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CHAPTER 1. Chemistry and the Scientific Method

THE SCIENTIFIC METHOD

1-2. First the scientists must verify the results of the original experiment to be sure that no errors were made. Second, if the results are confirmed, then the theory must be either revised to accommodate the new data or discarded and replaced by a new theory.

1-4. What is meant by the statement is that no two snowflakes have yet been observed to be the same.

SCIENTIFIC NOTATION

1-6. We have in decimal form

(a) 299 800 000

(b) 0.000 548 580

(c) 0.000 000 000 05292

(d) 155 000 000 000 0000

1-8. 556.0×10^3

UNITS

1-10. (a) 10^{-12}; (b) 10^{9}; (c) 10^{-9}; (d) 10^{3}; (e) 10^{-18}; (f) 10^{-15}

1-12. The easiest way to order these quantities is to convert all the volumes to units of liters. We use the conversion factors according to the prefix as indicated in Table 1.2.

(a) 10 L

(b) $100 \times 10^{-3}\ \text{L} = 0.10\ \text{L}$

(c) $0.10 \times 10^{6}\ \text{L} = 1.0 \times 10^{5}\ \text{L}$

(d) $1.0 \times 10^{3} \times 10^{-6}\ \text{L} = 1.0 \times 10^{-3}\ \text{L}$

(e) $20 \times 10^{-2}\ \text{L} = 0.20\ \text{L}$

(f) $10 \times 10^{4} \times 10^{-9}\ \text{L} = 1.0 \times 10^{-5}\ \text{L}$

Thus, the order is f < d < b < e < a < c.

1-14. The volume of the cube is given by $V = l^3$. If we substitute in the given value of l, then we have that

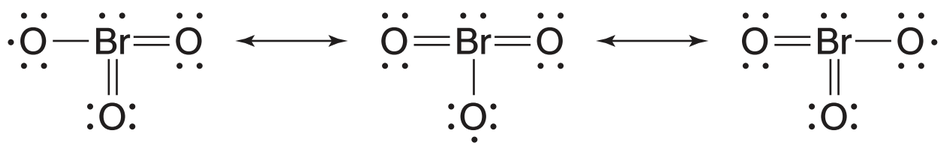
$$V = l^3 = (200.0\ \text{pm})^3 = (200.0 \times 10^{-12}\ \text{m})^3 = 8.000 \times 10^{-30}\ \text{m}^3$$

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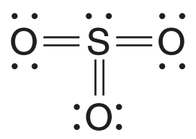
FREE RADICALS

7-24. (a) A BrO_3 molecule contains a total of 59 electrons and 25 valence electrons. The Lewis formulas for a BrO_3 molecule are

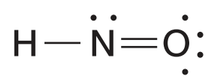


odd electron

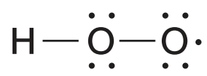
(b) A SO_3 molecule contains a total of 40 electrons and 24 valence electrons. The Lewis formula of a SO_3 molecule is



(c) A HNO molecule contains a total of 16 electrons and 12 valence electrons. The Lewis formula of a HNO molecule is

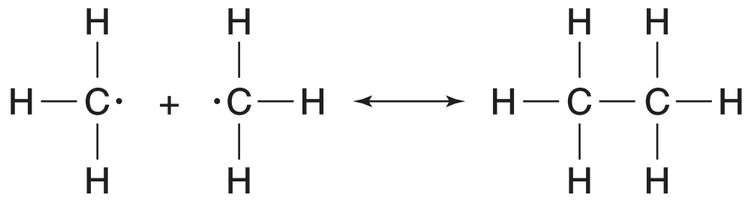


(d) A HO_2 molecule contains a total of 17 electrons and 13 valence electrons. The Lewis formula of a HO_2 molecule is

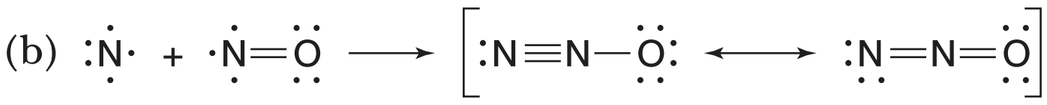


odd electron

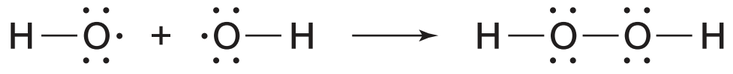
7-26. (a)



(b)

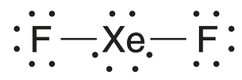


(c)

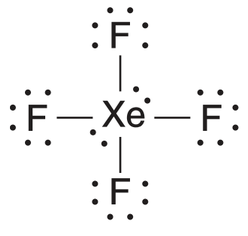


EXPANDED OCTETS

7-28. (a) A XeF_2 molecule has 22 valence electrons. We take Xe as the central atom. If we add one bond between each atom and then try to satisfy the octet rule about each of the atoms, we find that we have two additional electrons to account for. Because xenon is located in the fifth row of the periodic table ($n = 5$) it can expand its octet by using its $5d$ orbitals and so we place these additional two electrons on the xenon atom by expanding its octet, to obtain



(b) A XeF_4 molecule has 36 valence electrons or 18 electron pairs. Placing the Xe atom as the central atom, we have



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LIMITING REACTANT

11-50. Because we are given the quantities of two reactants, we must check to see if one of them is a limiting reactant. The number of moles of $P_4(s)$ is

$$\text{moles of } P_4 = (20.0 \text{ g}) \left(\frac{1 \text{ mol } P_4}{123.90 \text{ g } P_4} \right) = 0.1614 \text{ mol}$$

and the number of moles of $NaOH(s)$ is

$$\text{moles of NaOH} = (50.0 \text{ g}) \left(\frac{1 \text{ mol NaOH}}{40.00 \text{ g NaOH}} \right) = 1.250 \text{ mol}$$

Because one mole of $P_4(s)$ reacts with three moles of $NaOH(aq)$, we see that 0.1614 moles of $P_4(s)$ require 0.4842 moles of $NaOH(aq)$. Thus, $NaOH(aq)$ is in excess and $P_4(s)$ is the limiting reactant. The mass of $PH_3(g)$ produced is

$$\text{mass of } PH_3 = (0.1614 \text{ mol } P_4) \left(\frac{1 \text{ mol } PH_3}{1 \text{ mol } P_4} \right) \left(\frac{33.99 \text{ g } PH_3}{1 \text{ mol } PH_3} \right) = 5.49 \text{ g}$$

11-52. Because we are given the quantities of two reactants, we must check to see if one of them is a limiting reactant. The number of moles of NaBr is

$$\text{moles of NaBr} = (25.0 \text{ g}) \left(\frac{1 \text{ mol NaBr}}{102.89 \text{ g NaBr}} \right) = 0.243 \text{ mol}$$

and the number of moles of $Cl_2(g)$ is

$$\text{moles of } Cl_2 = (25.0 \text{ g}) \left(\frac{1 \text{ mol } Cl_2}{70.90 \text{ g } Cl_2} \right) = 0.353 \text{ mol}$$

Each mole of Cl_2 requires two moles of NaBr, or 0.353 moles of Cl_2 require 0.706 moles of NaBr. Thus, Cl_2 is in excess and NaBr is the limiting reactant. The mass of $Br_2(l)$ produced is

$$\begin{aligned} \text{mass of } Br_2 &= (0.243 \text{ mol NaBr}) \left(\frac{1 \text{ mol } Br_2}{2 \text{ mol NaBr}} \right) \left(\frac{159.8 \text{ g } Br_2}{1 \text{ mol } Br_2} \right) \\ &= 19.4 \text{ g} \end{aligned}$$

11-54. (a) The balanced equation is

$$CaCO_3(s) + 2\,HCl(aq) \longrightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

(b) Because we are given the quantities of two reactants, we must check to see if one of them is a limiting reactant. We have the stoichiometric correspondences

$$25.0 \text{ g } CaCO_3 \eqsim 0.250 \text{ mol } CaCO_3$$
$$15.0 \text{ g HCl} \eqsim 0.411 \text{ mol HCl}$$

Therefore, HCl is the limiting reactant because 0.411 moles of HCl require only 0.205 moles of $CaCO_3$. The mass of calcium chloride produced is

$$\text{mass of } CaCl_2 = (0.411 \text{ mol HCl}) \left(\frac{1 \text{ mol } CaCl_2}{2 \text{ mol HCl}} \right) \left(\frac{110.98 \text{ g } CaCl_2}{1 \text{ mol } CaCl_2} \right) = 22.8 \text{ g}$$

(c) Only 0.205 moles of $CaCO_3$ will react, and so there is an excess of $(0.250 - 0.205)$ moles $=$ 0.045 moles of $CaCO_3$, or 4.50 grams remaining.

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(c) $2\,C_2H_6(g) + 7\,O_2(g) \longrightarrow 4\,CO_2(g) + 6\,H_2O(l)$

$$\begin{aligned}\Delta H^\circ_{rxn} &= \{4\,\Delta H^\circ_f[CO_2(g)] + 6\,\Delta H^\circ_f[H_2O(l)]\} - \{2\,\Delta H^\circ_f[C_2H_6(g)] + 7\,\Delta H^\circ_f[O_2(g)]\}\\ &= (4)(-393.5\ \text{kJ}\cdot\text{mol}^{-1}) + (6)(-285.8\ \text{kJ}\cdot\text{mol}^{-1})\\ &\quad - (2)(-84.0\ \text{kJ}\cdot\text{mol}^{-1}) - (7)(0\ \text{kJ}\cdot\text{mol}^{-1})\\ &= -3120.8\ \text{kJ}\cdot\text{mol}^{-1}\end{aligned}$$

Two moles, or 60.14 grams, of $C_2H_6(g)$ are burned, and so the enthalpy of combustion per gram is

$$\text{enthalpy of combustion per gram} = \frac{-3120.8\ \text{kJ}}{60.14\ \text{g}} = -51.89\ \text{kJ}\cdot\text{g}^{-1}$$

The enthalpy of combustion per gram increases as the number of hydrogen atoms increases.

14-84. The equation for the net ionic reaction is

$$3\,Cu(s) + 8\,H^+(aq) + 2\,NO_3^-(aq) \longrightarrow 3\,Cu^{2+}(aq) + 2\,NO(g) + 4\,H_2O(l)$$

Thus, we have for ΔH°_{rxn}

$$\begin{aligned}\Delta H^\circ_{rxn} &= \{3\,\Delta H^\circ_f[Cu^{2+}(aq)] + 2\,\Delta H^\circ_f[NO(g)] + 4\,\Delta H^\circ_f[H_2O(l)]\}\\ &\quad - \{3\,\Delta H^\circ_f[Cu(s)] + 8\,\Delta H^\circ_f[H^+(aq)] + 2\,\Delta H^\circ_f[NO_3^-(aq)]\}\\ &= (3)(64.39\ \text{kJ}\cdot\text{mol}^{-1}) + (2)(91.3\ \text{kJ}\cdot\text{mol}^{-1}) + (4)(-285.8\ \text{kJ}\cdot\text{mol}^{-1})\\ &\quad - (3)(0\ \text{kJ}\cdot\text{mol}^{-1}) - (8)(0\ \text{kJ}\cdot\text{mol}^{-1}) - (2)(-207.35\ \text{kJ}\cdot\text{mol}^{-1})\\ &= -352.7\ \text{kJ}\cdot\text{mol}^{-1}\end{aligned}$$

14-86. The equation for the reaction is

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$$

For 100 milliliters of 0.100 M $HCl(aq)$ or $NaOH(aq)$, we have

$$n = (0.100\ \text{mol}\cdot\text{L}^{-1})(0.100\ \text{L}) = 0.0100\ \text{mol}$$

Therefore,

$$\Delta H = (0.0100\ \text{mol})(-55.7\ \text{kJ}\cdot\text{mol}^{-1}) = -0.557\ \text{kJ}$$

The temperature change of the resulting solution (0.200 L) is given by Equation 14.36 as

$$\begin{aligned}\Delta H &= -c_{P,\text{cal}}\Delta T\\ -557\,\text{J} &= -(200\ \text{mL})\left(\frac{1.00\ \text{g}}{1.00\ \text{mL}}\right)\left(\frac{1\ \text{mol}}{18.02\ \text{g}}\right)(75.3\,\text{J}\cdot\text{mol}^{-1})\Delta T\end{aligned}$$

or $\Delta T = 0.666°\text{C}$.

14-88. The standard enthalpy is given by

$$\Delta H_{rxn} \approx \Delta U_{rxn} = -c_P\Delta T = -(38.70\ \text{kJ}\cdot\text{K}^{-1})(2.89\ \text{K}) = -112\ \text{kJ}$$

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18-20. From step 1 of the reaction mechanism, the fast equilibrium allows us to write

$$k_1[O_2NNH_2] = k_{-1}[O_2NNH^-][H^+]$$

and so the rate equation for the second step (rate determining) of the reaction mechanism becomes

$$\text{rate of reaction} = k_2[O_2NNH^-] = k_2\left(\frac{k_1}{k_{-1}}\right)\frac{[O_2NNH_2]}{[H^+]} = k\frac{[O_2NNH_2]}{[H^+]}$$

This is consistent with the observed rate law with

$$k = \frac{k_2k_1}{k_{-1}}$$

18-22. The observed rate law is (from Problem 18-19)

$$\text{rate of reaction} = k[Cl_2]^{3/2}[CO]$$

From step 3 of the reaction mechanism, we write

$$\text{rate of reaction} = k_3[Cl_3][CO] \qquad (1)$$

Because steps 2 and 1 establish a fast equilibrium, we write

$$k_2[Cl][Cl_2] = k_{-2}[Cl_3] \qquad (2)$$

Also,

$$k_1[Cl_2] = k_{-1}[Cl]^2$$

and so

$$[Cl] = \left(\frac{k_1}{k_{-1}}\right)^{1/2}[Cl_2]^{1/2}$$

Substituting this expression for [Cl] into equation 2 gives

$$[Cl_3] = \frac{k_2}{k_{-2}}\left(\frac{k_1}{k_{-1}}\right)^{1/2}[Cl_2]^{3/2}$$

and substituting this expression into equation 1 gives

$$\text{rate of reaction} = \frac{k_3k_2k_1^{1/2}}{k_{-2}k_{-1}^{1/2}}[Cl_2]^{3/2}[CO] = k[Cl_2]^{3/2}[CO]$$

which corresponds to the observed rate law. To determine whether this mechanism or the one given in Problem 18-19 occurs, we might determine whether a Cl_3 intermediate is produced during the reaction.

CATALYSIS

18-24. When $[H_2O_2]_0$ is doubled with $[I^-]_0$ and $[H^+]_0$ constant, the initial rate doubles. Therefore, the reaction is first order in $[H_2O_2]$. When $[I^-]_0$ is doubled with $[H^+]_0$ and $[H_2O_2]_0$ constant, the initial rate quadruples. The reaction is second order in $[I^-]$. When $[H^+]_0$ is doubled with

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The solubility due to the first equation is

$$s = [Cr^{3+}] = \frac{K_{sp}}{[OH^-]^3} = \frac{(6.3 \times 10^{-31}\ M^4)[H_3O^+]^3}{(1.0 \times 10^{-14}\ M^2)^3} = (6.3 \times 10^{11}\ M^{-2})[H_3O^+]^3$$

The solubility due to the second equation is

$$s = [Cr(OH)_4^-] = K[OH^-] = \frac{(0.04)(1.0 \times 10^{-14}\ M^2)}{[H_3O^+]} = \frac{4.0 \times 10^{-16}\ M^2}{[H_3O^+]}$$

The total solubility is given by

$$s = [Cr^{3+}] + [Cr(OH)_4^-] = (6.3 \times 10^{11}\ M^{-2})[H_3O^+]^3 + \frac{4.0 \times 10^{-16}\ M^2}{[H_3O^+]}$$

For $Sn(OH)_2(s)$, the two relevant chemical equations are

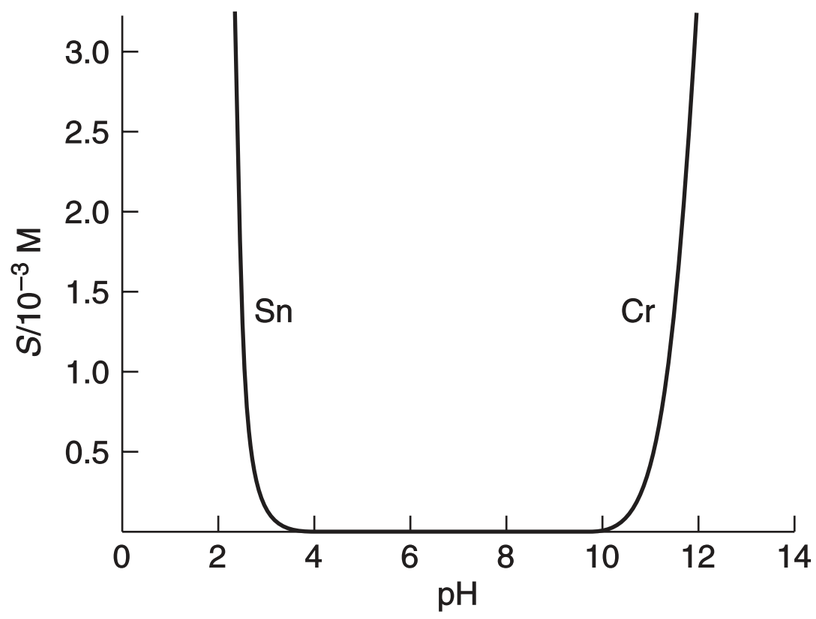
$$Sn(OH)_2(s) \rightleftharpoons Sn^{2+}(aq) + 2\,OH^-(aq) \qquad K_{sp} = 5.5 \times 10^{-27}\ M^3$$

$$Sn(OH)_2(s) + 2\,OH^-(aq) \rightleftharpoons [Sn(OH)_4]^{2-}(aq) \qquad K_f = 0.01\ M^{-1}$$

The total solubility is given by

$$\begin{aligned} s &= [Sn^{2+}] + \left[Sn(OH)_4^{2-}\right] = \frac{K_{sp}}{[OH^-]^2} + K_f[OH^-]^2 \\ &= \frac{(5.5 \times 10^{-27}\ M^3)[H_3O^+]^2}{(1.0 \times 10^{-14}\ M^2)^2} + \frac{(0.01\ M^{-1})(1.0 \times 10^{-14}\ M^2)^2}{[H_3O^+]} \\ &= (55\ M^{-1})[H_3O^+]^2 + \frac{1 \times 10^{-30}\ M^3}{[H_3O^+]^2} \end{aligned}$$

The solubilities are plotted against pH in the following figure:



Thus, we see that the best separation is achieved between pH = 4 and pH = 7.

22-96.* Using the method and the results of the previous problem, we have

pH	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0
s/M	3.3	1.0	0.33	0.11	0.055	0.045	0.044	0.044	0.044	0.044

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