298}. Suitable fuels will have $\Delta G < 0$ and $\Delta H < 0$.

(a) $\Delta G^\circ_{298} = \Delta G^\circ_{f_{N_2(g)}} + 3\Delta G^\circ_{f_{H_2(g)}} - 2\Delta G^\circ_{f_{NH_3(g)}} = 0 + 3(0) - 2(-16.5) = 33\text{ kJ}$

$\Delta H^\circ_{298} = \Delta H^\circ_{f_{N_2(g)}} + 3\Delta H^\circ_{f_{H_2(g)}} - 2\Delta H^\circ_{f_{NH_3(g)}} = 0 + 3(0) - 2(-46.11) = 92.22\text{ kJ}$

(b) $\Delta G^\circ_{298} = 2\Delta G^\circ_{f_{B(g)}} + 3\Delta G^\circ_{f_{H_2(g)}} - \Delta G^\circ_{f_{B_2H_6(g)}} = 2(518.8) + 3(0) - 86.6 = 951\text{ kJ}$

$\Delta H^\circ_{298} = 2\Delta H^\circ_{f_{B(g)}} + 3\Delta H^\circ_{f_{H_2(g)}} - \Delta H^\circ_{f_{B_2H_6(g)}} = 2(562.7) + 3(0) - 36 = 1089\text{ kJ}$

(c) $\Delta G^\circ_{298} = \Delta G^\circ_{f_{N_2(g)}} + 2\Delta G^\circ_{f_{H_2(g)}} - \Delta G^\circ_{f_{N_2H_4(g)}} = 0 + 2(0) - 159.3 = -159.3\text{ kJ}$

$\Delta H^\circ_{298} = \Delta H^\circ_{f_{N_2(g)}} + 2\Delta H^\circ_{f_{H_2(g)}} - \Delta H^\circ_{f_{N_2H_4(g)}} = 0 + 2(0) - 95.4 = -95.4\text{ kJ}$

(d) $\Delta G^\circ_{298} = \Delta G^\circ_{f_{H_2O(g)}} + \frac{1}{2}\Delta G^\circ_{f_{O_2(g)}} - \Delta G^\circ_{f_{H_2O_2(l)}} = 0 + \frac{1}{2}(0) - 120.4 = -120.4\text{ kJ}$

$\Delta H^\circ_{298} = \Delta H^\circ_{f_{H_2O(g)}} + \frac{1}{2}\Delta H^\circ_{f_{O_2(g)}} - \Delta H^\circ_{f_{H_2O_2(l)}} = 0 + \frac{1}{2}(0) - 187.8 = -187.8\text{ kJ}$

Both reactions (c) and (d) are suitable under the given conditions.

39. Calculate $\Delta G°$ for each of the following reactions from the equilibrium constant at the temperature given.

(a) $\text{N}_2(g) + \text{O}_2(g) \longrightarrow 2\text{NO}(g)$ T = 2000 °C $K_P = 4.1 \times 10^{-4}$

(b) $\text{H}_2(g) + \text{I}_2(g) \longrightarrow 2\text{HI}(g)$ T = 400 °C $K_P = 50.0$

(c) $CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g)$ T = 980 °C $K_P = 1.67$

(d) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$ T = 900 °C $K_P = 1.04$

(e) $HF(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + F^-(aq)$ T = 25 °C $K_a = 7.2 \times 10^{-4}$

(f) $AgBr(s) \longrightarrow Ag^+(aq) + Br^-(aq)$ T = 25 °C $K_{sp} = 3.3 \times 10^{-13}$

Solution
(a) $\Delta G° = -RT \ln K_P = -(8.314 \text{ J K}^{-1})(2273.15 \text{ K})(\ln 4.1 \times 10^{-4}) = 147 \text{ kJ} = 1.5 \times 10^2 \text{ kJ}$;
(b) $\Delta G° = -(8.314 \text{ J K}^{-1})(673.15 \text{ K})(\ln 50.0) = -21{,}893 \text{ J} = -21.9 \text{ kJ}$;
(c) $\Delta G° = -(8.314 \text{ J K}^{-1})(1253.15 \text{ K})(\ln 1.67) = -5.34 \text{ kJ}$;
(d) $\Delta G° = -(8.314 \text{ J K}^{-1})(1173.15 \text{ K})(\ln 1.04) = -0.383 \text{ kJ}$;
(e) $\Delta G° = -(8.314 \text{ J K}^{-1})(298.15 \text{ K})(\ln 7.2 \times 10^{-4}) = 17{,}937 \text{ J} = 18 \text{ kJ}$;
(f) $\Delta G° = -(8.314 \text{ J K}^{-1})(298.15 \text{ K})(\ln 3.3 \times 10^{-13}) = 71{,}240 \text{ J} = 71 \text{ kJ}$

40. Calculate $\Delta G°$ for each of the following reactions from the equilibrium constant at the temperature given.

(a) $Cl_2(g) + Br_2(g) \longrightarrow 2BrCl(g)$ T = 25 °C $K_P = 4.7 \times 10^{-2}$

(b) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ T = 500 °C $K_P = 48.2$

(c) $H_2O(l) \rightleftharpoons H_2O(g)$ T = 60 °C $K_P = 0.196$

(d) $CoO(s) + CO(g) \rightleftharpoons Co(s) + CO_2(g)$ T = 550 °C $K_P = 4.90 \times 10^2$

(e)
$CH_3NH_2(aq) + H_2O(l) \longrightarrow CH_3NH_3^+(aq) + OH^-(aq)$ T = 25 °C $K_b = 4.4 \times 10^{-4}$

(f) $PbI_2(s) \longrightarrow Pb^{2+}(aq) + 2I^-(aq)$ T = 25 °C $K_{sp} = 8.7 \times 10^{-9}$

Solution
(a) $\Delta G° = -RT\ln K_p = (8.314 \text{ J K}^{-1})(298.15 \text{ K})(\ln 4.7 \times 10^{-2}) = 7579 \text{ J} = 7.6 \text{ kJ}$;
(b) $\Delta G° = -(8.314 \text{ J K}^{-1})(773.15 \text{ K})(\ln 48.2) = 24{,}911 \text{ J} = 24.9 \text{ kJ}$;
(c) $\Delta G° = -(8.314 \text{ J K}^{-1})(333.15 \text{ K})(\ln 0.196) = 4513.8 \text{ J} = 4.51 \text{ kJ}$;
(d) $\Delta G° = -(8.314 \text{ J K}^{-1})(823.15 \text{ K})(\ln 4.90 \times 10^2) = -42{,}392 \text{ J} = -42.4 \text{ kJ}$;
(e) $\Delta G° = -(8.314 \text{ J K}^{-1})(298.15 \text{ K})(\ln 4.4 \times 10^{-4}) = 19{,}158 \text{ J} = 19 \text{ kJ}$;
(f) $\Delta G° = -(8.314 \text{ J K}^{-1})(298.15 \text{ K})(\ln 8.7 \times 10^{-19}) = 103{,}084 \text{ J} = 1.0 \times 10^2 \text{ kJ}$

41. Calculate the equilibrium constant at 25°C for each of the following reactions from the value of $\Delta G°$ given.

(a) $O_2(g) + 2F_2(g) \longrightarrow 2OF_2(g)$ $\Delta G° = -9.2 \text{ kJ}$

(b) $I_2(s) + Br_2(l) \longrightarrow 2IBr(g)$ $\Delta G° = 7.3 \text{ kJ}$

(c) $2LiOH(s) + CO_2(g) \longrightarrow Li_2CO_3(s) + H_2O(g)$ $\Delta G° = -79 \text{ kJ}$

(d) $N_2O_3(g) \longrightarrow NO(g) + NO_2(g)$ $\Delta G° = -1.6 \text{ kJ}$

(e) $SnCl_4(l) \longrightarrow SnCl_4(l)$ $\Delta G° = 8.0 \text{ kJ}$

Solution
Equilibrium constants are calculated from $\ln K = \frac{-\Delta G°}{RT}$. Note that K is a function of T and thus changes as T changes.

(a) $\ln K = -\left[\frac{-9.2 \times 10^3 \text{ J}}{\left(8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}\right)}\right] = 3.71, K = 41;$

(b) $\ln K = \frac{-7300 \text{ J}}{\left(8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}\right)} = -2.945, K = 0.053;$

(c) $\ln K = -\left[\frac{-79 \times 10^3 \text{ J}}{\left(8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}\right)}\right] = 31.870, K = 6.9 \times 10^{13};$

(d) $\ln K = -\left[\frac{-1.6 \times 10^3 \text{ J}}{\left(8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}\right)}\right] = 0.645, K = 1.9;$

(e) $\ln K = \frac{-8 \times 10^3 \text{ J}}{\left(8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}\right)} = -3.227, K = 0.04$

42. Determine $\Delta G°$ for the following reactions.
(a) Antimony pentachloride decomposes at 448 °C. The reaction is:

$$SbCl_5(g) \longrightarrow SbCl_3(g) + Cl_2(g)$$

An equilibrium mixture in a 5.00 L flask at 448 °C contains 3.85 g of $SbCl_5$, 9.14 g of $SbCl_3$, and 2.84 g of Cl_2.
(b) Chlorine molecules dissociate according to this reaction:

$$Cl_2(g) \longrightarrow 2Cl(g)$$

1.00% of Cl_2 molecules dissociate at 975 K and a pressure of 1.00 atm.

Solution
(a) Find the equilibrium constant by first calculating the number of moles of each component.
molar masses: $SbCl_5 = 299.11 \text{ g mol}^{-1}$
$SbCl_3 = 228.11 \text{ g mol}^{-1}$
$Cl_2 = 70.9054 \text{ g mol}^{-1}$

$$\text{mol } SbCl_5 = \frac{3.85 \text{ g}}{299.01 \text{ g mol}^{-1}} = 0.0129 \text{ mol}$$

$$\text{mol } SbCl_3 = \frac{9.14 \text{ g}}{228.11 \text{ g mol}^{-1}} = 0.0401 \text{ mol}$$

$$\text{mol } Cl_2 = \frac{2.84 \text{ g}}{70.9054 \text{ g mol}^{-1}} = 0.0401 \text{ mol}$$

$$K = \frac{[SbCl_3][Cl_2]}{[SbCl_5]} = \frac{\left(\frac{0.0401 \text{ mol}}{5.00 \text{ L}}\right)\left(\frac{0.0401 \text{ mol}}{5.00 \text{ L}}\right)}{\left(\frac{0.0129 \text{ mol}}{5.00 \text{ L}}\right)} = 0.0249 \text{ mol L}^{-1}$$

At 448 °C = 721.15 K,

$$\Delta G° = -RT \ln K = -(8.314 \text{ J K}^{-1})(721.15 \text{ K})(\ln 0.0249) = -2.21 \times 10^4 \text{ J} = -22.1 \text{ kJ}$$

(b) Determine the value of K and then determine the value of $\Delta G°$ from the value of K. Molar concentrations are required to find K. The concentration of Cl_2 at 1.00 atm and 975 K is determined from the ideal gas law, $PV = nRT$

$$\frac{n}{V} = \frac{P}{RT} = \frac{1.00 \text{ atm}}{0.08206 \frac{\text{L atm}}{\text{K mol}} (975 \text{ K})} = 0.0125 \, M$$

Since the Cl_2 gas is 1.00% dissociated, the concentration of Cl_2 is $0.9900 \times 0.0125 \, M = 0.0124 \, M$. The concentration of Cl_2 is $2 \times 0.0100 \times 0.0125 = 0.000250 \, M$ (we have to use the factor of two since each dissociated Cl_2 molecule produces two Cl particles).

$$K = \frac{[Cl]^2}{[Cl_2]} = \frac{0.000250^2}{0.0124} = 5.04 \times 10^{-6}$$

Using this result, $\Delta G^o = -RT \ln K = -8.314 \text{ J/mol K} \times 975 \text{ K} \ln(5.04 \times 10^{-6}) = 98{,}900 \text{ J/mol} = 98.9 \text{ kJ/mol}$.

43. Given that the ΔG_f° for $Pb^{2+}(aq)$ and $Cl^-(aq)$ is –24.3 kJ/mole and –131.2 kJ/mole respectively, determine the solubility product, K_{sp}, for $PbCl_2(s)$.

Solution

The reaction of interest is: $PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$

$$\Delta G_{298}^\circ = \sum \nu \Delta G_f^\circ (\text{products}) - \sum \nu \Delta G_f^\circ (\text{reactants})$$

$$\Delta G_{298}^\circ = \left[1 \text{ mol}(-24.3 \text{ kJ/mol}) + 2 \text{ mol}(-131.2 \text{ kJ/mol})\right] - \left[1 \text{ mol}(-314.1 \text{ kJ/mol})\right]$$

$$= 27.4 \text{ kJ}$$

$$\Delta G_{298}^\circ = -RT \ln K$$

$27.4 \times 10^3 = -8314 \times 2981.15 \ln K$

$K_{sp} = 1.6 \times 10^{-5}$

44. Determine the standard free energy change, ΔG_f°, for the formation of $S^{2-}(aq)$ given that the ΔG_f° for $Ag^+(aq)$ and $Ag_2S(s)$ are 77.1 kJ/mole and –39.5 kJ/mole respectively, and the solubility product for $Ag_2S(s)$ is 8×10^{-51}.

Solution

The reaction of interest is: $Ag_2S(s) \rightleftharpoons 2Ag^+(aq) + S^{2-}(aq)$ $\qquad K_{sp} = 8 \times 10^{-51}$

$$\Delta G_{298}^\circ = -RT \ln K$$

$$\Delta G_{298}^\circ = -8.314 \times 298.15 \cdot \ln 8 \times 10^{-51}$$

$$\Delta G_{298}^\circ = 286 \text{ kJ}$$

$$\Delta G_{298}^\circ = \sum \nu \Delta G_f^\circ (\text{products}) - \sum \nu \Delta G_f^\circ (\text{reactants})$$

$$286 = \left[1 \text{ mol}\left(\Delta G_f^\circ S^{2-} \text{ kJ/mol}\right) + 2 \text{ mol}(77.1 \text{ kJ/mol})\right] - \left[1 \text{ mol}(-39.5 \text{ kJ/mol})\right]$$

$$\Delta G_f^\circ S^{2-} = 90 \text{ kJ/mol}$$

45. Determine the standard enthalpy change, entropy change, and free energy change for the conversion of diamond to graphite. Discuss the spontaneity of the conversion with respect to the

enthalpy and entropy changes. Explain why diamond spontaneously changing into graphite is not observed.

Solution

The reaction of interest is: $\mathrm{C}(s,\ \text{diamond}) \longrightarrow \mathrm{C}(s,\ \text{graphite})$

$$\Delta G^\circ_{298} = \sum \nu \Delta G^\circ_f(\text{products}) - \sum \nu \Delta G^\circ_f(\text{reactants})$$

$$\Delta H^\circ_{298} = \left[1\ \text{mol}(0\ \text{kJ/mol})\right] - \left[1\ \text{mol}(1.89\ \text{kJ/mol})\right] = -1.89\ \text{kJ}$$

$$\Delta S^\circ_{298} = \sum \nu \Delta S^\circ(\text{products}) - \sum \nu \Delta S^\circ(\text{reactants})$$

$$\Delta S^\circ_{298} = \left[1\ \text{mol}\left(5.74\frac{\text{J}}{\text{mol•K}}\right)\right] - \left[1\ \text{mol}\left(2.38\frac{\text{J}}{\text{mol•K}}\right)\right] = 3.36\frac{\text{J}}{\text{mol•K}}$$

$$\Delta G^\circ_{298} = \sum \nu \Delta G^\circ_f(\text{products}) - \sum \nu \Delta G^\circ_f(\text{reactants})$$

$$\Delta G^\circ_{298} = \left[1\ \text{mol}\left(0\frac{\text{J}}{\text{mol•K}}\right)\right] - \left[1\ \text{mol}\left(2.90\frac{\text{J}}{\text{mol•K}}\right)\right] = -2.90\frac{\text{J}}{\text{mol•K}}$$

The conversion is spontaneous, $\Delta G^\circ_{298} < 0$, and is both enthalpy driven (exothermic, $\Delta H^\circ_{298} < 0$) and entropy driven, $\Delta S^\circ_{298} > 0$. However, the conversion is so slow that diamonds are effectively very stable.

46. The evaporation of one mole of water at 298 K has a standard free energy change of 8.58 kJ.

$\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2O}(g) \qquad \Delta G^\circ_{298} = 8.58\ \text{kJ}$

(a) Is the evaporation of water under standard thermodynamic conditions spontaneous?
(b) Determine the equilibrium constant, K_P, for this physical process.
(c) By calculating ΔG, determine if the evaporation of water at 298 K is spontaneous when the partial pressure of water, $P_{\mathrm{H_2O}}$, is 0.011 atm.

(d) If the evaporation of water were always nonspontaneous at room temperature, wet laundry would never dry when placed outside. In order for laundry to dry, what must be the value of $P_{\mathrm{H_2O}}$ in the air?

Solution

(a) Under standard thermodynamic conditions, the temperature is 298 K, and the pressure of water vapor would be 1 atm (or 1 bar). Under these conditions, the evaporation is nonspontaneous as indicated by $\Delta G^\circ_{298} > 0$. (b) $\Delta G^\circ_{298} = -RT \ln K$, $8.58 \times 10^3 = -8.314 \times 2981.15 \ln K$, $K_p = 0.031$; (c) $Q = P_{\mathrm{H_2O}} = 0.011\ \text{atm}$, $\Delta G = \Delta G^\circ_{298} + RT \ln Q$, $\Delta G = 8.58 \times 10^3 + (8.314 \times 298 \times \ln 0.011) = -2.6\ \text{kJ}$, Under these conditions, the evaporation of water is spontaneous; (d) $P_{\mathrm{H_2O}}$ must always be less than K_P or less than 0.031 atm. 0.031 atm represents air saturated with water vapor at 25 °C, or 100% humidity.

47. In glycolysis, the reaction of glucose (Glu) to form glucose-6-phosphate (G6P) requires ATP to be present as described by the following equation:

$\mathrm{Glu} + \mathrm{ATP} \longrightarrow \mathrm{G6P} + \mathrm{ADP} \qquad \Delta G^\circ_{298} = -17\ \text{kJ}$

In this process, ATP becomes ADP summarized by the following equation:

$\text{ATP} \longrightarrow \text{ADP} \qquad \Delta G^\circ_{298} = -30 \text{ kJ}$

Determine the standard free energy change for the following reaction, and explain why ATP is necessary to drive this process:

$\text{Glu} \longrightarrow \text{G6P} \qquad \Delta G^\circ_{298} = ?$

Solution

Adding together the reactions $\text{ATP} \longrightarrow \text{ADP}$ and $\text{Glu} \longrightarrow \text{G6P}$ generate $\text{Glu} + \text{ATP} \longrightarrow \text{G6P} + \text{ADP}$. Therefore, $\Delta G^\circ_{298}(\text{Glu} \longrightarrow \text{G6P}) + (-30 \text{ kJ}) = -17 \text{ kJ}$, $\Delta G^\circ_{298}(\text{Glu} \longrightarrow \text{G6P}) = 13 \text{ kJ}$. As this is a nonspontaneous process, it needs to be coupled to the hydrolysis of ATP to become spontaneous.

48. One of the important reactions in the biochemical pathway glycolysis is the reaction of glucose-6-phosphate (G6P) to form fructose-6-phosphate (F6P):

$\text{G6P} \rightleftarrows \text{F6P} \qquad \Delta G^\circ_{298} = 1.7 \text{ kJ}$

(a) Is the reaction spontaneous or nonspontaneous under standard thermodynamic conditions?
(b) Standard thermodynamic conditions imply the concentrations of G6P and F6P to be 1 *M*, however, in a typical cell, they are not even close to these values. Calculate ΔG when the concentrations of G6P and F6P are 120 μ*M* and 28 μ*M* respectively, and discuss the spontaneity of the forward reaction under these conditions. Assume the temperature is 37 °C.

Solution

(a) Nonspontaneous as $\Delta G^\circ_{298} > 0$; (b)$\Delta G = \Delta G° + RT \ln Q$,

$\Delta G = 1.7 \times 10^3 + \left(8.314 \times 310 \times \ln \frac{28}{120}\right) = -2.1 \text{ kJ}$. The forward reaction to produce F6P is spontaneous under these conditions.

49. Without doing a numerical calculation, determine which of the following will reduce the free energy change for the reaction, that is, make it less positive or more negative, when the temperature is increased. Explain.

(a) $\text{N}_2(g) + 3\text{H}_2(g) \longrightarrow 2\text{NH}_3(g)$

(b) $\text{HCl}(g) + \text{NH}_3(g) \longrightarrow \text{NH}_4\text{Cl}(s)$

(c) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7(s) \longrightarrow \text{Cr}_2\text{O}_3(s) + 4\text{H}_2\text{O}(g) + \text{N}_2(g)$

(d) $2\text{Fe}(s) + 3\text{O}_2(g) \longrightarrow \text{Fe}_2\text{O}_3(s)$

Solution

Reaction (c). This reaction is the only one where entropy increases from reactants to products.

50. When ammonium chloride is added to water and stirred, it dissolves spontaneously and the resulting solution feels cold. Without doing any calculations, deduce the signs of ΔG, ΔH, and ΔS for this process, and justify your choices.

Solution

ΔG is negative as the process is spontaneous. ΔH is positive as with the solution becoming cold, the dissolving must be endothermic. ΔS must be positive as this drives the process, and it is expected for the dissolution of any soluble ionic compound.

51. An important source of copper is from the copper ore, chalcocite, a form of copper(I) sulfide. When heated, the Cu_2S decomposes to form copper and sulfur described by the following equation:

$Cu_2S(s) \longrightarrow Cu(s) + S(s)$

(a) Determine ΔG°_{298} for the decomposition of $Cu_2S(s)$.

(b) The reaction of sulfur with oxygen yields sulfur dioxide as the only product. Write an equation that describes this reaction, and determine ΔG°_{298} for the process.

(c) The production of copper from chalcocite is performed by roasting the Cu_2S in air to produce the Cu. By combining the equations from Parts (a) and (b), write the equation that describes the roasting of the chalcocite, and explain why coupling these reactions together makes for a more efficient process for the production of the copper.

Solution

(a) $\Delta G^\circ_{298} = \sum \nu \Delta G^\circ_f(\text{products}) - \sum \nu \Delta G^\circ_f(\text{reactants})$

$\Delta G^\circ_{298} = \left[1\ \text{mol}(0\ \text{kJ/mol}) + 1\ \text{mol}(0\ \text{kJ/mol})\right] - \left[1\ \text{mol}(-86.5\ \text{kJ/mol})\right] = 86.5\ \text{kJ}$; (b)

$S(s) + O_2(g) \longrightarrow SO_2(g)$

$\Delta G^\circ_{298} = \sum \nu \Delta G^\circ_f(\text{products}) - \sum \nu \Delta G^\circ_f(\text{reactants})$

$\Delta G^\circ_{298} = \left[1\ \text{mol}(-300.1\ \text{kJ/mol})\right] - \left[1\ \text{mol}(0\ \text{kJ/mol}) + 1\ \text{mol}(0\ \text{kJ/mol})\right] = -300.1\ \text{kJ}$;

(c)

$Cu_2S(s) \longrightarrow Cu(s) + S(s) \qquad \Delta G^\circ_{298} = 86.5\ \text{kJ}$

$S(s) + O_2(g) \longrightarrow SO_2(g) \qquad \Delta G^\circ_{298} = -300.1\ \text{kJ}$

$Cu_2S(s) + O_2(g) \longrightarrow Cu(s) + SO_2(g) \qquad \Delta G^\circ_{298} = 86.5\ \text{kJ} - 300.1\ \text{kJ} = -213.6\ \text{kJ}$

Coupling these reactions together makes the nonspontaneous production of copper by direct decomposition of chalcocite spontaneous, as it is now taking place with the spontaneous oxidation of sulfur.

52. What happens to ΔG° (becomes more negative or more positive) for the following chemical reactions when the partial pressure of oxygen is increased?

(a) $S(s) + O_2(g) \longrightarrow SO_2(g)$

(b) $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$

(c) $HgO(s) \longrightarrow Hg(l) + O_2(g)$

Solution

(a) Increasing P_{O_2} will shift the equilibrium toward the products, which increases the value of *K*. ΔG° therefore becomes more negative.

(b) Increasing P_{O_2} will shift the equilibrium toward the products, which increases the value of *K*. ΔG° therefore becomes more negative.

(c) Increasing P_{O_2} will shift the equilibrium the reactants, which decreases the value of *K*. ΔG° therefore becomes more positive.

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Chemistry: Atoms First 2e
14: Acid-Base Equilibria
14.1: Brønsted-Lowry Acids and Bases

1. Write equations that show NH_3 as both a conjugate acid and a conjugate base.

Solution

One example for NH_3 as a conjugate acid: $NH_2^- + H^+ \longrightarrow NH_3$; as a conjugate base:

$NH_4^+(aq) + OH^-(aq) \longrightarrow NH_3(aq) + H_2O(l)$

2. Write equations that show $H_2PO_4^-$ acting both as an acid and as a base.

Solution

$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3PO_4(aq) + OH^-(aq)$; as an acid:

$H_2PO_4^-(aq) + H_2O(aq) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(aq)$

3. Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:

(a) H_3O^+

(b) HCl

(c) NH_3

(d) CH_3CO_2H

(e) NH_4^+

(f) HSO_4^-

Solution

(a) $H_3O^+(aq) \longrightarrow H^+(aq) + H_2O(l)$; (b) $HCl(l) \longrightarrow H^+(aq) + Cl^-(aq)$; (c) $NH_3(aq) \longrightarrow H^+(aq) + NH_2^-(aq)$; (d) $CH_3CO_2H(aq) \longrightarrow H^+(aq) + CH_3CO_2^-(aq)$; (e) $NH_4^+(aq) \longrightarrow H^+(aq) + NH_3(aq)$; (f) $HSO_4^-(aq) \longrightarrow H^+(aq) + SO_4^{2-}(aq)$

4. Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:

(a) HNO_3

(b) PH_4^+

(c) H_2S

(d) CH_3CH_2COOH

(e) $H_2PO_4^-$

(f) HS^-

Solution

In a Brønsted-Lowry acid, the acid must supply an H^+. (a) $HNO_3(aq) \longrightarrow H^+(aq) + NO_3^-(aq)$; (b) $PH_4^+(aq) \longrightarrow H^+(aq) + PH_3(aq)$; (c) $H_2S(aq) \longrightarrow H^+(aq) + HS^-(aq)$; (d) $C_2H_5CO_2H(aq) \longrightarrow H^+(aq) + C_2H_5CO_2^-(aq)$; (e) $H_2PO_4^-(aq) \longrightarrow H^+(aq) + HPO_4^{2-}(aq)$; (f) $HS^-(aq) \longrightarrow H^+(aq) + S^{2-}(aq)$

5. Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry base:

(a) H_2O

(b) OH^-

(c) NH_3
(d) CN^-
(e) S^{2-}
(f) $H_2PO_4^-$

Solution
(a) $H_2O(l) + H^+(aq) \longrightarrow H_3O^+(aq)$; (b) $OH^-(aq) + H^+(aq) \longrightarrow H_2O(l)$; (c) $NH_3(aq) + H^+(aq) \longrightarrow NH_4^+(aq)$; (d) $CN^-(aq) + H^+(aq) \longrightarrow HCN(aq)$; (e) $S^{2-}(aq) + H^+(aq) \longrightarrow HS^-(aq)$; (f) $H_2PO_4^-(aq) + H^+(aq) \longrightarrow H_3PO_4(aq)$

6. Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry base:
(a) HS^-
(b) PO_4^{3-}
(c) NH_2^-
(d) C_2H_5OH
(e) O^{2-}
(f) $H_2PO_4^-$

Solution
In a Brønsted-Lowry base, the base must accept an H^+.
(a) $HS^- + H^+ \longrightarrow H_2S$; (b) $PO_4^{3-} + H^+ \longrightarrow HPO_4^{2-}$; (c) $NH_2^- + H^+ \longrightarrow NH_3$ (d) $C_2H_5OH + H^+ \longrightarrow C_2H_5OH_2^+$; (e) $O^{2-} + H^+ \longrightarrow OH^-$; (f) $HPO_4^{2-} + H^+ \longrightarrow H_2PO_4^-$

7. What is the conjugate acid of each of the following? What is the conjugate base of each?
(a) OH^-
(b) H_2O
(c) HCO_3^-
(d) NH_3
(e) HSO_4^-
(f) H_2O_2
(g) HS^-
(h) $H_5N_2^+$

Solution
(a) H_2O, O^{2-}; (b) H_3O^+, OH^-; (c) H_2CO_3, CO_3^{2-}; (d) NH_4^+, NH_2^-; (e) H_2SO_4, SO_4^{2-}; (f) $H_3O_2^+$, HO_2^-; (g) H_2S; S^{2-}; (h) $H_6N_2^{2+}$, H_4N_2

8. What is the conjugate acid of each of the following? What is the conjugate base of each?
(a) H_2S
(b) $H_2PO_4^-$
(c) PH_3
(d) HS^-
(e) HSO_3^-

(f) $H_3O_2^+$
(g) H_4N_2
(h) CH_3OH

Solution
(a) H_3S^+, HS^-; (b) $H_3PO_4^-$, HPO_4^{2-}; (c) PH_4^+, PH_2^-; (d) H_2S, S^{2-}; (e) H_2SO_3, SO_3^{2-}; (f) $H_4O_2^{2+}$, H_2O_2; (g) $H_5N_2^+$, $H_3N_2^-$; (h) $CH_3OH_2^+$, CH_3O^-

9. Identify and label the Brønsted-Lowry acid, its conjugate base, the Brønsted-Lowry base, and its conjugate acid in each of the following equations:
(a) $HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-$
(b) $CN^- + H_2O \longrightarrow HCN + OH^-$
(c) $H_2SO_4 + Cl^- \longrightarrow HCl + HSO_4^-$
(d) $HSO_4^- + OH^- \longrightarrow SO_4^{2-} + H_2O$
(e) $O^{2-} + H_2O \longrightarrow 2\,OH^-$
(f) $[Cu(H_2O)_3(OH)]^+ + [Al(H_2O)_6]^{3+} \longrightarrow [Cu(H_2O)_4]^{2+} + [Al(H_2O)_5(OH)]^{2+}$
(g) $H_2S + NH_2^- \longrightarrow HS^- + NH_3$

Solution
The labels are Brønsted-Lowry acid = BA; its conjugate base = CB; Brønsted-Lowry base = BB; its conjugate acid = CA. (a) HNO_3(BA), H_2O(BB), H_3O^+(CA), NO_3^-(CB); (b) CN^-(BB), H_2O(BA), HCN(CA), OH^-(CB); (c) H_2SO_4(BA), Cl^-(BB), HCl(CA), HSO_4^-(CB); (d) HSO_4^-(BA), OH^-(BB), SO_4^{2-}(CB), H_2O(CA); (e) O^{2-}(BB), H_2O(BA) OH^-(CB and CA); (f) $[Cu(H_2O)_3(OH)]^+$(BB), $[Al(H_2O)_6]^{3+}$(BA), $[Cu(H_2O)_4]^{2+}$(CA), $[Al(H_2O)_5(OH)]^{2+}$(CB); (g) H_2S(BA), NH_2^-(BB), HS^-(CB), NH_3(CA)

10. Identify and label the Brønsted-Lowry acid, its conjugate base, the Brønsted-Lowry base, and its conjugate acid in each of the following equations:
(a) $NO_2^- + H_2O \longrightarrow HNO_2 + OH^-$
(b) $HBr + H_2O \longrightarrow H_3O^+ + Br^-$
(c) $HS^- + H_2O \longrightarrow H_2S + OH^-$
(d) $H_2PO_4^- + OH^- \longrightarrow HPO_4^{2-} + H_2O$
(e) $H_2PO_4^- + HCl \longrightarrow H_3PO_4 + Cl^-$
(f) $[Fe(H_2O)_5(OH)]^{2+} + [Al(H_2O)_6]^{3+} \longrightarrow [Fe(H_2O)_6]^{3+} + [Al(H_2O)_5(OH)]^{2+}$
(g) $CH_3OH + H^- \longrightarrow CH_3O^- + H_2$

Solution
The labels are Brønsted-Lowry acid = BA; its conjugate base = CB; Brønsted-Lowry base = BB; and its conjugate acid = CA. (a) NO_2^-(BB), H_2O(BA), HNO_2(CA), OH^-(CB); (b) HBr(BA), H_2O(BB), H_3O^+(CA), Br^-(CB); (c) HS^-(BB), H_2O(BA), H_2S(CA), OH^-(CB)$^-$; (d) $H_2PO_4^-$(BA), OH^-(BB), HPO_4^{2-}(CB), H_2O(CA); (e) $H_2PO_4^-$(BB), HCl(BA), H_3PO_4(CA), Cl^-(CB); (f)

$[Fe(H_2O)_5(OH)]^{2+}$ (BB), $[Al(H_2O)_6]^{3+}$ (BA), $[Fe(H_2O)_6]^{3+}$ (CA), $[Al(H_2O)_5(OH)]^{2+}$ (CB); (g) CH_3OH(BA), H^-(BB), CH_3O^- (CB), H_2(CA)

11. What are amphiprotic species? Illustrate with suitable equations.

Solution
Amphiprotic species may either gain or lose a proton in a chemical reaction, thus acting as a base or an acid. An example is H_2O. As an acid: $H_2O(aq) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$. As a base: $H_2O(aq) + HCl(aq) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$

12. State which of the following species are amphiprotic and write chemical equations illustrating the amphiprotic character of these species:
(a) H_2O
(b) $H_2PO_4^-$
(c) S^{2-}
(d) CO_3^{2-}
(e) HSO_4^-

Solution
amphiprotic:
(a) $H_2O(l) + HBr(aq) \longrightarrow H_3O^+(aq) + Br^-(aq)$,
$H_2O(l) + CN^-(aq) \longrightarrow HCN(aq) + OH^-(aq)$;
(b) $H_2PO_4^-(aq) + HBr(aq) \longrightarrow H_3PO_4(aq) + Br^-(aq)$,
$H_2PO_4^-(aq) + OH^-(aq) \longrightarrow HPO_4^{2-}(aq) + H_2O(l)$; (e)
$HSO_4^-(aq) + HClO_4(aq) \longrightarrow H_2SO_4(aq) + ClO_4^-(aq)$,
$HSO_4^-(aq) + OH^-(aq) \longrightarrow SO_4^{2-}(aq) + H_2O(l)$;not amphiprotic: (c) S^{2-}, (d) CO_3^{2-}

13. State which of the following species are amphiprotic and write chemical equations illustrating the amphiprotic character of these species.
(a) NH_3
(b) HPO_4^{2-}
(c) Br^-
(d) NH_4^+
(e) ASO_4^{3-}

Solution
(a) $NH_3 + H_3O^+ \longrightarrow NH_4OH + H_2O$, $NH_3 + OCH_3^- \longrightarrow NH_2^- + CH_3OH$; (b)
$HPO_4^{2-} + OH^- \longrightarrow PO_4^{3-} + H_2O$, $HPO_4^{2-} + HClO_4 \longrightarrow H_2PO_4^- + ClO_4^-$;
not amphiprotic: (c) Br^-; (d) NH_4^+; (e) AsO_4^{3-}

14. Is the self ionization of water endothermic or exothermic? The ionization constant for water (K_w) is 2.9×10^{-14} at 40 °C and 9.3×10^{-14} at 60 °C.

Solution
Because K_w increases with increasing temperature, the reaction in endothermic. When the temperature of the system is increased, the reaction shifts toward the product side, making *K*

bigger. According to Le Châtelier's principle, the reaction shifts away from the heat term, so the heat term must be on the reactant side of the equation. Therefore, the reaction is endothermic.

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Chemistry: Atoms First 2e
14: Acid-Base Equilibria
14.2: pH and pOH

15. Explain why a sample of pure water at 40 °C is neutral even though $[H_3O^+] = 1.7 \times 10^{-7}\ M$. K_w is 2.910×10^{-14} at 40 °C.

Solution
In a neutral solution $[H_3O^+] = [OH^-]$. At 40 °C,

$$\left[H_3O^+\right] = \left[OH^-\right] = (2.910^{-14})^{1/2} = 1.7 \times 10^{-7}.$$

16. The ionization constant for water (K_w) is 2.9×10^{-14} at 40 °C. Calculate $[H_3O^+]$, $[OH^-]$, pH, and pOH for pure water at 40 °C.

Solution
$K_w = [H_3O^+][OH^-] = 2.9 \times 10^{-14}$

$$[H_3O^+] = [OH^-] = \sqrt{2.9 \times 10^{-14}} = 1.70 \times 10^{-7} = 1.7 \times 10^{-7}\ M$$

pH = pOH = –log(1.70×10^{-7}) = 6.769 = 6.77

17. The ionization constant for water (K_w) is 9.311×10^{-14} at 60 °C. Calculate $[H_3O^+]$, $[OH^-]$, pH, and pOH for pure water at 60 °C.

Solution
For water, $[H_3O^+] = [OH^-] = x$.
$K_w = 9.311 \times 10^{-14} = x^2$
$x = 3.051 \times 10^{-7} M = [H_3O^+] = [OH^-]$
pH = –log 3.051×10^{-7} = –(–6.5156) = 6.5156
pOH = pH = 6.5156

18. Calculate the pH and the pOH of each of the following solutions at 25 °C for which the substances ionize completely:
(a) 0.200 *M* HCl
(b) 0.0143 *M* NaOH
(c) 3.0 *M* HNO_3
(d) 0.0031 *M* $Ca(OH)_2$

Solution
pH = –log$[H_3O^+]$, pOH = –log$[OH^-]$; (a) Hydrochloric acid is a strong acid; therefore, the hydronium ion concentration is the same as the molar concentration of HCl. pH = – log(0.200) = –(–0.699) = 0.699; pOH = 14.00 – pH = 14.00 – 0.699 = 13.30; (b) NaOH is a strong base that is completely ionized in dilute solution. Therefore, since $[OH^-] = 0.0143\ M$, pOH = –log(0.0143) = –(–1.8447) = 1.845; pH = 14.00 – pOH = 14.00 – 1.845 = 12.16; (c) pH = –log(3.0) = –(0.477) =

–0.48; pOH = 14.00 – pH = 14.00 – (–0.477) = 14.477 = 14.48; (d) $[OH^-] = 2(0.0031) = 0.0062$ *M*; pOH = –log(0.0062) = –(–2.208) = 2.21; pH = 14.00 – 2.208 = 11.792 = 11.79

19. Calculate the pH and the pOH of each of the following solutions at 25 °C for which the substances ionize completely:
(a) 0.000259 *M* $HClO_4$
(b) 0.21 *M* NaOH
(c) 0.000071 *M* $Ba(OH)_2$
(d) 2.5 *M* KOH

Solution
(a) pH = –log(0.000259) = –(–3.5867) = 3.587; pOH = 14.0000 – 3.5867 = 10.4133 = 10.413; (b) pOH = –log(0.21) = –(–0.678) = 0.68; pH = 14.000 – 0.678 = 13.322 = 13.32; (c) since $[OH^-] = 2(0.000071) = 0.000142$ *M*; pOH = –log(0.000142) = –(–3.848) = 3.85; pH = 14.000 – 3.848 = 10.152 = 10.15;(d) pOH = –log(2.5) = –(0.398) = –0.40; pH = 14.000 – (–0.398) = 14.398 = 14.4

20. What are the pH and pOH of a solution of 2.0 *M* HCl, which ionizes completely?

Solution
HCl is a strong acid that undergoes complete ionization in pure water.
$[H_3O^+]$ = molarity of HCl = 2.0 *M*
$pH = -\log[H_3O^+] = -\log(2.0) = -0.30$
pOH = 14.00 – pH = 14.00 – (–0.30) = 14.30

21. What are the hydronium and hydroxide ion concentrations in a solution whose pH is 6.52?

Solution
$[H_3O^+] = 10^{-6.52} = 3.0 \times 10^{-7}$ *M*; pOH = 14.00 – pH; pOH = 14.00 – 6.52 = 7.48; $[OH^-] = 10^{-7.48} = 3.3 \times 10^{-8}$ *M*

22. Calculate the hydrogen ion concentration and the hydroxide ion concentration in wine from its pH. See Figure 14.2 for useful information.

Solution
$[H_3O^+] = 3 \times 10^{-4}$, $[OH^-] = 3 \times 10^{-11}$ *M*

23. Calculate the hydronium ion concentration and the hydroxide ion concentration in lime juice from its pH. See Figure 14.2 for useful information.

Solution
From Figure 14.2 the pH of lime juice is equal to 2. The hydronium ion concentration is pH = 2 = $-\log[H_3O^+]$; $[H_3O^+] = 1 \times 10^{-2}$ *M*; pH + pOH = 14; pOH = 14 – 2 = 12; $[OH^-] = 1 \times 10^{-12}$ *M*

24. The hydronium ion concentration in a sample of rainwater is found to be 1.7×10^{-6} *M* at 25 °C. What is the concentration of hydroxide ions in the rainwater?

Solution
$[H_3O^+][OH^-] = 1.0 \times 10^{-14}$; $[1.7 \times 10^{-6}][OH^-] = 1.0 \times 10^{-14}$;

$$[OH^-] = \frac{1.00 \times 10^{-14}}{1.7 \times 10^{-6}} = 5.9 \times 10^{-9}\ M$$

25. The hydroxide ion concentration in household ammonia is 3.2×10^{-3} *M* at 25 °C. What is the concentration of hydronium ions in the solution?

Solution
$[H_3O^+][OH^-] = 1.0 \times 10^{-14}$; $[H_3O^+][3.2 \times 10^{-3}] = 1.0 \times 10^{-14}$;

$$[OH^-] = \frac{1.00 \times 10^{-14}}{3.2 \times 10^{-3}} = 3.1 \times 10^{-12}\ M$$

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Chemistry: Atoms First 2e
14: Acid-Base Equilibria
14.3: Relative Strengths of Acids and Bases

26. Explain why the neutralization reaction of a strong acid and a weak base gives a weakly acidic solution.

Solution
The reaction forms the conjugate acid of the weak base. The conjugate acid of a weak base is a weak acid and ionizes to a slight extent giving an acidic solution.

27. Explain why the neutralization reaction of a weak acid and a strong base gives a weakly basic solution.

Solution
The salt ionizes in solution, but the anion slightly reacts with water to form the weak acid. This reaction also forms OH^-, which causes the solution to be basic. An example is NaCN. The CN^- reacts with water as follows: $CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq)$

28. Use this list of important industrial compounds (and Figure 14.8) to answer the following questions regarding: $Ca(OH)_2$, CH_3CO_2H, HCl, H_2CO_3, HF, HNO_2, HNO_3, H_3PO_4, H_2SO_4, NH_3, NaOH, Na_2CO_3.
(a) Identify the strong Brønsted-Lowry acids and strong Brønsted-Lowry bases.
(b) Identify the compounds that can behave as Brønsted-Lowry acids with strengths lying between those of H_3O^+ and H_2O.
(c) Identify the compounds that can behave as Brønsted-Lowry bases with strengths lying between those of H_2O and OH^-.

Solution
(a) strong Brønsted-Lowry acids: HCl, HNO_3, H_3PO_4, H_2SO_4; strong Brønsted-Lowry bases: $Ca(OH)_2$, NaOH; (b) CH_3CO_2H, H_2CO_3, HF, HNO_2; (c) NH_3, Na_2CO_3

29. The odor of vinegar is due to the presence of acetic acid, CH_3CO_2H, a weak acid. List, in order of descending concentration, all of the ionic and molecular species present in a 1-*M* aqueous solution of this acid.

Solution
$[H_2O] > [CH_3CO_2H] > [H_3O^+] \approx [CH_3CO_2^-] > [OH^-]$

30. Household ammonia is a solution of the weak base NH_3 in water. List, in order of descending concentration, all of the ionic and molecular species present in a 1-*M* aqueous solution of this base.

Solution
$[H_2O] > [NH_3] > [NH_4^+] \approx [OH^-] > [H^+]$

31. Explain why the ionization constant, K_a, for H_2SO_4 is larger than the ionization constant for H_2SO_3.

Solution
The oxidation state of the sulfur in H_2SO_4 is greater than the oxidation state of the sulfur in H_2SO_3.

32. Explain why the ionization constant, K_a, for HI is larger than the ionization constant for HF.

Solution
The radius of I is larger than the radius of F. This is why the H-I bond is weaker than the H-F bond, HI is easier to break than HF, and the Ka for HI is greater

33. Gastric juice, the digestive fluid produced in the stomach, contains hydrochloric acid, HCl. Milk of Magnesia, a suspension of solid $Mg(OH)_2$ in an aqueous medium, is sometimes used to neutralize excess stomach acid. Write a complete balanced equation for the neutralization reaction, and identify the conjugate acid-base pairs.

Solution

$$\underset{\text{BB}}{Mg(OH)_2(s)} + \underset{\text{BA}}{HCl(aq)} \longrightarrow \underset{\text{CB}}{Mg^{2+}(aq)} + 2Cl^-(aq) + \underset{\text{CA}}{2H_2O(l)}$$

34. Nitric acid reacts with insoluble copper(II) oxide to form soluble copper(II) nitrate, $Cu(NO_3)_2$, a compound that has been used to prevent the growth of algae in swimming pools. Write the balanced chemical equation for the reaction of an aqueous solution of HNO_3 with CuO.

Solution

$$\underset{\text{BB}}{CuO(s)} + \underset{\text{BA}}{2HNO_3(aq)} \longrightarrow \underset{\text{CB}}{Cu^{2+}(aq)} + 2NO_3^-(aq) + \underset{\text{CA}}{H_2O(l)}$$

35. What is the ionization constant at 25 °C for the weak acid $CH_3NH_3^+$, the conjugate acid of the weak base CH_3NH_2, $K_b = 4.4 \times 10^{-4}$.

Solution
$K_w = K_a \times K_b$

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.4 \times 10^{-4}} = 2.3 \times 10^{-11}$$

36. What is the ionization constant at 25 °C for the weak acid $(CH_3)_2NH_2^+$, the conjugate acid of the weak base $(CH_3)_2NH$, $K_b = 5.9 \times 10^{-4}$?

Solution
$K_w = K_a \times K_b$

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{5.9 \times 10^{-4}} = 1.7 \times 10^{-11}$$

37. Which base, CH_3NH_2 or $(CH_3)_2NH$, is the strongest base? Which conjugate acid, $(CH_3)_2NH_2^+$ or $CH_3NH_3^+$, is the strongest acid?

Solution
The strongest base or strongest acid is the one with the larger K_b or K_a, respectively. In these two examples, they are $(CH_3)_2NH$ and $CH_3NH_3^+$.

38. Which is the stronger acid, NH_4^+ or HBrO?

Solution
Look up (Appendix H) K_a for HBrO. Using the value of K_b for NH_3, calculate its K_a. Then compare the values:
$K_a(HBrO) = 2.8 \times 10^{-9}$

$$K_b(NH_3) = 1.8 \times 10^{-5} = \frac{K_w}{K_a},\ K_a(NH_4^+) = 5.6 \times 10^{-10}$$

39. Which is the stronger base, $(CH_3)_3N$ or $H_2BO_3^-$?

Solution
Look up (Appendix I) the value of K_b for $(CH_3)_3N$ and the value of K_a for H_3BO_3. From the latter, calculate the value of K_b for $H_2BO_3^-$. Then compare values:
$K_b(CH_3)_3N = 6.3 \times 10^{-5}$

$$K_a(H_3BO_3) = 5.4 \times 10^{-10} = \frac{K_w}{K_b},\ K_b = \frac{1.0 \times 10^{-14}}{5.4 \times 10^{-10}} = 1.9 \times 10^{-5}$$

A comparison shows that the larger K_b is that of triethylamine.

40. Predict which acid in each of the following pairs is the stronger and explain your reasoning for each.
(a) H_2O or HF
(b) $B(OH)_3$ or $Al(OH)_3$
(c) HSO_3^- or HSO_4^-
(d) NH_3 or H_2S
(e) H_2O or H_2Te

Solution
(a) HF; F is more electronegative than O. (b) $B(OH)_3$; B is more electronegative than Al. Accordingly $Al(OH)_3$ is more basic than $B(OH)_3$. (c) HSO_4^-; S has a +6 oxidation state in HSO_4^-, but a +4 oxidation state in HSO_3^-. Increasing the oxidation state of the central element in oxyacids increases acidity. (d) H_2S; NH_3 is a weak base and H_2S is a very weak acid. Therefore, NH_3 as an acid is weaker than H_2S. (e) H_2Te; Te is below O in group 16. Heavier members in acid-forming groups make stronger acids than lighter members of those groups.

41. Predict which compound in each of the following pairs of compounds is more acidic and explain your reasoning for each.
(a) HSO_4^- or $HSeO_4^-$
(b) NH_3 or H_2O
(c) PH_3 or HI
(d) NH_3 or PH_3
(e) H_2S or HBr

Solution
(a) HSO_4^-; higher electronegativity of the central ion. (b) H_2O; NH_3 is a base and water is neutral, or decide on the basis of K_a values. (c) HI; PH_3 is weaker than HCl; HCl is weaker than HI. Thus, PH_3 is weaker than HI. (d) PH_3; in binary compounds of hydrogen with nonmetals, the acidity increases for the element lower in a group. (e) HBr; in a period, the acidity increases from left to right; in a group, it increases from top to bottom. Br is to the left and below S, so HBr is the stronger acid.

42. Rank the compounds in each of the following groups in order of increasing acidity or basicity, as indicated, and explain the order you assign.
(a) acidity: HCl, HBr, HI
(b) basicity: H_2O, OH^-, H^-, Cl^-
(c) basicity: $Mg(OH)_2$, $Si(OH)_4$, $ClO_3(OH)$ (Hint: Formula could also be written as $HClO_4$.)
(d) acidity: HF, H_2O, NH_3, CH_4

Solution

(a) HCl < HBr < HI; H-X bond energy decreases going down a group. This consideration is more significant than the decrease in electronegativity. (b) $Cl^- < H_2O < OH^- < H^-$; Cl^- has no tendency to basic action; water forms OH^- in a very low concentration; OH^- is very basic; and H^- is even more willing to donate a pair of electrons. (c) $ClO_3(OH) < Si(OH)_4 < Mg(OH)_2$; the more nonmetallic the central atom, the more acidic the substance. As a result, base strength increases in the opposite direction. (d) $CH_4 < NH_3 < H_2O < HF$; this series can be envisioned in terms of increasing electronegativity of the atom attached to hydrogen. The greater the electronegativity, the stronger a binary acid in the same period of the periodic table.

43. Rank the compounds in each of the following groups in order of increasing acidity or basicity, as indicated, and explain the order you assign.
(a) acidity: $NaHSO_3$, $NaHSeO_3$, $NaHSO_4$
(b) basicity: BrO_2^-, ClO_2^-, IO_2^-
(c) acidity: HOCl, HOBr, HOI
(d) acidity: HOCl, HOClO, $HOClO_2$, $HOClO_3$
(e) basicity: NH_2^-, HS^-, HTe^-, PH_2^-
(f) basicity: BrO^-, BrO_2^-, BrO_3^-, BrO_4^-

Solution
(a) $NaHSeO_3 < NaHSO_3 < NaHSO_4$; in polyoxy acids, the more electronegative central element—S, in this case—forms the stronger acid. The larger number of oxygen atoms on the central atom (giving it a higher oxidation state) also creates a greater release of hydrogen atoms, resulting in a stronger acid. As a salt, the acidity increases in the same manner. (b) $ClO_2^- < BrO_2^- < IO_2^-$; the basicity of the anions in a series of acids will be the opposite of the acidity in their oxyacids. The acidity increases as the electronegativity of the central atom increases. Cl is more electronegative than Br, and I is the least electronegative of the three. (c) HOI < HOBr < HOCl; in a series of the same form of oxyacids, the acidity increases as the electronegativity of the central atom increases. Cl is more electronegative than Br, and I is the least electronegative of the three. (d) $HOCl < HOClO < HOClO_2 < HOClO_3$; in a series of oxyacids of the same central element, the acidity increases as the number of oxygen atoms increases (or as the oxidation state of the central atom increases). (e) $HTe^- < HS^- << PH_2^- < NH_2^-$; PH_2^- and NH_2^- are anions of weak bases, so they act as strong bases toward H^+. HTe^- and HS^- are anions of weak acids, so they have less basic character. In a periodic group, the more electronegative element has the more basic anion. (f) $BrO_4^- < BrO_3^- < BrO_2^- < BrO^-$; with a larger number of oxygen atoms (that is, as the oxidation state of the central ion increases), the corresponding acid becomes more acidic and the anion consequently less basic.

44. Both HF and HCN ionize in water to a limited extent. Which of the conjugate bases, F^- or CN^-, is the stronger base?

Solution
CN^-; HCN is the weaker acid, so CN^- is the stronger base.

45. The active ingredient formed by aspirin in the body is salicylic acid, $C_6H_4OH(CO_2H)$. The carboxyl group ($–CO_2H$) acts as a weak acid. The phenol group (an OH group bonded to an aromatic ring) also acts as an acid but a much weaker acid. List, in order of descending concentration, all of the ionic and molecular species present in a 0.001-*M* aqueous solution of $C_6H_4OH(CO_2H)$.

Solution
$[H_2O] > [C_6H_4OH(CO_2H)] > [H^+] > [C_6H_4OH(CO_2)^-] \gg [C_6H_4O(CO_2H)^-] > [OH^-]$

46. Are the concentrations of hydronium ion and hydroxide ion in a solution of an acid or a base in water directly proportional or inversely proportional? Explain your answer.

Solution
Inversely proportional. The hydronoim ion and hydroxide ion are related by the K_w equilibrium equation
$K_w = [H^+][OH^-]$
from which we see the inverse relation.

47. What two common assumptions can simplify calculation of equilibrium concentrations in a solution of a weak acid?

Solution
1. Assume that the change in initial concentration of the acid as the equilibrium is established can be neglected, so this concentration can be assumed constant and equal to the initial value of the total acid concentration. 2. Assume we can neglect the contribution of water to the equilibrium concentration of H_3O^+.

48. Which of the following will increase the percent of NH_3 that is converted to the ammonium ion in water?
(a) addition of NaOH
(b) addition of HCl
(c) addition of NH_4Cl

Solution
The equilibrium is:
$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$
(a) The addition of NaOH adds OH^- to the system and, according to LeChâtelier's principle, the equilibrium will shift to the left. Thus, the percent of converted NH_3 will decrease. (b) The addition of HCl will add H_3O^+ ions, which will then react with the OH^- ions. Thus, the equilibrium will shift to the right, and the percent will increase. (c) The addition of NH_4Cl adds NH_4^+ ions, shifting the equilibrium to the left. Thus, the percent will decrease.

49. Which of the following will increase the percent of HF that is converted to the fluoride ion in water?
(a) addition of NaOH
(b) addition of HCl
(c) addition of NaF

Solution
The equilibrium is:
$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$
(a) The addition of NaOH adds OH^- to the system, which will then react with the H_3O^+ ions. According to LeChâtelier's principle, the equilibrium will shift to the right. Thus, the percent will increase. (b) The addition of HCl will add H_3O^+ ions. The equilibrium will shift to the left, and the percent will decrease. (c) The addition of NaF and F^- ions, shifting the equilibrium to the left. Thus, the percent will decrease.

50. What is the effect on the concentrations of NO_2^-, HNO_2, and OH^- when the following are added to a solution of KNO_2 in water:
(a) HCl
(b) HNO_2
(c) NaOH
(d) NaCl
(e) KNO_2

Solution
(a) Adding HCl will add H_3O^+ ions, which will then react with the OH^- ions, lowering their concentration. The equilibrium will shift to the right, increasing the concentration of HNO_2, and decreasing the concentration of NO_2^- ions. (b) Adding HNO_2 increases the concentration of HNO_2 and shifts the equilibrium to the left, increasing the concentration of NO_2^- ions and decreasing the concentration of OH^- ions. (c) Adding NaOH adds OH^- ions, which shifts the equilibrium to the left, increasing the concentration of NO_2^- ions and decreasing the concentrations of HNO_2. (d) Adding NaCl has no effect on the concentrations of the ions. (e) Adding KNO_2 adds NO_2^- ions and shifts the equilibrium to the right, increasing the HNO_2 and OH^- ion concentrations.

51. What is the effect on the concentration of hydrofluoric acid, hydronium ion, and fluoride ion when the following are added to separate solutions of hydrofluoric acid?
(a) HCl
(b) KF
(c) NaCl
(d) KOH
(e) HF

Solution
(a) Adding HCl will add H_3O^+ ions. The equilibrium will shift to the left, increasing the concentration of HF and decreasing the concentration of F^- ions. (b) Adding KF increases the concentration of F^- ions, and shifts the equilibrium to the left, increasing the concentration of F^- ions, and shifts the equilibrium to the left, increasing the concentration of HF and decreasing the concentration of H_3O^+ ions. (c) Adding NaCl has no effect on the concentrations of H_3O^+ ions. (d) Adding KOH adds OH^- ions, which will react with the H_3O^+ ions, lowering their concentration. The equilibrium will shift to the right, increasing the concentration of F^- ions and decreasing the concentration of HF. (e) Adding HF increases the HF concentration, and shifts the equilibrium to the right, increasing the H_3O^+ and F^- ion concentrations.

52. Why is the hydronium ion concentration in a solution that is 0.10 *M* in HCl and 0.10 *M* in HCOOH determined by the concentration of HCl?

Solution
The equations of the occurring chemical processes are:

$$HCl(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

This is a case in which the solution contains a mixture of acids of different ionization strengths. In solution, the HCO_2H exists primarily as HCO_2H molecules because the ionization of the weak

acid is suppressed by the strong acid. Therefore, the HCO_2H contributes a negligible amount of hydronium ions to the solution. The stronger acid, HCl, is the dominant producer of hydronium ions because it is completely ionized. In such a solution, the stronger acid determines the concentration of hydronium ions, and the ionization of the weaker acid is fixed by the $[H_3O^+]$ produced by the stronger acid.

53. From the equilibrium concentrations given, calculate K_a for each of the weak acids and K_b for each of the weak bases.

(a) CH_3CO_2H: $[H_3O^+] = 1.34 \times 10^{-3}\ M$;

$[CH_3CO_2^-] = 1.34 \times 10^{-3}\ M$;

$[CH_3CO_2H] = 9.866 \times 10^{-2}\ M$;

(b) ClO^-: $[OH^-] = 4.0 \times 10^{-4}\ M$;

$[HClO] = 2.38 \times 10^{-4}\ M$;

$[ClO^-] = 0.273\ M$;

(c) HCO_2H: $[HCO_2H] = 0.524\ M$;

$[H_3O^+] = 9.8 \times 10^{-3}\ M$;

$[HCO_2^-] = 9.8 \times 10^{-3}\ M$;

(d) $C_6H_5NH_3^+$: $[C_6H_5NH_3^+] = 0.233\ M$;

$[C_6H_5NH_2] = 2.3 \times 10^{-3}\ M$;

$[H_3O^+] = 2.3 \times 10^{-3}\ M$

Solution

(a) The reaction is $CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$

$$K_a = \frac{[CH_3CO_2^-][H_3O^+]}{[CH_3CO_2H]} = \frac{(1.34 \times 10^{-3})(1.34 \times 10^{-3})}{(9.866 \times 10^{-2})} = 1.82 \times 10^{-5};$$

(b) The reaction is $ClO^-(aq) + H_2O(l) \rightleftharpoons HClO(aq) + OH^-(aq)$

$$K_b = \frac{[HClO][OH^-]}{[ClO^-]} = \frac{(2.38 \times 10^{-4})(4.0 \times 10^{-4})}{(0.273)} = 3.5 \times 10^{-7};$$

(c) The reaction is $HCO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_2^-(aq)$

$$K_a = \frac{[HCO_2^-][H_3O^+]}{[HCO_2H]} = \frac{(9.8 \times 10^{-3})(9.8 \times 10^{-3})}{(0.524)} = 1.8 \times 10^{-4};$$

(d) The reaction is

$$K_a = \frac{[C_6H_5NH_2][H_3O^+]}{[C_6H_5NH_3^+]} = \frac{(2.3 \times 10^{-3})(2.3 \times 10^{-3})}{(0.233)} = 2.3 \times 10^{-5}$$

54. From the equilibrium concentrations given, calculate K_a for each of the weak acids and K_b for each of the weak bases.

(a) NH_3: $[OH^-] = 3.1 \times 10^{-3}\ M$;

$[NH_4^+] = 3.1 \times 10^{-3}\ M$;

$[NH_3] = 0.533\ M$;

(b) HNO_2: $[H_3O^+] = 0.011\ M$;

$[NO_2^-] = 0.0438\ M$;
$[HNO_2] = 1.07\ M$;
(c) $(CH_3)_3N$: $[(CH_3)_3N] = 0.25\ M$;
$[(CH_3)_3NH^+] = 4.3 \times 10^{-3}\ M$;
$[OH^-] = 3.7 \times 10^{-3}\ M$;
(d) NH_4^+: $[NH_4^+] = 0.100\ M$;
$[NH_3] = 7.5 \times 10^{-6} M$;
$[H_3O^+] = 7.5 \times 10^{-6} M$

Solution
(a) The reaction is $NH_3(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + NH_4^+(aq)$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(3.1 \times 10^{-3})(3.1 \times 10^{-3})}{(0.533)} = 1.8 \times 10^{-5};$$

(b) The reaction is $HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$

$$K_a = \frac{[NO_2^-][H_3O^+]}{[HNO_2]} = \frac{(0.0438)(0.011)}{(1.07)} = 4.5 \times 10^{-4};$$

(c) The reaction is $(CH_3)_3N(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + (CH_3)_3NH^+(aq)$

$$K_b = \frac{[(CH_3)_3NH^+][OH^-]}{[(CH_3)_3N]} = \frac{(3.7 \times 10^{-3})(4.3 \times 10^{-3})}{(0.25)} = 6.4 \times 10^{-5};$$

(d) The reaction is $NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = \frac{(7.5 \times 10^{-6})(7.5 \times 10^{-6})}{(0.100)} = 5.6 \times 10^{-10}$$

55. Determine K_b for the nitrite ion, NO_2^-. In a 0.10-*M* solution this base is 0.0015% ionized.

Solution
The reaction is $NO_2^-(aq) + H_2O(l) \rightleftharpoons HNO_2(aq) + OH^-(aq)$.
The concentrations at equilibrium are $[HNO_2^+] = [OH^-] = (1.5 \times 10^{-5})(0.10\ M) = 1.5 \times 10^{-6}\ M$.
$[NH_3] = 0.10\ M - 1.5 \times 10^{-5}\ M = 0.10\ M$

$$K_b = \frac{[HNO_2][OH^-]}{[NH_3]} = \frac{(1.5 \times 10^{-6})(1.5 \times 10^{-6})}{(0.10)} = 2.3 \times 10^{-11}$$

56. Determine K_a for hydrogen sulfate ion, HSO_4^-. In a 0.10-*M* solution the acid is 29% ionized.

Solution
The reaction is $HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$.
The concentrations at equilibrium are:
$[H_3O^+] = [SO_4^{2-}] = (0.29)(0.10\ M) = 0.029\ M$
$[HSO_4^-] = 0.10\ M - 0.029\ M = 0.071\ M$

$$K_a = \frac{[SO_4^{2-}][H_3O^+]}{[HSO_4^-]} = \frac{(0.029)(0.029)}{(0.071)} = 1.2 \times 10^{-2}$$

57. Calculate the ionization constant for each of the following acids or bases from the ionization constant of its conjugate base or conjugate acid:
(a) F^-
(b) NH_4^+
(c) AsO_4^{3-}
(d) $(CH_3)_2NH_2^+$
(e) NO_2^-
(f) $HC_2O_4^-$ (as a base)

Solution
(a) The fluoride ion reacts with water as a base in the following way:

$$F^-(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^-(aq)$$

An expression for the equilibrium is written in the usual way:

$$K_b = \frac{[HF][OH^-]}{[F^-]}$$

This expression is related to the ionization of HF:

$$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$$

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = 6.4 \times 10^{-4}$$

Inspection of the expressions for K_b and for K_a indicates an inverse relationship between K_a and K_b with the substitution of $[H_3O^+] = \frac{K_w}{[OH^-]}$ in the expression for K_a

$$K_b = \frac{[HF][OH^-]}{[F^-]} = \frac{\frac{K_w}{[H_3O^+]} \times [HF]}{[F^-]} = \frac{K_w[HF]}{[F^-][H_3O^+]}$$

$$K_b = K_w \times \frac{1}{K_a} = \frac{K_w}{K_a}$$

This final relationship turns out to be the general form for the reaction of an ion from either a weak acid or a weak base.
For the F^- ion:

$$K_b = \frac{1.0 \times 10^{-14}}{6.4 \times 10^{-4}} = 1.6 \times 10^{-11};$$

(b) This ion is the conjugate acid of the weak base ammonia. Reaction of NH_4^+ gives:

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = \frac{K_w}{K_b(NH_3)} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10};$$

(c) $K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{3.0 \times 10^{-12}} = 3.3 \times 10^{-3};$

(d) $K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{5.9 \times 10^{-4}} = 1.7 \times 10^{-11}$;

(e) $K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.6 \times 10^{-4}} = 2.2 \times 10^{-11}$;

(f) $K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.0 \times 10^{-2}} = 1.7 \times 10^{-13}$

58. Calculate the ionization constant for each of the following acids or bases from the ionization constant of its conjugate base or conjugate acid:
(a) HTe^- (as a base)
(b) $(CH_3)_3NH^+$
(c) $HAsO_4^{2-}$ (as a base)
(d) HO_2^- (as a base)
(e) $C_6H_5NH_3^+$
(f) HSO_3^- (as a base)

Solution
(a) $K_b = \frac{K_w}{K_a} = \frac{(1.00 \times 10^{-14})}{2.3 \times 10^{-3}} = 4.3 \times 10^{-12}$;

(b) $K_a = \frac{K_w}{K_b} = \frac{(1.00 \times 10^{-14})}{6.3 \times 10^{-5}} = 1.6 \times 10^{-10}$;

(c) $K_b = \frac{K_w}{K_a} = \frac{(1.00 \times 10^{-14})}{1.7 \times 10^{-7}} = 5.9 \times 10^{-8}$;

(d) $K_b = \frac{K_w}{K_a} = \frac{(1.00 \times 10^{-14})}{2.4 \times 10^{-12}} = 4.2 \times 10^{-3}$;

(e) $K_a = \frac{K_w}{K_b} = \frac{(1.00 \times 10^{-14})}{4.3 \times 10^{-10}} = 2.3 \times 10^{-5}$;

(f) $K_b = \frac{K_w}{K_a} = \frac{(1.00 \times 10^{-14})}{1.6 \times 10^{-2}} = 6.3 \times 10^{-13}$

59. Using the K_a values in 1.4×10^{-5}, place $Al(H_2O)_6^{3+}$ in the correct location in Figure 14.7.

Solution
The reaction is:

$$Al(H_2O)_6^{3+}(aq) + H_2O(l) \rightleftharpoons Al(H_2O)_5OH^{2+}(aq) + H_3O^+(aq) \qquad K_a = 1.4 \times 10^{-5}$$

This is a comparatively weak acid. It lies between acetic acid at $K_a = 1.8 \times 10^{-5}$ and carbonic acid at $K_a = 4.3 \times 10^{-7}$.

60. Calculate the concentration of all solute species in each of the following solutions of acids or bases. Assume that the ionization of water can be neglected, and show that the change in the initial concentrations can be neglected.
(a) 0.0092 *M* HClO, a weak acid

(b) 0.0784 *M* $C_6H_5NH_2$, a weak base
(c) 0.0810 *M* HCN, a weak acid
(d) 0.11 *M* $(CH_3)_3N$, a weak base
(e) 0.120 *M* $Fe(H_2O)_6^{2+}$ a weak acid, $K_a = 1.6 \times 10^{-7}$

Solution

(a) The reaction is: $HClO(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + ClO^-(aq)$

The equilibrium expression is:

$$K_a = \frac{[H_3O^+][ClO^-]}{[HClO]} = 2.9 \times 10^{-8}$$

The initial and equilibrium concentrations for this system can be written as follows:

	[HClO]	$[H_3O^+]$	$[ClO^-]$
Initial concentration (*M*)	0.0092	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.0092 - x$	x	x

Substituting the equilibrium concentrations into the equilibrium expression and making the assumption that $(0.0092 - x) \approx 0.0092$ gives:

$$\frac{[H_3O^+][ClO^-]}{[HClO]} = \frac{(x)(x)}{(0.0092 - x)} \approx \frac{(x)(x)}{0.0092} = 2.9 \times 10^{-8}$$

Solving for x gives $1.63 \times 10^{-5} M$. This value is less than 5% of 0.0092, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$[H_3O^+] = [ClO^-] = 1.6 \times 10^{-5} M$

$[HClO^-] = 0.0092 - 1.63 \times 10^{-5} = 0.00918 = 0.0092\ M$

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{1.63 \times 10^{-5}} = 6.1 \times 10^{-10}\ M;$$

(b) The reaction is: $C_6H_5NH_2(aq) + H_2O(l) \rightleftharpoons C_6H_5NH_3^+(aq) + OH^-(aq)$

The equilibrium expression is:

$$K_a = \frac{[C_6H_5NH_3^+][OH^-]}{[C_6H_5NH_2]} = 4.3 \times 10^{-10}$$

The initial and equilibrium concentrations for this system can be written as follows:

	$[C_6H_5NH_2]$	$[C_5H_5NH_3^+]$	$[OH^-]$
Initial concentration (*M*)	0.0784	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.0784 - x$	x	x

Substituting the equilibrium concentrations into the equilibrium expression and making the assumption that $(0.0784 - x) \approx 0.0784$ gives:

$$\frac{[C_6H_5NH_3^+][OH^-]}{[C_6H_5NH_2]} = \frac{(x)(x)}{(0.0784 - x)} \approx \frac{(x)(x)}{0.0784} = 4.3 \times 10^{-10}$$

Solving for x gives $5.81 \times 10^{-6}\,M$. This value is less than 5% of 0.0784, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$[C_6H_5NH_2] = [OH^-] = 5.8 \times 10^{-6}\,M$

$[C_6H_5NH_2] = 0.0784 - 5.81 \times 10^{-6} = 0.07839 = 0.0784\,M$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{5.81 \times 10^{-6}} = 1.7 \times 10^{-9}\,M;$$

(c) The reaction is $HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$.

The equilibrium expression is:

$$K_a = \frac{[H_3O^+][CN^-]}{[HCN]} = 4.9 \times 10^{-10}$$

The initial and equilibrium concentrations for this system can be written as follows:

	[HClO]	$[H_3O^+]$	$[CN^-]$
Initial concentration (*M*)	0.0810	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.0810 - x$	x	x

Substituting the equilibrium concentrations into the equilibrium expression and making the assumption that $(0.0810 - x) \approx 0.0810$ gives:

$$\frac{[H_3O^+][CN^-]}{[HCN]} = \frac{(x)(x)}{(0.0810 - x)} \approx \frac{(x)(x)}{0.0810} = 4 \times 10^{-10}$$

Solving for x gives $6.30 \times 10^{-6}\,M$. This value is less than 5% of 0.0810, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$[H_3O^+] = [CN^-] = 6.3 \times 10^{-6}\,M$

$[HCN] = 0.0810 - 6.30 \times 10^{-6} = 0.08099 = 0.0810\,M$

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{6.30 \times 10^{-6}} = 1.6 \times 10^{-9}\,M;$$

(d) The reaction is:

$(CH_3)_3N(aq) + H_2O(l) \rightleftharpoons (CH_3)_3NH^+(aq) + OH^-(aq)$

The equilibrium expression is:

$$K_b = \frac{[(CH_3)_3NH^+][OH^-]}{[(CH_3)_3N]} = 6.3 \times 10^{-5}$$

The initial and equilibrium concentrations for this system can be written as follows:

	$[(CH_3)_3N]$	$[(CH_3)_3NH^+]$	$[OH^-]$
Initial concentration (*M*)	0.11	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.11 - x$	x	x

Substituting the equilibrium concentrations into the equilibrium expression and making the assumption that $(0.11 - x) \approx 0.11$ gives:

$$\frac{[(CH_3)_3NH^+][OH^-]}{[(CH_3)_3N]} = \frac{(x)(x)}{(0.11 - x)} \approx \frac{(x)(x)}{0.11} = 6.3 \times 10^{-5}$$

Solving for x gives $2.63 \times 10^{-3}\,M$. This value is less than 5% of 0.11, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$[(CH_3)_3NH^+] = [OH^-] = 2.6 \times 10^{-3}\,M$

$[(CH_3)_3N] = 0.11 - 2.63 \times 10^{-3} = 0.107 = 0.11\,M$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{2.63 \times 10^{-3}} = 3.8 \times 10^{-12}\,M;$$

(e) The reaction is:

$$Fe(H_2O)_6^{2+}(aq) + H_2O(l) \rightleftharpoons Fe(H_2O)_5(OH)^+(aq) + H_3O^+(aq)$$

The equilibrium expression is:

$$K_a = \frac{[Fe(H_2O)_5(OH)^+][H_3O^+]}{[Fe(H_2O)_6^{2+}]} = 1.6 \times 10^{-7}$$

The initial and equilibrium concentrations for this system can be written as follows:

	$[Fe(H_2O)_6^{2+}]$	$[H_3O^+]$	$[Fe(H_2O)_5(OH)^+]$
Initial concentration (*M*)	0.120	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.120 - x$	x	x

Substituting the equilibrium concentrations into the equilibrium expression and making the assumption that $(0.120 - x) \approx 0.120$ gives:

$$\frac{[Fe(H_2O)_5(OH)^+][H_3O^+]}{[Fe(H_2O)_6^{2+}]} = \frac{(x)(x)}{(0.120 - x)} \approx \frac{(x)(x)}{0.120} = 1.6 \times 10^{-7}$$

Solving for x gives $1.39 \times 10^{-4} M$. This value is less than 5% of 0.120, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$[Fe(H_2O)_5(OH)^+] = [H_3O^+] = 1.4 \times 10^{-4}\,M$

$[Fe(H_2O)_6^{2+}] = 0.120 - 1.39 \times 10^{-4} = 0.1199 = 0.120\,M$

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{1.39 \times 10^{-4}} = 7.2 \times 10^{-11}\,M$$

61. Propionic acid, $C_2H_5CO_2H$ ($K_a = 1.34 \times 10^{-5}$), is used in the manufacture of calcium propionate, a food preservative. What is the pH of a 0.698-*M* solution of $C_2H_5CO_2H$?

Solution
The reaction is:

$$C_2H_5CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_2H_5CO_2^-(aq)$$

The equilibrium expression is:

$$K_a = \frac{[C_2H_5CO_2^-][H_3O^+]}{[C_2H_5CO_2H]} = 1.34 \times 10^{-5}$$

The initial and equilibrium concentrations for this system can be written as follows:

	$[C_2H_5CO_2H]$	$[H_3O^+]$	$[C_2H_5CO_2^-]$
Initial concentration (*M*)	0.698	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.698 - x$	x	x

Substituting the equilibrium concentrations into the equilibrium expression and making the assumption that $(0.698 - x) \approx 0.698$ gives:

$$\frac{[C_2H_5CO_2^-][H_3O^+]}{[C_2H_5CO_2H]} = \frac{(x)(x)}{(0.698 - x)} \approx \frac{(x)(x)}{0.698} = 1.34 \times 10^{-5}$$

Solving for x gives $3.058 \times 10^{-3}\ M$. Because this value is 5% of 0.698, our assumption is correct. The equilibrium concentration of hydronium ion is therefore:

$$[H_3O^+] = 3.058 \times 10^{-3}\ M$$

$$pH = -\log(3.058 \times 10^{-3}) = 2.5146 = 2.515$$

62. White vinegar is a 5.0% by mass solution of acetic acid in water. If the density of white vinegar is 1.007 g/cm^3, what is the pH?

Solution
First, find the mass of acetic acid. $d = 1.007$ g/cm^3. Take 1.0 L of solution to have the quantities on a mole basis. Then, since 1000 cm^3 = 1.0 L, 1000 cm^3 × 1.007 g/cm^3 = 1007 g in 1.0 L. Then, 5.00% of this is the mass of acetic acid:

$$\text{Mass (acetic acid)} = 1007\ \text{g} \times \frac{5.0\%}{100\%} = 50.35\ \text{g}$$

Now calculate the number of moles of acetic acid present. Themolar mass of acetic acid is 60.053 g/mol:

$$\text{mol acetic acid} = \frac{50.35\ \cancel{\text{g}}}{60.053\ \cancel{\text{g}}\ \text{mol}^{-1}} = 0.838\ \text{mol}$$

From the moles of acetic acid and K_a, calculate $[H_3O^+]$:

$$K_a = 1.8 \times 10^{-5} = \frac{[CH_3CO_2^-][H_3O^+]}{[CH_3CO_2H]}$$

	$[CH_3CO_2H]$	$[H_3O^+]$	$[CH_3CO_2^-]$
Initial concentration (*M*)	0.838	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.838 - x$	x	x

Substitution gives:

$$K_a = 1.8 \times 10^{-5} = \frac{x^2}{0.838 - x}$$

Drop x because it is small in comparison with 0.838 *M*.

$x^2 = 0.838(1.8 \times 10^{-5}) = (1.508 \times 10^{-5})^{1/2} = 3.88 \times 10^{-3}\ M$

$pH = -\log(3.88 \times 10^{-3}) = 2.41$

63. The ionization constant of lactic acid, $CH_3CH(OH)CO_2H$, an acid found in the blood after strenuous exercise, is 1.36×10^{-4}. If 20.0 g of lactic acid is used to make a solution with a volume of 1.00 L, what is the concentration of hydronium ion in the solution?

Solution

$$CH_3CHOHCO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CHOHCO_2^-(aq)$$

$$M\ CH_3CHOHCO_2H = 20.0\ \cancel{g} \times \frac{1\ \text{mol}}{90.0788\ \cancel{g}} = \frac{0.2220\ \text{mol}}{1.00\ \text{L}} = 0.2220\ M\ CH_3CHOHCO_2H$$

	$[CH_3CHOHCO_2H]$	$[H_3O^+]$	$[CH_3CHOHCO_2^-]$
Initial concentration (*M*)	0.2220	~0	~0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.2220 - x$	x	x

At equilibrium:

$$\frac{[H_3O^+][CH_3CHOHCO_2^-]}{[CH_3CHOHCO_2H]} = 1.36 \times 10^{-4} = K_a$$

$$\frac{(x)(x)}{(0.2220 - x)} = 4.5 \times 10^{-4}$$

Assume that x is small:

$$\frac{(x)(x)}{(0.2220)} = 1.36 \times 10^{-4}$$

$x^2 = (0.2220) \times 1.36 \times 10^{-4} = 3.02 \times 10^{-5}$

$x = [H_3O^+] = 0.00549$

To check our assumption:

$$\frac{0.00549}{0.2220} = 0.0248\ (2.48\%)$$

Another approximation is not needed.

64. Nicotine, $C_{10}H_{14}N_2$, is a base that will accept two protons ($K_{b1} = 7 \times 10^{-7}$, $K_{b2} = 1.4 \times 10^{-11}$). What is the concentration of each species present in a 0.050-*M* solution of nicotine?

Solution

$C_{10}H_{14}N_2(aq) + H_2O(l) \rightleftharpoons C_{10}H_{14}N_2H^+(aq) + OH^-(aq) \qquad (K_{b1} = 7 \times 10^{-7})$

$C_{10}H_{14}N_2H^+(aq) + H_2O(l) \rightleftharpoons C_{10}H_{14}N_2H_2^{2+}(aq) + OH^-(aq) \qquad (K_{b2} = 1.4 \times 10^{-11})$

First set up a concentration table:

	$[C_{10}H_{14}N_2]$	$[C_{10}H_{14}N_2H^+]$	$[OH^-]$
Initial concentration (*M*)	0.050	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.050 - x$	x	x

Substituting the equilibrium concentrations into the equilibrium equation and making the assumption that $(0.050 - x) = 0.050$, we get:

$$K_{b1} = \frac{[C_{10}H_{14}N_2H^+][OH^-]}{[C_{10}H_{14}N_2]} = 7 \times 10^{-7}$$

$$= \frac{(x)(x)}{(0.050 - x)} = \frac{x^2}{0.050} = 7 \times 10^{-7}$$

Solving for x gives $1.87 \times 10^{-4} = 2 \times 10^{-4} M = [OH^-]$

Because x is less than 5% of 0.050 and $[OH^-]$ is greater than $4.5 \times 10^{-7} M$, our customary assumptions are justified. We can calculate $[C_{10}H_{14}N_2] = 0.050 - x = 0.050 - 2 \times 10^{-4} = 0.048$ *M*; $[OH^-] = [C_{10}H_{14}N_2H^+] = x = 2 \times 10^{-4} M$. Now calculate the concentration of $C_{10}H_2N_2H_2^{2+}$ in a solution with $[OH^-]$ and $[C_{10}H_2N_2H_2^{2+}]$ equal to $2 \times 10^{-4}\,M$. The equilibrium between these species is $C_{10}H_{14}N_2H^+(aq) + H_2O(l) \rightleftharpoons C_{10}H_{14}N_2H_2^{2+}(aq) + OH^-(aq)$. We know $[C_{10}H_{14}N_2H^+]$ and $[OH^-]$, so we can calculate the concentration of $C_{10}H_2N_2H_2^{2+}$ from the equilibrium expression:

$$K_{b2} = \frac{[C_{10}H_{14}N_2H_2^{2+}][OH^-]}{[C_{10}H_{14}N_2H^+]} = 1.4 \times 10^{-11}$$

$$= \frac{[C_{10}H_{14}N_2H_2^{2+}][2 \times 10^{-4}]}{[2 \times 10^{-4}]}$$

$[C_{10}H_{14}N_2H_2^{2+}] = 1.4 \times 10^{-11}\ M$

The concentration of OH^- produced in this ionization is equal to the concentration of $C_{10}H_2N_2H_2^{2+}$, $1.4 \times 10^{-11} M$, which is much smaller than the $2 \times 10^{-4} M$ produced in the first ionization; therefore, we are justified in neglecting the OH^- formed from $C_{10}H_{14}N_2H^+$.

We can now calculate the concentration of H_3O^+ present from the ionization of water:

$K_a = 1 \times 10^{-14} = [H_3O^+][OH^-]$

$$[H_3O^+] = \frac{1 \times 10^{-14}}{[OH^-]} = \frac{1 \times 10^{-14}}{1.9 \times 10^{-4}} = 5.3 \times 10^{-11}\ M$$

We can now summarize the concentrations of all species in solution as follows:

$[C_{10}H_{14}N_2] = 0.049\ M$

$[C_{10}H_{14}N_2H^+] = 1.9 \times 10^{-4}\ M$
$[C_{10}H_{14}N_2H_2^{2+}] = 1.4 \times 10^{-11}\ M$
$[OH^-] = 1.9 \times 10^{-4}\ M$
$[H_3O^+] = 5.3 \times 10^{-11}\ M$

65. The pH of a 0.23-*M* solution of HF is 1.92. Determine K_a for HF from these data.

Solution
The reaction is:

$$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$$

The concentrations at equilibrium are:
$[F^-] = [H_3O^+] = 10^{-pH} = 10^{-1.92} = 0.0120\ M$
$[HF] = 0.23\ M - 0.0120\ M = 0.218\ M$

$$K_a = \frac{[F^-][H_3O^+]}{[HF]} = \frac{(0.0120)(0.0120)}{(0.218)} = 6.6 \times 10^{-4}$$

66. The pH of a 0.15-*M* solution of HSO_4^- is 1.43. Determine K_a for HSO_4^- from these data.

Solution
The reaction is $HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_2^{2-}(aq)$.
The concentrations at equilibrium are $[SO_4^{2-}] = [H_3O^+] = 10^{-pH} = 10^{-1.43} = 0.0372\ M$
$[HF] = 0.15 - 0.0372\ M = 0.113\ M$

$$K_a = \frac{[SO_4^{2-}][H_3O^+]}{[HSO_4^-]} = \frac{(0.0372)(0.0372)}{(0.113)} = 1.2 \times 10^{-2}$$

67. The pH of a 0.10-*M* solution of caffeine is 11.70. Determine K_b for caffeine from these data:

$$C_8H_{10}N_4O_2(aq) + H_2O(l) \rightleftharpoons C_8H_{10}N_4O_2H^+(aq) + OH^-(aq)$$

Solution
The pOH can be determined from pOH = 14.00 – pH = 14.00 – 11.70 = 2.30. Therefore, the concentrations at equilibrium are:
$[C_8H_{10}N_4O_2H^+] = [OH^-] = 10^{-pOH} = 10^{-2.30} = 0.00501\ M$
$[C_8H_{10}N_4O_2] = 0.10 - 0.00501 = 0.095\ M$

$$K_b = \frac{[C_8H_{10}N_4O_2H^+][OH^-]}{[C_8H_{10}N_4O_2]} = \frac{(0.00501)(0.00501)}{(0.095)} = 2.6 \times 10^{-4}$$

68. The pH of a solution of household ammonia, a 0.950 *M* solution of NH_3, is 11.612. Determine K_b for NH_3 from these data.

Solution
The reaction is $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$.
The pOH can be determined from pOH = 14.000 – pH = 14.000 – 11.612 = 2.388. Therefore, the concentrations at equilibrium are $[NH_4^+] = [OH^-] = 10^{-pOH} = 10^{-2.388} = 0.004093\ M$
$[NH_3] = 0.950 - 0.004093 = 0.9459\ M$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(0.004093)(0.004093)}{(0.9459)} = 1.77 \times 10^{-5}$$

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Chemistry: Atoms First 2e
14: Acid-Base Equilibria
14.4: Hydrolysis of Salts

69. Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:
(a) $Al(NO_3)_3$
(b) RbI
(c) $KHCO_2$
(d) CH_3NH_3Br

Solution
(a) $Al(NO_3)_3$ dissociates into Al^{3+} ions (acidic metal cation) and NO_3^- ions (the conjugate base of a strong acid and therefore essentially neutral). The aqueous solution is therefore acidic. (b) RbI dissociates into Rb^+ ions (neutral metal cation) and I^- ions (the conjugate base of a strong acid and therefore essentially neutral). The aqueous solution is therefore neutral. (c) $KHCO_2$ dissociates into K^+ ions (neutral metal cation) and HCO_2^- ions (the conjugate base of a weak acid and therefore basic). The aqueous solution is therefore basic. (d) CH_3NH_3Br dissociates into $CH_3NH_3^+$ ions (a weak acid) and Br^- ions (the conjugate base of a strong acid and therefore neutral). The aqueous solution is therefore acidic.

70. Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:
(a) $FeCl_3$
(b) K_2CO_3
(c) NH_4Br
(d) $KClO_4$

Solution
(a) $FeCl_3$ dissociates into Fe^{3+} ions (acidic metal cation) and Cl^- ions (the conjugate base of a strong acid and therefore essentially neutral). The aqueous solution is therefore acidic. (b) K_2CO_3 dissociates into K^+ ions (neutral metal cation) and CO_3^{2-} ions (the conjugate base of a weak acid and therefore basic). The aqueous solution is therefore basic. (c) NH_4Brdissociates into NH_4^+ ions (a weak acid) and Br^- ions (the conjugate base of a strong acid and therefore essentially neutral). The aqueous solution is therefore acidic. (d) $KClO_4$ dissociates into K^+ ions (neutral metal cation) and ClO_4^- ions (the conjugate base of a strong acid and therefore neutral). The aqueous solution is therefore neutral.

71. Novocaine, $C_{13}H_{21}O_2N_2Cl$, is the salt of the base procaine and hydrochloric acid. The ionization constant for procaine is 7×10^{-6}. Is a solution of novocaine acidic or basic? What are $[H_3O^+]$, $[OH^-]$, and pH of a 2.0% solution by mass of novocaine, assuming that the density of the solution is 1.0 g/mL.

Solution
Using the abbreviation Pc for $C_{13}H_{20}O_2N_2$ (procaine), the formula for novocaine is PcHCl, which ionizes to form PcH^+ and Cl^-. The molar mass of novocaine is 272.774 g/mol. For convenience, start with 1.00 L of a 2.0% solution by mass:
$1.00 \times 10^3\ cm^3 \times 1.0\ g\ cm^{-3} = 1.00 \times 10^3\ g$

$$\frac{2.0}{100} \times 1.00 \times 10^3 \text{ g} = 20 \text{ g novocaine}$$

$$= \frac{20 \text{ g}}{272.774 \text{ g mol}^{-1}}$$

$$= 0.073 \text{ mol}$$

In exactly 1 L, there is 0.073 *M*. The cation reacts with water:

$$PcH^+(aq) + H_2O(l) \rightleftharpoons Pc(aq) + H_3O^+(aq)$$

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{7 \times 10^{-6}} = 1.4 \times 10^{-9}$$

It is convenient to set up a table of concentrations:

	$[C_{13}H_{21}O_2N_2H^+]$ or $[PcH^+]$	$[H_3O^+]$	$[C_{13}H_{21}O_2N_2]$ or [Pc]
Initial concentration (*M*)	0.073	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.073 - x$	x	x

$$1.4 \times 10^{-9} = \frac{[Pc][H_3O^+]}{[PcH^+]} = \frac{x^2}{0.073}$$

The change *x* compared with 0.073 *M* is small and, therefore, neglected:

$[H_3O^+] = x = 1.0 \times 10^{-5} = 1 \times 10^{-5} M$

The solution is acidic. The hydroxide ion concentration is:

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-5}} = 1 \times 10^{-9} \ M$$

$pH = -\log(1.0 \times 10^{-5}) = 5.00 = 5.0$

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Chemistry: Atoms First 2e
14: Acid-Base Equilibria
14.5: Polyprotic Acids

72. Which of the following concentrations would be practically equal in a calculation of the equilibrium concentrations in a 0.134-*M* solution of H_2CO_3, a diprotic acid: $[H_3O^+]$, $[OH^-]$, $[H_2CO_3]$, $\left[HCO_3^-\right]$, $\left[CO_3^{2-}\right]$? No calculations are needed to answer this question.

Solution

$[H_3O^+]$ and $[HCO_3^-]$ are equal in a 0.134-*M* solution of H_2CO_3. K_a of H_2CO_3 is significantly larger than K_a for HCO_3^-. Therefore, very little of HCO_3^- ionizes to give hydronium ions and CO_3^{2-} ions, and the concentrations of H_3O^+ and HCO_3^- are practically equal in an aqueous solution of H_2CO_3.

73. Calculate the concentration of each species present in a 0.050-*M* solution of H_2S.

Solution

$H_2S(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HS^-(aq) \qquad (K_{a1} = 8.9 \times 10^{-8})$

$HS^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + S^{2-}(aq) \qquad (K_{a2} = 1.0 \times 10^{-19})$

As indicated by the K_a values, H_2S is a much stronger acid than HS^-, so H_2S is a dominant producer of H_3O^+ in solution:

	$[H_2S]$	$[H_3O^+]$	$[HS^-]$
Initial concentration (*M*)	0.05	~0	~0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.05 - x$	x	x

Assume that $(0.05 - x) = 0.05$. Thus:

$$K_{a1} = \frac{[H_3O^+][HS^-]}{[H_2S]} = 8.9 \times 10^{-8}$$

$$= \frac{(x)(x)}{0.05} = \frac{x^2}{0.05}$$

$x^2 = 0.05 \times 8.9 \times 10^{-8}$

$x = 6.7 \times 10^{-5}$

$[H_2S] = 0.050 - x = 0.050 - 6.7 \times 10^{-5} = 0.050\ M$

$[H_3O^+] = [HS^-] = x = 6.7 \times 10^{-5}\ M$

$$K_{a2} = \frac{[H_3O^+][S^{2-}]}{[HS^-]} = 1.0 \times 10^{-19}$$

$$= \frac{(6.7 \times 10^{-5})[S^{2-}]}{6.7 \times 10^{-5}} = 1.0 \times 10^{-19}\ M$$

$$[S^{2-}] = \frac{(1.0 \times 10^{-19})(6.7 \times 10^{-5})}{6.7 \times 10^{-5}} = 1 \times 10^{-19}\ M$$

The $[OH^-]$ can be calculated from K_w as follows:

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{6.7 \times 10^{-5}} = 1.5 \times 10^{-10}\ M$$

In summary, the concentrations of all species present in a 0.050-*M* solution of H_2S are:

$[H_2S] = 0.050\ M$

$[HS^-] = 6.7 \times 10^{-5}\ M$

$[H_3O^+] = 6.7 \times 10^{-5}\ M$

$[S^{2-}] = 1 \times 10^{-19}\ M$

$[OH^-] = 1.5 \times 10^{-10}\ M$

74. Calculate the concentration of each species present in a 0.010-*M* solution of phthalic acid, $C_6H_4(CO_2H)_2$.

$$C_6H_4(CO_2H)_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_4(CO_2H)(CO_2)^-(aq) \qquad K_a = 1.1 \times 10^{-3}$$

$$C_6H_4(CO_2H)(CO_2)(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_4(CO_2)_2^{2-}(aq) \qquad K_a = 3.9 \times 10^{-6}$$

Solution

$[C_6H_4(CO_2H)_2]$ $7.2 \times 10^{-3} M$, $[C_6H_4(CO_2H)(CO_2)^-] = [H_3O^+]$ $2.8 \times 10^{-3} M$, $[C_6H_4(CO_2)_2^{2-}]$ $3.9 \times 10^{-6} M$, $[OH^-]$ $3.6 \times 10^{-12} M$]

75. Salicylic acid, $HOC_6H_4CO_2H$, and its derivatives have been used as pain relievers for a long time. Salicylic acid occurs in small amounts in the leaves, bark, and roots of some vegetation (most notably historically in the bark of the willow tree). Extracts of these plants have been used as medications for centuries. The acid was first isolated in the laboratory in 1838.

(a) Both functional groups of salicylic acid ionize in water, with $K_a = 1.0 \times 10^{-3}$ for the—CO_2H group and 4.2×10^{-13} for the–OH group. What is the pH of a saturated solution of the acid (solubility = 1.8 g/L).

(b) Aspirin was discovered as a result of efforts to produce a derivative of salicylic acid that would not be irritating to the stomach lining. Aspirin is acetylsalicylic acid, $CH_3CO_2C_6H_4CO_2H$. The–CO_2H functional group is still present, but its acidity is reduced, $K_a = 3.0 \times 10^{-4}$. What is the pH of a solution of aspirin with the same concentration as a saturated solution of salicylic acid (See Part a).

Solution

(a) First, find the concentration of the saturated solution. The molar mass of salicylic acid is 138.123 g/mol. This gives:

$$\frac{1.8 \text{ g L}^{-1}}{138.123 \text{ g mol}^{-1}} = 0.0130\ M$$

The reactions and equilibrium constants are:

$$HOC_6H_4CO_2H(aq) + H_2O(l) \rightleftharpoons HOC_6H_4CO_2^-(aq) + H_3O^+(aq) \qquad K_a = 1.0 \times 10^{-3}$$

$$HOC_6H_4CO_2H(aq) + H_2O(l) \rightleftharpoons HO_2CC_6H_4O^-(aq) + H_3O^+(aq) \qquad K_a = 4.2 \times 10^{-13}$$

Because the equilibrium constant for the first reaction is so much larger than for the second reaction, it will dominate. The equilibrium expression for this reaction is:

$$K_a = \frac{[HOC_6H_4CO_2^-][H_3O^+]}{[HOC_6H_4CO_2H]} = 1.0 \times 10^{-3}$$

The initial and equilibrium concentrations for this system can be written as follows:

	$[CH_3CO_2C_6H_4CO_2H]$	$[CH_3CO_2C_6H_4CO_2^-]$	$[H_3O^+]$
Initial concentration (*M*)	0.0130	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.0130 - x$	x	x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumption that $(0.0130 - x) \approx 0.0130$, gives:

$$\frac{[HOC_6H_4CO_2^-][H_3O^+]}{[HOC_6H_4CO_2H]} = \frac{(x)(x)}{(0.0130 - x)} \approx \frac{(x)(x)}{0.0130} = 1.0 \times 10^{-3}$$

Solving for x gives $3.61 \times 10^{-3} M$. Because this value is 28% of 0.0130 M, our assumption is incorrect. Therefore, use the quadratic formula. Using the provided data gives the quadratic equation:

$x^2 + 1.0 \times 10^{-3}x - 1.30 \times 10^{-5} = 0$

Using the quadratic formula gives ($a = 1$, $b = 1.0 \times 10^{-3}$, and $c = -1.30 \times 10^{-5}$)

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-(1.0 \times 10^{-3}) \pm \sqrt{(1.0 \times 10^{-3})^2 - 4(1)(-1.30 \times 10^{-5})}}{2(1)}$$

$$= \frac{-(1.0 \times 10^{-3}) \pm (7.28 \times 10^{-3})}{2} = 3.14 \times 10^{-3}\ M \quad \text{(positive root)}$$

Thus, $[H^+] = 3.14 \times 10^{-3}\ M$

$pH = -\log(3.14 \times 10^{-3}) = 2.503 = 2.50$;

(b) The reaction and equilibrium constant are:

$$CH_3CO_2C_6H_4CO_2H(aq) + H_2O(l) \rightleftharpoons CH_3CO_2C_6H_4CO_2^-(aq) + H_3O^+(aq)$$

$$K_a = 3.0 \times 10^{-4}$$

The equilibrium expression for this reaction is:

$$K_a = \frac{[CH_3CO_2C_6H_4CO_2^-][H_3O^+]}{[CH_3CO_2C_6H_4CO_2H]} = 3.0 \times 10^{-4}$$

For a 0.0130-M initial concentration, the initial and equilibrium concentrations for this system can be written as follows:

	$[CH_3CO_2C_6H_4CO_2H]$	$[CH_3CO_2C_6H_4CO_2^-]$	$[H_3O^+]$
Initial concentration (M)	0.0130	0	0
Change (M)	$-x$	$+x$	$+x$
Equilibrium (M)	$0.0130 - x$	x	x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumption that $(0.0130 - x) \approx 0.0130$, gives:

$$\frac{[CH_3CO_2C_6H_4CO_2^-][H_3O^+]}{[CH_3CO_2C_6H_4CO_2H]} = \frac{(x)(x)}{(0.0130 - x)} \approx \frac{(x)(x)}{0.0130} = 3.0 \times 10^{-4}$$

Solving for x gives $1.97 \times 10^{-3}\ M$. Because this value is 15% of 0.0130, our assumption is incorrect. Therefore, use the quadratic formula. Using the above data gives the quadratic equation:

$x^2 + 3.0 \times 10^{-4}x - 3.90 \times 10^{-6} = 0$

Using the quadratic formula gives ($a = 1$, $b = 3.0 \times 10^{-4}$, and $c = -3.90 \times 10^{-6}$)

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-(3.0 \times 10^{-4}) \pm \sqrt{(3.0 \times 10^{-4})^2 - 4(1)(-3.90 \times 10^{-6})}}{2(1)}$$

$$= \frac{-(3.0 \times 10^{-4}) \pm (3.96 \times 10^{-3})}{2} = 1.83 \times 10^{-3}\ M \quad \text{(positive root)}$$

Thus, $[H^+] = 1.83 \times 10^{-3}\ M$

$pH = -\log(1.83 \times 10^{-3}) = 2.737 = 2.74$

76. The ion HTe^- is an amphiprotic species; it can act as either an acid or a base.

(a) What is K_a for the acid reaction of HTe^- with H_2O?
(b) What is K_b for the reaction in which HTe^- functions as a base in water?
(c) Demonstrate whether or not the second ionization of H_2Te can be neglected in the calculation of $[HTe^-]$ in a 0.10 *M* solution of H_2Te.

Solution
(a) as an acid,

$$HTe^-(aq) + H_2O(l) \rightleftharpoons Te^{2-}(aq) + H_3O^+(aq)$$

$$K_{a2} = \frac{[Te^{2-}][H_3O^+]}{[HTe^-]} = 1.6 \times 10^{-11} \quad ;$$

(b) as a base,

$$HTe^-(aq) + H_2O(l) \rightleftharpoons H_2Te(aq) + OH^-(aq)$$

$$K_b = \frac{[H_2Te][OH^-]}{[HTe^-]} = \frac{K_w}{K_{a_1}} = \frac{1.0 \times 10^{-14}}{2.3 \times 10^{-3}} = 4.3 \times 10^{-12} \; ;$$

(c) The reactions and ionization constants are:

$$H_2Te(aq) + H_2O(l) \rightleftharpoons HTe^-(aq) + H_3O^+(aq) \qquad K_{a1} = 2.3 \times 10^{-3}$$

$$HTe^-(aq) + H_2O(l) \rightleftharpoons Te^{2-}(aq) + H_3O^+(aq) \qquad K_{a2} = 1.6 \times 10^{-11}$$

As a general rule, if the first ionization constant is larger than the second by a factor of at least 20, then the second ionization can be neglected. Since K_{a1} is 230-times larger than K_{a2}, the assumption should hold true for HTe^-. To test the assumptions, find $[HTe^-]$ from the first reaction. The equilibrium expression for this reaction is $K_{a1} = \frac{[HTe^-][H_3O^+]}{[H_2Te]} = 2.3 \times 10^{-3}$.

The initial and equilibrium concentrations for this system can be written as follows:

	$[H_2Te]$	$[HTe^-]$	$[H_3O^+]$
Initial concentration (*M*)	0.10	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.10 - x$	x	x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumption that $(0.10 - x) \approx 0.10$, gives $\frac{[HTe^-][H_3O^+]}{[H_2Te]} = \frac{(x)(x)}{(0.10 - x)} \approx \frac{(x)(x)}{0.10} = 2.3 \times 10^{-3}$.

Solving for x gives 0.0152 *M*. Because this value is 15% of 0.10 *M*, our assumption is incorrect. Therefore, use the quadratic formula. Using the data gives the quadratic equation:

$x^2 + 2.3 \times 10^{-3}x - 2.3 \times 10^{-4} = 0$

Using the quadratic formula gives ($a = 1$, $b = 2.3 \times 10^{-3}$, and $c = -2.3 \times 10^{-4}$)

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-(2.3 \times 10^{-3}) \pm \sqrt{(2.3 \times 10^{-3})^2 - 4(1)(-2.3 \times 10^{-4})}}{2(1)}$$

$$= \frac{-(2.3 \times 10^{-3}) \pm (0.0304)}{2} = 0.0141\,M \quad \text{(positive root)}$$

Thus $[HTe^-] = 0.014\ M$. For the second ionization, $K_{a2} = \frac{[Te^{2-}][H_3O^+]}{[HTe^-]} = 1.6 \times 10^{-11}$.

The initial and equilibrium concentrations for this system can be written as follows:

	$[HTe^-]$	$[Te^{2-}]$	$[H_3O^+]$
Initial concentration (*M*)	0.0141	0	0.0141
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.0141 - x$	x	$0.0141 + x$

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that $(0.0140 - x) \approx$ and $(0.0141 + x) \approx 0.0141$, gives:

$$\frac{[Te^{2-}][H_3O^+]}{[HTe^-]} = \frac{(x)(0.0141 + x)}{(0.0141 - x)} \approx \frac{(x)(0.0141)}{0.0141} = 1.6 \times 10^{-11}$$

Solving for x gives $1.6 \times 10^{-11}\ M$. Therefore, compared with 0.014 *M*, this value is negligible (1.1×10^{-7} %).

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Chemistry: Atoms First 2e
14: Acid-Base Equilibria
14.6: Buffers

77. Explain why a buffer can be prepared from a mixture of NH_4Cl and NaOH but not from NH_3 and NaOH.

Solution

OH^- is a base, and NH_4^+ is a weak acid. They react with one another to form NH_3, thereby setting up the equilibrium $NH_4^+(aq) + OH^-(aq) \rightleftharpoons NH_3(aq) + H_2O(l)$. Because both the base (NH_3) and the conjugate acid (NH_4^+) are present, a buffer is formed. However, in the second case, NH_3 and OH^- are both bases, so no buffer is possible.

78. Explain why the pH does not change significantly when a small amount of an acid or a base is added to a solution that contains equal amounts of the acid H_3PO_4 and a salt of its conjugate base NaH_2PO_4.

Solution

Excess H_3O^+ is removed primarily by the reaction:

$$H_3O^+(aq) + H_2PO_4^-(aq) \longrightarrow H_3PO_4(aq) + H_2O(l)$$

Excess base is removed by the reaction:

$$OH^-(aq) + H_3PO_4(aq) \longrightarrow H_2PO_4^-(aq) + H_2O(l)$$

79. Explain why the pH does not change significantly when a small amount of an acid or a base is added to a solution that contains equal amounts of the base NH_3 and a salt of its conjugate acid NH_4Cl.

Solution

A mixture of NH_3 and NH_4Cl is a buffer because it contains a weak base and its salt. If hydroxide ions are added, the ammonium ions in the buffer react with the hydroxide ions to form ammonia and water and reduce the hydroxide ion concentration toward its original value: $NH_4^+(aq) + OH^-(aq) \rightleftharpoons NH_3(aq) + H_2O(l)$. If hydronium ions are added, the ammonia molecules in the buffer react with them to form ammonium ions, reducing the hydronium ion concentration toward its original value: $H_3O^+(aq) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + H_2O(l)$

80. What is $[H_3O^+]$ in a solution of 0.25 *M* CH_3CO_2H and 0.030 *M* $NaCH_3CO_2$?

$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq) \qquad K_a = 1.8 \times 10^{-5}$

Solution
The equilibrium expression is:

$$K_a = \frac{[CH_3CO_2^-][H_3O^+]}{[CH_3CO_2H]} = 1.8 \times 10^{-5}$$

The initial and equilibrium concentrations for this system can be written as follows:

	$[CH_3CO_2H]$	$[H_3O^+]$	$[CH_3CO_2^-]$
Initial concentration (*M*)	0.25	0	0.030
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.25 - x$	x	$0.030 + x$

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that $(0.25 - x) \approx 0.25$ and $(0.030 - x) \approx 0.030$, gives:

$$\frac{[CH_3CO_2^-][H_3O^+]}{[CH_3CO_2H]} = \frac{(x)(0.030 + x)}{(0.25 - x)} \approx \frac{(x)(0.030)}{0.25} = 1.8 \times 10^{-5}$$

Solving for x gives $1.50 \times 10^{-4} M$. Because this value is less than 5% of both 0.25 and 0.030, our assumptions are correct. Therefore, $[H_3O^+] = 1.5 \times 10^{-4}\ M$.

This problem can also be solved using the Henderson-Hasselbalch equation:

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$; $pK_a = -\log(K_a) = -\log(1.8 \times 10^{-5}) = 4.74$; $[HA] \approx [HA]_0 =$ $[CH_3CO_2H]_0 = 0.25M$; $[A^-] \approx [NaCH_3CO_2] = 0.030\ M$. Using these data:

$$pH = 4.74 - \log\left(\frac{0.030\ M}{0.25\ M}\right) = 3.82\ ; [H_3O^+] = 10^{-pH}\ M = 10^{-3.82}\ M = 1.5 \times 10^{-4}\ M$$

81. What is $[H_3O^+]$ in a solution of 0.075 *M* HNO_2 and 0.030 *M* $NaNO_2$?

$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq) \qquad K_a = 4.6 \times 10^{-5}$

Solution
The equilibrium expression is $K_a = \frac{[NO_2^-][H_3O^+]}{[HNO_2]} = 4.6 \times 10^{-4}$.
The initial and equilibrium concentrations for this system can be written as follows:

	$[HNO_2]$	$[H_3O^+]$	$[NO_2^-]$
Initial concentration (*M*)	0.075	0	0.030
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.075 - x$	x	$0.030 + x$

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that $(0.075 - x) \approx 0.075$ and $(0.030 - x) \approx 0.030$, gives:

$$\frac{[NO_2^-][H_3O^+]}{[HNO_2]} = \frac{(x)(0.030 - x)}{(0.075 - x)} \approx \frac{(x)(0.030)}{0.075} = 4.6 \times 10^{-4}$$

Solving for x gives $1.15 \times 10^{-3} M$. Because this value is less than 5% of both 0.075 and 0.030, our assumptions are correct. Therefore, $[H_3O^+] = 1.2 \times 10^{-3} M$.

82. What is $[OH^-]$ in a solution of 0.125 *M* CH_3NH_2 and 0.130 *M* CH_3NH_3Cl?

$$CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq) \qquad K_b = 4.4 \times 10^{-4}$$

Solution

The equilibrium expression is:

$$K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]} = 4.4 \times 10^{-4}$$

The initial and equilibrium concentrations for this system can be written as follows:

	$[CH_3NH_2]$	$[CH_3NH_3^+]$	$[OH^-]$
Initial concentration (*M*)	0.125	0.130	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.125 - x$	$0.130 + x$	x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that $(0.125 - x) \approx 0.125$ and $(0.130 - x) \approx 0.130$, gives:

$$\frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]} = \frac{(0.130 - x)(x)}{(0.125 - x)} \approx \frac{(0.130)(x)}{0.125} = 4.4 \times 10^{-4}$$

Solving for x gives $4.23 \times 10^{-4} M$. Because this value is less than 5% of both 0.125 and 0.130, our assumptions are correct. Therefore, $[OH^-] = 4.2 \times 10^{-4} M$.

83. What is $[OH^-]$ in a solution of 1.25 *M* NH_3 and 0.78 *M* NH_4NO_3?

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad K_b = 1.8 \times 10^{-5}$$

Solution

The equilibrium expression is $K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$.

The initial and equilibrium concentrations for this system can be written as follows:

	$[NH_3]$	$[NH_4^+]$	$[OH^-]$
Initial concentration (*M*)	1.25	0.78	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.125 - x$	$0.78 + x$	x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that $(1.25 - x) \approx 1.25$ and $(0.78 + x) \approx 0.78$, gives:

$$\frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(0.78 - x)(x)}{(1.25 - x)} \approx \frac{(0.78)(x)}{1.25} = 1.8 \times 10^{-5}$$

Solving for x gives $2.88 \times 10^{-5} M$. Because this value is less than 5% of both 1.25 and 0.78, our assumptions are correct. Therefore, $[OH^-] = 2.9 \times 10^{-5} M$.

This problem can also be solved using the Henderson-Hasselbalch equation:

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

Let us rewrite the reaction in the reversed fashion:

$$NH_4^+(aq) \longrightarrow NH_3(aq) + H^+(aq)$$

In this case, A^- is NH_3 and AH is NH_4^+; $[NH_3] \approx [NH_3]_0 = 1.25\ M$; $[NH_4^+] \approx [NH_4NO_3] = 0.78\ M$.

$$K_a = \frac{[NH_3][H^+]}{[NH_4^+]}$$

$[H^+][OH^-] = K_w$, so $[H^+] = \frac{K_w}{[OH^-]}$, and $K_a = \frac{[NH_3]K_w}{([NH_4^+][OH^-])}$.

The Henderson-Hasselbalch equation becomes:

$$pH = pK_w - pK_b + \log\left(\frac{[NH_3]}{[NH_4NO_3]}\right)$$

Since $[H^+][OH^-] = K_w$, $pH = pK_w - pOH$, and

$$pOH = -\log([OH^-]) = pK_b - \log\left(\frac{[NH_3]}{[NH_4NO_3]}\right) = 4.74 - 0.20 = 4.54$$

$$[OH^-] = 10^{-pOH}\ M = 10^{-4.54}\ M = 2.9 \times 10^{-5} M$$

84. What is the effect on the concentration of acetic acid, hydronium ion, and acetate ion when the following are added to an acidic buffer solution of equal concentrations of acetic acid and sodium acetate:
(a) HCl
(b) KCH_3CO_2
(c) NaCl
(d) KOH
(e) CH_3CO_2H

Solution
The reaction and equilibrium constant are:

$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq) \qquad K_a = 1.8 \times 10^{-5}$

(a) The added HCl will increase the concentration of H_3O^+ slightly, which will react with $CH_3CO_2^-$ and produce CH_3CO_2H in the process. Thus, $[CH_3CO_2^-]$ decreases and $[CH_3CO_2H]$ increases.

(b) The added KCH_3CO_2 will increase the concentration of $[CH_3CO_2^-]$ which will react with H_3O^+ and produce CH_3CO_2H in the process. Thus, $[H_3O^+]$ decreases slightly and $[CH_3CO_2H]$ increases.

(c) The added NaCl will have no effect on the concentration of the ions.

(d) The added KOH will produce OH^- ions, which will react with the H_3O^+, thus reducing $[H_3O^+]$. Some additional CH_3CO_2H will dissociate, producing $[CH_3CO_2^-]$ ions in the process. Thus, $[CH_3CO_2H]$ decreases slightly and $[CH_3CO_2^-]$ increases.

(e) The added CH_3CO_2H will increase its concentration, causing more of it to dissociate and producing more $[CH_3CO_2^-]$ and H_3O^+ in the process. Thus, $[H_3O^+]$ increases slightly and $[CH_3CO_2^-]$ increases.

85. What is the effect on the concentration of ammonia, hydroxide ion, and ammonium ion when the following are added to a basic buffer solution of equal concentrations of ammonia and ammonium nitrate:

(a) KI
(b) NH_3
(c) HI
(d) NaOH
(e) NH_4Cl

Solution

The reaction and equilibrium constant are:

$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad K_b = 1.8 \times 10^{-5}$

(a) The added KI will have no effect on the concentrations of the ions.

(b) The added NH_3 will increase its concentration, causing more of it to dissociate and producing more OH^- and NH_4^+ in the process. Thus, $[OH^-]$ increases slightly and $[NH_4^+]$ increases.

(c) The added HI will increase the concentrations of H_3O^+, which will then react with some OH^- thus reducing $[OH^-]$ slightly. Some additional NH_3 will dissociate, producing NH_4^+ in the process. Thus $[NH_3]$ decreases and $[NH_4^+]$ increases.

(d) The added NaOH will increase the concentration of OH^- slightly, which will react with NH_4^+ and produce NH_3 in the process. Thus, $[NH_4^+]$ decreases and $[NH_3]$ increases.

(e) The added NH_4Cl will dissociate to yield $[NH_4^+]$, increasing its concentration. It will then react with some OH^- ions, thus reducing $[OH^-]$ slightly. Some additional NH_3 will form in the process. Thus, $[NH_3]$ increases.

86. What will be the pH of a buffer solution prepared from 0.20 mol NH_3, 0.40 mol NH_4NO_3, and just enough water to give 1.00 L of solution?

Solution

The reaction and equilibrium constant are:

$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad K_b = 1.8 \times 10^{-5}$

The equilibrium expression is:

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

The initial concentrations of NH_3 and NH_4^+ are 0.20 *M* and 0.40 *M*, respectively. The equilibrium concentrations for this system can be written as follows:

	$[NH_3]$	$[NH_4^+]$	$[OH^-]$
Initial concentration (*M*)	0.20	0.40	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.20 - x$	$0.40 + x$	x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that $(0.20 - x) \approx 0.20$ and $(0.40 + x) \approx 0.40$, gives:

$$\frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(0.40 + x)(x)}{(0.20 - x)} \approx \frac{(0.40)(x)}{0.20} = 1.8 \times 10^{-5}$$

Solving for x gives 9.00×10^{-6} *M*. Because this value is less than 5% of both 0.20 and 0.40, our assumptions are correct. Therefore, $[OH^-] = 9.00 \times 10^{-6}$ *M*. Thus:

$pOH = -\log(9.00 \times 10^{-6}) = 5.046$

$pH = 14.000 - pOH = 14.000 - 5.046 = 8.954 = 8.95$

87. Calculate the pH of a buffer solution prepared from 0.155 mol of phosphoric acid, 0.250 mole of KH_2PO_4, and enough water to make 0.500 L of solution.

Solution

The reaction and equilibrium constant are:

$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_4^-(aq) \qquad K_a = 7.5 \times 10^{-3}$

The equilibrium expression is $K_a = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} = 7.5 \times 10^{-3}$.

The initial and concentrations of H_3PO_4 and $H_2PO_4^-$ are 0.310 *M* and 0.500 *M*, respectively. The equilibrium concentrations for this system can be written as follows:

	$[H_3PO_4]$	$[H_3O^+]$	$[H_2PO_4^-]$
Initial concentration (*M*)	0.310	0	0.500
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.310 - x$	x	$0.500 + x$

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that $(0.310 - x) \approx 0.310$ and $(0.500 + x) \approx 0.500$, gives:

$$\frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} = \frac{(x)(0.500 + x)}{(0.310 - x)} \approx \frac{(x)(0.500)}{0.310} = 7.5 \times 10^{-3}$$

Solving for x gives 4.65×10^{-3} M. Because this value is less than 5% of both 0.310 and 0.500, our assumptions are correct. Therefore, $[H_3O^+] = 4.65 \times 10^{-3}$ M. Thus:

$pH = -\log(4.65 \times 10^{-3}) = 2.333 = 2.33$

88. How much solid $NaCH_3CO_2 \cdot 3H_2O$ must be added to 0.300 L of a 0.50-M acetic acid solution to give a buffer with a pH of 5.00? (Hint: Assume a negligible change in volume as the solid is added.)

Solution

This problem is most conveniently solved using the Henderson-Hasselbalch equation:

$pH = pK_a + \log [base] / [acid]$

where the base is acetate ion and the acid is acetic acid.

The pK_a for acetic acid is

$pK_a = -\log K_a = -\log 1.8 \times 10^{-5} = 4.74$

Substitution of this value and the provided pH into the Henderson-Hasselbalch equation and rearranging to isolate the conjugate acid/base ratio yields

$[C_2H_3O_2^-] / [HC_2H_3O_2] = 10^{(5.00 - 4.74)} = 10^{0.26} = 1.82$

The small K_a for acetic acid means very little will undergo acid ionization, and so its concentration will be ~0.50 M. The molarity of acetate ion required is therefore

$[C_2H_3O_2^-] = [HC_2H_3O_2] \times 1.82 = 0.50 \times 1.82 = 0.91$ M

The mass of sodium acetate trihydrate required is then

0.91 mol/L × 136.1 g/mol × 0.300 L = 37 g

89. What mass of NH_4Cl must be added to 0.750 L of a 0.100-M solution of NH_3 to give a buffer solution with a pH of 9.26? (Hint: Assume a negligible change in volume as the solid is added.)

Solution

This problem is most conveniently solved using the Henderson-Hasselbalch equation:

$pH = pK_a + \log [base] / [acid]$

where the base is ammonia and the acid is ammonium ion.

The pK_a for ammonium ion is

$pK_a = pK_w - pK_b = 14.00 - (-\log K_b) = 14.00 - 4.74 = 9.26$

Substitution of this value and the provided pH into the Henderson-Hasselbalch equation and rearranging to isolate the conjugate acid/base ratio yields

$[NH_3] / [NH_4^+] = 10^{(9.26 - 9.26)} = 10^{0.00} = 1.0$

The small K_b for ammonia means very little will undergo base ionization, and so its concentration will be ~0.100 M. The molarity of ammonium ion required is therefore

$[NH_4^+] = [NH_3] / 1.0 = 0.100 / 1.00 = 0.10$ M

The mass of ammonium chloride required is then

0.10 mol/L × 53.49 g/mol × 0.750 L = 4.0 g

90. A buffer solution is prepared from equal volumes of 0.200 *M* acetic acid and 0.600 *M* sodium acetate. Use 1.80×10^{-5} as K_a for acetic acid.
(a) What is the pH of the solution?
(b) Is the solution acidic or basic?
(c) What is the pH of a solution that results when 3.00 mL of 0.034 *M* HCl is added to 0.200 L of the original buffer?

Solution
(a) The reaction and equilibrium constant are:

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq) \qquad K_a = 1.8 \times 10^{-5}$$

The equilibrium expression is:

$$K_a = \frac{[CH_3CO_2^-][H_3O^+]}{[CH_3CO_2H]} = 1.8 \times 10^{-5}$$

The molar mass of NH_4Cl is 53.4912 g/mol. The moles of NH_4Cl are:

$$\frac{5.36 \text{ g}}{53.4912 \text{ g mol}^{-1}} = 0.1002 \text{ mol}$$

Assume 0.500 L of each solution is present. The total volume is thus 1.000 L. The initial concentrations of the ions is obtained using $M_1V_1 = M_2V_2$, or:

$$[CH_3CO_2H] = M_1 \times \frac{V_1}{V_2} = (0.200) \times \frac{0.500 \text{ L}}{1.000 \text{ L}} = 0.100\ M$$

$$[CH_3CO_2^-] = M_1 \times \frac{V_1}{V_2} = (0.600) \times \frac{0.500 \text{ L}}{1.000 \text{ L}} = 0.300\ M$$

The initial and equilibrium concentrations of this system can be written as follows:

	$[CH_3CO_2H]$	$[H_3O^+]$	$[CH_3CO_2^-]$
Initial concentration (*M*)	0.100	0	0.300
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.100 - x$	x	$0.300 + x$

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that $(0.100 - x) \approx 0.100$ and $(0.300 - x) \approx 0.300$, gives:

$$\frac{[H_3O^+][CH_3CO_2^-]}{[CH_3CO_2H]} = \frac{(x)(0.300 + x)}{(0.100 - x)} \approx \frac{(x)(0.300)}{0.100} = 1.80 \times 10^{-5}$$

Solving for x gives $6.000 \times 10^{-6}\ M$. Because this value is less than 5% of both 0.100 and 0.300, our assumptions are correct. Therefore $[H_3O^+] = 6.000 \times 10^{-6}\ M$:

pH = –log(6.000 × 10^{-6}) = 5.2218 = 5.222;
(b) The solution is acidic.

(c) Assume that the added H^+ reacts completely with an equal amount of $CH_3CO_2^-$, forming an equal amount of CH_3CO_2H in the process. The moles of H^+ added equal 0.034 *M* × 0.00300 L = 1.02 × 10^{-4} mol. For the acetic acid, the initial moles present equal 0.2000 *M* × 0.200 L = 0.0400 mol, and for acetate ion, 0.600 *M* × 0.200 L = 0.120 mol. Thus:
mol CH_3CO_2H = 0.4000 + 1.02 × 10^{-4} = 0.0401 mol

mol $CH_3CO_2^-$ = 0.120 − 1.02 × 10^{-4} = 0.120 mol
Final volume = 0.200 L + 3.00 × 10^{-3} L = 0.203 L
The initial concentrations are therefore:

$$[CH_3CO_2H] = \frac{0.0401 \text{ mol}}{0.203 \text{ L}} = 0.198\ M$$

$$[CH_3CO_2^-] = \frac{0.120 \text{ mol}}{0.203 \text{ L}} = 0.591\ M$$

The initial and equilibrium concentrations for this system can be written as follows:

	$[CH_3CO_2H]$	$[H_3O^+]$	$[CH_3CO_2^-]$
Initial concentration (*M*)	0.198	0	0.591
Change (*M*)	−*x*	+*x*	+*x*
Equilibrium (*M*)	0.198 − *x*	*x*	0.591 + *x*

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that $(0.198 - x) \approx 0.198$ and $(0.591 + x) \approx 0.591$, gives:

$$\frac{[H_3O^+][CH_3CO_2^-]}{[CH_3CO_2H]} = \frac{(x)(0.591 + x)}{(0.198 - x)} \approx \frac{(x)(0.591)}{0.198} = 1.80 \times 10^{-5}$$

Solving for *x* gives 6.03 × 10^{-6} *M*. Because this value is less than 5% of both 0.198 and 0.591, our assumptions are correct. Therefore, $[H_3O^+] = 6.03 \times 10^{-6} M$.
pH = –log(6.03 × 10^{-6}) = 5.2197 = 5.220

91. A 5.36–g sample of NH_4Cl was added to 25.0 mL of 1.00 *M* NaOH and the resulting solution diluted to 0.100 L.
(a) What is the pH of this buffer solution?
(b) Is the solution acidic or basic?
(c) What is the pH of a solution that results when 3.00 mL of 0.034 *M* HCl is added to the solution?

Solution
(a) The reaction and equilibrium constant are:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad K_b = 1.8 \times 10^{-5}$$

The equilibrium expression is $K_a = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$.

The molar mass of NH_4Cl is 53.4912 g/mol. The moles of NH_4Cl are: $\frac{5.36\text{ g}}{53.4912\text{ g mol}^{-1}} = 0.1002\text{ mol}$. The moles of OH^- ion are given by $1.00\ M \times 0.0250\text{ L} = 0.0250$ mol. Assume that the hydroxide ions react completely with an equal number of moles of NH_4^+ ions to form an equal number of moles of NH_3. Therefore, the initial numbers of moles are: mol $NH_4^+ = 0.1002 - 0.0250 = 0.0752$ mol; mol $NH_3 = 0.0250$ mol. The initial concentrations are:

$$[NH_4^+] = \frac{0.0752\text{ mol}}{0.100\text{ L}} = 0.752\ M$$

$$[NH_3] = \frac{0.0250\text{ mol}}{0.100\text{ L}} = 0.2500\ M$$

The initial and equilibrium concentrations of this system can be written as follows:

	$[NH_3]$	$[NH_4^+]$	$[OH^-]$
Initial concentration (*M*)	0.250	0.752	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.250 - x$	x	x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that $(0.250 - x) \approx 0.250$ and $(0.752 - x) \approx 0.752$, gives:

$$\frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(0.752 + x)(x)}{(0.250 - x)} \approx \frac{(0.752)(x)}{0.250} = 1.8 \times 10^{-5}$$

Solving for x gives $5.98 \times 10^{-6}\ M$. Because this value is less than 5% of both 0.250 and 0.752, our assumptions are correct. Therefore, $[OH^-] = 5.98 \times 10^{-6} M$:

$pOH = -\log(5.98 \times 10^{-6}) = 5.223$

$pH = 14.000 - pOH = 14.000 - 5.223 = 8.777 = 8.78$;

(b) The solution is basic.

(c) Assume that the added H^+ reacts completely with an equal amount of NH_3, forming an equal amount of NH_4^+ in the process. The moles of H^+ added equal $0.034\ M \times 0.00300\text{ L} = 1.02 \times 10^{-4}$ mol; mol $NH_3 = 0.02500 - 1.02 \times 10^{-4} = 0.02490$ mol; mol $NH_4^+ = 0.0752 + 1.02 \times 10^{-4} = 0.0753$ mol. Final volume $= 0.100\text{ L} + 3.00 \times 10^{-3}\text{ L} = 0.1030$ L. The initial concentrations are therefore $[NH_3] = \frac{0.02490\text{ mol}}{0.1030\text{ L}} = 0.2417\ M$ and $[NH_4^+] = \frac{0.0753\text{ mol}}{0.1030\text{ L}} = 0.731\ M$. The initial and equilibrium concentrations for this system can be written as follows:

	$[NH_3]$	$[NH_4^+]$	$[OH^-]$
Initial concentration (*M*)	0.2417	0.731	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.2417 - x$	$0.731 + x$	x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that $(0.2417 - x) \approx 0.2417$ and $(0.731 - x) \approx 0.731$, gives:

$$\frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(0.731 + x)(x)}{(0.2417 - x)} \approx \frac{(0.731)(x)}{0.2417} = 1.8 \times 10^{-5}$$

Solving for x gives $5.95 \times 10^{-6}\,M$. Because this value is less than 5% of both 0.2417 and 0.731, our assumptions are correct. Therefore, $[OH^-] = 5.95 \times 10^{-6}\,M$:

$pOH = -\log(5.98 \times 10^{-6}) = 5.226$

$pH = 14.000 - pOH = 14.000 - 5.226 = 8.774 = 8.77$

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Chemistry: Atoms First 2e
14: Acid-Base Equilibria
14.7: Acid-Base Titrations

92. Explain how to choose the appropriate acid-base indicator for the titration of a weak base with a strong acid.

Solution

At the equivalence point in the titration of a weak base with a strong acid, the resulting solution is slightly acidic due to the presence of the conjugate acid. Thus, pick an indicator that changes color in the acidic range and brackets the pH at the equivalence point. Methyl orange is a good example.

93. Explain why an acid-base indicator changes color over a range of pH values rather than at a specific pH.

Solution

The color in an indicator depends on the ratio of nonionized to ionized forms. The predominant color in acid requires at least a 1:10 ratio of forms, whereas the predominant color in base requires a 10:1 ratio of forms. The transition from one condition to the other comes about by addition of acid or base requiring, in general, a change of two pH units between colors.

94. Calculate the pH at the following points in a titration of 40 mL (0.040 L) of 0.100 *M* barbituric acid ($K_a = 9.8 \times 10^{-5}$) with 0.100 *M* KOH.

(a) no KOH added
(b) 20 mL of KOH solution added
(c) 39 mL of KOH solution added
(d) 40 mL of KOH solution added
(e) 41 mL of KOH solution added

Solution

(a) Let HA represent barbituric acid and A^- represent the conjugate base. The reaction and equilibrium constant are:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_3O^+(aq) \qquad K_a = 9.8 \times 10^{-5}$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = 9.8 \times 10^{-5}$$

The initial and equilibrium concentrations for this system can be written as follows:

	[HA]	$[H_3O^+]$	$[A^-]$
Initial concentration (*M*)	0.100	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.100 - x$	x	x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumption that $(0.100 - x) \approx 0.100$, gives:

$$\frac{[H_3O^+][A^-]}{[HA]} = \frac{(x)(x)}{(0.100 - x)} \approx \frac{(x)(x)}{0.100} = 9.8 \times 10^{-5}$$

Solving for x gives $3.13 \times 10^{-3} M$. Because this value is less than 5% of 0.100, our assumption is correct. Therefore, $[H_3O^+] = 3.13 \times 10^{-3}\ M$:

$\text{pH} = -\log(3.13 \times 10^{-3}) = 2.504 = 2.50$;

(b) The moles of OH^- added are given by:

$\text{mol } OH^- = M \times V = (0.100\ M) \times (0.020\ \text{L}) = 0.00200\ \text{mol}$

The initial moles of barbituric acid are given by:

$\text{mol HA} = M \times V = (0.100\ M) \times (0.040\ \text{L}) = 0.00400\ \text{mol}$

Assume that the added hydroxide ion reacts completely with an equal number of moles of HA, forming an equal number of moles of A^- in the process. Thus, the moles of the ions are given by:

$\text{mol HA} = 0.00400 - 0.00200 = 0.00200\ \text{mol}$

$\text{mol } A^- = 0.00200\ \text{mol}$

The total volume is:

$40.0\ \text{mL} + 20.0\ \text{mL} = 60.0\ \text{mL} = 0.0600\ \text{L}$

The initial concentrations of the ions are given by:

$$[HA] = \frac{0.00200\ \text{mol}}{0.0600\ \text{L}} = 0.0333\ M$$

$$[A^-] = \frac{0.00200\ \text{mol}}{0.0600\ \text{L}} = 0.0333\ M$$

The initial and equilibrium concentrations for this system can be written as follows:

	[HA]	$[H_3O^+]$	$[A^-]$
Initial concentration (*M*)	0.0333	0	0.0333
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.0333 - x$	x	$0.0333 + x$

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that $(0.0333 - x) \approx 0.0333$ and $(0.0333 + x) \approx 0.0333$, gives:

$$\frac{[H_3O^+][A^-]}{[HA]} = \frac{(x)(0.0333 + x)}{(0.0333 - x)} \approx \frac{(x)(0.0333)}{0.0333} = 9.8 \times 10^{-5}$$

Solving for x gives $9.8 \times 10^{-5} M$. Because this value is less than 5% of 0.0333, our assumptions are correct. Therefore, $[H_3O^+] = 9.8 \times 10^{-5} M$:

$\text{pH} = -\log(9.8 \times 10^{-5}) = 4.009 = 4.01$;

(c) The moles of OH^- added are given by:
mol $OH^- = M \times V = (0.100\ M) \times (0.039\ L) = 0.00390$ mol
The initial moles of barbituric acid are given by:
mol $HA = M \times V = (0.100\ M) \times (0.040\ L) = 0.00400$ mol
Assume that the added hydroxide ion reacts completely with an equal number of moles of HA, forming an equal number of moles of A^- in the process. Thus, the moles of the ions are given by:
mol HA = 0.00400 – 0.00390 = 0.00010 mol
mol A^- = 0.00930 mol
The total volume is:
40.0 mL + 39.0 mL = 79.0 mL = 0.0790 L
The initial concentrations of the ions are given by:

$$[HA] = \frac{0.00010\ \text{mol}}{0.0790\ \text{L}} = 0.00127\ M$$

$$[A^-] = \frac{0.00390\ \text{mol}}{0.0790\ \text{L}} = 0.0494\ M$$

The initial and equilibrium concentrations for this system can be written as follows:

	[HA]	$[H_3O^+]$	$[A^-]$
Initial concentration (*M*)	0.00127	0	0.0494
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.00127 - x$	x	$0.0494 + x$

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumption that $(0.00127 - x) \approx 0.00127$ and $(0.0494 + x) \approx 0.0494$, gives:

$$\frac{[H_3O^+][A^-]}{[HA]} = \frac{(x)(0.0494 + x)}{(0.00127 - x)} \approx \frac{(x)(0.0494)}{0.00127} = 9.8 \times 10^{-5}$$

Solving for x gives $2.52 \times 10^{-6}\ M$. Because this value is less than 5% of 0.00127 and 0.0494, our assumptions are correct. Therefore, $[H_3O^+] = 2.52 \times 10^{-6}\ M$:
$pH = -\log(2.52 \times 10^{-6}) = 5.599 = 5.60$;
(d) The moles of OH^- added are given by:
mol $OH^- = M \times V = (0.100\ M) \times (0.040\ L) = 0.00400$ mol
The initial moles of barbituric acid are given by:
mol $HA = M \times V = (0.100\ M) \times (0.040\ L) = 0.00400$ mol
This is the equivalence point, where the moles of base added equal the moles of acid present initially. At the equivalence point:
mol A^- = 0.00400 mol
The total volume is:
40.0 mL + 40.0 mL = 80.0 mL = 0.0800 L
The initial concentration of the conjugate base is:

$$[A^-] = \frac{0.00400\ \text{mol}}{0.0800\ \text{L}} = 0.0500\ M$$

The reaction and equilibrium constant are:

$$A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq)$$

$$K_b = \frac{[HA][OH^-]}{[A^-]} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{9.8 \times 10^{-4}} = 1.08 \times 10^{-10}$$

The initial and equilibrium concentrations for this system can be written as follows:

	$[A^-]$	[HA]	$[OH^-]$
Initial concentration (*M*)	0.0500	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.0500 - x$	x	x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumption that $(0.0500 - x) \approx 0.0500$, gives:

$$\frac{[HA][OH^-]}{[A^-]} = \frac{(x)(x)}{(0.0500 - x)} \approx \frac{(x)(x)}{0.0500} = 1.02 \times 10^{-10}$$

Solving for x gives 2.26×10^{-6} *M*. Because this value is less than 5% of 0.0500, our assumption is correct. Therefore, $[OH^-] = 2.26 \times 10^{-6}$ *M*:
pOH = $-\log(2.26 \times 10^{-6}) = 5.646$
pH = 14.000 – pOH = 14.000 – 5.646 = 8.354 = 8.35;
(e) The moles of OH^- added are given by:
mol $OH^- = M \times V = (0.100\ M) \times (0.041\ L) = 0.00410$ mol
The initial moles of barbituric acid are given by:
mol $HA = M \times V = (0.100\ M) \times (0.040\ L) = 0.00400$ mol
This is past the equivalence point, where the moles of base added exceed the moles of acid present initially. The excess moles of hydroxide ion are given by:
mol $OH^- = 0.00410 - 0.00400 = 0.00010$ mol
The total volume is:
40.0 mL + 41.0 mL = 81.0 mL = 0.0810 L
The concentration of OH^- is:

$$[OH^-] = \frac{0.00010\ \text{mol}}{0.0810\ \text{L}} = 0.0012\ M$$

pOH = $-\log(0.0012) = 2.921$
pH = 14.000 – pOH = 14.000 – 2.921 = 11.079 = 11.08

95. The indicator dinitrophenol is an acid with a K_a of 1.1×10^{-4}. In a 1.0×10^{-4}-*M* solution, it is colorless in acid and yellow in base. Calculate the pH range over which it goes from 10% ionized (colorless) to 90% ionized (yellow).

Solution

$\mathrm{HIn}(aq)$ (colorless) $\rightleftharpoons$ $\mathrm{H_3O^+}(aq)$ + $\mathrm{In^-}(aq)$ (yellow)

$$[\mathrm{H_3O^+}]_{\text{acid form}} = \frac{K_a[\mathrm{HIn}]}{[\mathrm{In^-}]} = 1.1 \times 10^{-4}\,\frac{(9.0 \times 10^{-5})}{(1.0 \times 10^{-5})}$$

$$= 9.9 \times 10^{-4}\ M \qquad \mathrm{pH} = 3.00$$

$$[\mathrm{H_3O^+}]_{\text{base form}} = 1.1 \times 10^{-4}\,\frac{(1.0 \times 10^{-5})}{(9.0 \times 10^{-5})} = 1.22 \times 10^{-5} \qquad \mathrm{pH} = 4.91$$

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