Chemistry Review Manual

Introductory Chemistry I (McMaster University)

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Chemistry Review Manual
2nd Edition

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McMaster University
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Table of Contents

1. The Mole **5**
- **1.1 How do we use the mole? Counting atoms and molecules** 5
  - Example 1.1 How many helium atoms? 5
    - Equation 1.1 Moles from mass and molar mass 6
  - Example 1.2: How many water molecules? 6
- **1.2 Balancing Chemical Reactions** 6
  - Example 1.3: Balance the following chemical reactions 6
- **1.3 Stoichiometry and limiting reactant** 7
  - Example 1.4: Limiting reactant and yield 7
- **1.4 Density** 8
    - Equation 1.2: Mass from volume and density 8
  - Example 1.5: Mass of 1 mL cube of copper 8
  - Example 1.6: Mass of 1 m^3 cube of copper 8
- **1.5 Solutions** 9
    - Equation 1.3: Moles from concentration and volume 9
  - Example 1.7: How much HCl? 9
  - Example 1.8: Water volume added to achieve dilution 9
- **1.6 Titration and solution stoichiometry** 9
  - Example 1.9: Titration of NaOH solution 10
  - Example 1.10: Titration of Na_2CO_3 solution 10
- **Problems** 11
- **Solutions** 12

2. The Ideal Gas Law **14**
- **2.1 The Gas Laws** 14
    - Equation 2.1: The ideal gas law 14
  - Example 2.1: Molar mass of a gas 14
  - Example 2.2: Temperature change accompanying volume change 15
  - Example 2.3: Pressure change accompanying volume change 15
  - Example 2.4: Temperature change accompanying pressure change 16
  - Example 2.5: Yield of HCl 16
- **2.2 Partial Pressure** 17
    - Equation 2.2: Sum of partial pressues 17
  - Example 2.6: The mole fraction of water in saturated air 17
- **Problems** 18
- **Solutions** 19

3. Acids and bases **22**
- **3.1 Brønsted-Lowry Theory** 22
  - Example 3.1: Identify acid and base in a given reaction 22
- **3.2 Strong and Weak Acids and Bases** 23
    - Table 3.1. Strong acids and a few weak acids 24
    - Table 3.2. Strong bases and a few weak bases 24
  - Example 3.2: Ordering acids and bases according to strength 25
- **3.3 Types of Acids and Bases** 25
    - Table 3.3. Oxoacids and oxoanions 26
    - Table 3.4. Some simple organic acids and bases 27
- **Problems** 27
- **Solutions** 29

4. Bonding **31**
- **4.1 Types of Bonding** 31

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Example 4.1: Type of bonding 31
4.2 Solutions 32
Figure 4.1 Solvation of sodium and chloride ions in aqueous solution 33
Figure 4.2 Lewis structure and molecular shape of water 33
Figure 4.3. Lewis structure of CCl_4 34
Example 4.2: Electrolyte solutions 34
Example 4.3: Pairs of compounds forming solutions 35
Problems 35
Solutions 37

5. Chemical Equilibrium 39
5.1 Dynamic equilibrium 39
5.2 The equilibrium constant 39
Equation 5.1: Activity 39
Equation 5.2: Equilibrium constant, K 40
Equation 5.3: Acid ionization constant, K_a 40
Equation 5.4: Base ionization constant, K_b 41
Equation 5.5: Solubility product, K_{sp} 41
Example 5.1: Expressions for K 41
Example 5.2: Determining unknown concentration 42
Equation 5.6: K for a sum of reactions 43
5.3 The reaction quotient 43
Example 5.3: Net forward or reverse reaction 43
5.4 Shift in equilibrium – le Châtelier's principle 44
Example 5.4: Shift in equilibrium 45
Example 5.5: Hydrogen and iodine 47
5.5 Solubility 49
Example 5.6: Solubilities of $BaSO_4$ and CaF_2 49
Example 5.7: Common ion effect 52
5.6 Acid base equilibrium 53
Example 5.8: pH of a concentrated weak acid solutions 54
Example 5.9: pH of a dilute weak acid solution 56
Example 5.10: pH of concentrated and dilute weak base solutions 57
Problems 58
Solutions 61

6. Thermochemistry 67
6.1 System and Properties - Energy 67
6.2 Heat 67
Equation 6.1: Heat from ΔT, mass and specific heat capacity 68
Example 6.1: Heat flow into water 68
Example 6.2: Heat flow from copper to water 68
6.3 Work 69
Figure 6.1: Gas in cylinder with piston 69
Equation 6.2: Work for a constant pressure process 69
Example 6.3: Compression – work done on a gas 70
Example 6.4: Work done on or by a gas 70
6.4 Energy Conservation – the 1st Law of Thermodynamics 71
Equation 6.3: 1st law of thermodynamics 71
Example 6.5: Heating and compressing a gas 71
6.5 Enthalpy 71
Equation 6.4: Definition of enthalpy 71
Equation 6.5: Heat for a constant volume process 72
Equation 6.6: Heat for a constant pressure process 72
Example 6.6: Calorimetry measures enthalpy change 72

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Example 6.7: Using Hess' Law 74
Equation 6.7: Δ*H* from enthalpies of formation 74
Figure 6.2: Graphical depiction of Hess' law for formation reactions 75
Example 6.8: Δ*H* from enthalpies of formation 75
Equation 6.8: Δ*H* from bond enthalpies 76
Figure 6.3: Graphical depiction of Hess' law for bond dissociations 77
Example 6.9: Δ*H* from bond enthalpies 77
Problems 77
Solutions 79

7. Math Skills 83
7.1 Scientific Notation 83
Example 7.1: Scientific notation 83
Table 7.1. Units of Distance 84
7.2 Dimensional Analysis 84
Example 7.2: How many Cu atoms are there in a penny? 85
7.3 Solving for a variable 85
Example 7.3: New concentration after dilution 85
Example 7.4: Two equations and two unknowns 86
7.4 Logarithms 86

Periodic Table of the Elements 88

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1. The Mole

Early chemists discovered that substances combine in certain combinations to form new substances. For example, 32 g (grams) of oxygen combines with 4 g of hydrogen to form 36 g of water. Also, 32 g of oxygen combines with 12 g of carbon to form 44 g of carbon dioxide. Eventually people realized that substances are made of atoms, and that atoms combine in specific ratios. The various combinations of masses that were observed to react is explained when we account for different atoms having different masses.

The numbers of atoms encountered in everyday life is very large. Even a tiny quantity of a substance consists of a vast number of atoms. It is inconvenient to constantly talk about such large numbers of atoms when discussing chemical reactions – or substances in general. This approach to dealing with large numbers is actually quite common. For example, when discussing the national debt of the United States, we hear numbers like 14.3 trillion dollars. This number is expressed in units of trillions of dollars. This is much more convenient than writing the number as $14300000000000.

It turns out that there are typically a lot more atoms than there are dollars of national debt. Thus, the unit for numbers of particles used in chemistry is much bigger than 1 trillion. It is $N_A = 6.022\times10^{23}$ mol^{-1}, the Avogadro constant. The unit itself is called the mole (or mol). If we have 1 mol of hydrogen atoms, we have 6.022×10^{23} hydrogen atoms. This number arises because chemists wanted 1 mol of hydrogen atoms (the lightest atoms) to have a mass of about 1 g. They achieve this by setting the mass of 1 mol of carbon-12 atoms to exactly 12 g (carbon-12 is the common isotope of carbon). This convention defines the value of the Avogadro constant.

1.1 How do we use the mole? Counting atoms and molecules

The masses of 1 mol of each type of atom[1] are given in the periodic table. With this data, we can determine how many atoms are in a sample by measuring the mass of the sample.

Example 1.1: If a sample of Helium has a mass of 6.600 g, then how many helium atoms are in the sample?

Approach: Find mol of He. Convert to number of atoms.

The molar mass of helium (i.e., the mass of 1 mol of helium atoms) is expressed as 4.003 g mol^{-1}. You find this in the periodic table. Therefore, 6.500 g of helium consists of

$$\frac{6.600\ \text{g}}{4.003\ \text{g mol}^{-1}} = 1.648_8\ \text{mol of helium}$$ [2]

To get the number of helium atoms *not* in units of mol, we simply multiply by $N_A = 6.022\times10^{23}$ atoms mol^{-1}. The Avogadro constant has units of "particles" per mole. Here, the particle is a helium atom. Thus, there are

$$1.648_8\ \text{mol} \times 6.022\times10^{23}\ \text{atoms mol}^{-1} = 9.929\times10^{23}\ \text{atoms}$$

[1] Molar masses found in the periodic table are averages of isotope masses, weighted according to natural abundance.

[2] The final digit in 1.648_8 is written as a subscript to indicate that we are carrying the extra digit (the second 8) into the next step of the calculation. It is written as a subscript because it is *not a significant figure*. Carrying the extra figure reduces rounding errors during the steps of a calculation.

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Observe how the units cancel out, leaving the desired unit of atoms:

$$1.648_8 \text{ ~~mol~~} \times 6.022\times10^{23} \text{ atoms ~~mol~~}^{-1} = 9.929\times10^{23} \text{ atoms}$$

Dividing the mass of a sample of atoms by the molar mass of the atom gives the amount of the substance in mol.

$$\text{amount (in mol)} = \frac{\text{mass (in g)}}{\text{Molar mass (in g mol}^{-1})} \qquad n = \frac{m}{M} \qquad 1.1$$

Multiplying by N_A then gives the number of atoms. We can use the same formula to count the number of molecules in a sample.

Example 1.2: How many water molecules are in 20.0 g of water?

Approach: Find number of moles of water. Convert to number of molecules.

$$\text{amount of water (mol)} = \frac{\text{mass of water}}{\text{Molar mass of water}}$$
$$= \frac{20.0 \text{ g}}{18.015 \text{ g mol}^{-1}} = 1.11_0 \text{ mol}$$

This is the amount of water. To answer the question, we must multiply by the Avogadro constant.

$$1.11_0 \text{ mol} \times 6.022\times10^{23} \text{ molecules mol}^{-1} = 6.68 \times10^{23} \text{ molecules}$$

The Avogadro constant has units of "particles" per mole. Here, the particle is a water molecule. The "particle" can be any unit we need.

1.2 Balancing Chemical Reactions

Chemical reactions are happening all the time. Some are slow, and barely noticeable. Others are fast. Some of these involve the release of energy in the form of heat, light and/or sound. Chemical reactions are conversions of one set of compounds – the *reactants* – into another set of compounds – the *products*. They readily occur when there are stable products that can be reached through some rearrangement of the atoms of the reactants. A principal feature of any chemical reaction is that the total number of each type of atom, among reactants, must equal the same tally for the products. Atoms are neither created nor destroyed in a chemical reaction (this is the Law of Conservation of Mass). This allows us to balance chemical reactions and use the associated stoichiometric coefficients to determine the expected amounts of the various products.

Example 1.3: Balance the following chemical reactions:

(a) $Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$
(b) $Ca(s) + O_2(g) \rightarrow CaO(s)$
(c) $CH_4(g) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$

(a) This chemical equation is already balanced. There are two chlorine atoms and one magnesium on each side of the equation.

(b) Calcium is already balanced – one Ca on each side. To balance oxygen, we need two mol of CaO on the right. This changes the calcium balance, which is fixed by having two mol of Ca on the left. The result is

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$$2\ Ca(s) + O_2(g) \rightarrow 2\ CaO(s)$$

It is also acceptable to balance this reaction using ½ as the coefficient of $O_2(g)$ – i.e.

$$Ca(s) + \tfrac{1}{2}\ O_2(g) \rightarrow CaO(s)$$

(c) Carbon is already balanced. To balance H we need two mol H_2O on the right. Now we need two mol O_2 on the left two balance the four mol O on the right – two from CO_2 and two from 2 H_2O. The result is

$$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(g)$$

This method is called balancing by *inspection*. There are reactions that are more challenging to balance. Often these are oxidation-reduction reactions, which are balanced with the half-reaction method. This method will be reviewed in class.

1.3 Stoichiometry and limiting reactant

Knowing the amounts of substances is important because the coefficients in a chemical reaction give the relative *amounts* of the substances that react and are produced. For example, the balanced chemical equation

$$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$$

tells us that the amount of hydrogen needed to completely consume a sample of oxygen is twice the amount of oxygen in the sample. It also tells us that the amount of water produced equals the amount of hydrogen consumed.

Sometimes the relative amounts of reactants *actually used* in a reaction are not the same as the stoichiometric coefficients. In such cases we must determine the reactant that is completely consumed (the *limiting* reactant). The other reactant(s) is(are) in excess.

Example 1.4: Suppose we carry out the above reaction with 30.0 g of O_2 and 4.00 g of H_2.

(a) Which reactant is the limiting reactant?
(b) How much of the other reactant remains at the end of the reaction?
(c) What mass of water is produced?

Approach: Find the number of moles of each reactant. Use reaction stoichiometry to determine the limiting reactant.

$$\text{amount of } O_2 = \frac{30.0\ \text{g}}{31.9988\ \text{g mol}^{-1}} = 0.937_5\ \text{mol}$$

$$\text{amount of } H_2 = \frac{4.00\ \text{g}}{2.01588\ \text{g mol}^{-1}} = 1.98_4\ \text{mol}$$

(a) To completely consume 1.98_4 mol of H_2 requires $1.98_4/2 = 0.992_0$ mol of O_2. However, there is not enough O_2 (only 0.938 mol). Therefore, O_2 is the *limiting reactant*. The 0.938 mol of O_2 is consumed completely, and some H_2 remains unreacted.

(b) The amount of H_2 consumed is twice the amount of O_2 consumed. 1.876 mol of H_2 is consumed, leaving $1.98_4 - 1.876 = 0.10_8$ or 0.11 mol of H_2 unreacted.

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(c) Since the amount of H_2 consumed equals the amount of H_2O produced, 1.876 mol of H_2O is produced.

	$2\ H_2(g)$	+ $O_2(g)$	→ $2\ H_2O(l)$
Before	1.984 mol	**0.938 mol** limiting reactant	0 mol
After	0.108 mol	0	1.876 mol

We are asked for the mass of H_2O produced. This is the theoretical yield, determined by calculation based on amount of limiting reagent used.

$$\text{mass of water} = \text{amount of water} \times \text{Molar mass of water}$$
$$= 1.876\ \text{mol} \times 18.015\ \text{g mol}^{-1} = 33.80\ \text{g}$$

1.4 Density

Sometimes we are given the volume of a substance and not its mass. To determine the amount of the substance, we need to know the density of the substance. The density of a substance is the mass per unit volume. For example, the density of water under ordinary conditions is about 1.00 g mL^{-1}. If we know the volume of a substance, then we can determine its mass from its density.

$$\text{mass} = \text{volume} \times \text{density} \qquad \text{or} \qquad m = V \times d \qquad 1.2$$

Example 1.5: The density of copper is 8.94 g mL^{-1}. What is the mass of a cube of copper 1.00 cm × 1.00 cm × 1.00 cm ? Note that 1 mL = 1 cm^3.

Approach: Find cube volume. Use density and volume to solve for mass.

First, we need the volume of the cube in mL

$$1.00\ \text{cm} \times 1.00\ \text{cm} \times 1.00\ \text{cm} = 1.00\ \text{cm}^3 = 1.00\ \text{mL}$$

The mass of the copper cube is $m = V \times d$,

$$1.00\ \text{mL} \times 8.94\ \text{g mL}^{-1} = 8.94\ \text{g}$$

Sometimes more elaborate unit conversions are required.

Example 1.6: What is the mass of a cube of copper 1.00 m × 1.00 m × 1.00 m ?

Again, we need the volume of the cube in mL.[3] This time, we will use the definition of the litre, 1 L = 1 dm^3 = 10^3 mL. [Note that 1 dm = 10^{-2} m].

$$V = (1.00\ \text{m})^3 = (10.0\ \text{dm})^3 = 10.0^3\ \text{dm}^3 = 1.00 \times 10^3\ \text{dm}^3 = 1.00 \times 10^3\ \text{L}$$
$$= 1.00 \times 10^3\ \text{L} \times 10^3\ \text{mL/L} = 10^6\ \text{mL}$$

The mass of the copper cube is

$$10^6\ \text{mL} \times 8.94\ \text{g mL}^{-1} = 8.94 \times 10^6\ \text{g} = 8.94 \times 10^3\ \text{kg}$$

[3] Alternatively, we could convert the density to units of g m^{-3}.

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1.5 Solutions

Sometimes we are given a volume of a solution. We can determine the amount of a dissolved substance, if we know the concentration.

$$\text{amount} = \text{volume} \times \text{concentration} \quad \text{or, } n = c\,V \qquad 1.3$$

Example 1.7: How much HCl (mol) is in 250. mL of a solution with HCl concentration, [HCl], equal to 2.00 mol L^{-1}?

Approach: Use concentration and volume to find mol.

$$\text{amount of HCl (mol)} = 0.250\ \text{L} \times 2.00\ \text{mol L}^{-1} = 0.500\ \text{mol}$$

Note the conversion of volume in mL to volume in L because the concentration is given in mol L^{-1}.

The concentration of a substance is the number of moles per unit volume. Dissolved species can be very dilute (low concentration) or highly concentrated (high concentration).

A dilute solution can be prepared from a concentrated solution by adding pure water. This is called dilution.

Example 1.8: What volume of pure water (in mL) must be added to 100. mL of a [NaOH] = 2.00 mol L^{-1} sodium hydroxide solution to make a solution with [NaOH] = 0.500 mol L^{-1}?

Approach: Find mol NaOH. Use final concentration to find final volume. Take difference between final and initial volumes.

The amount of NaOH (mol) in the initial and final solutions is the same – only pure water is added. Therefore, since $n = cV$,

Amount of NaOH (mol) = amount initial = $c_i V_i$ = amount final = $c_f V_f$

(You may recognize this as $c_1 V_1 = c_2 V_2$)

$$\text{amount of NaOH} = 0.100\ \text{L} \times 2.00\ \text{mol L}^{-1} = V_f \times 0.500\ \text{mol L}^{-1}$$

where V_f is the final solution volume.

$$V_f = \frac{0.100\ \text{L} \times 2.00\ \text{mol L}^{-1}}{0.500\ \text{mol L}^{-1}} = 0.400\ \text{L}$$

The volume of water added is the change between the final and the initial volumes:

$$\Delta V = V_f - V_i = 0.400 - 0.100\ \text{L} = 0.300\ \text{L}$$

Therefore, 300. mL of pure water must be added to perform the dilution.

1.6 Titration and solution stoichiometry

A strong acid such as HCl will react completely with a base. The acid is said to *neutralize* the base. We can detect when the base is completely consumed by adding a small amount of an

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acid-base indicator such as phenolphthalein to the base solution. Phenolphthalein makes the solution pink until all the base is consumed, at which point the solution turns colorless.

An HCl solution with known concentration can be used to determine the unknown concentration of a base solution.

Example 1.9: Suppose 221.6 mL of a standard HCl solution with [HCl] = 1.007 mol L^{-1} are required to completely neutralize the NaOH in 100.0 mL of a sample solution of unknown NaOH concentration. NaOH and HCl react according to

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

What is the NaOH concentration of the sample solution?

Approach: Find mol NaOH. Use NaOH volume and mol to determine concentration.

Since the reaction is 1:1, for complete reaction, the amount of HCl (mol) added must equal the amount of NaOH (mol) in the sample solution. Therefore,

$$\text{amount of NaOH} = \text{amount of HCl} = 0.2216\ \text{L} \times 1.007\ \text{mol L}^{-1} = 0.2231_5\ \text{mol}$$

This amount of NaOH was present in 100.0 mL of the sample solution. Therefore, the NaOH concentration of the sample solution was $c = n/V$,

$$[\text{NaOH}] = \frac{0.2231_5\ \text{mol}}{0.1000\ \text{L}} = 2.232\ \text{mol L}^{-1}$$

Example 1.10: Suppose 178.1 mL of a standard HCl solution with [HCl] = 1.007 mol L^{-1} are required to completely neutralize the Na_2CO_3 in 100.0 mL of a sample solution of unknown Na_2CO_3 concentration. Na_2CO_3 and HCl react according to

$$Na_2CO_3(aq) + 2\ HCl(aq) \rightarrow 2\ NaCl(aq) + H_2O(l) + CO_2(g)$$

What is the Na_2CO_3 concentration of the sample solution?

Approach: Find mol Na_2CO_3. Use volume and mol to find concentration.

Take note of the stoichiometry of the *balanced* equation. The amount of HCl added must be twice the amount of Na_2CO_3 in the sample solution. Therefore,

$$\text{amount of Na}_2\text{CO}_3 = \frac{1}{2} \times \text{amount of HCl}$$

$$= \frac{1}{2} \times \left(0.1781\ \text{L} \times 1.007\ \text{mol L}^{-1}\right) = 0.08967_3\ \text{mol}$$

and

$$[\text{Na}_2\text{CO}_3] = \frac{0.08967_3\ \text{mol}}{0.1000\ \text{L}} = 0.8967\ \text{mol L}^{-1}$$

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Problems:

1.1 How many grams of calcium oxide, CaO, can be produced from the reaction of 4.20 g of calcium metal and 1.60 g of oxygen gas?

1.2 (a) How many water molecules are in an Olympic-sized swimming pool (volume 2500 m^3)? The density of water is 1.00 g/mL. (b) If each water molecule were replaced by a solid cube with volume 1.00 cm^3, what volume swimming pool (in km^3) would be required to hold all the cubes?

1.3 What mass of hydrogen is required to produce 40.0 mL of water (density = 1.00 g mL^{-1}) in the hydrogen fuel cell reaction:

$$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$$

1.4 What is the concentration of a KOH solution, if 107 mL are required to neutralize 250 mL of 1.09 mol L^{-1} nitric acid (HNO_3) solution?

1.5 What volume of 1.21 mol L^{-1} LiOH solution is required to neutralize 305 mL of 0.511 mol L^{-1} H_2SO_4 solution?

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Solutions:

1.1 First, write a balanced reaction:

$$2\ Ca(s) + O_2(g) \rightarrow 2\ CaO(s)$$

Initial amount of calcium:

$$n(\mathrm{Ca}) = \frac{m(\mathrm{Ca})}{M(\mathrm{Ca})} = \frac{4.20\ \mathrm{g}}{40.08\ \mathrm{g/mol}} = 0.104_8\ \mathrm{mol}$$

Initial amount of oxygen:

$$n(\mathrm{O_2}) = \frac{m(\mathrm{O_2})}{M(\mathrm{O_2})} = \frac{1.60\ \mathrm{g}}{31.9988\ \mathrm{g/mol}} = 0.0500\ \mathrm{mol}$$

Since O_2 and Ca react in a 1:2 ratio, O_2 is the limiting reactant – there is less than 0.0524 mol (the amount needed to consume the entire 0.104_8 mol of Ca).

Amount of CaO produced = 2 × (amount of O_2) = 2 x 0.500 mol = 0.100 mol

Mass of CaO produced = (0.100 mol) × (56.08 g/mol) = 5.61 g

1.2 (a) Because the density is expressed in g mL^{-1}, we must convert m^3 to mL. Since 1 m = 10^2 cm,

$$2500\ m^3 = 2500 \times (10^2\ cm)^3 = 2500 \times 10^6\ cm^3 = 2.500 \times 10^9\ mL$$

Mass of water = volume × density = 2.500×10^9 mL × 1.00 g / mL = 2.500×10^9 g

Amount of water =

$$n(\mathrm{H_2O}) = \frac{m(\mathrm{H_2O})}{M(\mathrm{H_2O})} = \frac{2.500\times10^9\ \mathrm{g}}{18.015\ \mathrm{g/mol}} = 1.387_7\times10^8\ \mathrm{mol}$$

Multiply by the Avogadro constant to get the number of water molecules:

$$1.387_7 \times10^8\ mol \times 6.022 \times10^{23}\ molecules\ mol^{-1} = 8.356_7 \times10^{31}\ molecules$$

(b) The total volume of $8.356_7 \times10^{31}$ cubes is

$$8.356_7 \times10^{31}\ cubes \times 1.00\ cm^3/cube = 8.356_7 \times10^{31}\ cm^3$$

$$= 8.356_7 \times10^{31}\ cm^3\ (10^{-5}\ km/cm)^3 = 8.357 \times10^{16}\ km^3$$

This volume corresponds to giant cube more than half of 1 million kilometers along each side.

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1.3 Mass of water produced = volume × density = 40.0 mL × 1.00 g /mL = 40.0 g

Amount of water produced:

$$n(\mathrm{H_2O}) = \frac{m(\mathrm{H_2O})}{M(\mathrm{H_2O})} = \frac{40.0\ \mathrm{g}}{18.015\ \mathrm{g/mol}} = 2.22_0\ \mathrm{mol}$$

From the balanced chemical equation,

$$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l),$$

we see there is a 1:1 ratio of hydrogen consumed to water produced. Therefore, 2.22_0 mol of hydrogen is required.

Mass of H_2 required = (2.22_0 mol) × (2.016 g mol^{-1}) = 4.48 g

1.4 First write the balanced chemical equation.

$$KOH(aq) + HNO_3(aq) \rightarrow KNO_3(aq) + H_2O(l)$$

We see that KOH and HNO_3 react in a 1:1 ratio. Therefore, the amount of KOH added must equal the amount of HNO_3 in the nitric acid solution. Therefore,

amount of KOH = amount of HNO_3 = 0.250 L × 1.09 mol L^{-1} = 0.272_5 mol

[KOH] = (amount of KOH) / (volume of KOH solution) = 0.272_5 mol / 0.107 L

= 2.55 mol L^{-1}

is the concentration of the KOH solution.

1.5 First write the balanced chemical equation.

$$2\ LiOH(aq) + H_2SO_4(aq) \rightarrow Li_2SO_4(aq) + 2\ H_2O(l)$$

We see that LiOH and H_2SO_4 react in a 2:1 ratio. Therefore, the amount of LiOH added must equal twice the amount of H_2SO_4 in the sulfuric acid solution. Therefore,

amount of LiOH = 2 × amount of H_2SO_4
= 2 × (0.305 L × 0.511 mol L^{-1}) = 0.311_7 mol

volume of LiOH solution = (amount of LiOH) / [LiOH] = 0.311_7 mol / 1.21 mol/L

= 0.258 L = 258 mL

is the volume of the LiOH solution required.

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2. The Ideal Gas Law

2.1 The Gas Laws

At low pressures all gases have the same behavior in the following sense:

1) With pressure and temperature fixed, the volume of the gas is proportional to the number of particles (atoms in the case of a monatomic gas such as Ne, or molecules in the case of a molecular gas such as CO_2). The proportionality constant is the same for all gases. This is Avogadro's Law:

$$V = \text{constant} \times n$$

2) If temperature is increased, with pressure fixed, the volume increases in proportion to the temperature (provided the temperature is measured on the absolute scale). This is Charles' Law:

$$V = \text{constant} \times T$$

3) If pressure is increased, with temperature fixed, the volume decreases inversely with the pressure. This is Boyle's law:

$$V = \text{constant} / p$$

4) If temperature is increased, with volume fixed, the pressure increases in proportion to the temperature. This law follows from Charles' and Boyle's Laws:

$$p = \text{constant} \times T$$

Note that each of these laws has a different constant that depends on the values of the fixed properties.

These observations are encapsulated in the ideal gas law:

$$pV = nRT \qquad 2.1$$

where R = 8.314 J mol^{-1} K^{-1} = 0.08206 L atm mol^{-1} K^{-1} is the gas constant. Gases that obey this law are said to be *ideal*. The law is valid at low pressure for all gases because, under these conditions, the atoms or molecules are so far apart that forces between them have no significant effect on the pressure of the gas.

The *first observation* allows us to determine the molar mass of a gas by measuring the mass of a known volume of the gas at known temperature and pressure.

Example 2.1: Suppose a 1.000 L sample of a gas at 1.000 atm pressure and 293.0 K has a mass of 1.830 g. What is the molar mass of the gas?

Approach: Solve for the amount of gas. Divide mass by amount to give the molar mass of the gas.

The amount of gas is determined, from $pV = nRT$, by

$$n = \frac{pV}{RT} = \frac{1.000\ \text{atm} \times 1.000\ \text{L}}{0.08206\ \text{L atm mol}^{-1}\text{K}^{-1} \times 293.0\ \text{K}}$$
$$= 0.04159_1\ \text{mol}$$

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The molar mass is determined from

$$\text{molar mass} = \frac{\text{mass}}{\text{amount}} = \frac{1.830\ \text{g}}{0.04159_1\ \text{mol}}$$
$$= 44.00\ \text{g mol}^{-1}$$

The gas is likely CO_2.

The *second observation*: Changes in volume indicate changes in temperature – if pressure is fixed.

Example 2.2: A balloon of gas increases in volume from 10.0 L to 12.8 L at 1.000 atm pressure. If the gas was initially at 295 K, what is its final temperature?

Approach: The amount of gas does not change. Equate the initial and final amounts. Cancel out *R* and the pressure which also does not change.

The pressure and the amount of gas are constant. Therefore,

$$n = \frac{pV_i}{RT_i} = \frac{pV_f}{RT_f}$$

or

$$\frac{V_i}{T_i} = \frac{V_f}{T_f}$$

or

$$T_f = \frac{V_f}{V_i} T_i = \frac{12.8\ \text{L}}{10.0\ \text{L}} \times 295\ \text{K}$$
$$= 378\ \text{K}$$

The *third observation*: Changes in volume indicate changes in pressure – if temperature is fixed.

Example 2.3: A balloon of gas increases in volume from 10.0 L to 15.6 L at 298 K. If the gas was initially at 1.00 atm pressure, what is its final pressure?

Approach: Equate the initial and final amounts. Cancel out *R* and the temperature which also does not change.

The temperature and the amount of gas are constant. Therefore,

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$$n = \frac{p_i V_i}{RT} = \frac{p_f V_f}{RT}$$

or

$$p_i V_i = p_f V_f$$

or

$$p_f = \frac{V_i}{V_f} p_i = \frac{10.0 \text{ L}}{15.6 \text{ L}} \times 1.00 \text{ atm}$$

$$= 0.641 \text{ atm}$$

The *fourth observation*: Changes in pressure indicate changes in temperature – if volume is fixed.

Example 2.4: A gas is held in a cylinder with fixed volume of 10.0 L. The pressure at is observed to increase from 1.00 atm to 15.0 atm. If the gas was initially at 298 K, what is its final temperature?

Approach: Equate the initial and final amounts. Cancel out *R* and the volume which also does not change.

The volume and the amount of gas are constant. Therefore,

$$n = \frac{p_i V}{RT_i} = \frac{p_f V}{RT_f}$$

or

$$\frac{p_i}{T_i} = \frac{p_f}{T_f}$$

or

$$T_f = \frac{p_f}{p_i} T_i = \frac{15.0 \text{ atm}}{1.00 \text{ atm}} \times 298 \text{ K}$$

$$= 4470 \text{ K}$$

Because the volume of a gas is proportional to amount (mol), we are sometimes faced with reaction stoichiometry questions that provide volume data for reactant gases.

Example 2.5: H_2 and Cl_2 react according to

$$H_2(g) + Cl_2(g) \rightarrow 2\ HCl(g)$$

Suppose 3.00 L of hydrogen gas is mixed with 4.00 L of chlorine gas, at 1.00 atm pressure and 298 K, then ignited. How much HCl is produced?

Approach: Determine the amount of the limiting reactant. The reaction stoichiometry then determines the amount of product.

Under the same conditions of pressure and temperature, a smaller volume means a smaller amount. Since the gases combine in a 1:1 ratio, the gas with the smaller volume is the limiting reactant. The limiting reactant is H_2 since it has the lesser volume.

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$$\text{amount of } H_2 \text{ consumed} = n = \frac{pV}{RT}$$
$$= \frac{1.00 \text{ atm} \times 3.00 \text{ L}}{0.08206 \text{ L atm mol}^{-1}\text{K}^{-1} \times 298 \text{ K}}$$
$$= 0.122_7 \text{ mol}$$

According to the reaction stoichiometry, the amount of HCl produced is twice this amount; i.e.,

amount of HCl = $2 \times 0.122_7$ mol = 0.245 mol

2.2 Partial Pressure

When we have a mixture of gases in a vessel, each gas contributes to the total pressure in the vessel – each gas has its own *partial pressure*. The total pressure in the vessel is the sum of the partial pressures of all gases in the vessel. For example, if we have a mixture of gases, A, B, C, …, the total pressure would be expressed as:

$$p_{TOTAL} = p_A + p_B + p_C + \ldots \qquad 2.2$$

The partial pressure of any gas in a mixture can be determined if we know the total pressure of the mixture and the mole fraction of the gas of interest. The mole fraction, x, of any gas in a mixture is its proportion with respect to the whole quantity. For example, if we have our mixture of gases A, B and C, and we know that we have 2.0 mol A, 1.5 mol B and 1.5 mol C, then the mole fraction of gas A is:

x_A = 2.0 mol / (2.0 + 1.5 + 1.5) mol = 2.0/5.0 or 0.40

If the total pressure of the mixture under a given set of conditions were 1.4 atm, then the partial pressure of gas A would be the total pressure multiplied by the mole fraction of gas A:

$p_A = p_{TOTAL} \times x_A$ = (1.4 atm) (0.40) = 0.56 atm

Example 2.6: The vapor pressure of water at 298 K is 24 torr (1 atm = 760 torr). This is the partial pressure of water in air saturated with water at 298 K. What is the mole fraction of water in 1.00 atm air at 298 K with 100% humidity (i.e. the air is saturated with water)?

Approach: Mole fraction is proportional to partial pressure, and we know the total pressure – i.e. 1.00 atm.

Total air pressure = 1.00 atm x 760 torr atm^{-1} = 760 torr
x_{water} = 24 torr / 760 torr = 0.031_6

The mole fraction of water vapor in air with 100% humidity is 0.032.

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Problems:

2.1 (a) Determine the density of He, N_2 and Ar at 1 atm pressure and 298 K.
(b) Which gas can be used to displace air in a cylinder, by pouring the gas into the cylinder?

2.2 What volume (in L) of CO_2 is consumed by reaction with 1.00 kg of CaO at 298 K and 1.00 atm pressure?

$$CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$$

2.3 Hydrochloric acid reacts with aluminum to produce hydrogen gas:

$$2\ Al(s) + 6\ HCl(aq) \rightarrow 2\ AlCl_3(s) + 3\ H_2(g)$$

An impure sample of aluminum contains an unknown amount of Al and other impurities. Suppose 110 mL of H_2, at 1.00 atm and 298 K, are collected from the reaction with HCl of all the aluminum in the 3.65 g impure sample. What percentage (by mass) of the sample is Al? Assume that the other components of the sample do not react with HCl.

2.4 Because the reaction in question 2.3 is carried out in aqueous solution, any gas collected from such a reaction will be a mixture of the product gas – in this case, hydrogen – and water vapor. Gases collected bubbling out of an aqueous are saturated with water. Thus, the 110 mL of H_2 collected in question 2.3 must be the dry volume – i.e., the volume after all of the water is removed (e.g. with a dessicant). Do question 2.3 again, but this time, suppose that the 110 mL of gas collected has not been dried – it contains water vapor. You must correct either the pressure or the volume of H_2 in order to get the actual amount (mol) of H_2.

2.5 Hydrogen peroxide decomposes into water and oxygen.

$$2\ H_2O_2(aq) \rightarrow 2\ H_2O(l) + O_2(g)$$

What volume of oxygen is liberated from the complete decomposition of 100. mL of a 3.00% hydrogen peroxide solution, at 1.00 atm and 293 K? The density of the hydrogen peroxide solution is 1.01 g mL^{-1}.

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Solutions:

2.1 (a) These three gases are essentially ideal under ordinary conditions. Therefore,

$$\frac{n}{V} = \frac{p}{RT} = \frac{1\text{ atm}}{0.08206\text{ L atm mol}^{-1}\text{ K}^{-1} \times 298\text{ K}} = 0.0408_9\text{ mol L}^{-1}$$

for all three gases. However, the gases have different molar masses, and consequently different densities. For example

$$d = m / V = n M / V$$

$$\text{density}(\text{He}) = \frac{m(\text{He})}{V} = \frac{nM(\text{He})}{V} = \frac{n}{V}M(\text{He})$$
$$= 0.0408_9\text{ mol L}^{-1} \times 4.002\text{ g mol}^{-1} = 0.164\text{ g L}^{-1}$$

Similarly,

$$\text{density}(\text{N}_2) = 0.0408_9\text{ mol L}^{-1} \times M(\text{N}_2)$$
$$= 0.0408_9\text{ mol L}^{-1} \times 28.013\text{ g mol}^{-1} = 1.15\text{ g L}^{-1}$$

and

$$\text{density}(\text{Ar}) = 0.0408_9\text{ mol L}^{-1} \times M(\text{Ar})$$
$$= 0.0408_9\text{ mol L}^{-1} \times 39.948\text{ g mol}^{-1} = 1.63\text{ g L}^{-1}.$$

(b) Denser gases can displace less dense gases. Air is mostly nitrogen, with 20% oxygen (which is a little denser). Only argon can displace air by pouring it into a cylinder. Nitrogen will not pour through air – it will mix slowly. Helium pours upwards because the surrounding air quickly displaces this less dense gas, forcing it to the ceiling and beyond.

2.2 Because molar masses are expressed in g mol^{-1}, we must convert kg to g:

1.00 kg = 1.00 × 10^3 g

Amount of calcium oxide consumed:

$$n(\text{CaO}) = \frac{m(\text{CaO})}{M(\text{CaO})} = \frac{1.00 \times 10^3\text{ g}}{56.08\text{ g mol}^{-1}} = 17.8_3\text{ mol}$$

From the balanced chemical equation,

$$\text{CaO(s)} + \text{CO}_2\text{(g)} \rightarrow \text{CaCO}_3\text{(s)},$$

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the amount of CO_2 consumed = amount of CaO consumed = 17.8_3 mol

At 298 K and 1.00 atm pressure, this corresponds to the volume of CO_2,

$$V = \frac{nRT}{p} = \frac{17.8_3 \text{ mol} \times 0.08206 \text{ L atm mol}^{-1}\text{K}^{-1} \times 298 \text{ K}}{1.00 \text{ atm}}$$
$$= 436 \text{ L}$$

2.3 To determine the amount of aluminum reacted, we need to calculate the amount of hydrogen gas:

$$n = \frac{pV}{RT} = \frac{1.00 \text{ atm} \times 0.110 \text{ L}}{0.08206 \text{ L atm mol}^{-1}\text{K}^{-1} \times 298 \text{ K}}$$
$$= 0.00449_8 \text{ mol}$$

From the reaction stoichiometry, we see that three mol of H_2 are produced for every 2 mol of Al.

Therefore, the amount of Al = (2/3) × 0.00449_8 mol = 0.00299_9 mol.

The mass of Al = 0.00299_9 mol × 26.9815 g/mol = 0.0809_2 g.
Since the mass of the sample was 3.65 g, the percentage Al (by mass) is

$$\frac{0.0809_2 \text{ g}}{3.65 \text{ g}} \times 100\% = 2.22\%$$

2.4 We must correct the volume, 110 mL, or pressure, 1.00 atm, of the collected gas to account for the water contribution. It is easier to correct for pressure since we are given the partial pressure of water in the collected gas – it is 24 torr or

24 torr / 760 torr atm^{-1} = 0.031_6 atm

The total pressure is 1.00 atm. This is the sum of the partial pressures of hydrogen and water. Therefore, the partial pressure of hydrogen is

1.00 atm − 0.031_6 atm = 0.96_8 atm

Now, we can follow the solution of question 2.3 with the partial pressure of hydrogen set to 0.96_8 atm rather than 1.00 atm. This by-passes determining the corrected collected volume – i.e., determining the dried volume of collected gas.[4]

The amount of hydrogen gas:

$$n = \frac{pV}{RT} = \frac{0.96_8 \text{ atm} \times 0.110 \text{ L}}{0.08206 \text{ L atm mol}^{-1}\text{K}^{-1} \times 298 \text{ K}}$$
$$= 0.0043_5 \text{ mol}$$

[4] The dried volume of product gas is just $\frac{0.96_8 \text{ atm}}{1.00 \text{ atm}} \times 110 \text{ mL} = 1.0_6 \times 10^2 \text{ mL}$

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The amount of Al = (2/3) × 0.0043_5 mol = 0.0029_0 mol.

The mass of Al = 0.0029_0 mol × 26.9815 g/mol = 0.078_2 g.
Since the mass of the sample was 3.65 g, the percentage Al (by mass) is

$$\frac{0.078_2\ \text{g}}{3.65\ \text{g}} \times 100\% = 2.1\%$$

2.5 The mass of hydrogen peroxide solution = volume × density

= 100 mL × 1.01 g/mL = 101 g

The solution is 3.00% (be mass) hydrogen peroxide.

Therefore, the mass of hydrogen peroxide in the solution = 0.0300 × 101 g = 3.03 g.

$$\text{the amount of } H_2O_2 \text{ decomposed} = \frac{3.03\ \text{g}}{34.015\ \text{g/mol}} = 0.0890_8\ \text{mol}$$

This corresponds to the volume,

$$V = \frac{nRT}{p} = \frac{0.0890_8\ \text{mol} \times 0.08206\ \text{L atm mol}^{-1}\text{K}^{-1} \times 293\ \text{K}}{1.00\ \text{atm}}$$
$$= 2.14_2\ \text{L}$$

The volume of O_2 is one half the volume of H_2O_2,

V = (2.14_2 L) / 2 = 1.07 L

Note that all of the above questions make use of the ideal gas law, *pV* = *nRT*, simply rearranged, as required, in order to solve for an unknown quantity.

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3. Acids and Bases

3.1 Brønsted-Lowry Theory

According to the Brønsted-Lowry definition of acids and bases, an acid reacts with a base by exchanging an H^+. For example,

$$HBr + NH_3 \rightarrow Br^- + NH_4^+$$

Here, HBr is the H^+ donor – the acid – while NH_3 is the H^+ acceptor – the base. The H^+ is able to leave the acid because the H-Br bond is polarized – the bonding electrons are shifted towards the bromine atom. The Lewis definition of acids and bases explains that NH_3 is able to accept the H^+ because there is a lone pair of electrons on the nitrogen atom. These electrons are shared to become the fourth N-H bond in NH_4^+.

Example 3.1: Identify the acid and base in the following reaction:

$$NH_2^- + HF \rightarrow NH_3 + F^-$$

Approach: Look for the reactant that gained an H^+, and that which lost an H^+.

The HF loses an H^+. It is the H^+ donor – i.e., it is the acid. NH_2^- accepts the H^+. It is the base. Note that an acid always has an H bonded to an electronegative atom (N, O, F, S, Cl, Br or I – often it is O). A base must have a lone pair of electrons to accept the H^+. The lone pair is usually on an N atom (often seen for uncharged basic molecules) or an O atom (mostly seen for anionic bases).

Acids and bases form acidic and basic aqueous solutions. Acids and bases can be molecules or ions.

Salts form aqueous solutions by splitting into positive and negative ions that are solvated by water. For example,

$$NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$$

Molecular compounds form aqueous solutions by becoming solvated by water. For example, acetic acid (vinegar) dissolves in water according to

$$CH_3COOH(l) \xrightarrow{H_2O} CH_3COOH(aq)$$

Acids and bases react with water when in aqueous solution. Acids react by donating H^+ to water. For example,

$$HCl(aq) + H_2O(l) \rightarrow Cl^-(aq) + H_3O^+(aq)$$

In this reaction, H_2O acts as a base. It accepts an H^+.

Bases react by accepting an H^+ from water. For example,

$$NH_2^-(aq) + H_2O(l) \rightarrow NH_3(aq) + OH^-(aq)$$

Here, H_2O acts as an acid. It donates an H^+. Some substances, such as water, can behave as either acids or bases depending on what they react with. They are called *amphoteric*.

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3.2 Strong and Weak Acids and Bases

All the chemical reactions shown above have arrows to the right indicating the reaction proceeds to completion. In reality, no reaction proceeds to completion; there is always a reverse reaction that returns products back to reactants. However, we frequently encounter reactions that essentially go to completion. All the reactions listed above are of this type. In such cases, the rate of the reverse reaction is very much smaller than the rate of forward reaction. When equilibrium is obtained – i.e., when the rate of reverse reaction equals the rate of forward reaction – there is very little reactant left. This amount is often negligible. However, there are also many reactions where the rate of reverse reaction is not negligible; in these cases there is a significant amount of "reactant" present at equilibrium.

Many acids and bases react with water only to a limited extent. For example, ammonia only reacts to a limited extent:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

The limited degree of reaction is indicated here by the double arrow (showing forward and reverse reactions). In fact, in an aqueous solution of ammonia there is only a small amount of $NH_4^+(aq)$. Most of the ammonia is unreacted. This is indicated by the asymmetry of the double arrow. For this reason, NH_3 is said to be a *weak base*. In contrast, the reaction of NH_2^- with water shown above goes essentially to completion. NH_2^- is a *strong base*.

Acids are similarly labeled as strong or weak depending on whether the reaction with water goes to completion. For example, acetic acid is a *weak acid* (we use a double arrow):

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

Nitric acid is *strong acid* (we use a single arrow):

$$HNO_3(aq) + H_2O(l) \rightarrow NO_3^-(aq) + H_3O^+(aq)$$

Note that the reverse of an acid base reaction is itself an acid base reaction. The acid and base of the reverse reaction are the products of the forward reaction – the result of the acid losing an H^+ and the result of the base having accepted an H^+. These are called the conjugate base and conjugate acid, respectively. For example,

$H_2SO_4(aq)$ +	$H_2O(l)$	$\rightarrow$	$HSO_4^-(aq)$	+	$H_3O^+(aq)$
acid	base		conjugate base of H_2SO_4		conjugate acid of H_2O

This reaction goes essentially to completion because H_2SO_4 is a stronger acid than H_3O^+. The equilibrium is always shifted *away* from the stronger acid. Above, this corresponds to the forward reaction. This is why we call H_2SO_4 a *strong acid*.

In contrast,

$HOCl(aq)$ +	$H_2O(l)$	$\rightleftharpoons$	$OCl^-(aq)$	+	$H_3O^+(aq)$
acid	base		conjugate base of HOCl		conjugate acid of H_2O

Here, the acid HOCl is weaker than H_3O^+ (the reaction shifts away from the stronger acid). Hence, HOCl is called a *weak acid*.

Now consider some reactions of bases. When NaOH dissolves in water, we get $OH^-(aq)$. Any alkali metal (Group 1) or alkaline earth (Group 2) metal hydroxide produces $OH^-(aq)$ when dissolved in water. Let us consider what the reaction of the $OH^-(aq)$ would be with water:

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$$\underset{\text{base}}{OH^-(aq)} + \underset{\text{acid}}{H_2O(l)} \rightleftharpoons \underset{\text{conjugate acid of } OH^-}{H_2O(aq)} + \underset{\text{conjugate base of } H_2O}{OH^-(aq)}$$

Here, the reactants and products are the same. This is a balanced equilibrium. The bases on both sides are the same and consequently equal in strength. We define OH^- to be a *strong base*. Any base stronger than OH^-, such as NH_2^- shown above, is also strong.

NH_3, shown above, is a weak base. It is weaker than OH^-, as seen in the shift of the equilibrium towards reactants. The equilibrium is always shifted *away* from the stronger base. Note that this rule always agrees with the "*away* from the stronger acid" rule given above – we always see the stronger acid and the stronger base on the same side of the reaction. OCl^- is also weaker than OH^-, and is a therefore a *weak base*.

$$\underset{\text{base}}{OCl^-(aq)} + \underset{\text{acid}}{H_2O(l)} \rightleftharpoons \underset{\text{conjugate acid of } OCl^-}{HOCl(aq)} + \underset{\text{conjugate base of } H_2O}{OH^-(aq)}$$

Table 3.1. Strong acids and a few weak acids

	Acid(s)	**Conjugate Base(s)**	
Strong Acids	HCl, HBr, HI HNO_3 H_2SO_4 $HClO_3$, $HClO_4$	Cl^-, Br^-, I^- NO_3^- HSO_4^- ClO_3^-, ClO_4^-	The conjugate bases are ***very* weak bases**
Weak Acids	HF HOCl H_3PO_4 acetic acid: CH_3COOH	F^- OCl^- $H_2PO_4^-$ CH_3COO^-	The conjugate bases are **weak bases**

Table 3.2. Strong bases and a few weak bases

	Base(s)	**Conjugate Acid(s)**	
Strong Bases	O^{2-}, oxide ion (e.g. Li_2O, Na_2O, CaO, SrO) OH^-, hydroxide ion (e.g. LiOH, NaOH, KOH, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$) NH_2^-, amide ion (e.g. $NaNH_2$) H^-, hydride ion (e.g. LiH)	OH^- H_2O NH_3 H_2	The conjugate acids are ***very* weak acids**
Weak Bases	NH_3 OCl^- methylamine: CH_3NH_2	NH_4^+ HOCl $CH_3NH_3^+$	The conjugate acids are **weak acids**

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Note that weak acids are conjugate to weak bases, whereas **strong** acids are conjugate to ***very weak*** bases and **strong** bases are conjugate to ***very weak*** acids.

Example 3.2: Given that

$$NH_2^-(aq) + H_2O(l) \rightarrow NH_3(aq) + OH^-(aq)$$
$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$
$$NH_4^+(aq) + OCl^-(aq) \rightleftharpoons HOCl(aq) + NH_3(aq)$$

(a) Order the bases (the species acting as a base in either the forward or reverse of one of these reactions) according to increasing strength as a base (from weakest to strongest).
(b) Order the acids according to increasing strength.

(a) In the first reaction, NH_2^- is the reactant base. This strongly product-favored reaction indicates that NH_2^- is a stronger base than OH^-. The shift to the left of the second equilibrium indicates that OH^- is a stronger base than NH_3. The shift to the left of the third equilibrium indicates that NH_3 is a stronger base than OCl^-. Therefore. in order of increasing strength as a base, we have

$$OCl^- < NH_3 < OH^- < NH_2^-$$

(b) The acids are just the conjugate acids to the bases listed. The order of acid strength is the reverse of the above order (with conjugate acids replacing the bases); i.e., according to strength as an acid,

$$NH_3 < H_2O < NH_4^+ < HOCl$$

3.3 Types of Acids and Bases

Binary Acids

The simplest class of acids is the binary acids consisting of H bonded to an electronegative atom. The most important of these are hydrosulfuric acid (H_2S).and the hydrohalic acids: hydrofluoric acid (HF), hydrochloric acid (HCl), hydrobromic acid (HBr) and hydroiodic acid (HI).

Oxoacids and Oxoanions

Many common acids are oxoacids. These are acids with a central atom bonded to one or more oxygen atoms, with one or more of those oxygen atoms in turn bonded to a hydrogen atom.[5] The bases conjugate to the oxoacids are oxoanions. Some oxoacids can donate more than one H^+ - they are polyprotic. The common set of oxoacids and associated oxoanions are shown in Table 3.3.

[5] There is one exception to this characterization of oxoacids: phosphorus acid (H_3PO_3), wherein a (non-acidic) H is bonded to the central atom – phosphorus in this case. However, the conjugate base rearranges such that both H atoms in $H_2PO_3^-$ are bonded to an O. $H_2PO_3^-$ is a diprotic acid that ultimately leads to PO_3^{3-}, the 3rd conjugate base of phosphorous acid.

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Table 3.3. Oxoacids and oxoanions

Oxoacid	1st Conjugate Base	2nd Conjugate Base	3rd Conjugate Base
H_2CO_3 carbonic acid	HCO_3^- hydrogen carbonate (bicarbonate)	CO_3^{2-} carbonate	
HNO_2 nitrous acid	NO_2^- nitrite		
HNO_3 nitric acid	NO_3^- nitrate		
H_3PO_3 phosphorous acid	$H_2PO_3^-$ dihydrogen phosphite	HPO_3^{2-} hydrogen phosphite	PO_3^{3-} phosphite
H_3PO_4 phosphoric acid	$H_2PO_4^-$ dihydrogen phosphate	HPO_4^{2-} hydrogen phosphate	PO_4^{3-} phosphate
H_2SO_3 sulfurous acid	HSO_3^- hydrogen sulfite	SO_3^{2-} sulfite	
H_2SO_4 sulfuric acid	HSO_4^- hydrogen sulfate	SO_4^{2-} sulfate	
HClO hypochlorous acid	OCl^- hypochlorite		
$HClO_2$ chlorous acid	ClO_2^- chlorite		
$HClO_3$ chloric acid	ClO_3^- chlorate		
$HClO_4$ perchloric acid	ClO_4^- perchlorate		

Note that some elements as central atoms (e.g. N, S, P and Cl) have more than one oxoacid. When there are two such species they are labeled ...ous acid and ...ic acid (e.g. nitrous and nitric acids). The oxoacid with more O atoms (for which the central atom has the highest oxidation number) is labeled ...ic acid, while that with fewer O atoms is labeled ...ous acid. The corresponding oxoanions are labeled ...ite and ...ate. In the case of chlorine, there are four oxoacids. The middle two (with respect to number of O atoms) acids are chlorous and chloric acid, respectively. That with one fewer O than chlorous acid is called hypochlorous acid. That with one more O than chloric acid is called perchloric acid. The conjugate base to hypochlorous acid is hypochlorite, while the conjugate base to perchloric acid is perchlorate. Other common oxoanions include the powerful oxidizing agents, dichromate, $Cr_2O_7^{2-}$, and permanganate, MnO_4^-.

Organic Acids and Bases

There are many organic acids. The simplest are the alkanoic (carboxylic) acids derived from the alkanes. The alkanes have the chemical formula, C_nH_{2n+2}. For example, for n = 1 and 2 we have methane, CH_4, and ethane, C_2H_6, respectively. The alkanoic acids are obtained by replacing 3 H atoms attached to one of the end carbon atoms with a doubly bonded O and an OH group (the O

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bonds to the carbon atom. The result is a compound with formula, $C_nH_{2n-1}OOH$ (or RCOOH). The simplest of these compounds are tabulated in Table 3.4.

Simple amines are also derived from alkanes. We obtain an amine from an alkane by replacing an H with an NH_2, to get a compound with chemical formula, $C_nH_{2n+1}NH_2$, The amines derived in this way are weak bases similar to ammonia. some of them are tabulated in Table 3.4.

Table 3.4. Some simple organic acids and bases

Alkane	Alkanoic acid	Conjugate Base - Alkanoate	Amine
CH_4 methane	HCOOH methanoic acid (also known as formic acid)	$HCOO^-$ methanoate (also known as formate)	CH_3NH_2 methylamine
C_2H_6 methane	CH_3COOH ethanoic acid (also known as acetic acid)	CH_3COO^- ethanoate (also known as acetate)	$CH_3CH_2NH_2$ ethylamine
C_3H_8 propane	CH_3CH_2COOH propanoic acid	$CH_3CH_2COO^-$ propanoate	$CH_3CH_2NH_2$ Propylamine
C_4H_{10} butane	$CH_3CH_2CH_2COOH$ butanoic acid	$CH_3CH_2CH_2COO^-$ butanoate	$CH_3CH_2NH_2$ Butylamine
C_5H_{12} pentane	$CH_3CH_2CH_2CH_2COOH$ pentanoic acid	$CH_3CH_2CH_2CH_2COO^-$ pentanoate	$CH_3CH_2CH_2CH_2CH_2NH_2$ Pentylamine
C_6H_{14} hexane	$CH_3CH_2CH_2CH_2CH_2COOH$ hexanoic acid	$CH_3CH_2CH_2CH_2CH_2COO^-$ hexanoate	$CH_3CH_2CH_2CH_2CH_2CH_2NH_2$ Hexylamine

Oxalic acid, $H_2C_2O_4$ is another related, commonly encountered, organic acid. It is a dicarboxylic acid. The associated 2nd conjugate base is oxalate, $C_2O_4^{2-}$.

Problems:

3.1 Which of the following reactions are acid-base reactions? For those that are acid-base reactions, identify the acid and the base.

(a) $2\ Li(s) + Cl_2(g) \rightarrow 2\ LiCl(s)$
(b) $LiOH(aq) + HBr(g) \rightarrow LiBr(aq) + H_2O(l)$
(c) $NH_3(aq) + HClO_3(aq) \rightarrow NH_4ClO_3(aq)$
(d) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
(e) $CH_3COOH(g) + NH_3(g) \rightarrow NH_4CH_3COO(s)$

3.2 Identify each of the following as a strong/weak acid/base, or neither acid nor base. What is the difference between a strong acid and a weak acid?

(a) HF (b) CH_4 (c) KOH (d) CH_3NH_2 (e) $HClO_4$

3.3 Identify the conjugate acid base pairs present in the following reactions:

(a) $H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + H_3O^+(aq)$

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(b) $CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$
(c) $HClO_4(aq) + H_2O(l) \rightarrow ClO_4^-(aq) + H_3O^+(aq)$

3.4 Some acids are cations, while some bases are anions. When we dissolve a salt in water, we get an acidic solution if the cation is an acid (strong or weak, but not very weak), and a basic solution if the anion is a base (strong or weak, but not very weak). If the salt is composed of an acid and a base, the pH of the resulting solution depends on the relative strength of the cation as acid and anion as base.

Which of the following salts will produce an acidic/basic solution when dissolved in water?

(a) LiF (b) NH_4Cl (c) KBr (d) CH_3NH_3Cl (e) NaOCl

3.5 Write out the chemical equilibria for the reactions of the acidic/basic ions (in question 3.4) with water. Indicate whether the equilibrium is shifted to the right or shifted to the left – i.e. use arrow size to depict the shift in equilibrium.

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Solutions:

3.1 (a) $2\ Li(s) + Cl_2(g) \rightarrow 2\ LiCl(s)$
is NOT an acid-base reaction. There is no H^+ transfer. This is an electron transfer reaction, an oxidation-reduction reaction.

(b) $LiOH(aq) + HBr(g) \rightarrow LiBr(aq) + H_2O(l)$
is an acid-base reaction. LiOH(aq) is really shorthand for $Li^+(aq) + OH^-(aq)$. In this reaction, HBr donates an H^+ to OH^-. Therefore, HBr is the acid and OH^- is the base.

(c) $KOCl(aq) + HClO_3(aq) \rightarrow KClO_3(aq) + HOCl(aq)$
is an acid-base reaction. KOCl(aq) is shorthand for $K^+(aq) + OCl^-(aq)$. Since $HClO_3$ is a strong acid, $HClO_3(aq)$ is shorthand for $H_3O^+(aq) + ClO_3^-(aq)$. Thus, in this reaction, it is really H_3O^+ acting as an acid and donating an H^+ to OCl^-. However, as written, the reaction shows $HClO_3$ donating an H^+ to OCl^-. Here, $HClO_3$ is the acid and OCl^- is the base.

(d) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
is NOT an acid-base reaction. It is a gas-forming decomposition reaction.

(e) $CH_3COOH(g) + NH_3(g) \rightarrow NH_4CH_3COO(s)$
is an acid-base reaction. CH_3COOH donates an H^+ to NH_3. Therefore, CH_3COOH is the acid and NH_3 is the base. *Note*: the reaction shown does not take place in water. However, the above is an acid-base reaction according to the Brønsted-Lowry and Lewis definitions.

3.2 (a) HF is a weak acid.

(b) CH_4 is neither acid not base.

(c) KOH is a strong base.

(d) CH_3NH_2 is a weak base.

(e) $HClO_4$ is a strong acid.

A strong acid fully dissociates in water - the equilibrium wherein the acid donates an H^+ to H_2O is strongly shifted to the right. A weak acid is mostly undissociated in water - the equilibrium wherein the acid donates an H^+ to H_2O is shifted to the left.

3.3 (a) $H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + H_3O^+(aq)$
Here, $H_2PO_4^-$ is the base conjugate to the weak acid, H_3PO_4, while H_3O^+ is the acid conjugate to the (very weak) base, H_2O.

(b) $CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$
Here, OH^- is the base conjugate to the (very weak) acid, H_2O, while $CH_3NH_3^+$ is the acid conjugate to the weak base, CH_3NH_2.

(c) $HClO_4(aq) + H_2O(l) \rightarrow ClO_4^-(aq) + H_3O^+(aq)$
Here, ClO_4^- is the (very weak) base conjugate to the strong acid, $HClO_4$, while H_3O^+ is the acid conjugate to the (very weak) base, H_2O.

3.4 (a) LiF will produce a basic solution. LiF is an ionic material that dissolves in water to form $Li^+(aq)$ and $F^-(aq)$. Li^+ is NOT an acid (nor a base). In fact, all Group 1 cations are

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neutral in water, as they do not react with water. However, F^- is the weak base conjugate to the weak acid, HF. It will react with water *via*

$$F^-(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^-(aq)$$

to sufficient extent to make the solution noticeably basic.

(b) NH_4Cl will produce an acidic solution. NH_4Cl is an ionic material that dissolves in water to form $NH_4^+(aq)$ and $Cl^-(aq)$. Cl^- is a very weak base - it is conjugate to a strong acid. It does not react to noticeable extent with water – i.e., we can say that it is not a base. However, NH_4^+ is the weak acid conjugate to the weak acid, NH_3. It will react with water *via*

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

to sufficient extent to make the solution noticeably acidic.

(c) KBr will produce a neutral solution. Neither K^+ (a Group 1 cation), not Br^-, reacts with water to a noticeable extent. Br^- is the very weak base conjugate to the strong acid, HBr.

(d) CH_3NH_3Cl will produce an acidic solution. This is an ionic material that dissolves in water to form $CH_3NH_3^+(aq)$ and $Cl^-(aq)$. Cl^- does not react with water – see part (b) above. $CH_3NH_3^+$ is the weak acid conjugate to the weak acid, CH_3NH_2. It will react with water *via*

$$CH_3NH_3^+(aq) + H_2O(l) \rightleftharpoons CH_3NH_2(aq) + H_3O^+(aq)$$

to sufficient extent to make the solution noticeably acidic.

(e) NaOCl will produce a basic solution. NaOCl dissolves in water to form $Na^+(aq)$ and $OCl^-(aq)$. Na^+ (a Group 1 cation) does not react with water. However, OCl^- is the weak base conjugate to the weak acid, HOCl. It will react with water *via*

$$OCl^-(aq) + H_2O(l) \rightleftharpoons HOCl(aq) + OH^-(aq)$$

to sufficient extent to make the solution noticeably basic.

3.5 The requested chemical equilibria are shown in the solution to question 3.4. The shifts in the equilibria are indicated by the size of the forward and reverse arrows.

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4. Bonding

4.1 Types of Bonding

The physical and chemical properties of a substance are largely determined by the nature of the bonding between atoms of the substance. Different types of bonding are possible.

Ionic

When a metal reacts with a non-metal, the product is generally an ionic material. Non-metal atoms take electrons from metal atoms to form anions. Metal atoms lose electrons and become cations. An ionic material is an alternating lattice of cations and anions held together by the strong electrostatic attraction between oppositely charged ions. The bonding in such a material is called *ionic*. For example, NaCl(s) is an ionic material consisting of Na^+ and Cl^- ions. Ionic materials are typically hard, brittle solids with high melting points.

Covalent

Non-metal atoms form *covalent bonds*, wherein they share valence electrons with a neighboring non-metal atom. A covalent bond can be polar (as it is in case of H-Cl), wherein the bonding electrons are closer to the more electronegative atom. A covalent bond can also be completely non-polar (as it is in the case Cl-Cl, or any other homonuclear diatomic). An ionic bond is, in a sense, the extreme of a polarized covalent bond. Covalent bonding frequently extends only over a limited number of atoms. This defines a *molecule*. The associated material is called *molecular*. In the case of a solid or liquid molecular material, the molecules are held together by *intermolecular forces*. These forces are weaker, and such materials generally have lower melting and boiling points than other types of materials (e.g. metals, covalent networks). Most materials consisting of small molecules are gases or liquids. CO_2(g), H_2O(l) and sucrose,$C_{12}H_{24}O_{12}$(s), are examples of molecular materials.

Covalent bonding can extend over an array of vast numbers of atoms. In such a case, the "molecule" is a vast network of atoms connected by covalent bonds. These materials are called *network covalent solids*. They are generally very hard, and have high melting points. For example, diamond is a 3-dimensional network of carbon atoms.

Metallic

In metallic solids, metal atoms share their valence electrons over an array of vast numbers of atoms. This type of bonding is called *metallic*, and is responsible for the unique properties of metals familiar in everyday life. For example, metals are typically solid, often with high melting points. They are also shiny, and mostly silver-colored. They conduct electricity and are somewhat malleable.

Example 4.1: What type of bonding is present in the following substances? (states are shown for each substance at 25°C).

(a) KF(s)	(b) Cu(s)	(c) $LiNO_3$(s)	(d) SF_6(g)	(e) SiO_2(s)
(f) Na(s)	(g) $CaBr_2$(s)	(h) C_2H_6(g)	(i) $MgCO_3$(s)	(j) Br_2(l)

(a) Ionic bonding. KF(s), potassium fluoride, is a compound formed from a metal (potassium) and a non-metal (fluorine). It is ionic, consisting of K^+ and F^- ions. The formula, KF, tells us that there is a one to one ratio of K^+ to F^- ions to balance the charge.

(b) Metallic bonding. Cu(s) is a metal. The chemical formula simply says that the material consists only of copper atoms.

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(c) Ionic and covalent bonding. $LiNO_3(s)$ is an ionic compound composed of Li^+ and NO_3^- (nitrate) ions. The nitrate ion is a *polyatomic ion*. It consists of covalently bonded N and O atoms, with a net charge of −1.
(d) Covalent bonding. $SF_6(g)$ is a gas consisting of distinct SF_6 molecules. Each SF_6 molecule is an S atom covalently bonded to six F atoms; both elements are non-metals.
(e) Covalent bonding. Quartz, $SiO_2(s)$, is a network covalent solid. The chemical formula for a network covalent solid tells us the relative amounts of the different types of atoms – here, Si and O. Because it is a continuous network it can be represented as $(SiO_2)_n$.
(f) Metallic bonding. Na(s) is a metal.
(g) Ionic bonding. $CaBr_2(s)$ is an ionic compound composed of Ca^{2+} and Br^- ions. Because the calcium has a +2 charge, whereas bromide is only −1, there are two bromide ions for every calcium ion.
(h) Covalent bonding. Ethane, $C_2H_6(g)$, is a gas of C_2H_6 molecules. The chemical formula for molecular compounds tells us the actual number of each type of atom in one molecule – it is not just the relative amounts of atoms. Here, there are two C atoms and 6 H atoms in every ethane molecule.
(i) Ionic and covalent bonding. $MgCO_3(s)$ is an ionic compound composed of Mg^{2+} and CO_3^{2-} (carbonate) ions. The carbonate ion is a *polyatomic ion*. It consists of covalently bonded C and O atoms, with a net charge of −2.
(j) Covalent bonding. $Br_2(l)$ is a liquid consisting distinct of Br_2 molecules. Covalent bonding holds each Br_2 molecule together.

4.2 Solutions

The different types of materials described above have distinguishing properties when those materials are dissolved in a solvent (often, but not necessarily, water). For example, ionic materials (salts) dissolve in water to form electrolyte solutions – though some salts have extremely small solubility. An electrolyte solution conducts electricity. This is because the ions of the ionic material move around freely in the water solution. They can carry electricity. In contrast, an ionic solid does not conduct electricity as the ions are fixed in lattice positions and cannot move to carry current.

Salts dissolve in water because the ions can be solvated by water molecules (or, 'hydrated'). Solvation is an example of intermolecular forces – forces of attraction that exist between molecules or between molecules and ions. In this case, we have ions and water molecules. Solvation is strong here because water molecules are polar and are able to align themselves to interact favorably with either a positive or negative ion. This is an example of an ion-dipole force.

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e.g.

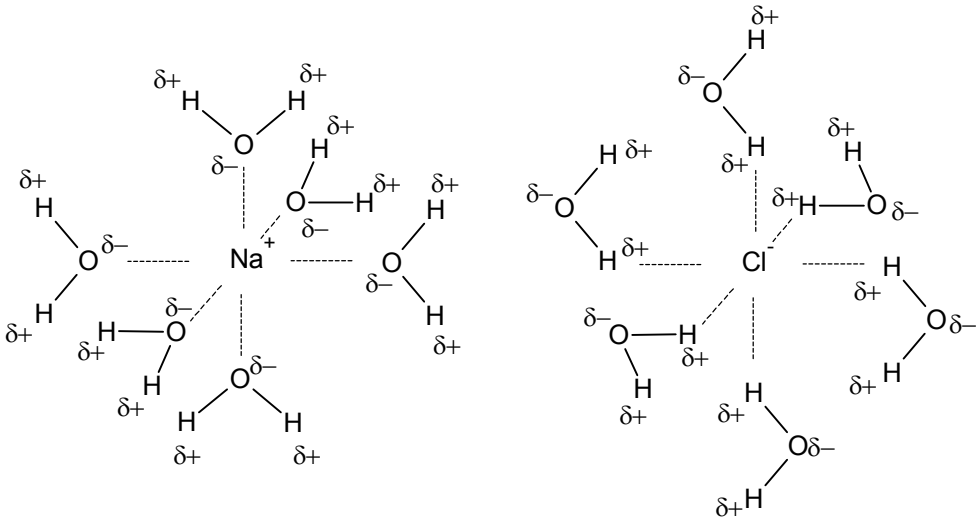

Figure 4.1 Solvation of sodium and chloride ions in aqueous solution. The δ+ and δ– are the partial charges on H and O atoms associated with the polarity of the OH bond.

Water is polar because it is an asymmetric molecule with polar covalent bonds. The H-O bonds are polar because oxygen is more electronegative than hydrogen. Thus, the bonding electrons are shifted toward the O atom. The O atom is slightly negatively charged (δ–), while the H atoms are slightly positively charged (δ+), where δ indicates a partial charge Each water molecule has a permanent, or 'net', dipole.

In water, the two H-O bond dipole moments do not cancel. This is because two lone pairs of electrons on the O atom push the H-O bonds to one side of the molecule.

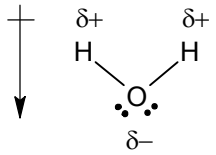

Figure 4.2 Lewis structure and molecular shape of water, showing the partial charges, and the net dipole moment vector (on the left).

Molecular compounds can also dissolve in water. This is again because of intermolecular forces. Compounds with the highest solubilities are those consisting of molecules with net dipole moments – i.e., polar molecules like water. When molecular compounds dissolve in water, in the absence of reaction with water (e.g. acids and bases excluded), the result is a *non-electrolyte solution*. Such solutions do not conduct electricity. When the molecular compound is an acid or a base, it reacts when dissolved in water (see Section 3) producing H_3O^+ or OH^- ions, respectively. These ions move freely in solution, and will carry a current. The solutions of an acid or a base are *electrolyte* solutions.

Dissolution of compounds in other molecular solvents is also important. Many organic solvents (e.g. CCl_4) are non-polar. These solvents best dissolve other non-polar materials. This is because a polar molecule has stronger intermolecular forces when it is surrounded by other polar molecules. The polar compound will not readily dissolve in a non-polar solvent, as it would be

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solvated by weaker intermolecular forces than are already present in the compound. In summary, "*like dissolves like*".

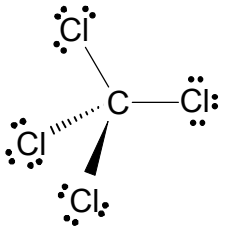
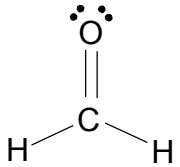
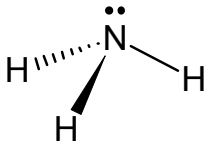


Figure 4.3. Lewis structure of CCl_4: The molecule has polar bonds. However, it is a symmetric molecule (it has a tetrahedral shape). The "wedge" bond indicates a bond coming forward out of the plane of the page, and the "dashed" bond indicates a bond going back behind the plane of the page. In such a way we try to show a 3-dimensional shape in a 2-dimensional drawing. Because of the symmetry all of the bond dipoles cancel out, and it has no permanent dipole (it is a non-polar molecule).

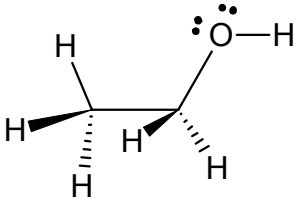
Example 4.2: Consider the following Lewis structures:



Lewis structure and shape of formaldehyde, CH_2O



Lewis structure and shape of ammonia NH_3



Lewis structure of ethanol, C_2H_5OH, showing shape around the O atom – and the C atoms (these atoms appear only as vertices from which four bonds emerge)

Which of the following are electrolyte solutions?

(a) potassium chlorate solution: $KClO_3(aq)$
(b) formaldehyde solution (pH = 7): $CH_2O(aq)$
(c) acetic acid solution (pH = 3): $CH_3COOH(aq)$
(d) sodium bromide: $NaBr(aq)$
(e) ammonia solution (pH = 10): $NH_3(aq)$
(f) ethanol solution (pH = 7): $C_2H_5OH(aq)$

(a) Electrolyte solution. $KClO_3(aq)$ consists of K^+ and ClO_3^- ions in aqueous solution. These ions move freely and therefore can conduct electricity.
(b) Non-electrolyte solution. Formaldehyde solution contains CH_2O molecules solvated by water molecules. Formaldehyde is neither an acid nor a base in water. The information

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that pH = 7 tells us that the solution is neutral. The H atoms in CH_2O are bonded to carbon. They are not acidic. Though the O atom has lone electron pairs, it does not accept H^+ from water. Formaldehyde remains neutral in solution. While it moves freely, it cannot conduct electricity.

(c) Electrolyte solution. CH_3COOH is a weak acid, as indicated by the information that pH = 3. It donates an H^+ to H_2O to form H_3O^+. The H_3O^+ and CH_3COO^- ions move freely in solution and can conduct electricity.

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

(d) Electrolyte solution. NaBr(aq) consists of Na^+ and Br^- ions in aqueous solution. The hydrated Na^+ and Br^- ions can conduct electricity.

(e) Electrolyte solution. NH_3 is a weak base. It accepts an H^+ from H_2O to leaving OH^- and NH_4^+ ions.. The OH^- and NH_4^+ ions move freely in solution and can conduct electricity.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

Note also that, because the equilibrium is shifted to the left, this will be a *weak* electrolyte solution. It will only weakly conduct electricity.

(f) Non-electrolyte solution. A molecular solution, and ethanol is neither an acid nor a base in water (pH = 7).

Example 4.3: Which of the following pairs of compounds form solutions?

(a) potassium iodide and water
(b) methane, CH_4, and water
(c) methane, CH_4, and carbon tetrachloride, CCl_4
(d) formaldehyde, CH_2O, and water
(e) formaldehyde, CH_2O, and carbon tetrachloride, CCl_4
(f) ethanol, C_2H_5OH, and water

(a) Solution. KI is ionic. It dissolves in water to form solvated K^+ and I^- ions.
(b) No solution. CH_4 is symmetrical and non-polar. It has very little solubility in a polar solvent such as water.
(c) Solution. CCl_4 is symmetrical and non-polar. It dissolves non-polar compounds like methane.
(d) Solution. CH_2O is asymmetrical. It has a dipole moment arising mainly from the polar C-O bond (a double bond in formaldehyde). It dissolves in polar solvents like water.
(e) No solution. Polar formaldehyde does not dissolve in non-polar carbon tetrachloride.
(f) Solution. Ethanol is polar (primarily because of the O-H bond) and dissolves in polar water.

Problems:

4.1 Identify the types of bonding present in the following materials. Label the material as ionic, molecular, network covalent, or metallic.

(a) $Cl_2(g)$
(b) LiOH(s)
(c) $H_2SO_4(l)$
(d) Fe(s)
(e) $CaCO_3(s)$
(f) C(diamond)
(g) brass – an alloy of mostly copper, zinc and (sometimes) Sn.

4.2 Which of the pairs of material form solutions?

(a) ethane, C_2H_6, and butane, C_4H_{10}.
(b) ethanol, C_2H_5OH, and water

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(c) carbon dioxide and carbon tetrachloride, CCl_4
(d) lithium bromide, LiBr, and water
(e) sodium nitrate, $NaNO_3$, and carbon tetrachloride, CCl_4

4.3 Electrolytes can be strong or weak. For example, most acids are molecules that dissociate in water. They react with water to form an anion (the conjugate base) and hydronium ion, H_3O^+. The ions formed can conduct electricity. So, the resulting solution is an electrolyte solution. However, most acids are weak which means they only dissociate to a small extent. Consequently, the ion concentration in solution is small, and the electrical conductivity is also small. Weak acids are therefore *weak electrolytes*. Weak bases are similarly *weak electrolytes*. Ionic materials and strong acids and bases are *strong electrolytes*.

Label each of the following materials as a strong or weak electrolyte, or as a non-electrolyte.

(a) nitric acid, HNO_3
(b) lithium hydroxide, LiOH
(c) ethanol, C_2H_5OH
(d) potassium iodide, KI
(e) ammonia, NH_3
(f) hypochlorous acid, HOCl
(g) sodium hypochlorite, NaOCl

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Solutions:

4.1 (a) $Cl_2(g)$. The bonding is covalent. This is a molecular gas. Chlorine gas consists of pairs of chlorine atoms covalently bonded to form molecules.

(b) LiOH(s). Ionic and covalent bonding are present. This is an ionic material. Lithium hydroxide consists of Li^+ and OH^- ions arranged in a lattice. Hydroxide, OH^-, is a diatomic anion with an oxygen atom covalently bonded to a hydrogen atom.

(c) $H_2SO_4(l)$. The bonding is covalent within the sulfuric acid molecules. Since the material is a liquid, there are also intermolecular forces holding the molecules together. These are weaker forces. At room temperature, the sulfuric acid molecules have enough thermal energy to easily move around one another. Consequently, sulfuric acid is a liquid at room temperature.

(d) Fe(s). The bonding is metallic. The material is a metal. Iron atoms share valence electrons over vast arrays of nuclei arranged in a dense lattice to optimize the sharing.

(e) $CaCO_3(s)$. Ionic and covalent bonding are present. This is an ionic material. Calcium carbonate consists of Ca^{2+} and CO_3^{2-} ions arranged in a lattice. Carbonate, CO_3^{2-}, is a polyatomic anion with three oxygen atoms covalently bonded to a carbon atom.

(f) C(diamond). Only covalent bonding is present. Diamond is a network covalent solid. It consists of a network (lattice) of carbon atoms held together by covalent bonds between neighboring atoms.

(g) brass – an alloy of mostly copper, zinc and (sometimes) Sn. The bonding is metallic. The material is a metal. It consists of vast arrays of copper, zinc and (sometimes) Sn nuclei with valence electrons shared as a “sea” over the network.

4.2 (a) ethane, C_2H_6, and butane, C_4H_{10}. These materials form a solution. They are both non-polar molecules.

(b) ethanol, C_2H_5OH, and water. They form a solution. They are both polar molecules.

(c) carbon dioxide and carbon tetrachloride, CCl_4. They form a solution, as they are both non-polar molecules.

(d) lithium bromide, LiBr, and water. These form a solution, as LiBr is an ionic material that dissolves in water and splits into ions that are solvated by the polar water molecules.

(e) sodium nitrate, $NaNO_3$, and carbon tetrachloride, CCl_4. These do not form a solution, as carbon tetrachloride is non-polar molecular liquid and the ionic $NaNO_3$ requires a polar solvent to dissolve it and solvate its ions.

4.3 (a) nitric acid, HNO_3. Nitric acid is a strong electrolyte. It is a strong acid - it fully dissociates in water.

(b) lithium hydroxide, LiOH. Lithium hydroxide is a strong electrolyte. It is an ionic material. It is also a strong base. However, since hydroxide is already ionic, reaction with water is not needed to produce an electrolyte solution. In the case of hydroxide, the products of reaction with water are water and hydroxide – there is no effect on the composition of the solution.

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(c) ethanol, C_2H_5OH. Ethanol is a non-electrolyte. It dissolves in water as neutral, solvated ethanol molecules. It is not an acid, though it has an H bonded to an O as do many acids.[6]

(d) potassium iodide, KI. Potassium iodide is a strong electrolyte – another ionic material.

(e) ammonia, NH_3. Ammonia is a weak electrolyte. It dissolves in water as neutral, solvated NH_3 molecules. However, as ammonia is a weak base, some of these molecules react with water to form ammonium, NH_4^+, and hydroxide, OH^-. These ions conduct electricity, giving an electrolyte solution. However, the reaction occurs only to a small extent. It is a weak electrolyte solution.

(f) hypochlorous acid, HOCl. Hypochlorous acid is a weak electrolyte. It dissolves in water as neutral HOCl molecules. However, as HOCl is a weak acid, some of the HOCl molecules react with water and form hypochlorite ion, OCl^-, and hydronium ion, H_3O^+. These ions conduct electricity, gving an electrolyte solution. However, the reaction occurs only to a small extent. It is a weak electrolyte solution.

(g) sodium hyochlorite, NaOCl. Sodium hypochlorite is a strong electrolyte. It is an ionic material – it splits into solvated ions in water. Now, OCl^- is a weak base. As such, to a small extent, it reacts with water to form HOCl and OH^-. This makes the solution slightly basic. However, it simply replaces some (a small amount) of the OCl^- with OH^-. This has no impact on the conductivity – it is still a strong electrolyte solution.

[6] Ethanol is like water with one of the H atoms replaced by an ethyl group, C_2H_5 (think of H-O-H *vs*. H-O-C_2H_5). The carbon atom of the ethyl group bonded to the O atom is not very electronegative. It cannot pull electrons away from the O atom. In contrast, oxo acids (like HOCl) have electrons pulled away from O atoms bonded to H. This makes the O atoms pull electrons away from the H making donation of H^+ occur more readily.

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5. Chemical Equilibrium

5.1 Dynamic equilibrium

We often speak of systems at equilibrium. This is a state where the properties of the system – including chemical composition – do not change with time. As such, it seems as though all chemical reactions have ceased at equilibrium. But this is not so - chemical reactions continue. For every forward reaction, there is a reverse reaction. The rate of a forward reaction generally depends on the concentrations of reactants, while the rate of a reverse reaction depends on the concentrations of products (partial pressures for gas reactions). When these rates are unequal, net reaction proceeds, changing the concentrations of reactants and products such that the rates approach each other. Chemical equilibrium occurs when the rate of forward reaction equals the rate of reverse reaction, and there is no further net reaction even though the forward and reverse reactions continue.

All reactions are equilibrium reactions. However, for some reactions, products are strongly favored. In such a case, the rate of forward reaction exceeds the reverse reaction until almost no reactant remains – the reaction essentially goes to completion. When the reactants are strongly favored, no reaction is observed. As seen in Section 5.3, there are cases between these extremes, reactions where neither reactant nor product concentration is negligible at equilibrium. These reactions are characterized by an *equilibrium constant*, which is neither extremely big nor extremely small.

5.2 Equilibrium constant

At equilibrium, the concentrations of dissolved species, and partial pressures of gases, stop changing. Sets of experiments show that the final equilibrium concentrations of reactants and products (consider reactions of aqueous species, for example) depend on the initial concentrations – i.e., the concentrations at the start of the experiment. However, there is a combination of concentrations that is the same for every experiment performed at the same temperature. The value of this combination of concentrations is called the equilibrium constant.

Careful studies show that the equilibrium constant is actually a combination of reactant and product *activities*, a. For a species A in solution, at low concentration, the activity is approximately equal to the concentration of the species, [A] in mol L^{-1}. For a gas, the activity is approximately the gas partial pressure, p_A in atm. For pure (or almost pure) liquids and solids, the activity is approximately 1. We take these approximations as exact, and henceforth adopt the following definition the activity, a_A, of species A:

$$a_A = \begin{cases} [A] & \text{for A in solution} \\ p_A & \text{for A in the gas phase} \\ 1 & \text{for pure liquid or solid A} \end{cases} \qquad 5.1$$

The units of [A] and p_A are mol L^{-1} and atm, respectively. However, these units are dropped from activity; activity is dimensionless because an activity is a concentration (or a pressure) divided by a standard concentration (or pressure) of 1. The *standard conditions* for chemical reactions (as defined in thermochemical studies – see Chapter 6) are 1 mol L^{-1} concentration of dissolved species and 1 atm partial pressure for gases. Thus, the activity of an aqueous species is really [A] / (1 mol L^{-1}). It is the concentration relative to its value under standard conditions, 1 mol L^{-1}. Further, the activities of pure liquids and solids are taken to be 1, so these species do not appear in equilibrium constant expressions (see below).

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The equilibrium constant, K, for the reaction,

$$c_A\,A + c_B\,B \rightleftharpoons c_Y\,Y + c_Z\,Z$$

is given by

$$K = \frac{a_Y^{c_Y} a_Z^{c_Z}}{a_A^{c_A} a_B^{c_B}} \qquad 5.2$$

where a_A, a_B , a_Y and a_Z are the activities of A, B, Y and Z under equilibrium conditions, and c_A, c_B, c_Y and c_Z are the stoichiometric coefficients of A, B, Y and Z, respectively. Moreover, any combination of a_A, a_B , a_Y and a_Z satisfying this equation constitutes equilibrium conditions. The equilibrium constant depends only temperature.

For more general reactions, there are additional $a_X^{c_X}$ factors in the numerator, if there are additional products; and in the denominator, if there are additional reactants. Examples are provided as follows:

Reaction	Equilibrium constant
$Br_2(g) + Cl_2(g) \rightleftharpoons 2\,BrCl(g)$	$K = \dfrac{p_{BrCl}^2}{p_{Br_2}\,p_{Cl_2}}$
$H_2(g) + I_2(s) \rightleftharpoons 2\,HI(g)$	$K = \dfrac{p_{HI}^2}{p_{H_2}}$
$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$	$K = \dfrac{p_{NH_3}^2}{p_{N_2}\,p_{H_2}^3}$
$CaO(s) + H_2O(l) \rightleftharpoons Ca^{2+}(aq) + 2\,OH^-(aq)$	$K = [Ca^{2+}][OH^-]^2$
$HClO(aq) + H_2O(l) \rightleftharpoons ClO^-(aq) + H_3O^+(aq)$	$K = K_a = \dfrac{[H_3O^+][ClO^-]}{[HClO]}$ or $\dfrac{[H^+][ClO^-]}{[HClO]}$
$NaF(s) \rightleftharpoons Na^+(aq) + F^-(aq)$	$K = K_{sp} = [Na^+][F^-]$

The last two examples show named equilibrium constants, K_a and K_{sp}, the acid ionization constant and the solubility product, respectively.

In general, acids are characterized by the acid ionization constant,

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}, \qquad 5.3$$

the equilibrium constant for the acid ionization reaction,

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)\,.$$

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Bases are characterized by the base ionization constant,

$$K_b = \frac{[\mathrm{HB}^+][\mathrm{OH}^-]}{[\mathrm{B}]}, \qquad 5.4$$

the equilibrium constant for the base ionization reaction,

$$\mathrm{B(aq)} + \mathrm{H_2O(l)} \rightleftharpoons \mathrm{HB^+(aq)} + \mathrm{OH^-(aq)}\ .$$

Salts are characterized by the solubility product,

$$K_{sp} = [\mathrm{M}^{c+}]^a[\mathrm{X}^{a-}]^c \qquad 5.5$$

the equilibrium constant for the dissolution of the salt,

$$\mathrm{M}_a\mathrm{X}_c\mathrm{(s)} \rightleftharpoons a\ \mathrm{M^{c+}(aq)} + c\ \mathrm{X^{a-}(aq)}\ .$$

Example 5.1: Write down the equilibrium constant, *K*, for each of the following reactions.

(a) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
(b) $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$
(c) $NO(g) + O_3(g) \rightleftharpoons NO_2(g) + O_2(g)$
(d) $Cl_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + Cl^-(aq) + HClO(aq)$
(e) $Cl_2(g) + 2\ Fe^{2+}(aq) \rightleftharpoons 2\ Cl^-(aq) + 2\ Fe^{3+}(aq)$

Approach: Look for gases or aqueous species. The equilibrium constant is constructed from the partial pressures of gases and the concentrations of aqueous species, raised to the associated stoichiometric coefficients in the balanced chemical reaction. Products appear in the numerator, while reactants appear in the denominator.

(a) $K = p_{\mathrm{CO_2}}$

The equilibrium constant is just the partial pressure of carbon dioxide. *K* here is the vapour pressure of solid carbon dioxide. In an enclosed space, $CO_2(s)$ will sublimate until the partial pressure of $CO_2(g)$ equals *K* and the solid and gas are in equilibrium.

(b) $K = p_{\mathrm{NH_3}}\, p_{\mathrm{H_2S}}$

$NH_4HS(s)$ does not appear in the equilibrium constant because it is a pure solid. All solids and liquids you will encounter in chemical reactions are pure (water, in aqueous reactions, is treated as though it were pure).

(c) $K = \dfrac{p_{\mathrm{NO_2}}\, p_{\mathrm{O_2}}}{p_{\mathrm{NO}}\, p_{\mathrm{O_3}}}$

(d) $K = \dfrac{[\mathrm{H^+}][\mathrm{Cl^-}][\mathrm{HClO}]}{[\mathrm{Cl_2}]}$

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$H_2O(l)$ does not appear. It is treated as a pure liquid. The concentration of pure water, $[H_2O]$, is about 56 mol L^{-1}. Changes in this value caused by dissolved aqueous species are small, and neglected.

(e) $K = \dfrac{[Cl^-]^2[Fe^{3+}]^2}{p_{Cl_2}[Fe^{2+}]^2}$

This reaction has a gas and three aqueous species. In this case, the equilibrium constant is constructed from a partial pressure and three concentrations. Note the stoichiometric coefficients in the exponents.

An equilibrium constant is evaluated by preparing an equilibrium mixture of reactants and products, then measuring the resulting concentrations and partial pressures. The value of *K* obtained does not depend on how the mixture was prepared. It depends only on temperature. Thus, temperature is generally noted when an equilibrium constant is given.

Once an equilibrium constant is known, an unknown concentration or partial pressure can be determined in an equilibrium mixture – if the other concentrations and partial pressures are known. For example, the equilibrium constant for the combustion of sulfur dioxide at 350°C is $K = 5.60\times10^4$.

$$2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$$

If the partial pressures of O_2 and SO_3 are both 0.500 atm, then the partial pressure of SO_2 is given by substituting all known quantities into the equilibrium constant equation and solving for p_{SO_2}. Specifically,

$$K = \frac{p_{SO_3}^2}{p_{SO_2}^2 p_{O_2}} = \frac{0.500^2}{p_{SO_2}^2\, 0.500} = 5.60\times10^4$$

from which we get

$$p_{SO_2}^2 = \frac{0.500^2}{5.60\times10^4\times0.500} = 8.92_9\times10^{-6}$$

and

$$p_{SO_2} = 2.99\times10^{-3}\ \text{atm}$$

Example 5.2: What is the concentration of OH^- in an equilibrium solution with $[CO_3^{2-}] = [HCO_3^-] = 1.0$ mol L^{-1}, given the following equilibrium constant?

$$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq) \qquad K = 2.1\times10^{-4}$$

Approach: Write down the equilibrium constant expression. Substitute the known concentrations. Solve for the unknown concentration.

$$K = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]} = \frac{1.0\times[OH^-]}{1.0} = [OH^-] = 2.1\times10^{-4}$$

Therefore, $[OH^-] = 2.1\times10^{-4}$ mol L^{-1}.

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Suppose we have a table of equilibrium constants for a set of reactions that does not include a reaction of interest. If the reaction of interest can be expressed as a combination of the tabulated reactions, then the equilibrium constant can be expressed as a product or quotient of the tabulated equilibrium constants.

The simplest case is when the reaction of interest is the reverse of a tabulated reaction. Considering the above definition of the equilibrium constant in terms of activities, one can deduce

$$K_{\text{reverse}} = \frac{1}{K_{\text{forward}}}$$

This follows because the reactants of the reverse reaction are the products of the forward reaction, and vice versa. If the reaction of interest is 2× a tabulated reaction, then the equilibrium constant of interest is the square of the tabulated equilibrium constant. This follows because all the stoichiometric coefficients are doubled if a reaction is doubled. To see this, write down expressions for K_1 and K_2 – the equilibrium constants for the following reactions - and see that $K_2 = K_1^2$.

Rxn 1	A → B + C	K_1
Rxn 2	2A → 2 B + 2 C	K_2

In general, the equilibrium constant of interest is a product of tabulated equilibrium constants, each raised to a power - the coefficient of the tabulated reaction in the combination required to reproduce the reaction of interest.

$$K = K_1^{n_1} K_2^{n_2} K_3^{n_3} \cdots, \qquad 5.6$$

where

$$\text{Reaction of interest} = \sum_i n_i \left(i\text{th tabulated reaction} \right),$$

n_i is negative for tabulated reactions that need to be reversed.

5.3 The reaction quotient

The above expressions for the equilibrium constant only hold under equilibrium conditions – i.e. the concentrations and partial pressures are for an equilibrium reaction mixture. When a reaction mixture is not at equilibrium, combining the concentrations and partial pressures as they are in the equilibrium constant gives the *reaction quotient*, Q. The reaction quotient can be computed under equilibrium or non-equilibrium conditions. If $Q = K$, then the system is at equilibrium. Otherwise, $Q \neq K$ and there is net forward or reverse reaction.

If $Q < K$, there is net forward reaction. Net forward reaction depletes reactants, reducing the denominator of Q. At the same time, product concentrations/partial pressures increase, increasing the numerator of Q. The net effect is an increase in Q. Net forward reaction continues until $Q = K$.

If $Q > K$, there is net reverse reaction. Net reverse reaction increases reactant concentrations/partial pressures, increasing the denominator of Q. At the same time, product is depleted, decreasing the numerator of Q. The net effect is a decrease in Q. Net reverse reaction continues until $Q = K$.

Example 5.3: Consider each of the following reaction mixtures. Is the mixture at equilibrium, or is there net forward or reverse reaction?

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(a) Solid calcium carbonate and calcium oxide at 700°C are in a vessel with 0.1 atm partial pressure carbon dioxide. At 700°C, K = 0.056 for the decomposition of $CaCO_3$(s) into CaO(s) and CO_2(g).

(b) Consider the following equilibrium:

$$Cu^{2+}(aq) + 4\ NH_3(aq) \rightleftharpoons Cu(NH_3)_4^{2+}(aq) \qquad K = 6.7\times10^{12} \text{ at } 25°C$$

Suppose $[Cu^{2+}] = [Cu(NH_3)_4^{2+}] = 1.0$ mol L^{-1}, while $[NH_3] = 5.0\times10^{-4}$ mol L^{-1} at 25°C.

(c) Consider the following equilibrium:

$$SnO_2(s) + 2\ CO(g) \rightleftharpoons Sn(s) + 2\ CO_2(g) \qquad K = 11 \text{ atm at some } T$$

Suppose the partial pressure of CO_2 is 3 atm, while that of CO is 1 atm at the required T.

Approach: Compute Q and compare it with K.

(a) $Q = p_{CO_2} = 0.1 > 0.056$. Therefore, there is net reverse reaction. At this partial pressure, CO_2 in the gas phase combines with available CaO(s) to form $CaCO_3$(s).

(b) Here,

$$Q = \frac{[Cu(NH_3)_4^{2+}]}{[Cu^{2+}][NH_3]^4} = \frac{1.0}{1.0\left(5.0\times10^{-4}\right)^4} = 1.6\times10^{13} > K$$

Again, $Q > K$ and there is net reverse reaction.

(c) Here,

$$Q = \frac{p_{CO_2}^2}{p_{CO}^2} = \frac{3^2}{1} = 9 < 11$$

In this case, $Q < K$ and there is net forward reaction.

5.4 Shift in equilibrium – le Châtelier's principle

Non-equilibrium conditions can result, starting with an equilibrium mixture, by adding or removing a reactant or a product. For example, if we have an equilibrium solution with the reaction

$$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq) \qquad K = 2.1\times10^{-4}$$

and we dissolve a small amount of NaOH(s) into the solution, a non-equilibrium initial state results. Increasing the concentration of hydroxide makes Q larger (a factor in the numerator is increased). Since Q is now larger than K, there is net reverse reaction – product concentrations decrease, while the reactant concentration increases. Net reaction continues until $Q = K$ is restored. When equilibrium is re-established, the hydroxide concentration is smaller than it was immediately after the added NaOH(s) dissolves, but larger than it was before the NaOH(s) was added.

We can also add a small amount of concentrated sulfuric acid (so as not to significantly change the total volume) to the solution. The added strong acid reacts completely with OH^- present, and reduces the hydroxide concentration. As such, it removes a product from the chemical reaction. This has the effect of making Q smaller. Net forward reaction results until equilibrium is re-established.

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Whether we add or remove product, the net reaction acts to reduce the change imposed on the system – the addition or removal of some hydroxide. The hydroxide concentration moves back towards (but does not reach[7]) its value before the change was imposed. This is a general principle called *le Châtelier's principle*:

> When a change is imposed on an equilibrium system, the change is followed by net reaction that reduces the change.

If a reactant is added – in the above example, some $Na_2CO_3(s)$ can be dissolved in the solution - le Châtelier's principle tells us that there will be net forward reaction consuming some of the added CO_3^{2-}. This is consistent with reaction quotient considerations. Note that the principle only applies to changes in activity. Changes in the amount of a pure solid or liquid do not affect an equilibrium. Thus, changing the amount of $CaCO_3(s)$ or $CaO(s)$ in an equilibrium mixture with $CO_2(g)$ does not affect the partial pressure of the gas.
Le Châtelier's principle also applies to the effect of changing temperature. The equilibrium constant generally depends upon temperature. Thermodynamics shows that K increases or decreases with temperature in accord with the sign of ΔH (change in enthalpy – see more in Chapter 6). Specifically, K increases with T for endothermic reactions ($\Delta H > 0$), and decreases with T for exothermic reactions ($\Delta H < 0$). If K increases with T, as it does for endothermic reactions, products will be favored at higher T. Thus, increasing T for an endothermic reaction causes net forward reaction until the new (product favored) equilibrium is established. This is consistent with le Châtelier's principle in the following sense: Increasing T makes more heat "available". A net forward endothermic reaction consumes some of this additional heat. In general, the endothermic direction of reaction (the reverse reaction, in the case of an exothermic reaction) is favored with increasing temperature. Thus, reactants are favored at high T in the case of an exothermic reaction.

Example 5.4: Predict the direction each of the following equilibriums shifts when the indicated changes are imposed.

$$NO(g) + O_3(g) \rightleftharpoons NO_2(g) + O_2(g) \qquad \Delta H^\circ = -200.8 \text{ kJ mol}^{-1}$$

(a) The O_3 partial pressure is increased
(b) Some NO_2 is removed from the reaction mixture
(c) The reaction mixture is transferred to a vessel with twice the volume
(d) Temperature is increased

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g) \qquad \Delta H^\circ = 176.2 \text{ kJ mol}^{-1}$$

(e) The HCl partial pressure is increased
(f) Some solid NH_4Cl is added to the mixture
(g) Temperature is decreased

Approach: Is a reactant or product activity changed – i.e., a partial pressure or concentration? If so, apply le Châtelier's principle. If temperature changes, note the sign of the enthalpy of reaction.

(a) O_3 is a reactant. Increasing its partial pressure results in net forward reaction – to consume some of the added O_3.

[7] In the case of an equilibrium with just one activity – for example, the decomposition of $CaCO_3(s)$ – if the activity is changed, it will return to original value. Otherwise, shifts in other activities will prevent a changed activity from returning to its original value.

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(b) NO_2 is a product. Removing it from the reaction mixture results in net forward reaction. This is a common means of improving product yield. Removing the product from a reaction mixture drives the reaction in the forward direction.

(c) Doubling the volume of the vessel reduces all partial pressures to 1/2 their initial values. However, this does not change the reaction quotient because there are two partial pressure factors in both the numerator and denominator of *Q* and they have the same exponents. Decreasing all partial pressures by the same factor thus has no affect on the reaction quotient. Therefore, the system is still at equilibrium. This is consistent with le Châtelier's principle, which says that the reaction will shift to the side with more moles of gas so as to counter the reduction in total pressure caused by the increase in volume. However, neither forward nor reverse reaction increases the moles of gas. Therefore, the mixture remains at equilibrium.

(d) The reaction is exothermic. Increasing temperature favors reactants (the endothermic direction of reaction) – i.e., there is net reverse reaction.

(e) HCl is a product. Increasing its partial pressure results in net reverse reaction.

(f) $NH_4Cl(s)$ is a pure solid. Adding it or removing some of it from the reaction mixture has no effect on the equilibrium as long as some of the solid remains. No net reaction results.

(g) The reaction is endothermic. Decreasing temperature favors reactant (the exothermic direction of reaction) – i.e., there is net reverse reaction.

The equilibrium constant allows quantitative determination of final equilibrium conditions. Such determinations are carried out by constructing an *ICE* table to relate equilibrium activities to the extent of reaction. This begins with the balanced chemical reaction. Below that are three rows. The first row shows the *initial* (I), non-equilibrium concentrations/partial pressures of reactants and products. The second row expresses the *changes* (*C*) in these concentrations (that occur upon achieving equilibrium) in terms of the unknown extent of reaction. This row accounts for the stoichiometric coefficients in the reaction. The third row is the sum of the first two rows. It gives the concentrations/partial pressures at *equilibrium* (E). For example, consider the reaction of water vapor and carbon monoxide, both initially at 1.00 atm partial pressure. $K = 0.63$ for this reaction at a certain *T*.

	$H_2O(g)$	+	$CO(g)$	$\rightleftharpoons$	$H_2(g)$	+	$CO_2(g)$
Initial	1.00		1.00		0		0
Change	$-x$		$-x$		$+x$		$+x$
Equilibrium	$1.00 - x$		$1.00 - x$		x		x

Here, *x* is the *extent of reaction*, appearing as a change in partial pressure. If one of the species had a stoichiometric coefficient greater than 1, it would multiply *x* in the associated cell. Having expressed the equilibrium concentrations in terms of the unknown *x*, we construct the equilibrium constant equation in terms of *x*.

$$K = \left(\frac{p_{H_2} p_{CO_2}}{p_{H_2O} p_{CO}} \right)_{eqm} = \frac{x\,x}{(1.00 - x)(1.00 - x)} = 0.63$$

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from which we get

$$\left(\frac{x}{(1.00-x)}\right)^2 = 0.63$$

$$\frac{x}{(1.00-x)} = \sqrt{0.63} = 0.79_4$$

$$x = 0.79_4(1.00-x)$$

$$x = \frac{0.79_4}{1.79_4} = 0.44_3$$

With x = 0.44_3, we can get the equilibrium partial pressures – the bottom row in the ICE table. Specifically,

$$p_{H_2O} = p_{CO} = 1.00 - x = 0.56 \text{ atm}$$

and

$$p_{H_2} = p_{CO_2} = x = 0.44 \text{ atm}$$

The above equation for x is easily solved because the right side of the first line is a perfect square (resulting from the reaction stoichiometry and because we started with equal partial pressures of H_2O and CO). For a simple equilibrium, a linear equation might result directly. However, in general, a polynomial equation is obtained. For many important reactions this is a quadratic reaction that can be solved approximately, or exactly using the formula for the solution of a quadratic equation – see below.

Example 5.5: Consider the gas phase equilibrium of hydrogen and iodine,

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g) \qquad K = 33 \text{ at some temperature, } T$$

(a) Suppose a vessel is filled to 0.100 atm of both H_2 and I_2. What is the partial pressure of HI when equilibrium is established at *T*?

(b) Suppose the vessel is filled to 1.00 atm of H_2 and 0.100 atm of I_2. What is the partial pressure of HI when equilibrium is established at *T*?

Approach: Construct an ICE table. Substitute into the equilibrium constant equation and solve for the unknown extent of reaction. Evaluate the equilibrium partial pressures in the third row of the ICE table.

(a)

	H_2	+	I_2	$\rightleftharpoons$	2 HI
Initial	0.100		0.100		0
Change	$-x$		$-x$		$+2x$
Equilibrium	$0.100 - x$		$0.100 - x$		$2x$

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Substitute the equilibrium partial pressures into the equilibrium constant equation.

$$K = \frac{p_{\mathrm{HI}}^2}{p_{\mathrm{H_2}} p_{\mathrm{I_2}}} = \frac{(2x)^2}{(0.100 - x)(0.100 - x)} = 33$$

This equation simplifies.

$$\left(\frac{2x}{(0.100 - x)}\right)^2 = 33$$

$$\frac{2x}{(0.100 - x)} = \sqrt{33} = 5.7_4$$

$$2x = 5.7_4(0.100 - x)$$

$$x = \frac{0.57_4}{7.7_4} = 0.074_2$$

Thus, the final equilibrium partial pressure of HI is

$$p_{\mathrm{HI}} = 2x = 2 \times 0.074_2 = 0.148 \text{ atm}$$

(b)

	H_2	+	I_2	$\rightleftharpoons$	2 HI
Initial	1.00		0.100		0
Change	$-x$		$-x$		$+2x$
Equilibrium	$1.00 - x$		$0.100 - x$		$2x$

Substitute the equilibrium partial pressures into the equilibrium constant equation.

$$K = \frac{p_{\mathrm{HI}}^2}{p_{\mathrm{H_2}} p_{\mathrm{I_2}}} = \frac{(2x)^2}{(1.00 - x)(0.100 - x)} = 33$$

This equation requires solution of a quadratic equation.

$$\frac{4x^2}{(0.100 - 1.10x + x^2)} = 33$$

$$4x^2 = 33(0.100 - 1.10x + x^2)$$

$$29x^2 - 36._3 x + 3.3 = 0$$

$$ax^2 + bx + c = 0$$

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The solution of this quadratic equation is

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$= \frac{36._3 \pm \sqrt{36._3{}^2 - 4 \times 29 \times 3.3}}{2 \times 29}$$

$$= \begin{cases} 1.1_5 \\ 0.098_7 \end{cases}$$

We get two solutions for x. However, only one of them is admissible. The choice of $x = 1.1_5$ yields negative equilibrium partial pressures for H_2 and I_2. It is an inadmissible solution. Thus,

$$x = 0.098_7$$

is the correct solution, and

$$p_{HI} = 2x = 2 \times 0.098_7 = 0.197 \text{ atm}$$

5.5 Solubility

When the equilibrium corresponds to the dissolution of an ionic solid (a salt), the equilibrium constant is called a solubility product, K_{sp}. The K_{sp} value determines the concentration of the ions in equilibrium with the solid. If excess salt is added to pure water, the resulting cation and anion concentrations are related by the stoichiometric coefficients in the dissolution process.
For example, the equilibrium constant of the reaction,

$$Ba_3(PO_4)_2(s) \rightleftharpoons 3\ Ba^{2+}(aq) + 2\ PO_4^{3-}(aq)$$

is K_{sp} for $Ba_3(PO_4)_2(s)$. The overall concentration of the salt is called the *molar solubility*. Thus, the molar solubility of $Ba_3(PO_4)_2(s)$ is 1/3 the barium concentration, or 1/2 the phosphate concentration at equilibrium, as per the stoichiometry of the K_{sp} expression.

Example 5.6: Determine the molar solubilities of the following salts at 25°C. (K_{sp} values are for 25°C.)

(a) $BaCO_3$ $K_{sp} = 2.6 \times 10^{-9}$
(b) CaF_2 $K_{sp} = 3.45 \times 10^{-11}$

Approach: Construct an ICE table for the addition of excess solid salt to pure water. Solve for the extent of reaction and evaluate the equilibrium concentrations.

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(a)

	$BaCO_3(s)$	$\rightleftharpoons$	$Ba^{2+}(aq)$	+	$CO_3^{2-}(aq)$
Initial			0		0
Change			$+x$		$+x$
Equilibrium			x		x

Substitute the equilibrium ion concentrations into the solubility product equation.

$$K_{sp} = [Ba^{2+}][CO_3^{2-}] = x^2 = 2.6 \times 10^{-9}$$

which gives

$$x = \sqrt{2.6 \times 10^{-9}} = 5.1 \times 10^{-5}$$

At equilibrium,

$[Ba^{2+}] = [CO_3^{2-}] = 5.1 \times 10^{-5}$ mol L^{-1}

In this case, the molar solubility is just the barium or carbonate concentration, i.e., 5.1×10^{-5} mol L^{-1}.

(b)

	$CaF_2(s)$	$\rightleftharpoons$	$Ca^{2+}(aq)$	+	$2\ F^-(aq)$
Initial			0		0
Change			$+x$		$+2\,x$
Equilibrium			x		$2\,x$

Substitute the equilibrium ion concentrations into the solubility product equation.

$$K_{sp} = [Ca^{2+}][F^-]^2 = x(2x)^2 = 3.45 \times 10^{-11}$$

which gives

$$x = \left(\frac{3.45 \times 10^{-11}}{4}\right)^{1/3} = 2.05 \times 10^{-4}$$

At equilibrium,

$[Ca^{2+}] = x = 2.05 \times 10^{-4}$ mol L^{-1}
$[F^-] = 2\,x = 4.10 \times 10^{-4}$ mol L^{-1}

In this case, the molar solubility is just the calcium concentration or 1/2 the fluoride concentration, i.e. 2.05×10^{-4} mol L^{-1}.

If we attempt to dissolve a salt in a solution that already contains a solvated ion in common with an ion in the salt, less of the salt will dissolve. This is called the *common ion effect*. For example,

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consider dissolving $CaCO_3(s)$ in a saturated solution of $CaF_2(s)$. K_{sp} = 3.36 × 10^{-9} for calcium carbonate at 25°C. Construct the ICE table for this process.

	$CaCO_3(s)$	$\rightleftharpoons$	$Ca^{2+}(aq)$	+	$CO_3^{2-}(aq)$
Initial			2.05×10^{-4}		0
Change			$+x$		$+x$
Equilibrium			$2.05 \times 10^{-4} + x$		x

Note that the initial concentration of calcium is not zero – it is the calcium concentration of a solution saturated in calcium fluoride.

Substitute the equilibrium ion concentrations into the solubility product equation.

$$K_{sp} = [Ca^{2+}][CO_3^{2-}] = \left(2.05\times10^{-4} + x\right)x = 3.36\times10^{-9}$$

which gives

$$x^2 + 2.05\times10^{-4}x - 3.36\times10^{-9} = 0$$

Using the quadratic formula,

$$\begin{aligned} x &= \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \\ &= \frac{-2.05\times10^{-4} \pm \sqrt{\left(2.05\times10^{-4}\right)^2 + 4\times3.36\times10^{-9}}}{2} \\ &= \begin{cases} 1.52_6 \times10^{-5} \\ -2.20_3 \times10^{-4} \end{cases} \end{aligned}$$

The negative solution produces a negative carbonate concentration at equilibrium and is therefore inadmissible.

At equilibrium,

$[Ca^{2+}]$ = 2.05 × 10^{-4} + 1.53 × 10^{-5} mol L^{-1} = 2.20 × 10^{-4} mol L^{-1}
$[CO_3^{2-}]$ = 1.53 × 10^{-5} mol L^{-1}

If the initial calcium concentration had been zero, K_{sp} equation would have given

$$K_{sp} = [Ca^{2+}][CO_3^{2-}] = x^2 = 3.36\times10^{-9}$$
$$x = \sqrt{3.36\times10^{-9}} = 5.80\times10^{-5}$$

In the absence of an initial calcium ion concentration, the extent of reaction (dissolution of calcium carbonate) is larger; 5.80 × 10^{-5} versus 1.53 × 10^{-5}. If the original solution contained neither calcium nor carbonate ions (e.g. a potassium bromide solution), then the dissolution of calcium carbonate would be unaffected.[1]

[1] Actually, the presence of ions already in solution does have an affect on the dissolution of $CaCO_3$. This is because concentrations are not good approximations for ions in solutions. We

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Example 5.7: What is the extent of dissolution of AgCl(s) (K_{sp} = 1.8 × 10^{-10}) in the following solutions when equilibrium is established? What are the equilibrium ion concentrations?

(a) 1.0 × 10^{-3} mol L^{-1} KBr(aq)
(b) 1.0 × 10^{-3} mol L^{-1} KCl(aq)

Approach: Construct ICE tables. Look for common ions. Substitute equilibrium concentrations into the solubility product and solve for the extent of reaction (extent of dissolution in this case).

In the first case, there are no initial common ions. In the second case, there are chloride ions already present.

(a) Initially, there are potassium and bromide ions present in solution, but no lead or chloride.

	AgCl(s)	$\rightleftharpoons$	**Ag^+(aq)**	**+**	**Cl^-(aq)**
Initial			0		0
Change			+ x		+ x
Equilibrium			x		x

Substitute the equilibrium ion concentrations into the solubility product equation.

$$K_{sp} = [Ag^+][Cl^-] = x^2 = 1.8\times10^{-10}$$

which gives the extent of dissolution,

$$x = \left(1.8\times10^{-10}\right)^{1/2} = 1.3_4\times10^{-5}\ \text{mol L}^{-1}$$

At equilibrium,

$[Ag^+]$ = $[Cl^-]$ = x = 1.3 × 10^{-5} mol L^{-1}

(b) Initially, there is 1.0 × 10^{-3} mol L^{-1} Cl^-(aq) – a common ion – present in solution.

	AgCl(s)	$\rightleftharpoons$	**Ag^+(aq)**	**+**	**Cl^-(aq)**
Initial			0		1.0 × 10^{-3}
Change			+ x		+ x
Equilibrium			x		1.0 × 10^{-3} + x

Substitute the equilibrium ion concentrations into the solubility product equation.

$$K_{sp} = [Ag^+][Cl^-] = \left(1.0\times10^{-3} + x\right)x = 1.8\times10^{-10}$$

---

must include a correction factor for each ion – the activity coefficient. The correction factor is different if there are already ions in solution, however we will not take this into account in Chem 1A03/1E03. A common ion has a much greater effect on solubility and we will take it into account.

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which gives

$$x^2 + 1.0\times10^{-3}x - 1.8\times10^{-10} = 0$$

Using the quadratic formula,

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$= \frac{-1.0\times10^{-3} \pm \sqrt{\left(1.0\times10^{-3}\right)^2 + 4\times1.8\times10^{-10}}}{2}$$

$$= \begin{cases} 1.8_0 \times 10^{-7} \\ -1.0_0 \times 10^{-3} \end{cases}$$

The negative solution produces a negative silver concentration at equilibrium and is therefore inadmissible. The extent of dissolution is therefore

$$x = 1.8 \times 10^{-7} \text{ mol L}^{-1}$$

At equilibrium,

$$[Ag^+] = 1.8 \times 10^{-7} \text{ mol L}^{-1}$$
$$[Cl^-] = 1.0 \times 10^{-3} + 1.8_0 \times 10^{-7} \text{ mol L}^{-1} = 1.0 \times 10^{-3} \text{ mol L}^{-1}$$

In this example, the extent of dissolution is reduced almost 100-fold when 1.0×10^{-3} mol L^{-1} is *already* present in solution. Note that the chloride ion concentration changes a negligible amount.

5.6 Acid base equilibrium

When the equilibrium corresponds to the dissociation an acid, HA(aq), into H^+(aq) and A^-(aq), the equilibrium constant is called K_a. K_a determines the extent of dissociation of the acid and the resulting H^+ concentration (and pH). Note that H^+ is actually transferred to water making H_3O^+(aq). H^+(aq) is a convenient shorthand for H_3O^+(aq), that eliminates the need to carry an extra water on the reactant side of the equation.

Strong acids dissociate completely and do not require an equilibrium analysis.

Consider the dissociation of ethanoic acid, a *weak* acid.

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq) \qquad K_a = 1.8 \times 10^{-5}$$

The equilibrium concentrations for a 1.00 mol L^{-1} ethanoic acid solution are determined in the usual way, starting with an ICE table.

	CH_3COOH(aq)	**+**	**H_2O(l)**	$\rightleftharpoons$	**CH_3COO^-(aq)**	**+**	**H_3O^+(aq)**
Initial	1.00				0		0
Change	$-x$				$+x$		$+x$
Equilibrium	$1.00 - x$				x		x

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Substitute the equilibrium concentrations into the equilibrium constant expression. Note that the activity of $H_2O(l)$ is 1 and does not appear in the K_a expression; pure liquids and solids do not appear in K expressions.

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = \frac{x^2}{1.00 - x} = 1.8 \times 10^{-5}$$

This equation can be rearranged to quadratic form,

$$x^2 + 1.8 \times 10^{-5} x - 1.8 \times 10^{-5} \times 1.00 = 0$$

with solution,

$$x = \frac{-1.8 \times 10^{-5} \pm \sqrt{\left(1.8 \times 10^{-5}\right)^2 + 4 \times 1.8 \times 10^{-5} \times 1.00}}{2}$$

$$= \begin{cases} 4.2_3 \times 10^{-3} \\ -4.2_5 \times 10^{-3} \end{cases}$$

Only the positive solution is admissible. Therefore, the extent of dissociation is 4.2×10^{-3} and the equilibrium concentrations are given by

$[CH_3COOH] = 1.00 - x = 0.99_6$ mol L^{-1} = 1.00 mol L^{-1}
$[CH_3COO^-] = [H_3O^+] = x = 4.2 \times 10^{-3}$ mol L^{-1}

Note that the extent of reaction is very small compared to the initial concentration of CH_3COOH. In fact, the final concentration of CH_3COOH is the same within the accuracy of the given data. This suggests an approximation method for solving the equilibrium equation.

Neglect x (i.e., assume x is small and negligible) in the denominator of the above expression for K_a; specifically, let $1.00 - x \approx 1.00$ (an excellent approximation in the current example). The equilibrium equation simplifies to

$$\frac{x^2}{1.00} = 1.8 \times 10^{-5}$$

$$x = \sqrt{1.8 \times 10^{-5} \times 1.00} = 4.2_4 \times 10^{-3}$$

The approximation gives the same extent of reaction as the quadratic formula, to within the accuracy of the given data.

Example 5.8: Use the approximation,

$$[HA]_{eqm} = [HA]_{initial} - x \approx [HA]_{initial}$$

to determine the pH of 2.00 mol L^{-1} solutions of

(a) HF $K_a = 6.3 \times 10^{-4}$
(b) HCN $K_a = 6.2 \times 10^{-10}$

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(c) H_2S $K_{a1} = 8.9 \times 10^{-8}$

Approach: Set up ICE table as above. Substitute equilibrium concentrations into the expression for the equilibrium constant. Determine *x* using the approximation method.

(a)

	HF(aq)	**+**	**H_2O(l)**	$\rightleftharpoons$	**F^-(aq)**	**+**	**H_3O^+(aq)**
Initial	2.00				0		0
Change	$-x$				$+x$		$+x$
Equilibrium	$2.00 - x$				x		x

Substitute the equilibrium concentrations into the equilibrium constant.

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = \frac{x^2}{2.00 - x} = 6.3 \times 10^{-4}$$

Upon invoking the approximation, $2.00 - x \approx 2.00$, this equation simplifies to

$$\frac{x^2}{2.00} = 6.3 \times 10^{-4}$$

$$x = \sqrt{6.3 \times 10^{-4} \times 2.00} = 3.5_5 \times 10^{-2}$$

Therefore,

$$[H_3O^+] = x = 3.5_5 \times 10^{-2} \text{ mol L}^{-1}$$

$$pH = -\log_{10}([H_3O^+]) = -\log_{10}(3.5_5 \times 10^{-2}) = 1.45$$

(b) The calculation is the same as in part (a) except that $K_a = 6.2 \times 10^{-10}$. Thus, the extent of reaction at equilibrium is given by

$$\frac{x^2}{2.00} = 6.2 \times 10^{-10}$$

$$x = \sqrt{6.2 \times 10^{-10} \times 2.00} = 3.5_2 \times 10^{-5}$$

Therefore,

$$[H_3O^+] = x = 3.5_2 \times 10^{-5} \text{ mol L}^{-1}$$

$$pH = -\log_{10}([H_3O^+]) = -\log_{10}(3.5_2 \times 10^{-5}) = 4.45$$

(c) Here, we have

$$x = \sqrt{8.9 \times 10^{-8} \times 2.00} = 4.2_2 \times 10^{-4}$$

and

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$$[H_3O^+] = x = 4.2_2 \times 10^{-4} \text{ mol L}^{-1}$$

$$pH = -\log_{10}([H_3O^+]) = -\log_{10}(4.2_2 \times 10^{-4}) = 3.37$$

How do we know when the acid is sufficiently concentrated to permit use of the above approximation? There is a rule based on the requirement that x be no more than $[HA]_{initial}/10$. Since $x \cong \sqrt{K_a[\text{HA}]_{\text{initial}}}$ (the approximation is good enough for this purpose), the rule takes the form,

$$\sqrt{K_a[\text{HA}]_{\text{initial}}} < \frac{[\text{HA}]_{\text{initial}}}{10}$$

or

$$\sqrt{\frac{[\text{HA}]_{\text{initial}}}{K_a}} > 10$$

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} > 100$$

If the initial HA concentration is too small (<100 K_a), we must solve the quadratic equation.

Example 5.9: What is the pH of a 1.00×10^{-3} mol L^{-1} solution of formic acid, HCOOH(aq) ($K_a = 1.8 \times 10^{-4}$)?

Approach: Set up the ICE table. Substitute equilibrium concentrations into expression for the equilibrium constant. Solve for the extent of reaction. Determine $[H_3O^+]$ and pH.

In this case, the initial HA concentration is less than 6 times bigger than K_a. We must solve the quadratic equation.

	HCOOH(aq)	**+**	**H_2O(l)**	$\rightleftharpoons$	**$HCOO^-$(aq)**	**+**	**H_3O^+(aq)**
Initial	1.00×10^{-3}				0		0
Change	$-x$				$+x$		$+x$
Equilibrium	$1.00 \times 10^{-3} - x$				x		x

Substitute the equilibrium concentrations into the equilibrium constant.

$$K_a = \frac{[H_3O^+][HCOO^-]}{[HCOOH]} = \frac{x^2}{1.00\times10^{-3} - x} = 1.8\times10^{-4}$$

This equation is rearranged to quadratic form,

$$x^2 + 1.8\times10^{-4}x - 1.8\times10^{-4}\times1.00\times10^{-3} = 0$$

with solution,

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$$x = \frac{-1.8\times10^{-4} \pm \sqrt{\left(1.8\times10^{-4}\right)^2 + 4\times1.8\times10^{-4}\times1.00\times10^{-3}}}{2}$$

$$= \begin{cases} 3.4_4\times10^{-4} \\ -5.2_4\times10^{-4} \end{cases}$$

Only the positive solution is admissible. Therefore, the extent of dissociation is 3.4×10^{-4} and the equilibrium concentrations are given by

$[HCOOH] = 1.00 \times 10^{-3} - x = 1.00 \times 10^{-3} - 3.4 \times 10^{-4} = 0.66$ mol L^{-1}
$[HCOO^-] = [H_3O^+] = x = 3.4 \times 10^{-4}$ mol L^{-1}

Weak bases can be treated in exactly the same fashion as weak acids. The equilibrium constant for the reaction of a base with water to form OH^- is called K_b. For example,

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad K_b = 1.8 \times 10^{-5}$$

Example 5.10: What is the pH of a (a) 1.00 mol L^{-1} and (b) 1.00×10^{-3} mol L^{-1} solution of ammonia, $NH_3(aq)$?

Approach: Exactly like a weak acid calculation, except that B replaces HA, HB^+ replaces A^- and OH^- replaces H_3O^+.

(a)

	$NH_3(aq)$	**+**	**$H_2O(l)$**	$\rightleftharpoons$	**$NH_4^+(aq)$**	**$OH^-(aq)$**
Initial	1.00				0	0
Change	$-x$				$+x$	$+x$
Equilibrium	$1.00 - x$				x	x

Substitute the equilibrium concentrations into the equilibrium constant.

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{x^2}{1.00 - x} = 1.8\times10^{-5}$$

The approximation, $1.00 - x \approx 1.00$ is good here. Therefore,

$$x^2 = 1.8\times10^{-5}\times1.00$$

$$x = \sqrt{1.8\times10^{-5}} = 4.2_4\times10^{-3}$$

Therefore,

$$[OH^-] = x = 4.2_4 \times 10^{-3} \text{ mol } L^{-1}$$

$$pOH = -\log_{10}([OH^-]) = -\log_{10}(4.2_4 \times 10^{-3}) = 2.37$$

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$$pH = 14.00 - pOH = 14.00 - 2.37 = 11.63$$

(b)

	$NH_3(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$NH_4^+(aq)$	+	$OH^-(aq)$
Initial	1.00×10^{-3}				0		0
Change	$-x$				$+x$		$+x$
Equilibrium	$1.00 \times 10^{-3} - x$				x		x

Substitute the equilibrium concentrations into the equilibrium constant.

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{x^2}{1.00\times10^{-3} - x} = 1.8\times10^{-5}$$

The solution is dilute, thus $1.00 \times 10^{-3} - x$ cannot be approximated. The equation is rearranged to quadratic form,

$$x^2 + 1.8\times10^{-5}x - 1.8\times10^{-5}\times1.00\times10^{-3} = 0$$

with solution,

$$x = \frac{-1.8\times10^{-5} \pm \sqrt{\left(1.8\times10^{-5}\right)^2 + 4\times1.8\times10^{-5}\times1.00\times10^{-3}}}{2}$$

$$= \begin{cases} 1.2_5\times10^{-4} \\ -1.4_3\times10^{-4} \end{cases}$$

The admissible solution ($x = 1.2_5 \times 10^{-4}$) gives

$$[OH^-] = x = 1.2_5 \times 10^{-4} \text{ mol L}^{-1}$$

$$pOH = -\log_{10}([OH^-]) = -\log_{10}(1.2_5 \times 10^{-4}) = 3.90$$

$$pH = 14.00 - pOH = 14.00 - 3.90 = 10.10$$

Problems:

5.1 Write down expressions for the equilibrium constants of the following reactions, in terms of equilibrium concentrations and/or partial pressures.

(a) $Cl_2(g) + Br_2(g) \rightleftharpoons 2\ BrCl(g)$
(b) $Fe^{3+}(aq) + Cu^+(aq) \rightleftharpoons Fe^{2+}(aq) + Cu^{2+}(aq)$
(c) $2\ IO_3^-(aq) + 5\ SO_3^{2-}(aq) + 2\ H^+(aq) \rightleftharpoons I_2(s) + 5\ SO_4^{2-}(aq) + H_2O(l)$
(d) $Ca_3(PO_4)_2(s) \rightleftharpoons 3\ Ca^{2+}(aq) + 2\ PO_4^{2-}(aq)$
(e) $HCN(aq) + H_2O(l) \rightleftharpoons CN^-(aq) + H_3O^+(aq)$

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5.2 An equilibrium mixture of N_2O_4 and NO_2, at 25°C, has a N_2O_4 partial pressure of 2.00 atm. What is the partial pressure of NO_2?

$$N_2O_4(g) \rightleftharpoons 2\ NO_2(g) \qquad K = 0.323 \text{ at } 25°C$$

5.3 Write down the equilibrium constants for the following reactions given the data table of equilibrium constants below.

(a) $Fe^{3+}(aq) + Cu^{+}(aq) \rightleftharpoons Fe^{2+}(aq) + Cu^{2+}(aq)$
(b) $2\ Fe^{2+}(aq) + Cl_2(aq) \rightleftharpoons 2\ Fe^{3+}(aq) + 2\ Cl^{-}(aq)$
(c) $2\ NaF(s) + Mg^{2+}(aq) \rightleftharpoons MgF_2(s) + 2\ Na^{+}(aq)$

DATA:

Reaction	Equilibrium Constant
1) $2\ Fe^{3+}(aq) + Cl_2(aq) + 2\ H_2O(l) \rightleftharpoons 2\ Fe^{2+}(aq) + 2\ HOCl(aq) + 2\ H^{+}(aq)$	K_1
2) $2\ HOCl(aq) + 2\ Cu^{+}(aq) + 2\ H^{+}(aq) \rightleftharpoons Cl_2(aq) + 2\ H_2O(l) + 2\ Cu^{2+}(aq)$	K_2
3) $2\ Cu^{+}(aq) + Cl_2(aq) \rightleftharpoons 2\ Cu^{2+}(aq) + 2\ Cl^{-}(aq)$	K_3
4) $MgF_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\ F^{-}(aq)$	K_4
5) $NaF(s) \rightleftharpoons Na^{+}(aq) + F^{-}(aq)$	K_5

5.4 Predict the direction each of the following equilibriums shifts when the indicated changes are imposed.

$$N_2O_4(g) \rightleftharpoons 2\ NO_2(g) \qquad \Delta H^{\circ} = 55.3 \text{ kJ mol}^{-1}$$

(a) The N_2O_4 partial pressure is increased
(b) Some NO_2 is removed from the reaction mixture
(c) The reaction mixture is transferred to a vessel with twice the volume
(d) Temperature is increased

$$MgF_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\ F^{-}(aq) \qquad \Delta H^{\circ} = -13.6 \text{ kJ mol}^{-1}$$

(e) Some KF is dissolved in the solution
(f) Some solid MgF_2 is added to the mixture
(g) Temperature is decreased

5.5 Determine the equilibrium partial pressure of all gases in the following equilibrium, after a vessel is prepared at 400°C with 10.0 atm partial pressure of both methane and bromine.

$$CH_4(g) + Br_2(g) \rightleftharpoons CH_3Br(g) + HBr(g) \qquad K = 0.012 \text{ at } 400°C$$

5.6 (a) What is the extent of dissolution of $Ba_3(PO_4)_2(s)$ ($K_{sp} = 3.4 \times 10^{-23}$), and the equilibrium ion concentrations, in a 1.0×10^{-5} mol L^{-1} KBr(aq) solution?
(b) How would the extent of dissolution of $Ba_3(PO_4)_2(s)$ be different in a 1.0×10^{-5} mol L^{-1} $K_3PO_4(aq)$ solution? (Just answer qualitatively – no calculations required.)

5.7 What is the pH of a (a) 1.00 mol L^{-1} and (b) 1.00×10^{-6} mol L^{-1} solution of hypochlorous acid? $K_a(HOCl) = 4.0 \times 10^{-8}$

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5.8 What is the pH of a (a) 1.00 mol L^{-1} and (b) 1.00×10^{-3} mol L^{-1} solution of ethylamine, $CH_3CH_2NH_2$? $K_b(CH_3CH_2NH_2) = 4.5 \times 10^{-4}$

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Solutions:

5.1 (a) $K = \dfrac{p_{\mathrm{BrCl}}^2}{p_{\mathrm{Cl_2}}\, p_{\mathrm{Br_2}}}$

(b) $K = \dfrac{[\mathrm{Fe^{2+}}][\mathrm{Cu^{2+}}]}{[\mathrm{Fe^{3+}}][\mathrm{Cu^{+}}]}$

(c) $K = \dfrac{[\mathrm{SO_4^{2-}}]^5}{[\mathrm{IO_3^-}]^2[\mathrm{SO_3^{2-}}]^5[\mathrm{H^+}]^2}$

The I_2(s) and H_2O(l) do not appear in this expression. Iodine is a pure solid, and the liquid water concentration varies very little except in very concentrated aqueous solutions.

(d) $K = K_{sp} = [\mathrm{Ca^{2+}}]^3[\mathrm{PO_4}^{2-}]^2$

Pure solid, $Ca_3(PO_4)_2$(s), does not appear. This is the solubility product of calcium phosphate.

(e) $K = K_a = \dfrac{[\mathrm{H_3O^+}][\mathrm{CN^-}]}{[\mathrm{HCN}]}$

Liquid water does not appear in the K_a expression.

5.2

$$K = \frac{p_{\mathrm{NO_2}}^2}{p_{\mathrm{N_2O_4}}} = \frac{p_{\mathrm{NO_2}}^2}{2.00} = 0.323$$

$$p_{\mathrm{NO_2}} = \sqrt{2.00 \times 0.323} = 0.804 \text{ atm}$$

5.3 (a) Since

1/2 × $2\ Fe^{3+}(aq) + Cl_2(aq) + 2\ H_2O(l) \rightleftharpoons 2\ Fe^{2+}(aq) + 2\ HOCl(aq) + 2\ H^+(aq)$

1/2 × $2\ HOCl(aq) + 2\ Cu^+(aq) + 2\ H^+(aq) \rightleftharpoons Cl_2(aq) + 2\ H_2O(l) + 2\ Cu^{2+}(aq)$

Net rxn: $Fe^{3+}(aq) + Cu^+(aq) \rightleftharpoons Fe^{2+}(aq) + Cu^{2+}(aq)$

$$K = K_1^{1/2}K_2^{1/2}$$

(b) Since

−1× $2\ Fe^{3+}(aq) + Cl_2(aq) + 2\ H_2O(l) \rightleftharpoons 2\ Fe^{2+}(aq) + 2\ HOCl(aq) + 2\ H^+(aq)$

−1× $2\ HOCl(aq) + 2\ Cu^+(aq) + 2\ H^+(aq) \rightleftharpoons Cl_2(aq) + 2\ H_2O(l) + 2\ Cu^{2+}(aq)$

1× $2\ Cu^+(aq) + Cl_2(aq) \rightleftharpoons 2\ Cu^{2+}(aq) + 2\ Cl^-(aq)$

Net rxn: $2\ Fe^{2+}(aq) + Cl_2(aq) \rightleftharpoons 2\ Fe^{3+}(aq) + 2\ Cl^-(aq)$

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$$K = \frac{K_3}{K_1 K_2}$$

(c) Since

−1×	$MgF_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\ F^-(aq)$
2×	$NaF(s) \rightleftharpoons Na^+(aq) + F^-(aq)$
Net rxn:	$2\ NaF(s) + Mg^{2+}(aq) \rightleftharpoons MgF_2(s) + 2\ Na^+(aq)$

$$K = \frac{K_5^2}{K_4}$$

5.4 (a) N_2O_4 is the reactant. Increasing reactant results in net forward reaction – consuming some of the added N_2O_4.

(b) Removing product results in net forward reaction.

(c) We start with an equilibrium mixture with

$$\frac{p^2_{NO_2,\text{eqm 1}}}{p_{N_2O_4,\text{eqm 1}}} = K$$

Doubling the volume decreases both partial pressures to 1/2 their initial values. The reaction quotient is now equal to

$$Q = \frac{\left(\frac{1}{2} p_{NO_2,\text{eqm 1}}\right)^2}{\frac{1}{2} p_{N_2O_4,\text{eqm 1}}} = \frac{1}{2}\frac{p^2_{NO_2,\text{eqm 1}}}{p_{N_2O_4,\text{eqm 1}}} = \frac{1}{2}K$$

Since Q < K, there is net forward reaction. This is predicted by le Châtelier's principle. The reaction shifts to the side with greater moles of gas when volume is increased (decreasing partial pressure). This increases the total pressure, countering the reduction caused by the increase in volume.

(d) This reaction is endothermic. The equilibrium constant increases with increasing temperature. Therefore, there is net forward reaction. In terms of le Châtelier's principle, the reaction shifts so as to consume some of the additional heat available at higher *T*.

(e) Dissolving some KF in the solution increases the fluoride concentration. Fluoride is a product. This causes net reverse reaction. Less of the $MgF_2(s)$ is dissolved when equilibrium is re-established. This is the common ion effect.

(f) Adding pure solid MgF_2 to the mixture has no effect on the equilibrium.

(g) This reaction is exothermic. The equilibrium constant increases with decreasing temperature. Therefore, there is net forward reaction. In terms of le Châtelier's principle, the reaction shifts, releasing heat, to counter the reduced availability of heat at lower *T*.

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5.5

	$CH_4(g)$	+	$Br_2(g)$	$\rightleftharpoons$	$CH_3Br(g)$	+	$HBr(g)$
Initial	10.0		10.0		0		0
Change	$-x$		$-x$		$+x$		$+x$
Equilibrium	$10.0 - x$		$10.0 - x$		x		x

$$K = \frac{p_{CH_3Br}\,p_{HBr}}{p_{CH_4}\,p_{Br_2}} = \frac{x\,x}{(10.0-x)(10.0-x)} = 0.012$$

from which we get

$$\left(\frac{x}{(10.0-x)}\right)^2 = 0.012$$

$$\frac{x}{(10.0-x)} = \sqrt{0.012} = 0.11_0$$

$$x = 0.11_0(10.0-x)$$

$$x = \frac{1.1_0}{1.11_0} = 0.99_1$$

With x = 0.99_1, we can get the equilibrium partial pressures. Specifically,

$$p_{CH_4} = p_{Br_2} = 10.0 - x = 9.0 \text{ atm}$$

and

$$p_{CH_3Br} = p_{HBr} = x = 0.99 \text{ atm}$$

5.6 (a) Initially, there are potassium and bromide ions present in solution. However, there are no barium or phosphate ions.

	$Ba_3(PO_4)_2(s)$	$\rightleftharpoons$	$3\ Ba^{2+}(aq)$	+	$2\ PO_4^{3-}(aq)$
Initial			0		0
Change			$+3x$		$+2x$
Equilibrium			$3x$		$2x$

Substitute the equilibrium ion concentrations into the solubility product equation.

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$$K_{sp} = [Ba^{2+}]^3[PO_4^{3-}]^2 = (3x)^3(2x)^2 = 3.4\times10^{-23}$$

which gives the extent of dissolution,

$$x = \left(\frac{3.4\times10^{-23}}{108}\right)^{1/5} = 1.2_6\times10^{-5}$$

At equilibrium,

$[Ba^{2+}] = 3x = 3.8 \times 10^{-5}$ mol L^{-1}
$[PO_4^{3-}] = 2x = 2.5 \times 10^{-5}$ mol L^{-1}

(b) Initially, there is 1.0×10^{-5} mol L^{-1} PO_4^{3-}(aq) present in solution. The phosphate already present suppresses the dissolution of $Ba_3(PO_4)_2$(s) – the common ion effect. The extent of dissolution is smaller in this case.

5.7 (a) What is the pH of a (a) 1.00 mol L^{-1} and (b) 1.00×10^{-3} mol L^{-1} solution of hypochlorous acid? K_a(HOCl) = 4.0×10^{-8}

	HOCl(aq)	**+**	**H_2O(l)**	$\rightleftharpoons$	**H_3O^+(aq)**	**OCl^-(aq)**
Initial	1.00				0	0
Change	$-x$				$+x$	$+x$
Equilibrium	$1.00 - x$				x	x

Substitute the equilibrium concentrations into the equilibrium constant expression.

$$K_a = \frac{[H_3O^+][OCl^-]}{[HOCl]} = \frac{x^2}{(1.00-x)} = 4.0\times10^{-8}$$

The approximation, $1.00 - x \approx 1.00$ is good here. Therefore,

$$x^2 = 4.0\times10^{-8}\times1.00 = 4.0\times10^{-8}$$

$$x = \sqrt{4.0\times10^{-8}} = 2.0\times10^{-4}$$

and

$[H_3O^+] = x = 2.0 \times 10^{-4}$ mol L^{-1}

pH = $-\log_{10}([H_3O^+]) = -\log_{10}(2.0 \times 10^{-4}) = 3.70$

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(b)

	HOCl(aq)	+	$H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	$OCl^-(aq)$
Initial	1.00×10^{-6}				0	0
Change	$-x$				$+x$	$+x$
Equilibrium	$1.00 \times 10^{-6} - x$				x	x

Substitute the equilibrium concentrations into the equilibrium constant expression.

$$K_a = \frac{[H_3O^+][OCl^-]}{[HOCl]} = \frac{x^2}{\left(1.00\times10^{-6} - x\right)} = 4.0\times10^{-8}$$

The solution is dilute, we cannot neglect x in $(1.00 \times 10^{-6} - x)$. The equation is rearranged to quadratic form,

$$x^2 + 4.0\times10^{-8}x - 4.0\times10^{-8}\times1.00\times10^{-6} = 0$$

with solution,

$$x = \frac{-4.0\times10^{-8} \pm \sqrt{\left(4.0\times10^{-8}\right)^2 + 4\times4.0\times10^{-8}\times1.00\times10^{-6}}}{2}$$

$$= \begin{cases} 1.8_1\times10^{-7} \\ -2.2_1\times10^{-7} \end{cases}$$

The admissible solution ($x = 1.8_1 \times 10^{-7}$) gives

$$[H_3O^+] = x = 1.8_1 \times 10^{-7} \text{ mol L}^{-1}$$

$$\text{pH} = -\log_{10}([H_3O^+]) = -\log_{10}(1.8_1 \times 10^{-7}) = 6.74$$

5.8 (a)

	$CH_3CH_2NH_3(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$CH_3CH_2NH_3^+(aq)$	$OH^-(aq)$
Initial	1.00				0	0
Change	$-x$				$+x$	$+x$
Equilibrium	$1.00 - x$				x	x

Substitute the equilibrium concentrations into the equilibrium expression.

$$K_b = \frac{[CH_3CH_2NH_3^+][OH^-]}{[CH_3CH_2NH_2]} = \frac{x^2}{1.00 - x} = 4.5\times10^{-4}$$

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The approximation, $1.00 - x \approx 1.00$ is good here. Therefore,

$$x^2 = 4.5\times10^{-4}\times1.00$$

$$x = \sqrt{4.5\times10^{-4}} = 2.1_2\times10^{-2}$$

Therefore,

$$[OH^-] = x = 2.1_2 \times 10^{-2}\ \text{mol L}^{-1}$$

$$pOH = -\log_{10}([OH^-]) = -\log_{10}(2.1_2 \times 10^{-2}) = 1.67$$

$$pH = 14.00 - pOH = 14.00 - 1.67 = 12.33$$

(b)

	$CH_3CH_2NH_3(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$CH_3CH_2NH_3^+(aq)$	$OH^-(aq)$
Initial	1.00×10^{-3}				0	0
Change	$-x$				$+x$	$+x$
Equilibrium	$1.00 \times 10^{-3} - x$				x	x

Substitute the equilibrium concentrations into the equilibrium constant expression.

$$K_b = \frac{[CH_3CH_2NH_3^+][OH^-]}{[CH_3CH_2NH_2]} = \frac{x^2}{1.00\times10^{-3} - x} = 4.5\times10^{-4}$$

The solution is dilute, $1.00 \times 10^{-3} - x$ cannot be approximated. The equation is rearranged to quadratic form,

$$x^2 + 4.5\times10^{-4}x - 4.5\times10^{-4}\times1.00\times10^{-3} = 0$$

with solution,

$$x = \frac{-4.5\times10^{-4} \pm \sqrt{\left(4.5\times10^{-4}\right)^2 + 4\times4.5\times10^{-4}\times1.00\times10^{-3}}}{2}$$

$$= \begin{cases} 4.8_3\times10^{-4} \\ -9.3_3\times10^{-4} \end{cases}$$

The admissible solution ($x = 4.8_3 \times 10^{-4}$) gives

$$[OH^-] = x = 4.8_3 \times 10^{-4}\ \text{mol L}^{-1}$$

$$pOH = -\log_{10}([OH^-]) = -\log_{10}(4.8_3 \times 10^{-4}) = 3.32$$

$$pH = 14.00 - pOH = 14.00 - 3.32 = 10.68$$

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6. Thermochemistry

Chemical reactions, such as $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$, and phase changes, such as $CO_2(s) \rightarrow CO_2(g)$, are accompanied by changes in energy. For example, two moles of liquid water has less energy than two moles of hydrogen and one mole of oxygen gases. Consequently, the chemical reaction of hydrogen and oxygen releases energy – ultimately in the form of heat. Chemical reactions are an important source of energy – e.g. heat in homes in winter, mechanical energy in the engine of a car, electrical energy in a cellphone battery. In order to predict the energy released by a given chemical reaction or physical process, chemists have measured the heat released by many processes and developed an energy scale for a wide range of substances. The closely related enthalpy scale is used to determine heat released under standard conditions - see Sec. 5.5. To understand this scale and how to use it requires the introduction of precise terminology.

6.1 System and Properties - Energy

We divide the universe into *system*(*s*) and *surroundings* (i.e. everything else). A *system* is an amount of a substance or collection of substances with a volume. If the system is in equilibrium (i.e. it is unchanging, or changing slowly), then it also has a temperature and pressure. It has other properties also. Most notably, the system has an energy, the sum total of all potential and kinetic energies of particles in the system. Enthalpy is another property – it is energy plus a small extra term. An energy or enthalpy scale for substances can be constructed from a sufficiently large set of measured energy or enthalpy changes. Changes in energy or enthalpy are determined by measuring the flow of heat to or from the system.

6.2 Heat

Heat is the energy that flows from a hot system to a cold system, when they are in *thermal contact* (this simply means they are touching, and not separated by thermal insulation). Heat flows until the final temperatures of the systems are the same. We use the symbol q to denote heat flow *into* a system, when there is one system of interest. When heat flows *from* the system, q is negative. When there are two systems, we use subscripts to distinguish the properties. When heat flows from system 2 to system 1 their q values are equal in magnitude but opposite in sign;

$$q_2 = -q_1$$

q_1 is positive because heat flowed into system 1, while q_2 is negative.

Temperature measurements are used to determine the amount of heat flow. When heat flows into a system, its temperature generally increases. The temperature change is proportional to the heat transferred, and vice versa. Thus, a measured temperature change can be used to determine the amount of heat transferred via

$$q = C\,\Delta T$$

C is the heat capacity of the system. It is proportional to the amount of substance – the size of the system. A system twice as big – but otherwise identical – has twice the heat capacity. Consequently, heat capacities for substances are tabulated for substances per mole, or per gram. Specific heat capacity,

$$s = C / m$$

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is the heat capacity per gram of substance; i.e. m is the mass in grams. Specific heat capacities are tabulated for various substances. The value for water is 4.18 J K^{-1} g^{-1} at 25°C and 1 atm pressure. We will use this value for water under any conditions. This is an approximation that greatly simplifies all our calculations. Copper has a much lower specific heat capacity, 0.385 J K^{-1} g^{-1} at 25°C and 1 atm pressure (we will treat s as independent of temperature for all substances). In terms of specific heat capacity, heat is related to temperature change according to

$$q = ms\,\Delta T \qquad 6.1$$

Example 6.1: How much heat must flow into a 100. g sample of water to raise its temperature from 20.00°C to 25.00°C? (s_{water} = 4.18 J K^{-1} g^{-1})

Approach: Substitute given mass, specific heat capacity and temperature difference into the above formula.

Note that

$$\Delta T = T_{final} - T_{initial} = 25.00\ °C - 20.00\ °C = 5.00\ °C \text{ or } 5.00\ K$$

Differences in temperature, ΔT, expressed in °C, can also be written with the unit K. A 1 °C difference is the same as 1 K difference.

The heat transferred is

$$\begin{aligned} q &= ms\,\Delta T \\ &= 100.\ g \times 4.18\ J\ K^{-1}\ g^{-1} \times 5.00\ K \\ &= 209_2\ J = 2.09\ kJ \end{aligned}$$

This example demonstrates how a calorimeter works. A chemical reaction or phase transition releases or absorbs heat within a calorimeter. The calorimeter has a well-defined heat capacity. Sometimes you will be given the heat capacity, C. Other times you are given a mass of a substance (usually it is water, or a dilute aqueous solution) and you use ms for the heat capacity. Occasionally, you must add the heat capacities of the (empty) calorimeter and a reacting solution. The temperature change inside the calorimeter is measured to determine how much heat was released or absorbed by the reaction or phase transition.

Example 6.2: A 20.0 g sample of copper at 300.°C is placed within a thermally insulated vessel containing 100. g of water at 20.0°C. What is the final temperature when thermal equilibrium is re-established? (s_{water} = 4.18 J K^{-1} g^{-1} and s_{copper} = 0.385 J K^{-1} g^{-1})

Approach: Express the heat lost by copper, and the heat gained by water, in terms of the respective changes in temperature. Equate these expressions and solve for the unknown final temperature, T_f. Note that heat *lost* by copper is $-q_{copper}$.

The heat lost by copper is

$$\begin{aligned} -q_{copper} &= -m_{copper}\, s_{copper}\, \Delta T_{copper} \\ &= -20.0\ g \times 0.385\ J\ K^{-1}\ g^{-1} \times (T_f - 300.\ °C) \\ &= 7.70\ J\ K^{-1}\ (300.\ °C - T_f) \end{aligned}$$

The heat gained by water is

$$\begin{aligned} q_{water} &= m_{water}\, s_{water}\, \Delta T_{water} \\ &= 100.\ g \times 4.18\ J\ K^{-1}\ g^{-1} \times (T_f - 20.\ °C) \\ &= 418\ J\ K^{-1}\ (T_f - 20.\ °C) \end{aligned}$$

Heat lost by copper is gained by water. So

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$$q_{\text{water}} = -q_{\text{copper}}$$

or

$$418 \text{ J K}^{-1} (T_f - 20. \text{ °C}) = 7.70 \text{ J K}^{-1} (300. \text{ °C} - T_f)$$

which rearranges to

$$(418 + 7.70)\, T_f = 7.70 \times 300. + 418 \times 20.$$

$$T_f = 10670/425._7 \text{ °C} = 25.1 \text{ °C}$$

The final temperature has units of °C because the initial temperatures of copper and water were expressed in °C. Only when dealing with temperature differences do we use °C in a thermodynamic formula. Otherwise, temperature must be expressed in Kelvin.

When there is a phase transition, heat can be absorbed or released without an accompanying change in temperature. Melting, vaporization and sublimation absorb heat, while the reverse processes – freezing, condensation and deposition – release heat while a constant temperature is maintained.

6.2 Work

The energy of a system can be changed in another way. Work can be done on a system (or *by* a system). Work is mechanical energy transferred when force applies over a distance. A system exchanges work with its surroundings when the boundary between them moves, increasing or decreasing the volume of the system. Consider the gas system depicted in Fig. 6.1. Here, the piston applies a force to a boundary of the gas. The boundary moves down a distance, *d*. Work is done on the gas, as its boundary moves and its volume decreases.

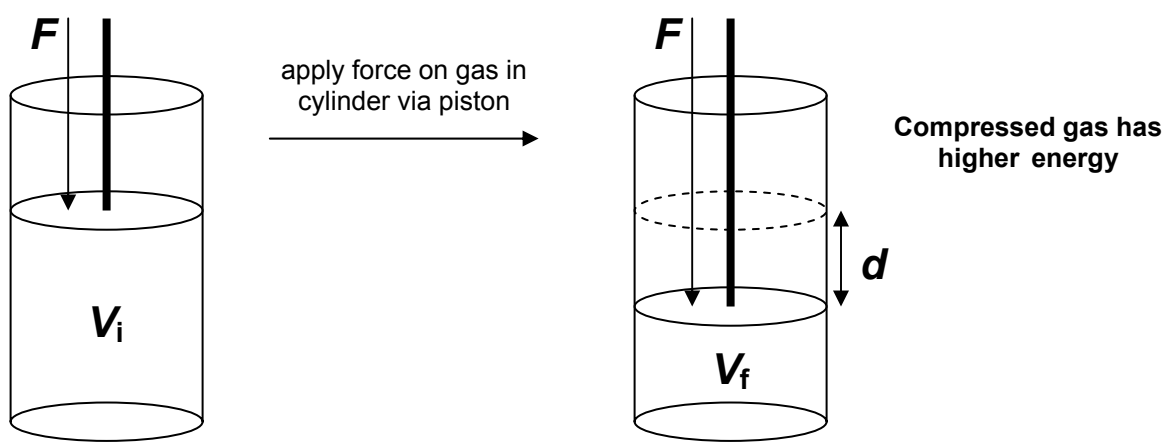

Figure 6.1. Force applied on a gas over a distance decreases the volume of the gas while increasing its energy.

The force on the piston is applied over the distance, *d*. The work done on the gas is

$$\begin{aligned} w &= F\,d \\ &= p\,A\,d \\ &= -p\,\Delta V \end{aligned} \qquad 6.2$$

where *A* is the area of the moving boundary and *p* is the pressure on that boundary (force per unit area). The third line follows from $A\,d = -\Delta V$; i.e., the volume of the gas *decreases* by this amount, $-\Delta V$ is negative.

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Example 6.3: How much work is done on the air in a bicycle pump when the volume of air is decreased by 50 mL under 5.0 atm pressure?

Approach: Substitute into the above formula for work.

$$\begin{aligned} w &= -p\,\Delta V \\ &= -5.0 \text{ atm} \times 0.050 \text{ L} = -0.25 \text{ L atm} \\ &= -101.3 \text{ J L}^{-1} \text{ atm}^{-1} \times 0.25 \text{ L atm} \\ &= 25 \text{ J} \end{aligned}$$

The L atm energy units are converted to J by the conversion factor 1.103 J = 1 L atm. This is an important step if you need to combine work and heat. Heat is determined in J.

Note that the conversion factor between L atm and J is just the ratio of the two forms of the gas constant.

$$101.3 \text{ J L}^{-1} \text{ atm}^{-1} = \frac{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}{0.082058 \text{ L atm K}^{-1} \text{ mol}^{-1}}$$

A system can gain or lose energy via work. The system gains energy when work is done on it – i.e. when it is compressed. The system loses energy when work is done by the system – it expands, compressing the surroundings. The sign of the work associated with a process is simply assessed by asking whether the volume of the system increased or decreased during the process. Because gases generally occupy much larger volumes than solids and liquids, the volume of a system is primarily determined by the number of moles of gas in the system. Moreover, changes in volume are generally connected with changes in the number of moles of gas. Thus, work is done by (i.e. $w < 0$) a system undergoing a reaction that increases the number of moles of gas. For example, a system of calcium carbonate decomposing into calcium oxide and carbon dioxide gas does work on the surroundings – i.e., work is done by the system. The energy is lost to the surroundings.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

Example 6.4: For which of the following processes is work positive – i.e., work is done on the system?

(a) $2\ Na(s) + 2\ H_2O(l) \rightarrow 2\ NaOH(aq) + H_2(g)$
(b) $C_3H_8(g) + 5\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(l)$
(c) $2\ NI_3NH_3(s) \rightarrow 2\ N_2(g) + 3\ I_2(s) + 3\ H_2(g)$
(d) $H_2O(g) \rightarrow H_2O(l)$
(e) $CO_2(s) \rightarrow CO_2(g)$

Approach: Count the number of moles of reactant and product gases. Work is positive if the number of moles of gas decreases.

(a) The only gas here is a product. $\Delta n_{gas} = n_{product\ gas} - n_{reactant\ gas} = 1$. Work is done by the system. $w < 0$
(b) $\Delta n_{gas} = -2$. Work is done **on** the system. $w > 0$
(c) $\Delta n_{gas} = 5$. Work is done by the system. $w < 0$
(d) $\Delta n_{gas} = -1$. Work is done **on** the system. $w > 0$
(e) $\Delta n_{gas} = 1$. Work is done by the system. $w < 0$

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6.4 Energy Conservation – the First Law of Thermodynamics

We have seen that energy can be transferred, either as heat or work, between systems, but is never created or destroyed. This is the *first law of thermodynamics* – energy is conserved. Thus, if the energy of a system changes it is because heat or work has been transferred between the system and surroundings. Specifically,

$$\Delta U = q + w \qquad 6.3$$

is the change in energy of the system expressed as the sum of heat flowing into the system and work done on the system - negative values accounting for reverse transfers. The above equation is the first law of thermodynamics in equation form.

Example 6.5: What is the change in energy for the following combinations of q and w?

(a) $q = 50$ J and $w = 50$ J
(b) $q = 0$ J and $w = 100$ J
(a) $q = 100$ J and $w = 0$ J

Approach: Add heat and work to get ΔU, the change in energy.

(a) $\Delta U = q + w = 50 \text{ J} + 50 \text{ J} = 100 \text{ J}$
(b) $\Delta U = q + w = 0 \text{ J} + 100 \text{ J} = 100 \text{ J}$
(c) $\Delta U = 100$ J

Note that the three combinations of q and w listed above produce the same change in the energy. The final energy depends only on the initial energy and the sum of heat and work transfers. In general, every system has a thermodynamic state with well-defined values of all of system properties – the *state functions* (they depend only on the state of the system). There are many paths connecting two final states. Paths correspond to processes that generally involve heat or work transfer. Heat and work are characteristics of processes – they are not state functions.

6.5 Enthalpy

Enthalpy is state function like energy (volume, pressure, temperature, etc). It is closely related to energy and we sometimes speak of energy of enthalpy as though they were interchangeable. Enthalpy, H, is just energy, U, plus an extra term:

$$H = U + p V \qquad 6.4$$

The extra term is the energy required to "make room" for the system in an environment with constant pressure, p. Solids and liquids occupy small spaces and the associated $p V$ term in the enthalpy is generally negligible. Gases occupy much larger volumes. The $p V$ term is small, but not negligible, for gases.

Enthalpy is introduced because it is common to perform heat measurements under constant pressure conditions. Calorimetry is used to measure heat. If the experiment takes place under constant pressure conditions, the change in energy is not equal to the measured q. The first law gives

$$\begin{aligned} \Delta U &= q + w \\ &= q - p\,\Delta V \end{aligned}$$

Under constant pressure conditions, the volume can change.

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Bomb calorimeters are calorimeters with *constant volume*. Heat measurements made with bomb calorimeters directly give ΔU (the work term is zero);

$$\Delta U = q + 0 = q_V \qquad 6.5$$

where q_V denotes heat for a constant volume process. However, bomb calorimeters require a strong, rigid (steel) container to withstand large pressure differences resulting from chemical reactions inside the calorimeter. Constant pressure calorimeters, known as coffee cup calorimeters, are much safer – but do not give ΔU directly. This is not a problem, however.

Under constant pressure conditions,

$$p\,\Delta V = \Delta(p\,V)$$

Work is thus the change in a state function (pressure × volume), when pressure is constant. This allows the first law to be rearranged to

$$\Delta U = q + w$$
$$\Delta U = q - p\,\Delta V$$
$$\Delta U + \Delta(p\,V) = q$$
$$\Delta(U + p\,V) = q$$

or

$$\Delta H = q = q_p \qquad 6.6$$

where q_p denotes heat for a constant pressure process, and $H = U + p\,V$ as introduced above. Here, we see that heat measured in a coffee cup calorimeter gives the change in enthalpy, a state function. It is sufficient (and convenient) to construct an enthalpy scale by doing a series of coffee cup calorimeter experiments. Each experiment measures the enthalpy difference between the reactants and products for some reaction – i.e., the *enthalpy of reaction*.

Example 6.6: The neutralization of 100. mL 0.200 M NaOH solution with 100. mL 0.200 HCl solution is performed in a coffee cup calorimeter. The temperature of the combined solution rises from 20.00°C to 21.34°C. What is the enthalpy of this reaction in kJ mol^{-1}? Assume the solution has density 1.00 g mL^{-1} and specific heat capacity 4.18 J K^{-1} g^{-1} – i.e., the properties of pure water at 20.00°C.

Approach: Determine the heat transferred from the temperature change and the heat capacity (use mass × specific heat capacity here). Write a net balanced chemical reaction and determined the number of moles reacted. Divide the heat by the number of moles to get the enthalpy of reaction in kJ mol^{-1}. The sign is negative because heat is released by the reaction and the temperature increased.

To use

$$q = m\,s\,\Delta T$$

we need the total mass of solution.

$$m = V\,d$$
$$= (100. + 100.\ \text{mL}) \times 1.00\ \text{g mL}^{-1} = 200.\ \text{g}$$

Therefore,

$$q = 200.\ \text{g} \times 4.18\ \text{J K}^{-1}\ \text{g}^{-1}\ (21.34 - 20.00)\ \text{K}$$
$$= 112_0\ \text{J} = 1.12\ \text{kJ}$$

The net balanced reaction is

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

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The number of moles of $H^+(aq)$ is the volume of the HCl solution × its concentration – i.e. 0.100 L × 0.200 mol L^{-1} = 0.0200 mol. The number of moles of OH^- is the same. They both react to completion. Therefore the number of moles reacted – the extent of reaction – is 0.0200 mol.

The enthalpy of reaction is

$$\Delta H = -1.12 \text{ kJ} / 0.0200 \text{ mol}$$
$$= -56.0 \text{ kJ mol}^{-1}$$

The sign reversal in the last step - recognizing that the reaction releases heat - can be confusing for students. The sign reversal results because the heat that determines ΔH is the heat that must be released to return the contents of the calorimeter to the initial temperature. The system – the calorimeter and its contents – would lose heat in this imagined process, a process not actually carried out since the calorimeter is thermally insulated. Nevertheless, the heat associated with the imagined process is calculated exactly as above, except that the sign of ΔT is reversed. In this process, 21.34°C is the initial temperature and 20.00°C is the final temperature. The heat determined in this way gives the enthalpy of reaction at 20.00°C.

In the above example, the reaction released heat and ΔH is negative. This is an *exothermic* reaction. Processes with positive ΔH absorb energy – they are called *endothermic* processes. For example, the dissolution of ammonium nitrate in water is endothermic.

$$NH_4NO_3(s) \rightarrow NH_4NO_3(aq) \qquad \Delta H = 24.9 \text{ kJ mol}^{-1}$$

This process is endothermic because strong ionic bonds in the reactant were broken in order to form weaker intermolecular forces (solvation of the separated ions) in solution. Other endothermic processes include melting, vaporization, sublimation and bond breaking. Bonds (covalent, ionic or intermolecular) are stronger in a solid, than in a liquid. In the gas phase intermolecular forces are essentially absent.

Exothermic reactions are reactions that beak weaker bonds to form stronger bonds. Condensation (the reverse of vaporization) is exothermic because it forms intermolecular bonds in the liquid without breaking any bonds.

Having measured a number of enthalpies of reaction, how do we go on to construct an enthalpy scale? The key is that because enthalpy is a state function, we can get the enthalpy of a specific reaction (the "target" reaction) by adding the enthalpies of reaction for a series of reactions as long as they begin with the specified reactants and end with the specified products. This is called *Hess' Law*.

The simplest application of *Hess' Law* is to combine a reaction with its reverse. In this case, the final products are just the reactants. $\Delta H = 0$ for the closed path. Therefore,

$$\Delta H = \Delta H_{forward} + \Delta H_{reverse} = 0$$

or

$$\Delta H_{reverse} = -\Delta H_{forward}$$

If a reaction must be scaled (e.g. doubled) so the stoichiometric coefficients match what is required to get the target reaction, then the enthalpy of the reaction is scaled by the same factor. For example, burning twice as much gas produces twice as much heat. If multiple reactions are combined to form a target reaction then their ΔH values are added together.

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Example 6.7: Determine the enthalpy of the following reaction given the data below.

$$Fe(s) + S(s) \rightarrow FeS(s)$$

n	Reaction	ΔH_n (kJ mol^{-1})
1	$2\ Fe(s) + O_2(g) \rightarrow 2\ FeO(s)$	−544.0
2	$2\ S(s) + 3\ O_2(g) \rightarrow 2\ SO_3(g)$	−791.4
3	$FeO(s) + SO_3(g) \rightarrow FeSO_4(s)$	−260.7
4	$FeS(s) + 2\ O_2(g) \rightarrow FeSO_4(s)$	−828.4

Approach: Manipulate and combine the given reactions as needed so they add up to the target reaction; perform the same manipulations to the ΔH values for each reaction. The target reaction ΔH is the combination of the given ΔH data after they have been manipulated. Look for the target reaction reactants and products in the given reaction.

Reaction 1 has reactant 2 Fe(s) among reactants. Scale reaction 1 by 1/2 to match the Fe(s) coefficient in the target reaction. Reaction 2 has 2 S(s) among reactants. Again, scale by 1/2. Reaction 4 has FeS(s) as a reactant, whereas FeS(s) is a product in the target reaction. Reverse reaction 4. Reaction 3 is needed to cancel out compunds that do not participate in the target reaction. Note that the ΔH values must be adjusted similarly.

		ΔH_n (kJ mol^{-1})
1/2 × Rxn 1	$Fe(s) + 1/2\ O_2(g) \rightarrow FeO(s)$	−272.0
1/2 × Rxn 2	$S(s) + 3/2\ O_2(g) \rightarrow SO_3(g)$	−395.7
−Rxn 4	$FeSO_4(s) \rightarrow FeS(s) + 2\ O_2(g)$	828.4
Rxn 3	$FeO(s) + SO_3(g) \rightarrow FeSO_4(s)$	−260.7
	$Fe(s) + S(s) \rightarrow FeS(s)$	−100.0

It is useful to have a more systematic approach to determining an enthalpy of reaction from known data. It turns out that the enthalpy of any reaction can be determined from a table of all formation reactions. The formation reaction of a compound is the reaction that forms the compound from its elements in their *standard state*. The standard state of an element is its stable form at 1.00 atm pressure and 25°C. Stable form refers to the stable allotrope (structure) of the element and the stable phase. The standard state of most elements is a solid. The noble gases, hydrogen, nitrogen, oxygen, fluorine and chlorine are gases, while bromine is a liquid. The standard state of carbon is graphite, C(graphite), not diamond, C(diamond).

Any reaction, under *standard conditions* (1.00 atm pressure and 25°C), can be written as the sum of the formation reactions of all products (weighted by the stoichiometric coefficients) plus the sum of the reverse formation reactions of all reactant (again, with stoichiometric weightings). Consequently, the enthalpy of reaction can correspondingly be expressed in terms of enthalpies of formation:

$$\Delta H^{o} = \sum_{\text{products, P}} c_P \Delta H_f^{o}[P] - \sum_{\text{reactants, R}} c_R \Delta H_f^{o}[R] \qquad 6.7$$

The superscript "o" refers to standard conditions. The terms c_P and c_R are the stoichiometric coefficients of products and reactants, respectively.

For example, the enthalpy of reaction of

$$Fe_2O_3(s) + 3\ SO_3(g) \rightarrow Fe_2(SO_4)_3(s)$$

is

$$\Delta H^{o} = \Delta H_f^{o}[Fe_2(SO_4)(s)] - \Delta H_f^{o}[Fe_2O_3(s)] - 3\Delta H_f^{o}[SO_3(g)]$$

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Note that an element in the standard state has an enthalpy of formation of zero, $\Delta H_f^{\circ} = 0$. The formation reaction in this case is a non-reaction.

The equation for enthalpy of reaction in terms of enthalpies of formation can be depicted graphically.

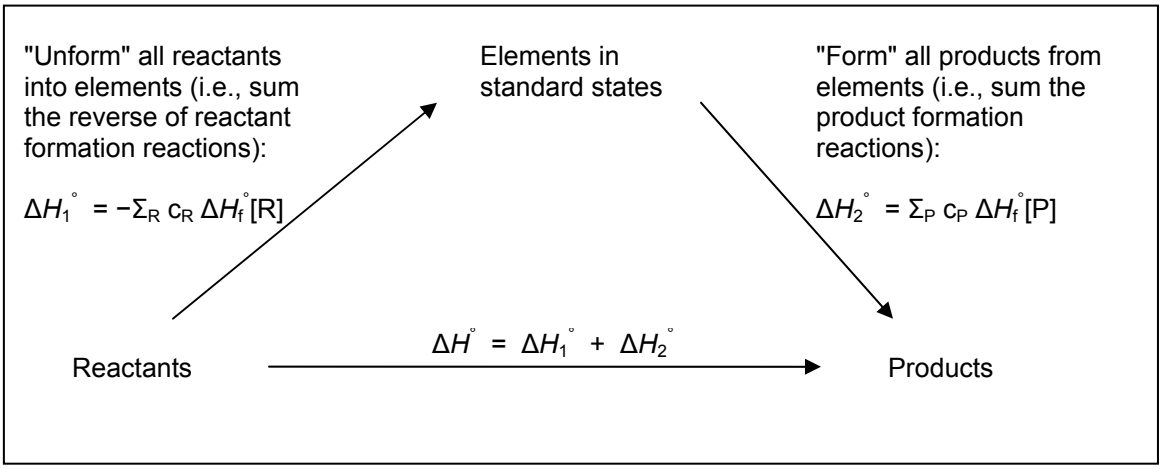

Figure 6.2. Graphical depiction of the expression of enthalpy of reaction in terms of enthalpies of formation – Equation 6.7 above.

Example 6.8: Determine the enthalpy of combustion of propane from the given enthalpies of formation.

Compound	ΔH_f° (kJ mol^{-1})
$CO_2(g)$	−393.5
$H_2O(l)$	−285.8
$C_3H_8(g)$	−103.8

Approach: Write down the balanced chemical reaction. Combine the enthalpies of formation as described above – products minus reactants.

$$C_3H_8(g) + 5\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(l)$$

$$\Delta H^{\circ} = 3\Delta H_f^{\circ}[CO_2(g)] + 4\Delta H_f^{\circ}[H_2O(l)] - \Delta H_f^{\circ}[C_3H_8(g)]$$
$$= 3(-393.5) + 4(-285.8) - (-103.8)\ \text{kJ mol}^{-1} = -2219.9\ \text{kJ mol}^{-1}$$

Note that the enthalpy of formation of oxygen is left out of the equation because it is zero.

A table of enthalpies of formation is not the only enthalpy we can construct. It is also convenient to determine enthalpies of reaction using *bond enthalpies*. A bond enthalpy is the enthalpy of a bond dissociation reaction – a reaction breaking a type of bond. For example, the bond enthalpy of the Cl-Cl bond, D(Cl-Cl), is ΔH for the dissociation of Cl_2 gas into Cl atoms:

$$Cl_2(g) \rightarrow 2\ Cl(g) \qquad \Delta H = D(\text{Cl-Cl})$$

Bond dissociation is an endothermic process. Bonds are broken – this requires energy – while no bonds are formed. D is always positive.

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For molecules with more than one bond, ΔH for the dissociation of the molecule into atoms is the sum of all bond enthalpies – one for each bond in the molecule. For example,

$$CHCl_3(g) \rightarrow C(g) + H(g) + 3\ Cl(g) \qquad \Delta H = D(\text{C-H}) + 3\ D(\text{C-Cl})$$

The enthalpy of any gas phase reaction can be written as the sum of all reactant bond enthalpies minus the sum of all product bond enthalpies:

$$\Delta H = \sum_{\text{reactant bonds, r}} n_{\text{r}} D[\text{r}] - \sum_{\text{product bonds, p}} n_{\text{p}} D[\text{p}] \qquad 6.8$$

where n_r is the number of occurrences of bond type r (e.g. C-Cl bond) in all reactant species. Similarly, n_p is the number of occurrences of bond type p among products.

The enthalpy of reaction for

$$C_2H_6(g) + 3\ Br_2(g) \rightarrow C_2H_3Br_3(g) + 3\ HBr(g)$$

is approximated by

$$\begin{aligned}\Delta H &= D[\text{C-C}] + 6D[\text{C-H}] + 3D[\text{Br-Br}] - D[\text{C-C}] - 3D[\text{C-H}] - 3D[\text{C-Br}] - 3D[\text{H-Br}] \\ &= 3D[\text{C-H}] + 3D[\text{Br-Br}] - 3D[\text{C-Br}] - 3D[\text{H-Br}]\end{aligned}$$

Note that some of the bonds are unchanged from reactant to product. The associated bond enthalpies cancel out leaving only the broken and formed bonds.

The structures of reactants and products must be drawn in order to identify the bonds present. Single, double and triple bonds are tabulated separately, as they have different bond enthalpies. In general, enthalpies of reaction determined from bond enthalpies are only approximate. This is because tabulated bond enthalpies are average bond enthalpies for each bond type – each distinct occurrence of a bond has a slightly different dissociation enthalpy.

The use of bond enthalpies to estimate reaction enthalpies is restricted to gas phase reactions. However, bond enthalpies can be used to determine enthalpies of reaction for reactions with liquids and/or solids, if the bond enthalpy data is supplemented with enthalpies of vaporization and/or sublimation. The target reaction is written as a gas phase reaction plus necessary phase transitions, making use of Hess' Law. For example, the combustion of propane at 25 °C can be written as the sum of a gas phase reaction and the condensation of water:

$$\begin{array}{c} C_3H_8(g) + 5\ O_2 \rightarrow 3\ CO_2(g) + 4\ H_2O(g) \\ \underline{4\times \quad H_2O(g) \rightarrow H_2O(l)} \\ C_3H_8(g) + 5\ O_2 \rightarrow 3\ CO_2(g) + 4\ H_2O(l) \end{array}$$

Therefore, the enthalpy of combustion of propane is just

$$\Delta H = \Delta H_{\text{gas phase reaction}} - 4\Delta H_{\text{vap}}[H_2O]$$

where

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$$\Delta H_{\text{gas phase reaction}} \cong 2D[\text{C-C}] + 8D[\text{C-H}] + 5D[\text{O=O}] - 3 \times 2D[\text{C=O}] - 4 \times 2D[\text{O-H}]$$

The equation for enthalpy of reaction in terms of bond enthalpies can be depicted graphically.

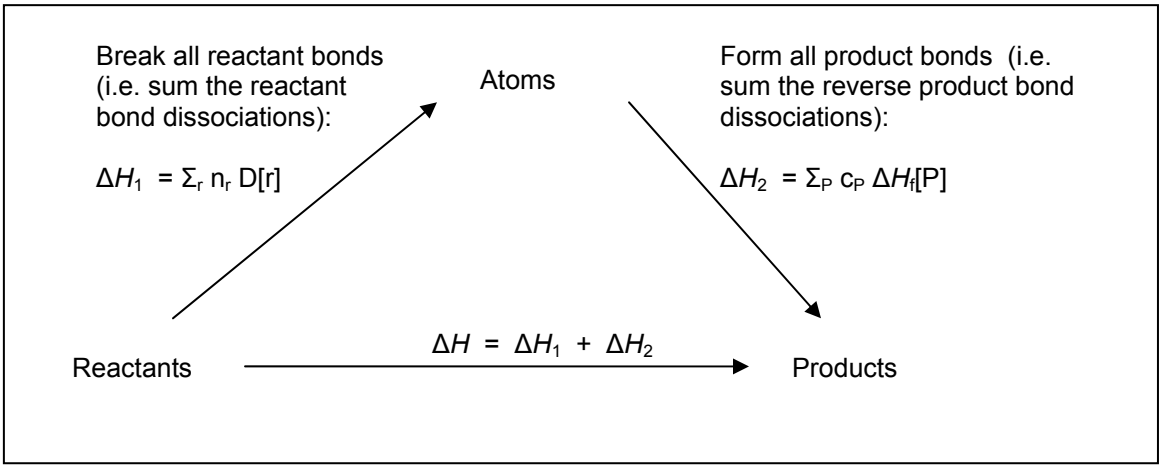

Figure 6.3. Graphical depiction of the expression of enthalpy of reaction in terms of bond enthalpies – Equation 6.8 above.

Example 6.9: Approximate the enthalpy of combustion of oxidation of $SO_2(g)$ to form $SO_3(g)$ from the given bond enthalpies.

Bond	D (kJ mol^{-1})
S=O	515
O=O	495

Approach: Write down the balanced chemical reaction. Combine the enthalpies of formation as described above – reactant bonds minus product bonds.

$$2\ SO_2(g) + O_2 \rightarrow 2\ SO_3(g)$$

$$\begin{aligned}\Delta H &\cong 2 \times 2D[\text{S=O}] + D[\text{O=O}] - 2 \times 3D[\text{S=O}] \\ &= D[\text{O=O}] - 2D[\text{S=O}] \\ &= 495 - 2(515)\ \text{kJ mol}^{-1} = -535\ \text{kJ mol}^{-1}\end{aligned}$$

Problems:

6.1 How much heat is released when 100. g of ethanol cools from 50.0°C to 20.0°C? (s_{ethanol} = 2.44 J K^{-1} g^{-1})

6.2 How much heat is required to produce steam at 150.°C from 200. mL of liquid water at 20.°C? ($s[H_2O(l)]$ = 4.18 J K^{-1} g^{-1}, $s[H_2O(g)]$ = 1.85 J K^{-1} g^{-1} and $\Delta H_{vap}°[H_2O]$ = 44.0 kJ mol^{-1})

6.3 When 8.16 g of $NH_4NO_3(s)$ is dissolved in 100. mL of water, in a calorimeter, the temperature is observed to drop from 19.5°C to 15.9°C. What is the enthalpy change for this dissolution process?

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6.4 The energy of a gas increases by 125 J, after its volume decreases by 2.00 L under 1.00 atm pressure. How much heat was absorbed/released by the gas?

6.5 For which of the following processes is (i) $q > 0$ (i.e. endothermic), or (ii) $w > 0$ (i.e., work is done on the system)?

(a) $Hg(l) \rightarrow Hg(g)$
(b) $Br_2(g) \rightarrow 2\ Br(g)$
(c) $H(g) + Cl(g) \rightarrow HCl(g)$
(d) $C(g) \rightarrow C(s)$
(e) $2\ S(s) + 3\ O_2(g) \rightarrow 2\ SO_3(g)$

6.6 Determine the enthalpy of the following reaction from the given data:

$$N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$$

n	Reaction	ΔH_n (kJ mol^{-1})
1	$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(g)$	−483.6
2	$N_2(g) + O_2(g) \rightarrow 2\ NO(g)$	182.6
3	$4\ NH_3(g) + 5\ O_2(g) \rightarrow 4\ NO(g) + 6\ H_2O(g)$	−260.7

6.7 Determine the enthalpy of the reaction below, known as the "mother of all bombs" reaction,

$$2\ Al(s) + NH_4NO_3(s) + O_2(g) \rightarrow Al_2O_3(s) + N_2(g) + 2\ H_2O(l)$$

from the given data. How much heat is released per gram of reactant (excluding oxygen – it is supplied by the atmosphere? What is the final temperature of 1.0 L of water at 20.°C, if it is heated by reaction of 10. g of this reactant?

Compound	$\Delta H_f°$ (kJ mol^{-1})
$NH_4NO_3(s)$	−356.6
$Al_2O_3(s)$	−1675.7
$H_2O(l)$	−285.8

6.8 Estimate the enthalpy of the oxidation of ethanol with hypochlorous acid using the given data.

$$CH_3CH_2OH(l) + 2\ HOCl(g) \rightarrow CH_3COOH(l) + 2\ HCl(g) + H_2O(l)$$

$\Delta H_{vap}°[CH_3CH_2OH] = 38.6$ kJ mol^{-1}
$\Delta H_{vap}°[CH_3COOH] = 23.7$ kJ mol^{-1}
$\Delta H_{vap}°[H_2O] = 44.0$ kJ mol^{-1}

Bond	D (kJ mol^{-1})
C-C	345
C-H	415
C-O	360
C=O	750
O-H	460
Cl-O	220
Cl-H	430

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Solutions:

6.1 Heat is related to temperature change of ethanol via

$$q = ms_{\text{ethanol}}\,\Delta T$$
$$= 100.\text{ g} \times 2.44\text{ J K}^{-1}\text{ g}^{-1} \times (20.0\text{ °C} - 50.0\text{ °C})$$
$$= 100.\text{ g} \times 2.44\text{ J K}^{-1}\text{ g}^{-1} \times (-30.0\text{ K})$$
$$= -732_0\text{ J} = -7.32\text{ kJ}$$

This heat is negative indicating heat is released by the ethanol as it cools.

6.2 There are three processes to consider here: (1) heat the water from 20.°C to 100.°C; (2) vaporize the $H_2O(l)$ to $H_2O(g)$ at 100.°C; (3) heat the $H_2O(g)$ from 100.°C to 150.°C.

First, get the mass of water from its volume and density:

$$m = d\,V = 200.\text{ mL} \times 1.00\text{ g mL}^{-1} = 200.\text{ g}$$

Next, determine the heat needed to raise the liquid water temperature to 100. °C - the boiling point of water.

$$q_1 = ms_{\text{water liq}}\,\Delta T$$
$$= 200.\text{ g} \times 4.18\text{ J K}^{-1}\text{ g}^{-1} \times (100.0\text{ °C} - 20.0\text{ °C})$$
$$= 668_{80}\text{ J} = 6.69\text{ kJ}$$

Now consider the vaporization of the $H_2O(l)$ to $H_2O(g)$ at 100.°C. The heat of vaporization is given as kJ mol^{-1}. The number of moles of water is

$$n = m/M = 200.\text{ g} / 18.015\text{ g mol}^{-1} = 11.1\text{ mol}$$

Vaporization of all the water requires

$$q_2 = n\,\Delta H_{\text{vap}}°[H_2O] = 11.1\text{ mol} \times 44.0\text{ kJ mol}^{-1} = 488._4\text{ kJ}$$

Finally, heating the water vapour from 100°C to 150°C requires

$$q_3 = ms_{\text{water vap}}\,\Delta T$$
$$= 200.\text{ g} \times 1.85\text{ J K}^{-1}\text{ g}^{-1} \times (150.0\text{ °C} - 100.0\text{ °C})$$
$$= 185_{00}\text{ J} = 1.85\text{ kJ}$$

The total heat required is

$$q = q_1 + q_2 + q_3$$
$$= 6.69 + 488._4 + 1.85\text{ kJ}$$
$$= 496._9\text{ kJ} = = 497\text{ kJ}$$

Note that the bulk of this heat is needed to vaporize the water.

6.3 We assume the solution has the same density and specific heat as pure water. The mass of solution is the mass of water (volume x density) plus the mass of NH_4NO_3,

$$m = 100.\text{ mL} \times 1.00\text{ g mL}^{-1} + 8.16\text{ g}$$

The drop in temperature indicates an endothermic reaction. The heat absorbed by the reaction (we include the sign reversal by reversing the final and initial temperatures) is given by

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$$q_{rxn} = ms_{water}(T_{initial} - T_{final})$$
$$= 108\ g \times 4.18\ J\ K^{-1}\ g^{-1} \times (19.5\ °C - 15.9\ °C)$$
$$= 16_{25}\ J = 1.6_{25}\ kJ$$

To get the enthalpy of dissolution per mole of NH_4NO_3, we must divide this heat by the moles of NH_4NO_3,

$$n = 8.16\ g / 80.04\ g\ mol^{-1} = 0.101_9\ mol$$

The enthalpy of dissolution is

$$\Delta H = q_{rxn} / n$$
$$= 1.6_{25}\ kJ / 0.101_9\ mol = 15.9\ kJ$$

6.4 The change in energy of the gas is given by the first law of thermodynamics,

$$\Delta U = q + w = 125\ J$$

The work done on the system is given by

$$w = -p\,\Delta V$$
$$= 1.00\ atm \times (-2.00\ L) = -2.00\ L\ atm \times (101.3\ J\ L^{-1}\ atm^{-1}) = 202\ J$$

Note the insertion of the conversion factor in the last step.
The first equation can now be solved for q,

$$q = \Delta U - w = 125 - 202\ J = -77\ J$$

Because this heat is negative, heat was released by the gas during the process.

6.5 (a) **(i)** Vaporization of mercury is endothermic ($q > 0$). The system requires input of heat to break the bonds between mercury atoms in the liquid. (ii) Work is done by the system ($w < 0$) because the volume increases. The volume of the system increases because one mole of gas is produced from one mole of liquid – gas occupies a much greater volume.

(b) **(i)** Atomization of bromine (breaking the diatomic molecule into atoms) is endothermic ($q > 0$). Breaking a bond requires energy input. (ii) Work is done by the system ($w < 0$), as volume increases.

(c) (i) Recombination of hydrogen and chlorine atoms is exothermic ($q < 0$). A bond is formed, releasing energy. **(ii)** Work is done on the system ($w > 0$), as volume decreases.

(d) (i) Deposition of carbon atoms into solid carbon is exothermic ($q < 0$) – bonds are formed. **(ii)** Work is done on the system ($w > 0$). Volume decreases.

(e) (i) In the combustion of sulfur, S-S and O=O bonds are broken, while S=O bonds are formed. In this case, experience tells us that this is exothermic ($q < 0$). The burning of sulfur (brimstone) releases energy. **(ii)** There are two moles of product gas and three moles of reactant gas. Work in done on the system ($w > 0$).

6.6 Use Hess' law. Reactions 1 and 2 have H_2 and N_2 as reactants. Reaction 3 has ammonia as a reactant. Reverse reaction 3 because ammonia is a product in the target reaction.

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$$\frac{3}{2}\times \quad 2H_2(g) + O_2(g) \longrightarrow 2H_2O(g) \qquad \Delta H^\circ = \frac{3}{2}\times(-483.6\ \text{kJ mol}^{-1})$$
$$N_2(g) + O_2(g) \longrightarrow 2NO(g) \qquad \Delta H^\circ = 182.6\,\text{kJ mol}^{-1}$$
$$\frac{1}{2}\times \quad 4NO(g) + 6H_2O(g) \longrightarrow 4NH_3(g) + 5O_2(g) \qquad \Delta H^\circ = -\frac{1}{2}\times(-260.7\,\text{kJ mol}^{-1})$$
$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g) \qquad \Delta H^\circ = -412.5\ \text{kJ mol}^{-1}$$

6.7 Subtract reactant enthalpies of formation from those of the products (leave out elements in their standard state – their contribution is zero):

$$\Delta H^\circ = \Delta H_f^\circ[Al_2O_3(s)] + 2\Delta H_f^\circ[H_2O(l)] - \Delta H_f^\circ[NH_4NO_3(s)]$$
$$= -1675.7 + 2(-285.8) - (-356.6)\ \text{kJ mol}^{-1} = -1890.7\ \text{kJ mol}^{-1}$$

The molar mass of reactants, not including oxygen, is 134.0 g mol^{-1}. Per gram of explosive, the heat released is

1890.7 kJ mol^{-1} / 134.0 g mol^{-1} = 14.11 kJ g^{-1}

Note the sign reversal because we are asked for the heat *released* (–*q*).

The heat released by 10. g of explosive is 141.1 kJ. This heat would increase the temperature of 1.0 L of water by

$$\Delta T = \frac{q_{\text{water}}}{m_{\text{water}}s_{\text{water}}} = \frac{141.1\ \text{kJ g}^{-1}}{1000\ \text{g} \times 4.18\ \text{J K}^{-1}\text{g}^{-1}} = 33.8\ \text{K}$$

Note a conversion from kJ to J is needed in the numerator of the above equation (1 kJ = 10^3 J) in order for all units to cancel appropriately.
The final temperature of 1.0 L of water initially at 20.°C is

= 20. + 33.8 °C = 54°C

6.8 First relate the reaction to a corresponding gas phase reaction by adding appropriate vaporization and condensation steps. (If solids were present sublimation and/or deposition processes would be included.) Specifically,

$$CH_3CH_2OH(g) + 2\ HOCl(g) \rightarrow CH_3COOH(g) + 2\ HCl(g) + 2\ H_2O(g) \qquad \Delta H^\circ = \Delta H^\circ_{\text{gas phase rxn}}$$
$$CH_3CH_2OH(l) \longrightarrow CH_3CH_2OH(g) \qquad \Delta H^\circ = \Delta H^\circ_{\text{vap}}[\text{ethanol}] = 38.6\,\text{kJ mol}^{-1}$$
$$CH_3COOH(g) \longrightarrow CH_3COOH(l) \qquad \Delta H^\circ = -\Delta H^\circ_{\text{vap}}[\text{ethanoic acid}] = -23.7\,\text{kJ mol}^{-1}$$
$$2\times \quad H_2O(g) \longrightarrow H_2O(l) \qquad \Delta H^\circ = -2\Delta H^\circ_{\text{vap}}[\text{water}] = -88.0\,\text{kJ mol}^{-1}$$
$$CH_3CH_2OH(l) + 2\ HOCl(g) \rightarrow CH_3COOH(l) + 2\ HCl(g) + 2\ H_2O(l) \qquad \Delta H^\circ = \Delta H^\circ_{\text{gas phase rxn}} - 73.1\ \text{kJ mol}^{-1}$$

Subtract product bond enthalpies from those of the reactants to estimate the enthalpy of the gas phase reaction. To identify all the bonds, rewrite the reaction using molecular structures:

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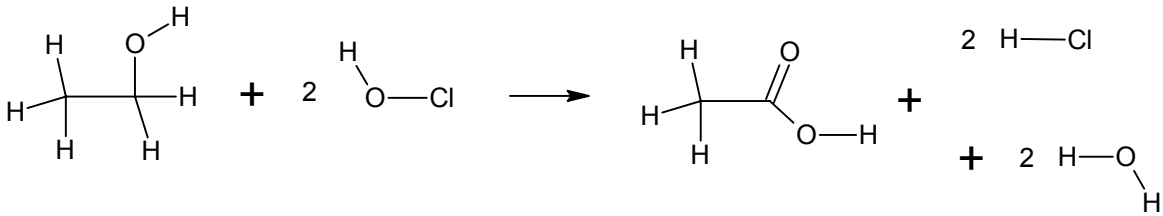

$$\Delta H_{\text{gas phase rxn}} \cong 5D[\text{C-H}] + D[\text{C-O}] + D[\text{O-H}] + 2D[\text{O-H}] + 2D[\text{Cl-O}]$$
$$- 3D[\text{C-H}] + D[\text{C-O}] - D[\text{C=O}] - D[\text{O-H}] - 4D[\text{O-H}] - 2D[\text{Cl-H}]$$
$$= 2D[\text{C-H}] + 2D[\text{Cl-O}] - D[\text{C=O}] - 2D[\text{O-H}] - 2D[\text{Cl-H}]$$
$$= 2 \times 415 + 2 \times 220 - 750 - 2 \times 460 - 2 \times 430 \ \text{ kJ mol}^{-1}$$
$$= -1260 \ \text{ kJ mol}^{-1}$$

Note that there is much cancelation of bond energies. Reactant bonds unchanged in the reaction (i.e. they also appear in the products) cancel out. The intermediate step, shown above, includes only the bonds that are changing – either broken (+*D*) or formed (□*D*).

The enthalpy of the oxidation of liquid ethanol to liquid ethanoic acid is therefore

$$\Delta H = \Delta H_{vap}°[CH_3CH_2OH] - 1260 \text{ kJ mol}^{-1} - \Delta H_{vap}°[CH_3COOH] - 2\,\Delta H_{vap}°[H_2O]$$
$$= 38.6 - 1260 - 23.7 - 2 \times 44.0 \text{ kJ mol}^{-1}$$
$$= -1333.1 \text{ kJ mol}^{-1}$$

Note that the terms of the above equation correspond to the following steps that, together, achieve the target reaction: (1) vaporize the ethanol, (2) carry out the reaction in the gas phase, (3) and (4) condense the ethanoic acid and water produced.

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7. Math Skills

Chemistry is a *quantitative* subject. This is its strength. Only through careful *measurement* and *calculation* are chemists able to reveal the world of atoms and molecules.

7.1 Scientific Notation

You may be asked to do chemical calculations. These calculations frequently involve very large or very small numbers. It is inconvenient (sometimes ridiculous) to write these numbers in the usual way – e.g. 0.00071, 0.012, 15, 3700, 450000. Scientific notation was introduced to let us leave out all the leading or trailing zeros otherwise needed to write numbers. The set of numbers listed above can be written as 7.1×10^{-4}, 1.2×10^{-2}, 1.5×10^{1}, 3.7×10^{3} and 4.5×10^{5}. The advantage of scientific notation is not necessarily evident here – e.g. we would rarely write 15 as 1.5×10^{1}. However, try to write the values 6.022×10^{23} or 6.626×10^{-34} without scientific notation!

Writing a number in scientific notation simply amounts to factoring the number into a power of 10 and a number in the range 1.0 to 9.999.... The exponent of 10 is the number of places the decimal moves to the left or minus the number of places the decimal moves to the right in order to get the number into the convenient range.

Example 7.1: Write the following numbers in scientific notation: (a) 53400 (b) 0.00618

> **Approach:** How many places do we need to move the decimal to get a number less than 10 or bigger than (or equal to) 1.0? The number of places moved to the left is the exponent of 10. Moving the decimal to the right means the exponent is negative.
>
> (a) If the decimal is moved 4 places to the left, we get 5.34. Therefore,
> $53400 = 5.34 \times 10^{4}$.
> (b) If the decimal is moved 3 places to the right, we get 6.18. Therefore,
> $0.00618 = 6.18 \times 10^{-3}$.

Scientific notation uses powers of 10 because our number system is the decimal system. Another way to get to work with more manageable numbers is to change the units. Again, powers of 10 are convenient for unit conversion. For example, we prefer to measure the distance between places in km rather than m. 1 km = 10^{3} m. Also, precision machine components must be accurate to within a micrometer (micron), 1 μm = 10^{-6} m. Powers of 10^{3} are common unit conversions in the metric system. Tiny masses might be measured in picograms (1 pg = 10^{-12} g), while very large masses measured in teragrams (1 Tg = 10^{12} g). The range of units spanned here is shown in the table.

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Table 7.1. Units of Distance

Distance measure	unit	relation to m
picometer	pm	10^{-12} m
nanometer	nm	10^{-9} m
micrometer	µm	10^{-6} m
millimeter	mm	10^{-3} m
centimeter	cm	10^{-2} m
decimeter	dm	10^{-1} m
Meter	m	1 m
kilometer	km	10^{3} m
megameter	Mm	10^{6} m
gigameter	Gm	10^{9} m
terameter	Tm	10^{12} m

7.2 Dimensional Analysis

It is important to pay close attention to units in order to do correct calculations. For example, if you are given density in g mL^{-1} and a volume of the material in L, then you must convert one of the given units so that only one volume unit, mL or L, is used. The mass is determined by multiplying density and volume. The volume units must be the same so that they cancel. for example,

$$\text{mass} = \text{density} \times \text{volume}$$

units:

$$\text{g} = \text{g mL}^{-1} \times \text{mL}$$

$$= \frac{\text{g}}{\text{mL}} \times \text{mL}$$

Attention to units can prevent use of incorrect formulas. The units must be the same on both sides of a formula. If they are not, the formula is wrong. Here are some examples with correct units:

$$\text{amount} = \frac{\text{mass}}{\text{molar mass}}$$

units:

$$\text{mol} = \frac{\text{g}}{\text{g mol}^{-1}}$$

$$= \frac{\text{g mol}}{\text{g}}$$

$$p = \frac{nRT}{V}$$

units:

$$\text{atm} = \frac{\text{mol} \left(\text{L atm K}^{-1}\text{mol}^{-1}\right) \text{K}}{\text{L}}$$

Prove to yourself that the mol, L and K units all cancel appropriately in the equation above!

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The value of the gas constant used in the ideal gas law, above, has the units, L atm K^{-1} mol^{-1}. The other form of the gas constant with units of J K^{-1} mol^{-1} is useful in work and other thermodynamic calculations.

Another common unit used in calculations is Avogadro's number, N_A, which has the value and unit of 6.0223×10^{23} mol^{-1}. We use this unit to scale quantities up to the molar scale, or down from the molar scale to the scale of individual particles. Carefully paying attention to this unit helps us use it correctly. We can have Avogadro's number of anything – atoms, molecules, ions, etc., so we can make the unit atoms mol^{-1}, molecules mol^{-1}, etc., as needed.

Example 7.2: How many Cu atoms are there in a penny? Let the mass of the penny be 3.35 g and assume it is pure copper.

> **Approach:** Determine number of moles of copper. Convert to number of atoms.
>
> Amount of Cu (mol) = mass / molar mass = 3.35 g / 63.546 g mol^{-1} = $5.27_2 \times 10^{-2}$ mol
> [Note: the final digit is shown as a subscript to indicate that it is not a significant digit. Rather, it is an extra digit which we will carry through the next stage of the calculation, in order to avoid rounding errors.]
>
> To convert to number of atoms,
>
> Number of atoms = $5.27_2 \times 10^{-2}$ mol $\times$ 6.0223×10^{23} atoms mol^{-1} = 3.17×10^{22} atoms

In this case we needed to multiply by Avogadro's number, in order to cancel the mol units.

7.3 Solving for a variable

Often in a calculation we are solving for at least one unknown quantity. Basic algebra skills will help us manipulate equations to isolate the variable we seek.

Example 7.3: A solution with volume 0.500 L and concentration 0.101 mol L^{-1} is diluted to 1.50 L. What is the new concentration?

> **Approach:** The number of moles of solute is unchanged.
> **Reality check:** The new concentration should be less than the initial.
>
> Since mol (initial) = mol (final), and $n = cV$, then $c_i V_i = c_f V_f$.
>
> $$0.101 \text{ mol L}^{-1} \times 0.500 \text{ L} = c_f \left(1.50 \text{ L}\right)$$
>
> So
>
> $$c_f = \frac{0.101 \text{ mol L}^{-1} \times 0.500 \text{ L}}{1.50 \text{ L}} = 0.0337 \text{ mol L}^{-1}$$

This matches our expectation (lower concentration). Notice how the units provide an excellent way to check that the calculation is set up correctly.

On occasion we may have more than one variable that is unknown. In such cases we will need more than one equation (or statement of variables) in order to solve for the unknowns. For example, if we have 2 unknowns, then we will need a minimum of 2 equations involving the variables, in order to solve for each one.

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Example 7.4: We have information that tells us the following relationships:
$x + y = 0.295$ mol and $0.20 = \log [\, y / (0.075 + x) \,]$

What are x and y?

We can use the first equation to write one variable in terms of the second one, then make a substitution in the second equation, in order to solve.

$$x = 0.295 - y$$

Substitute this into the second equation to get

$$0.20 = \log [\, y / (0.075 + 0.295 - y) \,]$$

Raise both sides to the power of 10 to remove the log statement on the right side

$$10^{0.20} = y / (0.370 - y)$$
$$1.58 = y / (0.370 - y)$$
$$1.58\,(0.370 - y) = y$$
$$0.584_6 - 1.58\,y = y$$
$$0.584_6 = y + 1.58\,y$$
$$0.584_6 = 2.58\,y$$
$$0.584_6/2.58 = y$$
$$0.227 = y$$

Now we can return and solve for x:

$$x + y = 0.295 \text{ mol}$$
$$x + 0.227 = 0.295$$
$$x = 0.295 - 0.227 = 0.068 \text{ mol}$$

Note that this last problem required taking the inverse of a log – i.e., we raised both sides of the equation in the third line of the solution to the power of 10. This is the inverse of a log (antilog).

7.4 Logarithms

Chemistry deals with quantities that can vary over vast ranges, as we have seen. This arises because many quantities vary exponentially. It is often convenient – and sometimes essential – to introduce the logarithm function, For example, acidity (or basicity) is generally expressed via the pH (the "potential of hydrogen").

$$\text{pH} = -\log_{10}(\, [H^+] \,)$$

A base 10 logarithm is used here. When we use the natural logarithm, we use the notation, ln.

pH can vary from below 0 to above 14. This corresponds to $[H^+]$ varying over more than 14 orders of magnitude.

The key properties of logarithms are as follows:

1. $y = 10^x$ is the inverse of the logarithm:

$$\text{if } y = \log x, \text{ then } 10^y = x$$

2. The sign of a log determines the size of the argument relative to 1:

$$\text{If } \log x > 0, \text{ then } x > 1$$

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If $\log x < 0$, then $0 < x < 1$.

Note that you cannot take the log of a negative number. Also, the argument of the logarithm (here, x) must not be negative.

3. The log of a product is the sum of the logarithms:

$$\log(x\,y) = \log x + \log y$$

4. The argument of a log must not have units. The $[H^+]$ that appears above in the definition of pH is the concentration of H^+ with the units of mol L^{-1} divided out. Note that we can take the log of an equilibrium constant because it has no units – any units of concentration (mol L^{-1}) and pressure (atm) are divided out.

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Periodic Table of the Elements

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Period	Main Group (s-block) 1 (IA)	2 (IIA)	Transition Metals (d-block) 3 (IIIB)	4 (IVB)	5 (VB)	6 (VIB)	7 (VIIB)	8	9 (VIIIB)	10	11 (IB)	12 (IIB)	Main Group (p-block) 13 (IIIA)	14 (IVA)	15 (VA)	16 (VIA)	17 (VIIA)	s-block (He only) 18 (VIIIA)
1	hydrogen 1 H 1.00794																	helium 2 He 4.002602
2	lithium 3 Li 6.941	beryllium 4 Be 9.012182											boron 5 B 10.811	carbon 6 C 12.0107	nitrogen 7 N 14.00674	oxygen 8 O 15.9994	fluorine 9 F 18.998403	neon 10 Ne 20.1797
3	sodium 11 Na 22.98977	magnesium 12 Mg 24.3050											aluminum 13 Al 26.981538	silicon 14 Si 28.0855	phosphorus 15 P 30.97376	sulfur 16 S 32.066	chlorine 17 Cl 35.4527	argon 18 Ar 39.948
4	potassium 19 K 39.0983	calcium 20 Ca 40.078	scandium 21 Sc 44.955910	titanium 22 Ti 47.867	vanadium 23 V 50.9415	chromium 24 Cr 51.9961	manganese 25 Mn 54.938049	iron 26 Fe 55.845	cobalt 27 Co 58.93320	nickel 28 Ni 58.6934	copper 29 Cu 63.546	zinc 30 Zn 65.409	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.92160	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.798
5	rubidium 37 Rb 85.4678	strontium 38 Sr 87.62	yttrium 39 Y 88.90585	zirconium 40 Zr 91.224	niobium 41 Nb 92.90638	molybdenum 42 Mo 95.94	technetium 43 Tc [98.9063]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.90550	palladium 46 Pd 106.42	silver 47 Ag 107.8682	cadmium 48 Cd 112.411	indium 49 In 114.818	tin 50 Sn 118.710	antimony 51 Sb 121.760	tellurium 52 Te 127.60	iodine 53 I 126.90447	xenon 54 Xe 131.29
6	cesium 55 Cs 132.90545	barium 56 Ba 137.327	57-71 *	hafnium 72 Hf 178.49	tantalum 73 Ta 180.9479	tungsten 74 W 183.84	rhenium 75 Re 186.207	osmium 76 Os 190.23	iridium 77 Ir 192.217	platinum 78 Pt 195.078	gold 79 Au 196.96655	mercury 80 Hg 200.59	thallium 81 Tl 204.3833	lead 82 Pb 207.2	bismuth 83 Bi 208.98038	polonium 84 Po [208.9824]	astatine 85 At [209.9871]	radon 86 Rn [222.0176]
7	francium 87 Fr [223.0197]	radium 88 Ra [226.0254]	89-103 **	rutherfordium 104 Rf [261.1089]	dubnium 105 Db [262.1144]	seaborgium 106 Sg [263.1186]	bohrium 107 Bh [264.12]	hassium 108 Hs [265.1306]	meitnerium 109 Mt [268]	darmstadtium 110 Ds [281]	roentgenium 111 Rg [272]	ununbium 112 Uub [285]	ununtriium 113 Uut [284]	unuquadium 114 Uuq [289]	ununpentium 115 Uup [288]	ununhexium 116 Uuh [292]		ununoctium 118 Uuo [294]

	d-block	f-block													
* lanthanoids	lanthanum 57 La 138.9055	cerium 58 Ce 140.116	praseodymium 59 Pr 140.90765	neodymium 60 Nd 144.24	promethium 61 Pm [144.9127]	samarium 62 Sm 150.36	europium 63 Eu 151.964	gadolinium 64 Gd 157.25	terbium 65 Tb 158.9253	dysprosium 66 Dy 162.500	holmium 67 Ho 164.93032	erbium 68 Er 167.26	thulium 69 Tm 168.9342	ytterbium 70 Yb 173.04	lutetium 71 Lu 174.967
** actinoids	actinium 89 Ac [227.0277]	thorium 90 Th 232.0381	protactinium 91 Pa 231.03588	uranium 92 U 238.0289	neptunium 93 Np [237.0482]	plutonium 94 Pu [244.0642]	americium 95 Am [243.0614]	curium 96 Cm [247.0703]	berkelium 97 Bk [247.0703]	californium 98 Cf [251.0796]	einsteinium 99 Es [252.0830]	fermium 100 Fm [257.0951]	mendelevium 101 Md [258.0984]	nobelium 102 No [259.1011]	lawrencium 103 Lr [262.110]

Rare Earth Elements

Solid
Liquid
Gas

The periodic table is based on the latest version recommended by IUPAC (2003, see http://www.iupac.org/reports/periodic_table/), however, IUPAC has not yet confirmed discovery of elements 113–116 and 118 (see http://www.iupac.org/publications/pac/2003/7510/7510x1601.html). Elements 113 and 115 were reported in February 2004. The symbols of the elements, their names, and their spellings are those recommended by the International Union of Pure and Applied Chemistry (IUPAC, 2001). Names have not yet been proposed for the most recently reported elements 113-116 and 118, so those listed are IUPAC's temporary systematic names. The name copernicium has been proposed for element 112 as of July 2009, however has not yet been formally endorsed by IUPAC. Atomic weights (mean relative masses) are the IUPAC 2001 values. Elements for which the atomic weight is contained within square brackets have no stable nuclides (*i.e.* are radioactive) and are represented by one of the element's more important isotopes. The symbols for naturally-occurring elements are colour-coded according to whether they exist as a solid, liquid or gas in their natural state at standard temperature and pressure. Synthetic elements are coloured white.

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