CHAPTER 1 – STOICHIOMETRY

Introduction

Chemistry – A Molecular Science (CAMS), the first half of this two-course sequence, stressed bonding, structure, and reactivity. The material was qualitative and stressed several types of reactions and the factors that affected their relative extents of reaction. However, as the title of this text suggests, chemistry is also a quantitative science. Chemists must not only predict the products of a reaction, they must also predict the amount of product that can be expected, and the amount of waste that must be removed. They also need to know how much energy is required or how much heat is generated by a reaction. They must also understand how the reaction occurs so that they can optimize the reaction conditions. These are the types of problems addressed in this text.

We begin our study of the quantitative aspects of chemistry with stoichiometry, the science that deals with the quantitative relationships between the elements in a compound (substance stoichiometry) and between the substances in a chemical reaction (reaction stoichiometry). It is the topic of this first chapter because a thorough knowledge of stoichiometry is vital to an understanding of the material presented in this course. Understanding how quantitative data and results are presented is also important, so you should review Appendix A, Reporting Quantitative Measurements and Results, for a treatment of precision, significant figures, and rounding errors. Finally, we will set up many problems using the factor label method, so please review Appendix B, The Factor Label Method, for a discussion of this procedure.

1.1 Mass and Moles

Introduction

Chemists use chemical equations to design possible routes to desired molecules and to discuss chemical processes. However, the individual molecules represented in the equations are far too small to be seen, so chemists must use a very large number of molecules in their reactions in order that the reactants and products can be observed. Indeed, the number of molecules required to make a visible sample is staggering. Consider that 1 μL of water—about 1/50th of a drop—contains about 100,000,000,000,000,000 or 10^{17} molecules and a typical reaction in the laboratory involves thousands of times that number. Such large numbers are cumbersome, so scientists use a more convenient unit when discussing numbers of molecules. The unit is the mole, the topic of this section.

Objectives

- Convert between numbers of moles and numbers of particles with Avogadro's number.
- Convert between mass and moles with molar mass.
- Convert between the pressure, volume, and temperature of a gas and the number of moles with the ideal gas law.

1.1-1. Avogadro's Number

Avogadro's number, which is given below, is simply the number of items in a mole, so it also defines the ***mole***, which is simply Avogadro's number of items.

$$N_\text{A} = 6.0221 \times 10^{23}\text{mol}^{-1} \qquad \text{Avogadro's Number}$$

A mole is used to indicate a number of items just as a dozen is used to indicate a number of eggs. Since Avodagro's number is so large, the mole is used only for the number of atoms or molecules, but it can be used for any item. For example, it is estimated that there are about 10^{23}–10^{24} stars in the universe, which is 1–10 moles. Converting from moles to atoms or molecules is done in the same way as converting dozens to items.
1.5 doz = (1.5 doz)(12 items/doz) = 18 items and 1.5 mol = (1.5 mol)(6.0×10^{23} atoms/mol) = 9.0×10^{23} atoms. The mole is used simply because it is much easier to discuss the number of atoms in moles than it is as individual items. 0.10 mol H_2O is a much more convenient expression than 6.0×10^{22} H_2O molecules.

1.1-2. Molar Mass (M_m)

Chemists need to be able to readily prepare mixtures of reactants that have the correct atom or molecule ratios for reaction, but they certainly cannot count such large numbers. Instead, they use other more easily determined properties that are related to the numbers of atoms and/or molecules. The first such method we examine is mass. Mass can be used to "count" atoms and molecules because a mole is the number of atoms present in one gram atomic weight (the atomic weight expressed in grams) of any atom or in one gram molecular weight of any molecule. Thus, the mass of a mole of any substance, which is known as its ***molar mass*** (M_m), equals its atomic or molecular weight expressed in grams. For example, the atomic weight of Mg is 24.3, so its molar mass 24.3 g/mol, and the molecular weight of CO_2 is 44.0, so its molar mass is 44.0 g/mol. Thus, molar mass allows us to quickly convert a mass into a number of moles or a number of moles into a mass. Chemists use this fact to quickly "count" the number of moles of substance by simply weighing it.

Mole ↔ mass conversions are most easily done with the factor label method. It uses the units of the given quantity and those of the conversion factors to assure the proper operations are performed. To use this method, arrange the factors so that the denominator of each factor cancels the numerator of the previous quantity until the units of the answer are obtained. (See The Factor Label Method.)

1.1-3. Determining Molar Mass Exercise

EXERCISE 1.1:

Determine the molar masses of the following. Express all answers to the nearest whole number.

N_2F_4
Atomic weight of N ________________

Atomic weight of F ________________

Molar mass of N_2F_4 ________________ g/mol

$Ca_3(PO_4)_2$
Atomic weight of Ca ________________

Atomic weight of P ________________

Atomic weight of O ________________

Molar mass of $Ca_3(PO_4)_2$ ________________ g/mol

1.1-4. Mass-Mole Conversion Exercises

EXERCISE 1.2:

What is the mass of 3.24 mol N_2O_5?

Molar mass $M_m =$ ________________ g/mol

Mass $m =$ ________________ g

How many moles of N_2O_5 are in 12.7 g?

Moles $n =$ ________________ mol

1.1-5. Moles-Items Exercise

EXERCISE 1.3:

How many Al atoms are present in 0.065 g Al?

Moles of atoms $n =$ ______________ mol

Individual atoms $N =$ ______________ atoms

1.1-6. Ideal Gas Law

The number of moles of molecules in a gas can also be determined with the ideal gas law.

$$PV = nRT \qquad \text{Ideal Gas Law} \tag{1.1}$$

- P is the pressure of the gas in atmospheres. 1 atm = 760 torr
- V is its volume in liters.
- n is the number of moles of gas.
- $R = 0.08206$ L·atm·K^{-1}·mol^{-1} is the ideal gas law constant.
- T is the temperature on the Kelvin scale (K = °C + 273.15).

1.1-7. Gas Law Exercise

EXERCISE 1.4:

How many moles of H_2 are in a 3.06 L container at 22 °C if its pressure is 742 torr?

$P =$ ______________ atm

$V =$ ______________ L

$R = 0.08206$ L·atm·K^{-1}·mol^{-1}

$T =$ ______________ K

$n =$ ______________ mol H_2

1.2 Determining Chemical Formulas

Introduction

The composition of a compound is given in terms of the mass percents of its component elements. In this section, we show how these fractions can be determined from the chemical formula of the compound and how the chemical formula can be determined from the fractions.

Objectives

- Determine the mass composition of a compound from experimental data.
- Determine the mass composition from the formula of the compound.
- Determine the amount of one element that is combined with a known amount of another element or is present in a known amount of compound.
- Determine the simplest formula of a compound from the relative amounts of each of the elements present in a sample.

- Determine a molecular formula from its simplest formula and molar mass.
- Use the empirical formula and the molar mass of a substance to determine its molecular formula.

1.2-1. Experimental Mass Composition

The mass fraction of an element in a compound is the mass of the element divided by the mass of the compound in which it is found.

$$\text{mass fraction of element A} = \frac{\text{mass of element A in compound}}{\text{mass of compound}}$$

The ***mass percent*** of an element in a compound is its mass fraction expressed as a percent.

$$\text{mass percent of element A} = \text{mass fraction of element A} \times 100\%$$

The ***elemental composition*** of a compound is frequently given by the mass percents of the elements. As shown in the following example, the elemental composition of lead(II) chloride is 74.4% Pb and 25.6% Cl by mass.

EXAMPLE:

Determine the percent lead in a sample if a 1.062 g sample contains 0.791 g Pb.

$$\text{\% mass of element} = \frac{0.791\text{ g Pb}}{1.062\text{ g compound}} \times 100\% = 74.4\%\text{ Pb}$$

1.2-2. Composition Exercise

EXERCISE 1.5:

A 0.2986 g sample of an oxide of iron contains 0.2161 g Fe. What is the percent iron in the sample?

$$\frac{\_\_\_\_\_\text{ g Fe}}{\_\_\_\_\_\text{ g compound}} \times 100\% = \_\_\_\_\_\text{ \% Fe}$$

1.2-3. Mass Composition from Chemical Formulas

The elemental composition of a compound can be determined from its formula because its molar mass and the mass contributed by each element to its molar mass are known.

<u>EXAMPLE</u>:

One mole of $PbCl_2$ contains:

$$\begin{aligned}(1 \text{ mol Pb})(207 \text{ g/mol Pb}) + (2 \text{ mol Cl})(35.5 \text{ g/mol Cl}) &= 207 \text{ g Pb} + 71.0 \text{ g Cl} \\ &= 278 \text{ g PbCl}_2\end{aligned}$$

Consequently, 278 g of $PbCl_2$ contains 207 g Pb and 71.0 g Cl, so the elemental composition of lead chloride can be expressed as follows:

$$\frac{207 \text{ g Pb}}{278 \text{ g of PbCl}_2} \times 100\% = 74.5\% \text{ Pb}$$

and

$$\frac{71.0 \text{ g Cl}}{278 \text{ g of PbCl}_2} \times 100\% = 25.5\% \text{ Cl}$$

In summary, one molar mass of A_aB_b contains:

- (a mol A)(molar mass of A) grams of A
- (b mol B)(molar mass of B) grams of B

Thus, its elemental composition can be determined as follows:

$$\%\text{A in } A_aB_b = \frac{a \times \text{ molar mass of A}}{\text{molar mass of } A_aB_b} \times 100\%$$

and

$$\%\text{B in } A_aB_b = \frac{b \times \text{molar mass of B}}{\text{molar mass of } A_aB_b} \times 100\%$$

1.2-4. Mass Percent Exercise

<u>EXERCISE 1.6</u>:

What is the mass percent of Na in Na_2SO_4? Express your answer as a percent to the nearest whole number.

The mass of one mole of Na_2SO_4 is:

_______________ g

The mass of Na in one mole of Na_2SO_4 is:

_______________ g

The fraction of the mass of Na_2SO_4 that is due to sodium expressed as a percent is:

_______________ %

1.2-5. Mass Percent Exercise

EXERCISE 1.7:

Determine the mass percent of P in $Ca_3(PO_4)_2$. Express your answer as a percent to the nearest whole number.

The mass of one mole of $Ca_3(PO_4)_2$ is:

______________ g

The mass of P in one mole of $Ca_3(PO_4)_2$ is:

______________ g

The fraction of the mass of $Ca_3(PO_4)_2$ that is due to phosphorus expressed as a percent is:

______________ %

1.2-6. Using Mass Percents

While an elemental mass fraction has no units, units are implied in factor label problems because the fraction is determined to be (mass of element)/(mass of compound). Consequently, mass fractions can be used to convert between the mass of an element and the mass of the compound. Similarly, the mass percent of an element in a compound can be viewed as the mass of the element present in 100 g of compound. Thus, the fact that XY is 30% X by mass implies that there are 30 g X/100 g XY. Furthermore, the sum of the elemental percents of all the elements in a compound must sum to 100%, so we can deduce the percent of one element in a compound if we know the percents of all other elements in the compound. Thus, if XY is 30% X by mass, then it must also be 70% Y by mass.

EXAMPLE:

Lead chloride is 74.4% lead by mass. How much lead is present in 23.4 g of lead chloride?

The percent is expressed as 74.4 g Pb/100 g compound, which is the factor required for the conversion.

$$23.4 \text{ g compound} \times \frac{74.4 \text{ g Pb}}{100 \text{ g compound}} = 17.4 \text{ g Pb}$$

What is the percent chloride in lead chloride?

The compound contains only Pb and Cl, so the sum of the percents of the two elements must be 100%. However, $PbCl_2$ is 74.4% Pb, so

$$\%\text{Cl} = 100\% - \%\text{Pb} = 100.0 - 74.4 = 25.6\%\text{Cl}$$

Thus, $PbCl_2$ is 74.4% Pb and 25.6% Cl by mass.

1.2-7. Composition Exercise

EXERCISE 1.8:

Hexane (C_6H_{14}) is 83.7% carbon by mass.

What portion, expressed as a percent, of the mass of hexane is due to hydrogen?

%H = ______________ %

How many grams of hexane contain 13.6 g C?

$$\underline{\hspace{3cm}}\ \text{g C} = \frac{\underline{\hspace{3cm}}\ \text{g } C_6H_{14}}{\underline{\hspace{3cm}}\ \text{g C}} = \underline{\hspace{3cm}}\ \text{g } C_6H_{14}$$

1.2-8. Empirical Formula

The elemental composition can be used to determine the ratio of elemental masses in a compound. Molar masses can then be used to convert the ratio of elemental masses into one of moles, and the ratio of moles is the ratio of subscripts in the compound. We cannot determine the actual subscripts without more information, but we can determine the simplest set of integers that results in the correct ratios. The formula of a compound that uses this simplest set of integers is called the ***empirical formula*** or the ***simplest formula***. To determine the empirical or simplest formula of a compound from its elemental composition:

1 Convert the amount of each element in a sample into moles of the element.

2 Determine the ratio of the moles by dividing each by the smallest.

3 If the result of Step 2 is not an integer, convert the ratio to a ratio of simple whole numbers. This is most easily accomplished by identifying the fraction that corresponds to the decimal, and then multiplying the ratio by the integer that makes the ratio an integer. See Table 1.1: Some Common Decimals and their Multipliers.

Step 2	**Multiplier**
0.125	8
0.167	6
0.200	5
0.250	4
0.333	3
0.375	8

Step 2	**Multiplier**
0.5	2
0.625	8
0.667	3
0.75	4
0.833	6
0.875	8

Table 1.1: Some Common Decimals and their Multipliers

For example, to convert a H:C mole ratio in Step 2 of 2.667 to a ratio of small whole numbers, you can recognize that the number means 2.667 mol H/1 mol C and that 0.667, which is a ratio of 2/3 or use the above table to determine that the multiplier must be 3. Multiply the numerator and denominator of the ratio by 3 to eliminate the fraction. The result is 3(2.667)/3(1) = 8 mol H/3 mol C. The formula of the compound is C_3H_8.

1.2-9. Empirical Formula Exercise

EXERCISE 1.9:

6.84 g of an oxide of chromium is found to contain 4.68 g Cr. What is the empirical formula of the oxide? Assume that the compound contains only Cr and O. Express all answers to three significant digits.

The number of moles of each element in the sample is:

moles of Cr (M_m = 52.0 g/mol) in the sample: ______________ mol Cr

moles of O in the sample: ______________ mol O

The ratio of the larger number of moles to the smaller number of moles (mol O/mol Cr) is:

____

The ratio determined in the previous step as a ratio of whole numbers (For example, 1.33 mol O/mol Cr would be expressed as 4/3) is:

____

The empirical formula is the following. (Denote any subscripts with an underscore. For example, NH_3 for NH_3.)

____

1.2-10. Empirical Formula Exercise

EXERCISE 1.10:

When hydrocarbons (compounds that contain only C and H) are burned, all of the carbon is converted into CO_2 and all of the hydrogen into H_2O. What is the empirical formula of a hydrocarbon that produces 0.200 mol CO_2 and 0.125 mol H_2O when burned?

The number of moles of carbon in the sample is:

____

The number of moles of hydrogen in the sample is:

____

The ratio of the larger to the smaller number of moles is:

____

The above number expressed as a ratio of whole numbers is:

____

The empirical formula of the hydrocarbon is the following. (Denote any subscripts with an underscore. For example, NH_3 for NH_3.)

____

1.2-11. Empirical Formulas from Elemental Compositions

To determine the empirical formula of a compound from its percent composition, use the percents as if they were masses in grams and proceed as in the previous topic.

Different samples of a compound are often used to determine each element in an elemental analysis, so compositions are usually presented as mass percents rather than absolute masses. The mass of each element in any amount of sample can be determined with the mass percents, so any sample size can be used. The most convenient sample size to use with mass percents is 100 g because the masses of the elements present in a 100 g sample are equal to the mass percents. For example, 100 g of a compound that is 60% C contains 60 g C or $60/12 = 5$ mol C. To determine an empirical formula from mass percents:

1 Divide the mass percent of each element by its molar mass to determine the number of moles of the element present in 100 g of sample.

2 Divide each of the moles determined in Step 1 by the smallest number of moles to get simple ratios.

3 If any of the results of Step 2 are not integers, multiply all of the numbers by the integer that makes them integers.

4 The integers determined in Step 3 are the subscripts in the empirical formula.

1.2-12. Empirical Formula from Elemental Composition Exercise

EXERCISE 1.11:

A hydrocarbon (a compound that contains only carbon and hydrogen) is found to be 82.66% C and 17.34% H by mass. What is the empirical formula of the hydrocarbon? Use molar masses of 12.01 g/mol and 1.008 g/mol for C and H, respectively.

The number of moles of C in 100 g of compound is:

____

The number of moles of H in 100 g of compound is:

____

The ratio expressed as a decimal of the smaller number to the larger number of moles is:

____

The ratio in Step 3 expressed as a ratio of whole numbers is:

____

The empirical formula is the following. (Denote any subscripts with an underscore. For example, NH_3 for NH_3.)

____

1.2-13. Molecular Formulas

A molecular formula of a compound, which shows the actual number of atoms present in a molecule, can be determined from its empirical formula and molar mass.

An empirical formula gives the simplest whole number ratios of the atoms, while a ***molecular formula*** shows the actual number of atoms present in each molecule. A molecular formula must contain an integral number of empirical units, so the molar mass of a compound must be an integer times the molar mass of the empirical unit. Consider the following table of compounds with the empirical formula CH; i.e., they all have molecular formulas of the type $(CH)_n$, where n is an integer. The molar mass on one empirical unit (CH) is 13 g/mol, so the molar mass of $(CH)_n$ is $13n$.

molecular formula	***n***	**molar mass (g/mol)**
$C_{12}H_{12}$	12	$13 \times 12 = 156$
C_6H_6	6	$13 \times 6 = 78$
C_4H_4	4	$13 \times 4 = 52$

Table 1.2

We use the fact that molar mass of the compound = $n \times$ molar mass of the empirical unit to determine the value of n as follows:

$$n = \frac{\text{molar mass of compound}}{\text{molar mass of empirical unit}} \qquad \text{empirical units} \tag{1.2}$$

Once we have the value of n, we can write the molecular formula by simply multiplying each of the subscripts in the empirical formula by n. For example, to determine the molecular formula of a compound with an empirical formula of CH_2 (M_m = 14 g/mol) and a molar mass of 112 g/mol, we would first determine n as

$$n = \frac{112\ \text{g/mol}}{14\ \text{g/mol}} = 8$$

The compound contains eight empirical units: $(CH_2)_8$, which would be written as C_8H_{16}.

1.2-14. Molecular Formula Exercise

EXERCISE 1.12:

Write the empirical formula for each of the following molecular formulas. (Denote any subscripts with an underscore. For example, NH_3 for NH_3.)

$C_4H_{10}N_4$: ________________ $C_{12}H_{24}N_5$: ________________ $C_8H_8N_4$: ________________

1.2-15. Molecular Formula from Empirical Formula Exercise

EXERCISE 1.13:

What is the molecular formula of a compound that has an empirical formula of C_2H_4O and a molar mass of 88 g/mol?

$$n = \frac{\underline{\qquad\qquad}\ \text{g/mol}}{\underline{\qquad\qquad}\ \text{g/mol}} = \underline{\qquad\qquad}$$

The empirical formula of the compound is the following. (Denote any subscripts with an underscore. For example, NH_3 for NH_3.)

____

1.2-16. Molecular Formula Exercise

EXERCISE 1.14:

What is the molecular formula of a compound that is 64.27% C, 7.19% H, and 28.53% O and has a molar mass of about 220 g/mol?

100.00 g of this compound contains how many moles of each element?

C ______________ mol H ______________ mol O ______________ mol

The number of moles of each element divided by the smallest number of moles is:

C ______________ mol H ______________ mol O ______________ mol

The empirical formula of the compound is the following. (Denote any subscripts with an underscore. For example, NH_3 for NH_3.)

____

The number of empirical units present in one molecular unit is:

____

The molecular formula is the following. (Denote any subscripts with an underscore. For example, NH_3 for NH_3.)

____

1.2-17. Molecular Formula from Combustion Exercise

EXERCISE 1.15:

It is common to determine formulas of organic compounds by burning them and determining the mass fractions of carbon and hydrogen from the amounts of CO_2 and H_2O that are produced in the combustion. If the compound contains oxygen, the mass of oxygen must be determined from the total mass of the sample and the masses of C and H that it contains.

What is the empirical formula of ascorbic acid (vitamin C) if combustion of 0.579 g of ascorbic acid produces 0.868 g of CO_2 and 0.237 g H_2O? Ascorbic acid also contains oxygen.

Convert mass of CO_2 and H_2O to moles.

moles of CO_2 produced: ______________ mol CO_2

moles of C present in the CO_2: ______________ mol C

moles of H_2O produced: ______________ mol H_2O

moles of H present in the H_2O: ______________ mol H

The sample contains oxygen, so its mass must be determined by difference. Therefore, the mass of C and H must be determined from the number of moles above. Note: this step would not be necessary if the sample contained no oxygen. We would simply determine the mol H/mol C ratio with the numbers of moles determined above to get the empirical formula.

mass of C in sample: ______________ g C

mass of H in sample: ______________ g H

mass of oxygen in sample: ______________ g O

moles of oxygen in sample: ______________ mol O

Determine the mole ratios.

mol C/mol C = ______________

mol H/mol C = ______________

mol O/mol C = ______________

Multiplier to be used to convert all of the above to integers:

____

The subscripts in the empirical formula:

subscript of C = ______________

subscript of H = ______________

subscript of O = ______________

The molar mass of ascorbic acid is 176 g/mol. What is its molecular formula?

The molar mass of the empirical unit = ______________ g/mol

The number of empirical units in a molecular unit = ______________ units

The subscripts in the molecular formula:

subscript of C = ______________

subscript of H = ______________

subscript of O = ______________

1.3 Substance or Composition Stoichiometry

Introduction

In a composition stoichiometry problem, the amount of one substance that is combined with another is determined with the use of the ratios of the subscripts in the chemical formula.

Objectives

- Determine and use stoichiometric links derived from chemical formulas.

1.3-1. Stoichiometric Link Video

A video or simulation is available online.

1.3-2. Stoichiometric Links and Chemical Formulas

The stoichiometric links for a substance are formed from the subscripts in a chemical formula.

A ***stoichiometric link*** is the ratio of the number of moles of one substance to the number of moles of another substance with which it combines. The stoichiometric link between two elements in a compound equals the ratio of the subscripts of the two elements in the compound. Consider the example of ammonia shown in Figure 1.1. One molecule of NH_3 contains one nitrogen atom and three hydrogen atoms, so we can write the following stoichiometric links between NH_3, N, and H.

$\frac{1 \text{ mol N}}{3 \text{ mol H}}$	$\frac{1 \text{ mol N}}{1 \text{ mol NH}_3}$	$\frac{3 \text{ mol H}}{1 \text{ mol NH}_3}$

Table 1.3

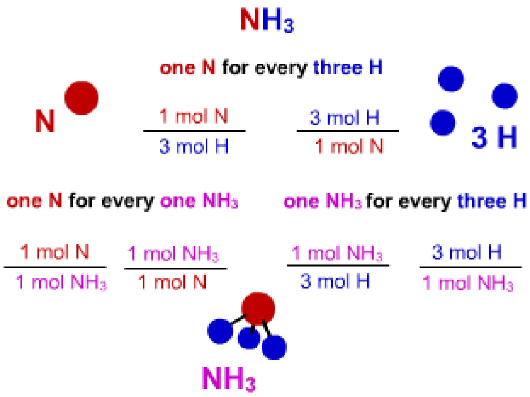


Figure 1.1: Substance Stoichiometry in $\mathbf{NH_3}$

The stoichiometric links available from the formula H_2SO_4 are:

Conversion factors using H in $\mathbf{H}_2\mathrm{SO}_4$			Conversion factors using S in $\mathrm{H}_2\mathbf{S}\mathrm{O}_4$			Conversion factors using O in $\mathrm{H}_2\mathrm{S}\mathbf{O}_4$		
$\frac{2 \text{ mol H}}{1 \text{ mol H}_2\text{SO}_4}$	$\frac{2 \text{ mol H}}{1 \text{ mol S}}$	$\frac{2 \text{ mol H}}{4 \text{ mol O}}$	$\frac{1 \text{ mol S}}{1 \text{ mol H}_2\text{SO}_4}$	$\frac{1 \text{ mol S}}{2 \text{ mol H}}$	$\frac{1 \text{ mol S}}{4 \text{ mol O}}$	$\frac{4 \text{ mol O}}{1 \text{ mol H}_2\text{SO}_4}$	$\frac{4 \text{ mol O}}{2 \text{ mol H}}$	$\frac{4 \text{ mol O}}{1 \text{ mol S}}$

Table 1.4

1.3-3. Using the Stoichiometric Link

Stoichiometric links can be combined with the factor label method to determine the amount of any element in a compound that is combined with a known amount of any other element in the compound.

The units of the denominator of the stoichiometric link must be the same as the given quantity, and the units of the numerator must be the same as those of the desired quantity. Thus, to **convert the amount of one atom or ion into the amount of another in the same compound, multiply the number of moles of a given substance by the appropriate stoichiometric link derived from the subscripts in the chemical formula**.

$$\text{moles of given} \times \frac{\text{subscript of desired}}{\text{subscript of given}} = \text{moles of desired} \qquad (1.3)$$

1.3-4. Mass-Mass Conversion

We have seen that the heart of a substance stoichiometry problem is multiplying the given number of moles by the appropriate stoichiometric link to obtain the number of moles of the desired substance. We now combine that operation with the molar masses of the given and desired substances to determine the mass of one substance (the desired substance) that is combined with a given mass of another (the given substance). The process involves the following three conversions:

1 **mass A → mol A**: Convert the given mass into given moles with the molar mass of the given substance.

2 **mol A → mol B**: Multiply the given moles calculated in Step 1 by the appropriate stoichiometric link to obtain the desired moles.

3 **mol B → mass B**: Convert the desired moles determined in Step 2 into grams with the molar mass of the desired substance.

Of course, all three steps can be combined into one extended multiplication with the factor label method. For example, the following shows how to determine the number of grams of oxygen ($M_m = 16.0$ g/mol) that are combined with 12.2 g of aluminum ($M_m = 27.0$ g/mol) in Al_2O_3.

$$12.2\ \cancel{\text{g Al}} \times \frac{1\ \cancel{\text{mol Al}}}{27.0\ \cancel{\text{g Al}}} \times \frac{3\ \cancel{\text{mol O}}}{2\ \cancel{\text{mol Al}}} \times \frac{16.0\ \text{g O}}{1\ \cancel{\text{mol O}}} = 10.8\ \text{g O}$$

We first divide the given mass of Al by its molar mass to obtain moles of Al. The moles of Al are then multiplied by the ratio of subscripts (stoichiometric link) to obtain the moles of O. Finally, the moles of O are multiplied by the molar mass of O to obtain grams of O. Note that all of the units cancel except grams of O, the desired quantity.

1.3-5. Mole Atom-Mole Molecule Conversion Exercise

EXERCISE 1.16:

How many moles of $MgCl_2$ contain 0.64 mol Cl atoms?

$$\boxed{}\ \text{mol Cl} \times \frac{\boxed{}\ \text{mol MgCl}_2}{\boxed{}\ \text{mol Cl}} = \boxed{}\ \text{mol MgCl}_2$$

1.3-6. Mole Atom-Mole Atom Conversion Exercise

EXERCISE 1.17:

How many moles of hydrogen atoms are in a sample of C_6H_{14} that contains 0.25 mol C?

$$\boxed{}\ \text{mol C} \times \frac{\boxed{}\ \text{mol H}}{\boxed{}\ \text{mol C}} = \boxed{}\ \text{mol H}$$

1.3-7. Mass Atom-Mass Molecule Conversion Exercise

EXERCISE 1.18:

What mass of Fe_3O_4 (M_m = 232 g/mol) contains 12 g of iron (M_m = 55.9 g/mol)?

$$\underline{\qquad}\ \text{g Fe} \times \frac{\underline{\qquad}\ \text{mol Fe}}{\underline{\qquad}\ \text{g Fe}} \times \frac{\underline{\qquad}\ \text{mol Fe}_3\text{O}_4}{\underline{\qquad}\ \text{mol Fe}} \times \frac{\underline{\qquad}\ \text{g Fe}_3\text{O}_4}{\underline{\qquad}\ \text{mol Fe}_3\text{O}_4} = \underline{\qquad}\ \text{g Fe}_3\text{O}_4$$

1.3-8. Mass Atom-Mass Atom Conversion Exercise

EXERCISE 1.19:

What mass of Fe (M_m = 55.9 g/mol) is combined with 26.3 g chlorine (M_m = 35.5 g/mol) in $FeCl_3$?

$$\underline{\qquad}\ \text{g C} \times \frac{\underline{\qquad}\ \text{mol Cl}}{\underline{\qquad}\ \text{g Cl}} \times \frac{\underline{\qquad}\ \text{mol Fe}}{\underline{\qquad}\ \text{mol Cl}} \times \frac{\underline{\qquad}\ \text{g Fe}}{\underline{\qquad}\ \text{mol Fe}} = \underline{\qquad}\ \text{g Fe}$$

1.4 Balancing Chemical Equations

Introduction

Neither the identity nor the number of atoms is changed in a chemical reaction, so chemical equations are balanced to assure that the number of each type of atom is the same on both sides. This is done by changing the number of each reacting and produced molecule by placing coefficients in front of each species. In this section, we show how to balance simple chemical equations by inspection.

Objectives

- Balance a chemical equation by inspection.

1.4-1. Balancing Chemical Equations Video

A video or simulation is available online.

1.4-2. Procedure for Balancing Equations

Chemical equations are balanced to assure that the number of each type of atom is the same on both sides of the equation. Only coefficients (not subscripts) can be changed to balance a chemical equation.

The following steps should lead to a balanced equation:

1 Pick the molecule with the greatest number of atoms and set its coefficient to "1" unless another choice is obviously better. For example, sometimes a "2" must be used to assure an even number of one of the atoms.

2 Determine which atoms are fixed by the coefficient set in Step 1, then balance those atoms on the other side of the equation.

3 Determine which atoms are fixed by the coefficient(s) created in Step 2, then balance those atoms on the other side of the equation.

4 Repeat Step 3 until the equation is balanced.

Note that coefficients of "1" are not usually included in the balanced equation.

<u>EXAMPLE</u>:

As an example, we will follow the steps above to balance the following chemical equation:

______ HCl + ______ MnO_2 → ______ $MnCl_2$ + ______ H_2O + ______ Cl_2

1 Make the coefficient of either MnO_2 or $MnCl_2$ one. We choose MnO_2.

______ HCl + **1** MnO_2 → ______ $MnCl_2$ + ______ H_2O + ______ Cl_2

2 The coefficient used in Step 1 fixes the number of Mn atoms at 1 and O atoms at 2, so we balance the Mn atoms with a coefficient of 1 for $MnCl_2$ and the oxygen atoms with a coefficient of 2 for water.

______ HCl + 1 MnO_2 → **1** $MnCl_2$ + **2** H_2O + ______ Cl_2

3 The coefficient of water fixes the number of hydrogen atoms at four, so we balance the H atoms with a coefficient of 4 for HCl. Note that the coefficient of $MnCl_2$ does not fix the number of Cl atoms because it is not the only source of Cl.

4 HCl + 1 MnO_2 → 1 $MnCl_2$ + 2 H_2O + ______ Cl_2

4 The coefficient of HCl fixes the number of chlorine atoms at four, but there are already 2 Cl atoms in 1 $MnCl_2$, so we balance the Cl atoms on the other side of the equation with a coefficient of 1 for Cl_2.

4 HCl + 1 MnO_2 → 1 $MnCl_2$ + 2 H_2O + **1** Cl_2

5 Each side of the equation contains 4 H atoms, 1 Mn atom, 2 O atoms, and 4 Cl atoms. The equation is now balanced, but ones are not usually written. Thus, the balanced equation is usually written as shown in the last step.

4 HCl + MnO_2 → $MnCl_2$ + 2 H_2O + Cl_2

1.4-3. Balancing Equations Exercise

<u>EXERCISE 1.20</u>:

Balance the following equations with the smallest whole-number coefficients. Include coefficients of “1” in your answer.

______ N_2 + ______ O_2 → ______ N_2O_5

______ Na + ______ H_2O → ______ $NaOH$ + ______ H_2

______ P_4 + ______ Cl_2 → ______ PCl_3

______ $C_6H_{12}O_6$ + ______ O_2 → ______ CO_2 + ______ H_2O

1.5 Reaction Stoichiometry

Introduction

The ratios of the coefficients of a balanced equation are conversion factors that allow us to calculate the amount of one substance that is produced by or reacts with a given amount of another substance. The only difference between this process and the one used to determine how much of one element was combined with a given amount of another element in a compound is the stoichiometric ratio or link: in one, the stoichiometric link is the ratio of the subscripts in the chemical formula; in the other, it is the ratio of the coefficients in the balanced equation. All other operations are the same in the two problem types.

Objectives

- Write the stoichiometric ratio relating two substances involved in a chemical reaction.
- Use the ratio to convert the amount of one substance involved in the reaction to the chemically equivalent amount of another substance in the same reaction.
- Identify the limiting reactant in a reaction.
- Determine the amount of product formed or of reactant consumed from the amount of limiting reactant that reacts.
- Determine the percent yield given the actual yield of a reaction or use the percent yield to determine the actual yield.
- Determine the complete composition of a reaction mixture after the reaction is complete.

1.5-1. Stoichiometric Links in Chemical Reactions

Stoichiometric links formed from the coefficients of balanced chemical equations are used to convert between equivalent amounts of reactants and products in a reaction.

Consider the following balanced chemical equation:

$$N_2 + 3\ H_2 \rightarrow 2\ NH_3$$

The coefficients indicate the relative number number of molecules that react, not the absolute number. That is, the equation does not indicate that three moles of H_2 react. Rather, it indicates that 3 mol H_2 react for every 1 mol N_2 that reacts or for every 2 mol NH_3 that form. Thus, we can write the following stoichiometric links for the reaction.

$\frac{1\text{ mol }N_2}{2\text{ mol }NH_3}$	$\frac{1\text{ mol }N_2}{3\text{ mol }H_2}$	$\frac{2\text{ mol }NH_3}{3\text{ mol }H_2}$

Table 1.5

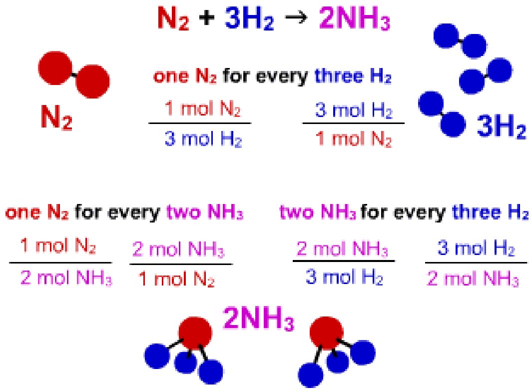


Figure 1.2: Reaction Stoichiometry in the Formation of NH_3 Reaction

1.5-2. Using Stoichiometric Links for Chemical Reactions

The stoichiometric links produced by the coefficients in a balanced equation can be used to determine the number of moles of one substance that are produced by or react with a given number of moles of another substance in the equation.

EXAMPLE:

The following shows how to determine the number of moles of nitrogen that are required and how many moles of NH_3 are produced in the reaction of 3.6 moles of hydrogen in the following:

$$3\ H_2 + N_2 \rightarrow 2\ NH_3$$

$$3.6 \text{ mol } H_2 \times \frac{1\text{mol } N_2}{3 \text{ mol } H_2} = 1.2 \text{ mol } N_2 \text{ are required}$$

$$3.6 \text{ mol } H_2 \times \frac{2 \text{ mol } NH_3}{3 \text{ mol } H_2} = 2.4 \text{ mol } NH_3 \text{ are produced}$$

Note that the stoichiometric link is simply the ratio of the coefficients in the balanced chemical equation. As in all applications of the factor label method, the units of the denominator of the stoichiometric link must be the same as the given quantity and the units of the numerator are those of the result.

1.5-3. Mole-Mole Conversion Exercise

EXERCISE 1.21:

How many moles of hydrogen are required to produce 2.8 mol NH_3? The chemical equation is

$$N_2 + 3\ H_2 \rightarrow 2\ NH_3$$

$$\boxed{}\ \text{mol } NH_3 \times \frac{\boxed{}\ \text{mol } H_2}{\boxed{}\ NH_3} = \boxed{}\ \text{mol } H_2$$

1.5-4. Method for Mass-Mass Conversions

We finish this lesson by showing how to determine the mass of one substance that reacts with or is produced by the reaction of a given mass of another substance in the chemical equation. The process, which is identical to that used in determining the mass of one element that is combined with a given mass of another element in a compound, involves the following three conversions:

1 **mass A → mol A**: Use the molar mass of the given compound to convert its mass to moles.

2 **mol A → mol B**: Use the stoichiometric link (ratio of coefficients) to convert the number of moles of given compound determined in Step 1 into the equivalent number of moles of desired substance.

3 **mol B → mass B**: Use the molar mass of the desired substance to convert the number of moles determined in Step 2 into the mass of the desired substance.

The three steps can be combined into one factor-label setup as shown in the following Example.

EXAMPLE:

The mass of Na_2O (M_m = 62 g/mol) that is produced in the reaction of 6.0 g Na (M_m = 23 g/mol) by the reaction $4\ Na + O_2 \rightarrow 2\ Na_2O$ is determined as follows:

$$6.0\text{ g Na} \times \frac{1\text{ mol Na}}{23\text{ g Na}} \times \frac{2\text{ mol Na}_2\text{O}}{4\text{ mol Na}} \times \frac{62\text{ g Na}_2\text{O}}{1\text{ mol Na}_2\text{O}} = 8.1\text{ g Na}_2\text{O}$$

$$6.0\text{ g Na} \rightarrow 0.26\text{ mol Na} \rightarrow 0.13\text{mol Na}_2\text{O} \rightarrow 8.1\text{ g Na}_2\text{O}$$

1.5-5. Mass-Mass Conversion Exercise

EXERCISE 1.22:

How many grams of fluorine must react to produce 24 g PF_5 (M_m = 126 g/mol)?

F_2 (M_m = 38 g/mol) reacts with P_4 (M_m = 126 g/mol) by the following reaction:

$$P_4 + 10\ F_2 \rightarrow 4\ PF_5$$

$$\boxed{}\text{ g PF}_5 \times \frac{\boxed{}\text{ mol PF}_5}{\boxed{}\text{ g PF}_5} \times \frac{\boxed{}\text{ mol F}_2}{\boxed{}\text{ mol PF}_5} \times \frac{\boxed{}\text{ g F}_2}{\boxed{}\text{ mol F}_2} = \boxed{}\text{ g F}_2$$

1.5-6. Limiting Reactants

Thus far, we have determined the amount of substance that reacts with or is formed by the reaction of another substance. However, there is usually more than one reactant and the reactants are not usually added in stoichiometric ratios. In such cases, one of the reactants, known as the ***limiting reactant***, is consumed before any other reactant. The other reactants are said to be in excess because they are still available after the limiting reactant is consumed.

The limiting reactant is identified as the reactant that is capable of producing the least amount of product. Thus, one way to determine which of several reactants is the limiting reactant is to determine the amount of product each reactant is capable of producing. The limiting reactant is the one that is capable of producing the least. Note, that the limiting reactant is not necessarily the reactant present in the smallest mass nor in the smallest number of moles.

To determine the limiting reactant, you would determine the number of moles of a substance B that is produced or reacts with a given number of moles of reactant A. The moles of B is formed from reactant A:

$$\text{mol A} \times \frac{\text{coefficient B}}{\text{coefficient A}} = \text{ mol B}$$

However, this can be rewritten as follows:

$$\frac{\text{mol A}}{\text{coefficient A}} \times \text{ coefficient B} = \text{ mol B}$$

The coefficient of B is constant, so the smallest amount of B would be produced by the reactant with the smallest mol/coefficient ratio. We conclude that **the limiting reactant is that reactant with the smallest (mol A/coefficient A) ratio**.

The amount of any product that forms or reactant that reacts is equal to the (reactant moles)/(reactant coefficient) ratio of the limiting reactant times the coefficient of the product or reactant whose amount is to be determined.

1.5-7. Mole-Mole Limiting Reactant Exercise

EXERCISE 1.23:

How many moles of NF_3 can be produced from the reaction of 0.50 mol N_2 and 0.90 mol F_2 in the following reaction?

$$N_2 + 3\ F_2 \rightarrow 2\ NF_3$$

Determine mole/coefficient ratios.

N_2 __________ F_2 __________

The limiting reactant is

N_2
F_2

Moles of NF_3 that can be produced by the limiting reactant is

__________ mol NF_3

1.5-8. Mass-Mass Limiting Reactant Exercise

EXERCISE 1.24:

How many grams of Ag_3PO_4 (M_m = 418.6 g/mol) form in the reaction of 3.21 g $AgNO_3$ (M_m = 169.9 g/mol) and 1.65 g K_3PO_4 (M_m = 212.3 g/mol)? How much of the excess reactant remains?

$$3\ AgNO_3 + K_3PO_4 \rightarrow Ag_3PO_4 + 3\ KNO_3$$

Determine the number of moles of each reactant.

$AgNO_3$ __________ mol K_3PO_4 __________ mol

Determine the mol/coefficient ratios.

$AgNO_3$ __________ K_3PO_4 __________

Identify the limiting reactant.

$AgNO_3$
K_3PO_4

Determine the amount of product formed.

__________ g Ag_3PO_4

Determine the amount of excess reactant that is unreacted.

Mass of excess reactant that reacts: __________ g

Mass of excess reactant that remains: __________ g

1.5-9. Percent Yield

The mass of a product determined from the amount of limiting reactant and the stoichiometry of the reaction is known as the ***theoretical yield***. However, the theoretical yield is not usually isolated in an actual experiment. The actual yield, which is the amount that is actually isolated in the experiment, can be less than the theoretical yield for the following reasons:

- The reaction may not be extensive, so all of the limiting reactant does not react.
- Product can be lost during purification. For example, some solid may remain on the filter paper or dissolve when washed.
- Competing reactions can consume some of the reactants.

The fraction of the theoretical yield that is actually isolated expressed as a percent is called the ***percent yield***.

$$\text{percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% \qquad \text{Percent Yield} \qquad (1.4)$$

EXAMPLE:

If stoichiometry predicts that 8.0 g of product should form, but only 6.0 g are actually obtained, the reaction would be reported to have a 75% yield.

$$\text{percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% = \frac{6.0\text{ g}}{8.0\text{ g}} \times 100\% = 75\%$$

1.5-10. Percent Yield Exercise

EXERCISE 1.25:

Aspirin ($C_9H_8O_4$, M_m = 180.16 g/mol) is prepared from the reaction of salicylic acid ($C_7H_6O_3$, M_m = 138.12 g/mol) and acetic anhydride ($C_4H_6O_3$, M_m = 102.09 g/mol) by the following reaction:

$$C_7H_6O_3 + C_4H_6O_3 \rightarrow C_9H_8O_4 + C_2H_4O_2$$

What is the percent yield of aspirin if the reaction of 20.00 g of salicylic acid and 17.00 g of acetic anhydride produces 22.36 g of aspirin?

theoretical yield of aspirin if salicylic acid is the limiting reactant: ________ g $C_9H_8O_4$

theoretical yield of aspirin if acetic anhydride is the limiting reactant: ________ g $C_9H_8O_4$

theoretical yield of aspirin: ________ g $C_9H_8O_4$

actual yield of aspirin: ________ g $C_9H_8O_4$

percent yield: ________ %

1.5-11. Reaction Table Lecture

A video or simulation is available online.

1.5-12. Lines of a Reaction Table

Reaction tables have three rows (initial, Δ, and final) and a column for each reactant and product in the chemical equation.

Reaction tables are completed for chemical reactions to show the amounts of all substances that react and are produced in order to determine the amounts that are present at the end of the reaction. They are constructed with three lines under the balanced equation: initial, Δ, and final.

1 **initial**: The initial line consists of the number of moles of each ingredient present before the reaction begins. Only the reactants are mixed in most reactions, so the entries under the products are zero in most reaction tables.

2 Δ: The delta (change) line shows how many moles of each reactant disappears and how many moles of each product are produced. All calculations on this line are based on the assumption that all of the limiting reactant disappears. The entries of all products are positive because they form during the reaction, but those of all reactants are negative because they disappear during the reaction.

3 **final**: The final line is the sum of the initial and delta lines and represents the final composition of the reaction mixture.

1.5-13. Reaction Table from Mass Exercise

EXERCISE 1.26:

Reaction tables are completed with either moles or concentrations, not with masses. However, initial amounts are often given as masses. In these cases, convert the masses into moles and proceed as in the previous example.

Construct the reaction table to determine the final **masses** of all substances remaining in the complete reaction of 10.00 g each of NH_3 and O_2. **Report the final masses to the nearest 0.01 g.**

	4 NH_3	+	5 O_2	→	4 NO	+	6 H_2O	
initial		+		→		+		mol
Δ								mol
final								mol
mass								g

1.6 Exercises and Solutions

Links to view either the end-of-chapter exercises or the solutions to the odd exercises are available in the HTML version of the chapter.

CHAPTER 2 – SOLUTIONS

Introduction

Solutions are all around us. Our atmosphere is a solution of gases in gases, carbonated beverages are solutions of gases in liquids, sweetened drinks are solutions of solids in liquids, and solder is a solution of solids in solids. Reactions are normally carried out in solutions of gases or liquids because the particles in these solutions are free to move and to collide. In this chapter, we define several terms relevant to the study of solutions and discuss some solution properties.

2.1. Concentration Units

Introduction

The properties of a solution depend upon the relative amounts of solvent and solute(s), which is given by the solute concentration in the solution. A concentrated solution is one in which the concentration of a solute is relatively large, while a dilute solution is one in which the solute concentrations are relatively low. However, the terms 'concentrated' and 'dilute' used in this manner are not quantitative. In this section, we present several different ways of reporting the concentrations of solutions in a quantitative manner.

Objectives

- Determine the concentration of a solution from the amount of solute and the amount of solution or solvent.
- Use the definition of a concentration unit to convert between the amount of solute and the amount of solution or solvent.
- Prepare a solution of known molarity.
- Use and understand the meaning of the prefixes m (milli), μ (micro) and n (nano).

2.1-1. Definitions

A solution consists of a solvent and one or more solutes.

Before we start into the quantitative aspects of solutions, we review some of the terms introduced in Section 10.1 of Chemistry – A Molecular Science (Chapter 10).

- A ***solution*** is a homogeneous mixture consisting of a solvent and one or more solutes. A homogeneous mixture is one whose composition is the same throughout. For example, sugar dissolves in water to make a homogeneous mixture in which the sugar concentration (sweetness) is the same throughout, so the mixture is a solution. Mixing water and oil forms a mixture whose composition varies from pure water to pure oil, so this mixture is heterogeneous and not a solution.
- The ***solvent*** is that substance that dictates the phase of the solution. If a liquid is present, it is usually the solvent. This course focuses on **aqueous solutions**, which are solutions in which water serves as the solvent.
- A ***solute*** is one of the substances that is dissolved in the solvent. Solutes of aqueous solutions can be solid (a sugar solution), liquid (alcoholic beverages contain liquid ethanol in water), and/or gas (carbonated beverages contain CO_2 in water).

When ionic substances dissolve in water, they break up into their component ions, i.e., they ionize or dissociate in water. A substance that ionizes or dissociates completely in water is said to be a strong ***electrolyte***. Ionic compounds are *strong electrolytes*. NaCl dissociates completely into Na^{1+} and Cl^{1-} ions in water, so it is a strong electrolyte. Molecular substances do not dissociate when in water and are classified as *nonelectrolytes*. Sugar dissolves in water as sugar molecules ($C_{12}H_{22}O_{11}$), so sugar is a nonelectrolyte. Acids and bases react with water to produce ions, so they too are electrolytes. Strong acids and bases react completely with water and are strong electrolytes, but weak acids and bases react only partially with water and are classified as *weak electrolytes*.

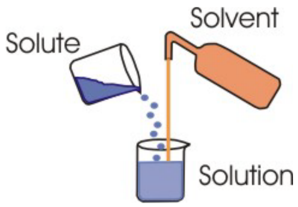


Figure 2.1: Components of a Solution A solution consists of a solvent and at least one solute. Almost all of the solutions considered in this course are aqueous solutions, which are solutions in which water is the solvent.

2.1-2. Molarity (M)

The ***molarity*** (M) of a solute is the number of moles of the solute in one liter of solution or the number of millimoles of solute in one milliliter of solution.

$$M = \frac{\text{moles of solute}}{\text{liters of solution}} = \frac{n}{V} = \frac{\text{mmoles of solute}}{\text{mL of solution}} \qquad \text{Molarity } (M) \qquad (2.1)$$

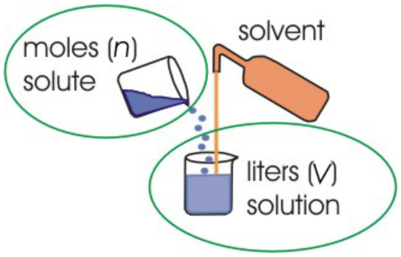


Figure 2.2: Molarity Molarity relates moles of solute to the volume of solution.

The molarity of a solute allows us to convert between the number of moles (or millimoles) of that **solute** and the number of liters (or milliliters) of **solution**.

To determine the number of moles of solute in a given volume of solution, we solve Equation 2.1 for n, the number of moles:

$$n = MV$$

Alternatively, we can use the units of molarity and the factor-label method to determine the number of moles.

$$\frac{M\text{mol solute}}{1 \text{ L solution}} \times V \text{ L of solution} = MV\text{mol solute}$$

If V is given in milliliters, then MV is millimoles of solute. **We will frequently use millimoles because volumes in a chemistry laboratory are most often given in milliliters.**

We can also solve Equation 2.1 for the volume of solution to determine what volume of solution contains a given number of moles of solute:

$$V = \frac{n}{M}$$

Or, using the factor-label method,

$$n \text{ mol solute} \frac{1 \text{ L solution}}{M \text{ mol solute}} = \frac{n}{M} \text{ L solution}$$

2.1-3. Preparing a Solution of Known Molarity

The denominator of molarity is the volume of the solution, not the volume of solvent. Thus, a solution of known molarity must be made by adjusting the volume after the solute and solvent have been thoroughly mixed. This is done with a volumetric flask of the appropriate volume (Figure 2.3) as follows.

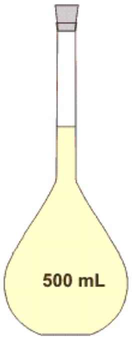


Figure 2.3: A 500-mL Volumetric Flask

1. Select a volumetric flask of the appropriate volume and determine the amount of solute that will be required. The flask in Figure 2.3 would be used to prepare 500 mL of solution.
2. Add solvent to the volumetric flask until it is about half full.
3. Add the required amount of solute and swirl the mixture until the solute has dissolved
4. Add solvent to the flask up to the fill line of the flask.
5. Invert the flask several times to assure homogeneity.

2.1-4. Preparing a Solution Exercise

EXERCISE 2.1:

How many mmoles of K_2HPO_4 are required to prepare 350. mL of 0.0865 M K_2HPO_4?

______________ mmol

How many grams of K_2HPO_4 (M_m = 174.17 g/mol) must be dissolved to make the solution?

______________ g

Molarity is the number of moles of solute per liter of **solution** not solvent, so the K_2HPO_4 would be dissolved in less than 350 mL of water (~250 mL). Water would then be added to adjust the volume of the resulting solution to 350 mL.

How many milliliters of the 0.0865 M solution of K_2HPO_4 are required to deliver 3.50 mmoles of K^{1+} ions?

V = ______________ mL

2.1-5. Molarity to Solute Mass Exercise

EXERCISE 2.2:

Ocean water is typically 0.53 M in chloride ion. How many grams of chloride ion are contained in 500. mL of ocean water?

mass = ______________ g Cl^{1-}

2.1-6. Molarity of Ions Exercise

EXERCISE 2.3:

$Ba(OH)_2$ is a strong electrolyte. What are the ion concentrations in a solution prepared by dissolving 0.210 g of $Ba(OH)_2$ in enough water to make 450. mL of solution?

The molarity of the $Ba(OH)_2$ solution is: ____________ *M*

The ion concentrations are:

$[OH^{1-}] =$ ____________ *M*

$[Ba^{2+}] =$ ____________ *M*

The number of millimoles of OH^{1-} in 275 mL of solution is: ____________ mmol

The number of milliliters of solution required to deliver 0.300 mmol of Ba^{2+} is: ____________ mL

2.1-7. Common Prefixes

1 *M* solutions are considered fairly concentrated, and most of the solutions encountered in the chemistry laboratory are much less concentrated. Indeed, some processes require only very dilute concentrations. For example, the maximum allowed level of mercury in drinking water is 0.000002 *M*, and a testosterone level of only 0.00000001 *M* initiates puberty in human males. Prefixes are used to avoid the preceding zeros or exponents when expressing these very dilute solutions.

Unit	Symbol	Value	
millimolar	m*M*	10^{-3} *M*	1 mmol·L^{-1}
micromolar	μM	10^{-6} *M*	1 μmol·L^{-1}
nanomolar	n*M*	10^{-9} *M*	1 nmol·L^{-1}

Table 2.1: Common Prefixes

Thus, the maximum allowed level of mercury in drinking water is $2 \times 10^{-6}\ M = 2\ \mu M$, and the testosterone level that initiates puberty is $10 \times 10^{-9}\ M = 10$ n*M*.

2.1-8. Using Prefixes Exercise

EXERCISE 2.4:

How many micrograms of testosterone ($C_{19}H_{28}O_2$, $M_m = 288$ g/mol) are in the blood (5.7 liters) of a person if the testosterone concentration is 12.5 n*M*?

mass = ____________ μg testosterone

2.1-9. Mole Fraction (*X*)

The ***mole fraction*** (*X*) of a substance in a solution is the number of the moles of that substance divided by the total number of moles of all substances (solutes and solvent) in solution. Because all of the substances comprise the whole mixture, **the sum of all mole fractions (including the solvent) must equal one**; i.e., $\sum_A X_A = 1$.

$$X_A = \frac{n}{n_{\text{tot}}} = \frac{\text{moles of } A \text{ in mixture}}{\text{total moles in mixture}} \qquad \text{Mole Fraction} \qquad (2.2)$$

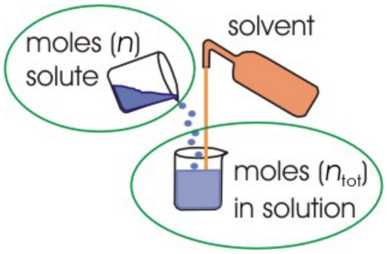


Figure 2.4: Mole Fraction The ***mole fraction*** of A equals the number of moles of A divided by the total number of moles of substances in the solution.

2.1-10. Mole Fraction Exercise

<u>EXERCISE 2.5</u>:

A sample of the alloy known as "yellow brass" is found to be 67.00% Cu and 33.00% Zn by mass. What are the mole fractions of Cu and Zn in the alloy?

Exactly 100 g of alloy contains:

________________ mol Cu

________________ mol Zn

________________ mol total in mixture

The mol fractions are

$X_{\text{Cu}} =$ ________________

$X_{\text{Zn}} =$ ________________

2.1-11. Mass Fraction (%, ppt, ppm)

The ***mass fraction*** relates the mass of a solute to the mass of the solution. It is commonly used for solutions where the solvent is not clearly defined.

$$\text{mass fraction} = \frac{\text{mass of solute}}{\text{mass of solution}} \qquad \text{Mass Fraction} \qquad (2.3)$$

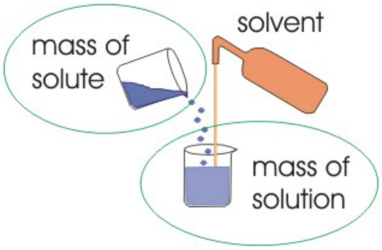


Figure 2.5: Mass Fraction The ***mass fraction*** relates the mass of a solute to the mass of the solution.

2.1-12. Mass Fraction Multipliers

Mass fractions represent a part of the whole, so they are always less than one. Indeed, mass fractions in dilute solutions can be so small that they are multiplied by powers of ten to eliminate the preceding zeros (see Table 2.2). Thus,

- a mass fraction of 0.012 would be reported as (0.012)(100%) = 1.2%
- a mass fraction of 1.2×10^{-8} would be reported as $(1.2 \times 10^{-8})(10^9 \text{ ppb}) = 12$ ppb.

Name	Multiplier	Useful Units
mass fraction	1	$\frac{\text{g } A}{\text{g mixture}}$
mass percent (%)	100	$\frac{\text{g } A}{\text{100g mixture}}$
parts per thousand (ppT)	1000	$\frac{\text{g } A}{\text{1000g mixture}}$
parts per million (ppm)	10^6	$\frac{\text{g } A}{10^6\text{g mixture}}$
parts per billion (ppb)	10^9	$\frac{\text{g } A}{10^9\text{g mixture}}$

Table 2.2: Common Multipliers Used with Mass Fraction

2.1-13. Mass Fraction Exercise

EXERCISE 2.6:

A mixture contains 6.0 g N_2, 16.0 g O_2 and 2.0 g He.
What are the mass fraction, mass percent, and mole fraction of each gas?

Mass Fractions

Total mass = ______________ g

Mass fraction of N_2 = ______________

Mass fraction of O_2 = ______________

Mass fraction of He = ______________

Mass Percents

Mass percent of N_2 = ______________ %

Mass percent of O_2 = ______________ %

Mass percent of He = ______________ %

Moles

Moles of N_2 = ______________ mol

Moles of O_2 = ______________ mol

Moles of He = ______________ mol

Total moles = ______________ mol

Mole Fractions

X_{N_2} = ______________

X_{O_2} = ______________

X_{He} = ______________

2.1-14. Molality (*m*)

The ***molality*** (m) of a solute is the number of moles of that solute per kilogram of solvent.

$$m = \frac{\text{moles of solute}}{\text{kg of solvent}} \qquad \text{Molality } (m) \tag{2.4}$$

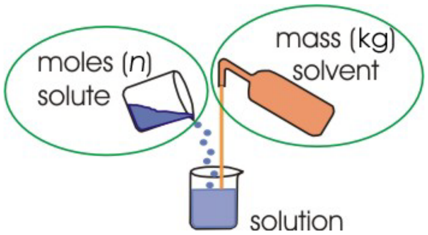


Figure 2.6: Molality Molality relates the moles of solute to the mass of solvent.

The volume of a solution varies with temperature, so the molarity (M) of the solution changes with temperature as well. Thus, molarity (M) is not a good unit of concentration to use in experiments involving temperature change. While volume is temperature dependent, mass is not, so molality (m), which involves no volumes, is commonly used for the concentration of any solution used in experiments that involve measurements resulting from temperature changes.

2.1-15. Molality Exercise

EXERCISE 2.7:

A solution is prepared by mixing 3.75 g of glucose ($C_6H_{12}O_6$, $M_m = 180.2$ g/mol) and 25.0 g of water. What is the molality of the resulting glucose solution?

moles of glucose in solution

_______________ mol $C_6H_{12}O_6$

kilograms of solvent present in solution

_______________ kg H_2O

the molality of the solution

_______________ m

2.2. Changing Concentrations Units

Introduction

It is sometimes necessary to change the units of concentration. This routine procedure is most often done when the concentration of a stock solution is given in units that are not convenient for a particular experiment. The procedure presented here entails converting the units of the numerator and denominator of the given concentration to those of the desired concentration and then dividing.

Objectives

- Convert between different concentration units.

2.2-1. Converting Concentration Units

To change concentration units, convert the numerator and denominator separately.

All concentrations are ratios of two quantities. The numerator indicates the amount of solute and the denominator the amount of solution or solvent. Use the following steps to convert one concentration unit into another:

1 Convert the given numerator into the numerator of the desired unit.

2 Convert the given denominator into the denominator of the desired unit.

3 Divide the result of step 1 by that of step 2 to obtain the desired concentration unit.

The numerators and denominators of the concentration units that we have dealt with are:

molarity	**mass fraction**	**mole fraction**	**molality**
$\frac{\text{moles of solute}}{\text{liters of solution}}$	$\frac{\text{mass of solute}}{\text{mass of solution}}$	$\frac{\text{moles of solute}}{\text{total moles (all solutes + solvent)}}$	$\frac{\text{moles of solute}}{\text{kilograms of } \textbf{solvent}}$

To convert between any of the above you need only some combination of the molar masses of solute and/or solvent, and/or the density of the solution.

Conversion	Requires
mol solute ↔ mass solute	molar mass of the solute
liters solution ↔ mass solution	density of solution
liters solution ↔ mol solute + mol solvent	density of solution, molar masses of solute and solvent
liters solution ↔ kg solvent	solution density, molar mass of solute
mass solution ↔ mol solute + mol solvent	molar masses of solute and solvent
mass solution ↔ kg solvent	molar mass of solute
mol solute + mol solvent ↔ kg solvent	molar masses of solute and solvent

Table 2.3: Converting Concentration Units

2.2-2. Molarity to Mass Percent Exercise

EXERCISE 2.8:

A solution of concentrated sulfuric acid is 18.00 *M* and has a density of 1.839 g/cm^3. What is the mass percent of H_2SO_4 in the concentrated acid solution? Molar mass of sulfuric acid = 98.08 g/mol.

The given units are molarity, while the desired units are mass fraction, which must be multiplied by 100 to obtain mass percent. Molarity has units of (mol solute)/(L solution), while mass fraction has units of (mass solute)/(mass solution). Thus, we must make the following conversions.

- numerator: 18.00 mol H_2SO_4 yields ↔ x grams H_2SO_4
- denominator: 1 L solution yields ↔ y grams solution

Convert the given numerator into the desired numerator.

18.00 mol H_2SO_4 = ______________ g H_2SO_4

Convert the denominator of the given concentration units into those of the desired concentration units.

1 L solution = ______________ g solution

The mass fraction of H_2SO_4 in the solution = ______________

The mass percent of H_2SO_4 in the solution = ______________ %

2.2-3. Molarity to Molality Exercise

EXERCISE 2.9:

Concentrated sulfuric acid is 18.00 *M* and has a density of 1.839 g/cm^3. What is the molality of H_2SO_4 in the concentrated acid solution?

The given units are molarity, while the desired units are molality. Molarity has units of (mol solute)/(L solution), while molality has units of (mol solute)/(kg solvent). Thus, we must make the following conversions:

- numerator: 18.00 mol H_2SO_4 → 18.00 mol H_2SO_4
- denominator: 1 L solution → y kilograms solvent

The numerators are the same (18.00 mol), so we need only change the denominator and then divide.

1 L solution contains ______________ kg solvent

Divide the numerator by the denominator to obtain molality: ______________ *m*

2.2-4. ppm to Molarity Exercise

EXERCISE 2.10:

What is the molarity of fluoride ion in drinking water that is 7.0 ppm F^{1-}?

The given units are ppm, (grams solute)/(10^6 g solution), while the desired units are molarity, (mol solute)/(L solution). Thus, the following conversions are required.

- numerator: 7.0 g $F^{1-} \rightarrow x$ mol F^{1-}
- denominator: 10^6 g solution $\rightarrow y$ liters of solution

Convert the given numerator into the desired numerator.

7.0 g F^{1-} = ______________ mol F^{1-}

Next, convert the denominator of the given concentration into that of the desired concentration. This solution is very dilute, so you can assume that the density of the solution is the same as the solvent (1.0 g/mL).

10^6 g solution = ______________ L solution

Finally, divide the two to obtain the desired concentration units.

$[F^{1-}]$ = ______________ M

2.2-5. Mass Percent to Molarity Exercise

EXERCISE 2.11:

What is the molarity of a 30.0% sulfuric acid solution if its density is 1.218 g/mL?

- numerator: 30.0 g $H_2SO_4 \rightarrow x$ mol H_2SO_4
- denominator: 100 g soln → y L soln

Convert the given numerator into the desired numerator.

30.0 g H_2SO_4 = ______________ mol H_2SO_4

Next, convert the denominator of the given concentration into that of the desired concentration.

100 g solution = ______________ L solution

Finally, divide the two to obtain the desired concentration units.

$[H_2SO_4]$ = ______________ M

2.3. Dilutions

Introduction

Stock solutions are often fairly concentrated and must be diluted before they are used. In this section, we show how to make a solution of known volume and molarity from a more concentrated stock solution.

Objectives

- Calculate the concentration of a solution after dilution.
- Prepare a dilute solution of known concentration from a more concentrated solution.

2.3-1. Dilution Lecture

A video or simulation is available online.

2.3-2. Equations of Dilution

The amount of solute does not change with the addition of solvent, so we can write the following:

$$C_\text{i} \times V_\text{i} = C_\text{f} \times V_\text{f} \qquad \text{Dilution Equation} \qquad (2.5)$$

where C is any concentration that indicates the amount of solute per unit volume of solution. Therefore, C can be molarity or g/mL, but not molality or mass percent. We solve Equation 2.5 for the final concentration, C_f to obtain the following

$$C_\text{f} = C_\text{i} \times \frac{V_\text{i}}{V_\text{f}} \qquad \text{Dilution Factor} \qquad (2.6)$$

where the ratio V_i/V_f is called the **dilution factor**. Thus, the final concentration equals the initial concentration times a dilution factor. If a solution is diluted successively several times, then the final concentration equals the initial concentration times the product of all of the successive dilution factors as shown in Equation 2.7.

$$C_\text{f} = C_1 \times \frac{V_1}{V_2} \times \frac{V_3}{V_4} \times \frac{V_5}{V_6} \qquad \text{Successive Dilutions} \qquad (2.7)$$

2.3-3. Molarity after Dilution Exercise

EXERCISE 2.12:

What is the molarity of sulfuric acid in a solution prepared by adding 30.0 mL of 18.0 M H_2SO_4 to enough water to make 500. mL of solution?

concentration = ______________ M H_2SO_4

2.3-4. Volume Required for Dilution Exercise

EXERCISE 2.13:

How many mL of 18.0 M H_2SO_4 are required to prepare 300. mL of 1.50 M H_2SO_4?

volume of 18.0 M H_2SO_4 = ______________ mL H_2SO_4

2.3-5. Concentration After Successive Dilutions Exercise

EXERCISE 2.14:

Solution A is prepared by diluting 20.0 mL of a stock 0.100 M HCl solution to 50.0 mL. Solution B is prepared by diluting 10.0 mL of solution A to 75.0 mL. Solution C is made by diluting 20.0 mL of solution B to 250.0 mL. What is the concentration of HCl in solution C? Note that the concentration is expressed as millimolar.

[HCl] in solution C = ______________ mM

2.3-6. Concentration of Initial Solution Exercise

EXERCISE 2.15:

50.00 mL of an unknown solution A is diluted to 500.00 mL to make solution B. 25.00 mL of solution B is diluted to 750.00 mL to make solution C. 15.00 mL of solution C is diluted to 1000.00 mL. What is the concentration of solution A, if the concentration of the final solution is 1.47 μM?

product of all dilution factors = ______________

concentration of solution A = ______________ M

2.4. Determining Concentrations

Introduction

Analyzing solutions to determine their concentration is an important part of analytical chemistry. In this section, we discuss two important methods used to carry out such an analysis: spectrometry and titration.

Objectives

- Use a color wheel to determine a complementary color.
- Use Beer's Law to determine the molarity of a solution.
- Determine the volume of one reactant that reacts with another reactant of known volume.
- Determine the limiting reactant from a balanced chemical equation and the concentrations and volumes of the reactants.
- Determine the concentrations of the excess reactants.

2.4-1. Complementary Colors

White light is the result of all visible colors. When white light shines on a colored substance, however, some of the colors are absorbed. Those colors that are not absorbed can be either reflected or transmitted to the eye. We perceive this reflected or transmitted portion as the color of the substance. Consequently, the characteristic color of a material is not the color of light that it absorbs; rather it is the mixture of the remaining, unabsorbed colors that are observed. In other words, it appears as its complementary color. The approximate relationship between observed and absorbed colors is summarized in a color wheel as shown in Figure 2.7. For example, a solution appears orange because it absorbs blue light. Thus, when white light shines on the solution, the blue portion of the spectrum is absorbed by the solution, which leaves only the orange portion to be detected by your eyes.

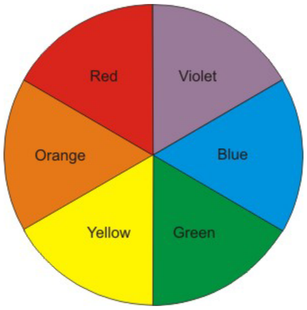


Figure 2.7: Color Wheel Complementary colors are opposite one another in a color wheel, so orange is the complement of blue.

2.4-2. Spectrometry

Spectrometry, measuring the amount of light that a solute absorbs at some wavelength, is a convenient way to determine the concentration of a solute in a solution. The amount of light that is absorbed by the sample is called the ***absorbance*** (A) of the sample. Consider the experiment shown in Figure 2.8 below. Orange light of intensity I_o

enters the cell, where some of it is absorbed by the blue solution, so the outgoing intensity I, is less than the initial I_o.

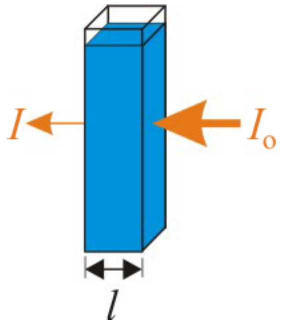


Figure 2.8: Absorbance and Beer's Law Orange light is absorbed by a blue solution. The amount of light that is absorbed by the solution is called the absorbance (A), which is defined as $-\log(I/I_o)$. The absorbance depends upon the concentration of the absorbing substance (c), the distance the light travels through the sample (l), and the molar absorptivity of the solute at the wavelength of the light (ϵ) as given by Beer's law.

The absorbance, which is defined as $A = -\log(I/I_o)$,depends upon three factors:

- how strongly the solute absorbs at the wavelength of light used in the experiment, which is known as the ***molar absorptivity*** (ϵ, epsilon);
- the concentration of the solute (c); and
- the path length of the light through the solution (l).

The relationship between these factors is given by Beer's Law.

$$A = \epsilon l c \qquad \text{Beer's Law} \tag{2.8}$$

2.4-3. Determining an Unknown Concentration

The following procedure is used to determine an unknown concentration in a solution:

1. Determine a good wavelength of light to use. The light should be absorbed by the solute to be determined, so it should be the complement of the color of the solution. The complement can be found as the color opposite the observed color on a color wheel. The light should not be absorbed by the rest of the solution, but the effect of the rest of the solution can be determined by measuring the absorbance of a blank. The ***blank*** should mimic the solution to be measured in all aspects except the presence of the solute to be measured. The absorbance of the blank is then subtracted from that of the sample to get a measurement of just the solute's absorbance.
2. Measure the absorbance of a ***standard solution***, which is simply a solution in which the concentration of the solute being measured is accurately known. The molar absorptivity of the solute can be determined from the measured absorbance, the known concentration, and the path length of the cell.
3. Measure the absorbance of the sample. The unknown concentration can be determined from the measured absorbance, the molar absorptivity determined in step 2, and the known path length of the cell.

Many solutes absorb very strongly, and the prepared solutions frequently absorb so strongly that too little light passes through the cell. In these cases, the solutions must be diluted before they can be measured. Indeed, it is often the case that they must be diluted several times in order to get a good reading of the absorbance. The following exercise takes you through this process except that no blank is used. Follow the above steps and dilute the samples to obtain the good absorbance readings. Don't forget to take into account your dilutions when doing the calculations.

2.4-4. Determining Concentration Exercise

EXERCISE 2.16:

Determine the concentration of an unknown solution.
A video or simulation is available online.

$\epsilon =$ ______________ $M^{-1}\cdot\text{cm}^{-1}$ $[X] =$ ______________ M

2.4-5. Titrations

Spectrometry is an easy way to determine an unknown concentration only if the solute absorbs light at a convenient wavelength (usually one in the visible). The concentration of a solute can also be determined by measuring the stoichiometric amount of a solution of known concentration required to react with the unknown solute. This method is called ***titration***. The known solution, whose volume is to be determined, is called the ***titrant***, while the solute being analyzed is the ***analyte***. The point at which the titrant and analyte are in stoichiometric amounts is called the ***equivalence point***. The equivalence point is usually approximated by an ***end point***, which is the point at which an indicator undergoes a color change.

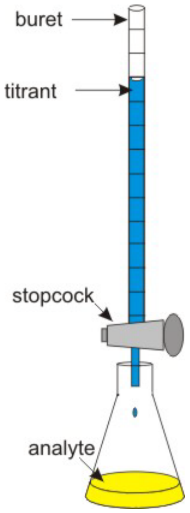


Figure 2.9: Titration Apparatus

2.4-6. Titration Method

Acid-base titrations are very common in the chemistry lab. The net chemical equation for the reaction of a strong acid and a strong base is:

$$H_3O^{1+} + OH^{1-} \longrightarrow 2H_2O$$

The above chemical equation shows that the reactants react in a 1:1 ratio, so the equivalence point is reached when the number of (milli)moles of base added equals the number of (milli)moles of acid present initially. However, the number of (milli)moles of a solute equals the volume of solution in (milli)liters times the molarity of the solute. Thus, the equivalence point in an acid base reaction is that point where

$$M_{\text{acid}}V_{\text{acid}} = M_{\text{base}}V_{\text{base}} \qquad \text{Acid Base Equivalence Point} \qquad (2.9)$$

If the acid is the unknown, then a known amount of acid, the analyte, would be added to the flask, so V_{acid} would be known. The concentration of the base (M_{base}), the titrant, would also be known and the volume of base required to reach the equivalence point (V_{base}) would be determined by the titration. M_{acid} would then be determined from Equation 2.9.

2.4-7. Titration Exercise

EXERCISE 2.17:

An indicator that changes color at the equivalence point is added to the analyte solution. The procedure is demonstrated in the following example. The indicator in this example turns a light pink at the equivalence point. When the color forms but then fades, you are close to the equivalence point. If the solution turns a dark red, you have passed the equivalence point. If you pass the equivalence point, you can simply add more acid until the color disappears. Be careful not to drain the buret below the bottom mark.

Determine the concentration of the unknown HCl (analyte) solution by titration with a 0.02597 *M* solution of NaOH (titrant).

A video or simulation is available online.

The molarity of the unknown acid is ______________ *M*

2.4-8. Precipitation Reactions

Solubility rules can help you determine the precipitate.

The concentration of a solution can also be determined from the amount of precipitate that forms when an excess of another reactant is added. The procedure is the following:

1 Use the solubility rules to decide upon a good reactant.

2 Add an excess of the reactant to a known volume of the solution to be analyzed.

3 Filter the solution to separate the precipitate from the solution. Add more reactant to the remaining solution to be certain no more precipitate forms.

4 Dry and weigh the precipitate then determine the number of moles of precipitate that were produced.

5 Use the results of step 4 to determine the number of moles of the solute that must have reacted.

6 Determine the concentration of the original solution from the number of moles of solute present (step 5) and the original volume.

Rule 1	Compounds of NH_4^{1+} and group 1A metal ions are soluble.
Rule 2	Compounds of NO_3^{1-}, ClO_4^{1-}, ClO_3^{1-} and $C_2H_3O_2^{1-}$ are soluble.
Rule 3	Compounds of Cl^{1-}, Br^{1-}, and I^{1-} are soluble *except* those of Ag^{1+}, Cu^{1+}, Tl^{1+}, Hg_2^{2+},and Pb^{2+}.
Rule 4	Compounds of SO_4^{2-} are soluble *except* those of Ca^{2+}, Sr^{2+}, Ba^{2+}, and Pb^{2+}
Rule 5	*Most* other ionic compounds are insoluble.

Table 2.4: Solubility Rules
Solubility rules for ionic compounds in water.

2.4-9. Precipitation Exercise

EXERCISE 2.18:

What is the concentration of Ag^{1+} ions in a solution if addition of excess $PO_4{}^{3-}$ ions to 25.00 mL of the solution produced 163.2 mg of Ag_3PO_4 (M_m = 418.6 g/mol)?

The net ionic equation is: $3\ Ag^{1+} + PO_4{}^{3-} \rightarrow Ag_3PO_4$

The number of millimoles of Ag_3PO_4 produced = ____________ mmol

The number of millimoles of Ag^{1+} required = ____________ mmol

The concentration of Ag^{1+} in the original solution = ____________ M

2.5. Colligative Properties

Introduction

The properties of a solution depend upon the concentrations of the solutes. Indeed, some solution properties depend only upon the concentration of particles in solution and not upon the identity of those particles. These properties are called ***colligative properties***. In this section, we discuss the following colligative properties.

- vapor pressure
- boiling point
- freezing point
- osmotic pressure

Objectives

- Determine the van't Hoff factor (i) for a compound.
- Convert a molarity or molality into a colligative molarity or colligative molality.
- Calculate the boiling point and melting point of a solution given its colligative molality and the boiling elevation and freezing point depression constants.
- Describe the causes of vapor pressure lowering at the molecular level.
- Calculate the vapor pressure of a solution given the mole fraction of the solute and the vapor pressure of the solvent.
- Describe osmosis at the molecular level.
- Determine the osmotic pressure of a solution of known concentration.
- Explain why osmosis is important.

2.5-1. van't Hoff Factor and Colligative Concentrations

Colligative properties depend upon the concentration of **particles** in solution, which is different than the solute concentration when the solute is ionic and dissociates in water. The solution concentration is converted to a concentration of particles with the ***van't Hoff factor*** (i), which is the number of moles of particles produced when one mole of solute dissolves. For example, $i = 3$ for $CaCl_2$ because dissolving one mole of $CaCl_2$ produces three moles of ions: $CaCl_2 \rightarrow Ca^{2+} + 2\ Cl^{1-}$.

The total particle concentration is called the colligative concentration. It is equal to the solute concentration times its van't Hoff factor. The following equations define the ***colligative molarity*** and ***colligative molality***.

$$\begin{aligned} M_c &= i \times M \\ m_c &= i \times m \end{aligned} \qquad \text{Colligative Concentrations} \qquad (2.10)$$

2.5-2. van't Hoff Exercise

EXERCISE 2.19:

What is the van't Hoff factor for each of the following?

$CaSO_4$: $i =$ _______________
CH_3OH: $i =$ _______________
NH_4ClO: $i =$ _______________
$Ba(OH)_2$: $i =$ _______________
HCl: $i =$ _______________
SF_4: $i =$ _______________

2.5-3. Colligative Molality Exercise

EXERCISE 2.20:

Determine the colligative molarity of each of the following solutions.

Solution	i	M_c
0.080 M K_3PO_4		
0.042 M $C_6H_{12}O_6$		

2.5-4. Phase Diagram

Figure 2.10 shows the phase diagrams of a pure substance and of a solution in which the substance is the solvent. The two diagrams are identical except for the region in blue, which is either a solid or gas in the pure substance but is all liquid in the solvent. Thus, the phase diagram of the solvent differs from that of the pure substance in three ways:

- The vapor pressure is lowered by ΔP at every temperature.
- The boiling point is elevated (raised) by ΔT_b.
- The freezing point is depressed (lowered) by ΔT_f.

The impact of these three effects is to increase the temperature-pressure range of the liquid state. The amount by which the liquid state is extended (shown in blue in the figure) depends only on the concentration of the solute particles, so freezing point depression, boiling point elevation, and vapor pressure lowering are all colligative properties, and we now examine the relationship between particle concentrations and their effect on each of these colligative properties. We then define a fourth colligative property, the osmotic pressure.

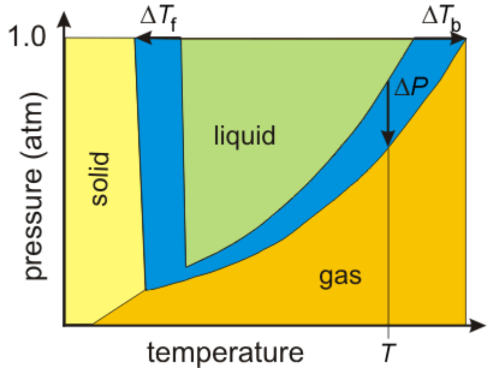


Figure 2.10: Phase diagrams of a solvent and a solution of the solvent. The solvent is liquid only in the green region, while the solution is liquid in both the green and blue regions; i.e., the blue region shows the extent to which the liquid state is expanded due to the presence of the solute particles.

2.5-5. Vapor Pressure Lowering

The vapor pressure of a solution is less than that of the pure solvent.

The liquid $\rightleftharpoons$ vapor equilibrium is a dynamic equilibrium that is established when the rate of evaporation equals the rate of condensation. The pressure of the vapor in equilibrium with the liquid at a given temperature is the vapor pressure of the liquid at that temperature. Evaporation occurs from the surface of the liquid, so the rate of evaporation depends upon the concentration of particles at the surface. Figure 2.11 compares a pure solvent with a solution in which the mole fraction of a nonvolatile solute is 0.2. A solute mole fraction of 0.2 means that 20% of the particles in solution are solute particles, so 20% of the sites on the surface are occupied by nonvolatile solute particles. Consequently, evaporation can occur from only 80% of the surface sites, which results in a 20% reduction in the rate of evaporation, which in turn, causes a 20% reduction in the vapor pressure. We conclude that ΔP, the amount by which the vapor pressure of the solvent at some temperature is lowered by the addition of a solute with a mole fraction of X_{solute}, is

$$\Delta P = X_{\text{solute}} P^\circ_{\text{solvent}} \qquad \text{Vapor Pressure Lowering of a Solvent} \qquad (2.11)$$

ΔP is the vapor pressure lowering; it is always positive because the vapor pressure of a solution is always lower than that of the pure solvent. P° is the vapor pressure of the pure solvent at the temperature under consideration. The vapor pressure of the solution is lower than that of the solvent by ΔP, so $P = P^\circ - \Delta P = P^\circ - X_{\text{solute}} P^\circ = (1 - X_{\text{solute}})P^\circ$. However, $1 - X_{\text{solute}} = X_{\text{solvent}}$, so we can rewrite Equation 2.11 as

$$P_{\text{soln}} = X_{\text{solvent}} P^\circ_{\text{solvent}} \qquad \text{Vapor Pressure of a Solution} \qquad (2.12)$$

The above indicates that the vapor pressure of a solution is equal to the vapor pressure of the pure solvent times the fraction of the surface sites occupied by the solvent; i.e., the mole fraction of the solvent.

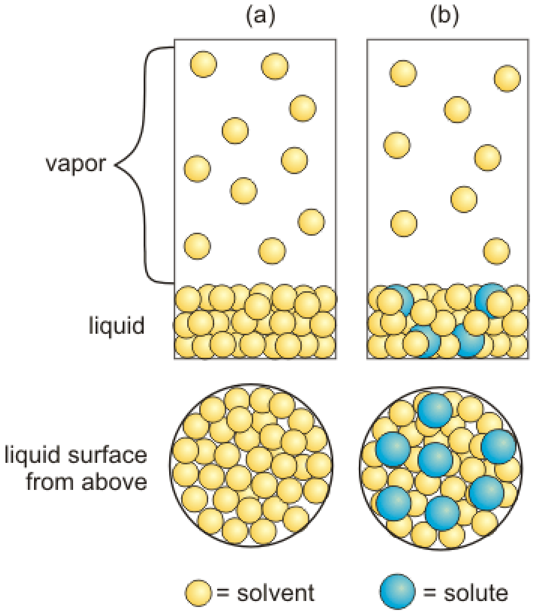


Figure 2.11: Vapor Pressure Lowering (a) Solvent: All of the surface sites are occupied by solvent molecules, which produces ten molecules in the vapor. (b) Solution: The mole fraction of the solute in the solution is ~0.2, so nonvolatile solute particles (blue spheres) occupy ~20% of the surface sites, which reduces the vapor pressure by ~20% as shown by the presence of only eight molecules in the vapor.

2.5-6. Vapor Pressure of Water

We will have made frequent use of the vapor pressure of water. The vapor pressure at 5 °C increments can be found in Table 2.5 and in the Resources.

T (°C)	P° (torr)	T (°C)	P° (torr)
0	4.6	50	92.5
5	6.5	55	118.0
10	9.2	60	149.9
15	12.8	65	187.5
20	17.5	70	233.7
25	23.8	75	289.1
30	31.8	80	355.1
35	41.2	85	433.6
40	55.3	90	525.8
45	71.9	95	633.9

Table 2.5: Vapor Pressure of Water at Selected Temperatures

2.5-7. Vapor Pressure Lowering Exercise

EXERCISE 2.21:

What is the vapor pressure at 25 °C of a solution prepared by dissolving 10.0 g NaCl in 100. g of water?

1. moles of NaCl in solution: ______________
2. moles of solute particles in solution: ______________
3. moles of solvent particles in solution: ______________
4. moles of solute and solvent particles in solution: ______________
5. mole fraction of solvent: ______________
6. vapor pressure of solvent at 25 °C (see Table 2.5): ______________ torr
7. vapor pressure of solution at 25 °C: ______________ torr

2.5-8. Boiling Point Elevation

The normal boiling point of a liquid is the temperature at which its vapor pressure is 1 atm. Although this is the definition of the normal boiling point, it is common to refer to it as simply the boiling point. The boiling point of water is 100 °C, so its vapor pressure at 100 °C is 1 atm, but the vapor pressure of an aqueous solution is less than 1 atm at 100 °C due to vapor pressure lowering. Consequently, an aqueous solution must be heated to a higher temperature to achieve a vapor pressure of 1 atm, so the boiling point of an aqueous solution is always higher than that of pure water. This reasoning can be applied to any solution, so we conclude that the boiling point of a solution is always higher than the boiling point of the pure solvent. The amount by which the boiling point of the solvent is increased by the addition of a nonvolatile solute is known as the ***boiling point elevation***, ΔT_b, which can be determined from the following equation:

$$\Delta T_\mathrm{b} = k_\mathrm{b} m_\mathrm{c} = i k_\mathrm{b} m \qquad \text{Boiling Point Elevation} \qquad (2.13)$$

k_b is the boiling point elevation constant, which has units of $°\mathrm{C}\cdot m^{-1}$ and depends on the solvent, and m_c is the colligative molality of the solute. ΔT_b is the amount by which the boiling point of the solvent (T_b°) is raised, so the boiling point of the solution (T_b) is given as

$$T_\mathrm{b} = T_\mathrm{b}^\circ + \Delta T_\mathrm{b}$$

2.5-9. Freezing Point Depression

Spreading salt on icy streets and sidewalks melts the ice because solute particles reduce the freezing point of a solvent in much the same way as they reduce its vapor pressure. That is, solute particles block sites on the solid where solvent molecules might otherwise freeze, thereby reducing the rate of freezing. The amount by which the freezing point is lowered is called the ***freezing point depression***, ΔT_f, and is shown in Equation 2.14:

$$\Delta T_\mathrm{f} = k_\mathrm{f} m_\mathrm{c} = i k_\mathrm{f} m \qquad \text{Freezing Point Depression} \tag{2.14}$$

k_f is the freezing point depression constant, which has units of °C$\cdot m^{-1}$ and depends on the solvent, and m_c is the colligative molality of the solute.

ΔT_f is the amount by which the freezing point of the solvent (T_f° is lowered, so the freezing point of the solution (T_f) is given as

$$T_\mathrm{f} = \Delta T_\mathrm{f}^\circ - \Delta T_\mathrm{f}$$

2.5-10. Solvent Constants

The solvent constants relevant for colligative properties are shown in Table 2.6 and in the Resources.

Solvent	**Freezing Point (°C)**	$\boldsymbol{k_\mathrm{f}}(^\circ\mathbf{C}\cdot\mathbf{m}^{-1})$	**Boiling Point (°C)**	$\boldsymbol{k_\mathrm{b}}(^\circ\mathbf{C}\cdot\mathbf{m}^{-1})$
Acetic acid	16.6	3.90	117.9	3.07
Benzene	5.5	4.90	80.1	2.53
Chloroform	−63.5	4.70	61.7	3.63
Cyclohexane	6.6	20.0	80.7	2.79
Ethanol	−117.3	1.99	78.5	1.22
para-Xylene	11.3	4.30		
Water	0.0	1.86	100.0	0.512

Table 2.6: Freezing Point Depression and Boiling Point Elevation Data for Some Solvents

2.5-11. Antifreeze Exercise

EXERCISE 2.22:

Antifreeze is ethylene glycol ($C_2H_6O_2$, $M_m = 62.1$ g/mol, $d = 1.11$ g/mL). What are the boiling and freezing points of an aqueous solution that is 50.% ethylene glycol by volume? Assume a density of 1.0 g/mL for water.

First, we determine the molality of the solution by assuming that water is the solvent and ethylene glycol is the solute. Thus, we need the number of kg of water and the number of moles of $C_2H_6O_2$. To determine the amounts, we must first choose an amount of solution. The easiest amount is exactly 1 L of solution.

The mass of H_2O in 1 L of solution = ______________ kg

The number of moles of $C_2H_6O_2$ in 1 L of solution = ______________ mol

The molality of $C_2H_6O_2$ = ______________ *m*

The van't Hoff factor for $C_2H_6O_2$ = ______________

The colligative molality of the solution = ______________ *m*

Use Table 2.6 to determine the following for water.

1. freezing point = ______________ °C
2. boiling point = ______________ °C
3. freezing point depression constant = ______________ °C/*m*
4. boiling point elevation constant = ______________ °C/*m*

The freezing point depression of the solution = ______________ °C

The boiling point elevation of the solution = ______________ °C

The freezing point of the solution = ______________ °C

The boiling point of the solution = ______________ °C

2.5-12. Salt Exercise

EXERCISE 2.23:

The salt that is commonly used to melt ice on roads and sidewalks is $CaCl_2$ ($M_m = 111$ g/mol). Consider a solution prepared by dissolving 62.3 g $CaCl_2$ in 100. g of water.

molality of $CaCl_2$ = ______________ *m*

colligative molality of the solution = ______________ *m*

freezing point of the solution = ______________ °C

boiling point of the solution = ______________ °C

mole fraction of solvent = ______________

vapor pressure of solvent at 20 °C = ______________ torr

vapor pressure of solution at 20 °C = ______________ torr

2.5-13. Molar Mass from Freezing Point Exercise

EXERCISE 2.24:

A common laboratory in general chemistry is the determination of a molar mass from the freezing point depression that it causes. In this example, we outline the procedure.

1.00 g of a non-dissociating solute is dissolved in 10.0 g of *para*-xylene. What is the molar mass of the solute, if the freezing point of the solution was 1.95 °C lower than that of the pure solvent? $k_\mathrm{f} = 4.30\ ^\circ\mathrm{C}/m$ for *para*-xylene.

Use Equation 2.14 to determine the molality of the solution: ____________ m

Use the molality and the mass of the solvent to determine the number of moles of solute in the solution: ____________ mol

Use the mass and number of moles of the solute to determine its molar mass: ____________ g/mol

2.5-14. Osmosis

Solvent molecules flow through a semipermeable membrane *from dilute* solutions to concentrated solutions.

A semipermeable membrane allows solvent molecules to pass through but denies passage of solute particles. The rate of passage of solvent molecules through the membrane is proportional to the concentration of the solvent molecules, so the rate is greater for a pure solvent than for a solution. When a solvent and a solution are separated by a semipermeable membrane, more solvent molecules move from the solvent to the solution than in the reverse direction. The net movement of the solvent molecules through the membrane from the solvent or a more dilute solution into a more concentrated one is called ***osmosis***.

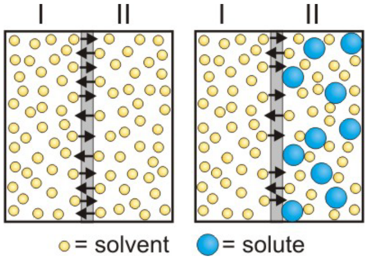


Figure 2.12: Osmosis (a) Rate of movement through the membrane is the same in both directions because the solvent concentration is the same on both sides. (b) A solute is added to side II, so the concentration of solvent is less in side II than in side I. Consequently, the rate of solvent motion I → II is greater than II → I.

2.5-15. Osmotic Pressure

Osmotic pressure depends on colligative *molarity*.

Osmosis of the solvent through the membrane from a solvent to a solution decreases the concentration of particles in the solution, but it also increases its volume while decreasing the volume of the solvent. These volume changes result in a height difference in the two columns as represented by h in Figure 2.13. The height difference results in a pressure differential at the membrane that increases the flow of solvent molecules from the solution side. Eventually, the combination of the increased pressure coupled with the decrease in concentration of the solute particles increases the flow of solvent particles from the solution back into the solvent to the point where the flow of solvent molecules through the membrane is the same in both directions. The pressure at which equilibrium is attained is called the osmotic pressure (Π) of the solution. The osmotic pressure that is developed is given in Equation 2.15

$$\Pi = M_c \times R \times T = i \times M \times R \times T \qquad \text{Osmotic Pressure} \qquad (2.15)$$

where R is the ideal gas law constant (R = 0.0821 L·atm/K·mol).

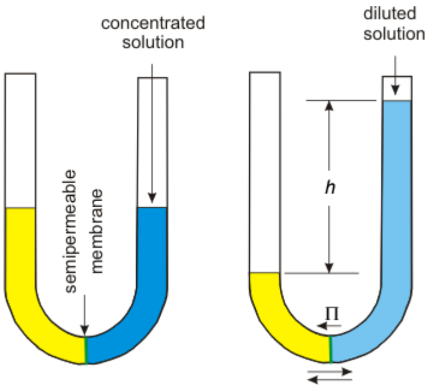


Figure 2.13: Osmotic Pressure Solvent molecules penetrate the semipermeable membrane, but solute molecules do not. Thus, there is a net flow of water molecules into the side with more solute.

A video or simulation is available online.

2.5-16. Osmotic Pressure of Sea Water Exercise

EXERCISE 2.25:

What is the osmotic pressure developed by seawater at 25 °C. Assume that seawater is a 0.53 M solution of NaCl.

$\Pi =$ ______________ atm

2.5-17. Molar Mass from Osmotic Pressure Exercise

EXERCISE 2.26:

1.00 L of an aqueous solution containing 0.40 g of a peptide has an osmotic pressure of 3.74 torr at 27 °C. What is the molar mass of the peptide?

$\Pi =$ ______________ atm

molar concentration of the peptide = ______________ M

number of moles of peptide in the solution = ______________ mol

molar mass of peptide = ______________ g/mol

2.5-18. Applications of Osmosis

Purification: Solvents can be purified by a process called reverse osmosis. If a pressure that exceeds the osmotic pressure is applied to a solution, solvent can be forced from the solution into the pure solvent. This process has been used to purify seawater in the Middle East. The challenge to purifying seawater lies in finding membranes that can withstand the large pressure (over 26 atm) required.

Biology: Cell membranes are semipermeable. When the solution around a cell has the same colligative concentration as within the cell, the cell maintains its size. However, if the cell is placed in water, water passes into the cell and can rupture it. Placing the cell in a solution with a greater colligative molarity causes water to leave the cell. This is why drinking seawater does not quench your thirst.

Water transport in plants: Water enters a tree through the membranes in the roots, but it evaporates from the leaves resulting in a substantial concentration difference between the roots and leaves. The large concentration difference can develop osmotic pressures of up to ~20 atm in tall trees.

2.6. Colloids

Introduction

Sometimes, rather than dissolving, one material will be suspended as small aggregates in another. Thus, sand will stay suspended in water as long as the water is stirred; but soon after the stirring has stopped, the sand settles to the bottom of the container. Because these mixtures do not meet the rigorous criterion of a solution, they are called dispersions or suspensions.

Objectives

- Identify common colloidal suspensions.

2.6-1. Types of Colloids

Suspensions in which the particle size is very small (1 nm to 1 μm) are called colloidal suspensions or simply ***colloids***. White paint is a colloidal suspension of SiO_2 and TiO_2 particles, which are used to make the paint opaque and white, respectively. Colloidal suspensions, which can be stable (will not settle) for years, are classified according to their composition. Whipped cream is a foam: a gas suspended in a liquid. Jellies and starch solutions are **sols**: solids suspended in a liquid. Milk is an **emulsion**: a liquid suspended in a liquid. **Aerosols** can be liquids suspended in a gas (hair sprays) or solids suspended in a gas (smoke). Fog is also an aerosol (water in air) and smog, the combination of smoke and fog, is also a colloidal suspension.

2.7. Exercises and Solutions

Links to view either the end-of-chapter exercises or the solutions to the odd exercises are available in the HTML version of the chapter.

CHAPTER 3 – THE 1^{ST} LAW OF THERMODYNAMICS

Introduction

In this chapter, we discuss the First Law of Thermodynamics (energy cannot be created or destroyed). In our discussion, we will define some important terms and demonstrate some valuable tools that are required to treat the energy flow in a chemical reaction.

3.1 Some Definitions and Conventions

Introduction

Determining the magnitude and direction of the energy flow is a common goal of thermodynamics. However, both the sign and magnitude depend upon the exact definition of the problem. In this section, we introduce some terms that will help us in this task.

Objectives

- Distinguish between a system, its surroundings, and the universe for a thermodynamic process.

3.1-1. Energy Flow

We first define three important terms:

- ***thermodynamic system***: That portion of the universe under investigation. It can be a volume in space or a carefully defined set of materials. It is the reference point for the direction of energy flow.
- ***thermodynamic surroundings***: That portion of the universe that interacts with the system. Energy flows between the system and its surroundings.
- ***thermodynamic universe***: A system and its surroundings.

The subscripts “univ” and “sur” are used to denote the universe and surroundings, but no subscripts are used for the system.

- ΔE = energy change of the system
- ΔE_{sur} = energy change in the surroundings
- ΔE_{univ} = energy change in the universe

Since the universe is simply the sum of the system and its surroundings, we can write

$$\Delta E_{\text{univ}} = \Delta E + \Delta E_{\text{sur}}$$

The sign or direction of energy flow is given by

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

Therefore, $\Delta E > 0$ means that $E_{\text{final}} > E_{\text{initial}}$, so the energy of the system increases, which requires energy to flow from the surroundings into the system, but $\Delta E < 0$ implies that $E_{\text{final}} < E_{\text{initial}}$, so there is a loss of energy in the system as energy flows out of the system and into the surroundings. Indeed, a negative sign is usually read as “lost” or “released.” For example, $\Delta E = -50$ J is usually read “50 J is released by the system,” while $\Delta E = +50$ J is read “50 J is absorbed by the system.”

3.1-2. Cash Flow Analogy

We now apply the definitions of system, surroundings, and sign to a cash flow problem where you write a check for \$50 to a friend. The first step in “setting up the books” is to define the system, which we will define as your account. In this problem, only your friend’s account interacts with (exchanges money with) the system, so it can be thought of as the surroundings. We define ΔB as the change in the balance of your account (the system); then $\Delta B = -\$50$ because money transferred out of the system, which caused your balance to decrease by \$50. Similarly, $\Delta B_{\text{sur}} = +\$50$

because money transferred into the surroundings, which increased the balance in your friend's account by \$50. Money was conserved in the process because money was neither created nor destroyed, it was simply transferred from the system to the surroundings. Thus, $\Delta B_{\text{univ}} = \Delta B + \Delta B_{\text{sur}} = -50 + 50 = 0$. If both accounts are held by the same bank, then the bank would be the universe for the problem as no money was tranferred into or out of the bank. However, it is important to realize that the value of ΔB depends upon our definitions. Consider the following possibilities:

- your account is the system: $\Delta B = -\$50$
- your friend's account is the system: $\Delta B = +\$50$
- the bank is the system: $\Delta B = 0$

Consequently, it is very important to clearly define the system.

3.2 Work, Heat, and Energy

Introduction

Heat and work are forms of energy transfer, and they represent the most common way for systems to exchange energy with their surroundings.

Objectives

- Calculate the heat absorbed by a system given its heat capacity and temperature change.
- Distinguish between heat capacity and specific heat.
- State the difference between the effects of work done *on* and work done *by* a system.

3.2-1. Work

Consider Figure 3.1, in which a larger mass M is attached to a smaller mass m through a pulley. Upon release, the larger mass would drop and its potential energy would decrease, but as it falls, it exerts a force on the other mass causing it to move up. ***Work***, w, is defined as a force through a distance, so the larger mass does work on the smaller one. For this discussion, we assume that 50 J of work is done. By convention, w is defined as the work done **on** the system.

So we would deduce that $w = -50$ J if the larger mass is the system, but $w = +50$ J if the smaller mass is the system.

The sign of w is given conversationally by using "on" or "by" as follows:

- $w > 0$: the work is done **on** the system
- $w < 0$: the work is done **by** the system

Thus, we would say that 50 J of work was done by the larger mass ($w < 0$) or that 50 J of work was done on the smaller mass ($w > 0$).

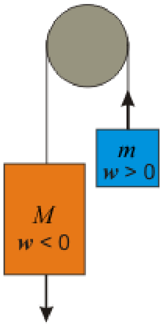


Figure 3.1: Work and the Sign of w

3.2-2. Sign of w Exercise

EXERCISE 3.1:

A person lifts a 70 kg mass to a height of 2.0 m, which changes the potential energy of the mass by 1.4 kJ.

1.4 kJ of work was done __________ the person, and 1.4 kJ of work was done __________ the mass.

First answer blank:	Second answer blank:
on	on
by	by

If the person is the system $w =$ __________ kJ

If the mass is the system $w =$ __________ kJ

3.2-3. Heat

Heat and work are the most common ways for energy to be transferred between a system and its surroundings.

Heat, q, is energy that is transferred as a result of a temperature difference. q is defined as the heat **absorbed by** the system. In Figure 3.2a, heat is absorbed by the system, so $q > 0$, which means that energy is transferred from the surroundings to the system increasing the energy of the system. In processes that absorb heat, heat enters the system, so they are said to be ***endothermic***. In Figure 3.2b, heat is given off, so $q < 0$ and energy is transferred from the system to the surroundings. In processes that give off heat, heat exits the system, so they are said to be ***exothermic***.

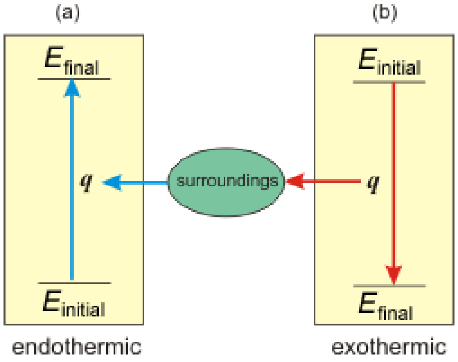


Figure 3.2: Heat and the Sign of q (a) Endothermic process: $q > 0$ and heat flows from the surroundings into the system. (b) Exothermic process: $q < 0$ and heat flows from the system into the surroundings.

3.2-4. Sign of q Exercise

EXERCISE 3.2:

A piece of metal is placed into hot water and 120 J of heat is transferred from the water to the metal.

If the *metal* is the system, $q =$ __________ J and the process is said to be __________.

- exothermic
- endothermic

If the *water* is the system, $q =$ __________ J and the process is said to be __________.

- exothermic
- endothermic

120 J of heat were ______________ by the metal and 120 J of heat were ______________ by the water.

First answer blank:
absorbed
given off

Second answer blank:
absorbed
given off

3.2-5. Heat Capacity and Specific Heat

The heat capacity of a substance depends upon its mass, but the specific heat does not.

Adding heat to a substance increases either its thermal energy (temperature) or its potential energy (phase change). Thus, adding heat to ice at −10 °C increases the temperature of the ice, while adding it at 0 °C causes the ice to melt but does not change the temperature. The temperature change that results is proportional to the heat added, and the proportionality constant is called the ***heat capacity***, C. The heat capacity is the amount of heat required to raise the temperature of the substance by 1 °C. It depends upon both the identity and the amount of substance. For example, the heat capacity of 4 g of water is four times that of 1 g.

$$q = C\Delta T \qquad \text{Heat, Heat Capacity, and Temperature Change} \qquad (3.1)$$

Tabulated values of heat capacities are not possible because they depend upon the mass, so we define the ***specific heat***, s, as the heat capacity of one gram of material; i.e., the specific heat is the amount of heat required to raise the temperature of one gram of substance by 1 °C. Thus, the heat capacity equals the specific heat times the mass.

$$C = ms \qquad \text{Specific Heat and Heat Capacity} \qquad (3.2)$$

Combining Equation 3.1 and Equation 3.2, we obtain the following expression for heat in terms of the specific heat and mass of the substance.

$$q = ms\Delta T \qquad \text{Heat, Specific Heat, and Temperature Change} \qquad (3.3)$$

Note that if the temperature increases, $\Delta T > 0$, so $q > 0$, which means that q joules must be absorbed when the temperature of a substance with mass m and specific heat s increases by ΔT degrees. If the temperature decreases, $\Delta T < 0$, so $q < 0$, and q joules would be given off when a substance with mass m and specific heat s cools by ΔT degrees.

The accompanying table gives the specific heats of some selected substances.

Substance	**Specific Heat ($\mathbf{J \cdot g^{-1} \cdot C^{-1}}$)**
$Al(s)$	0.90
$Cu(s)$	0.38
$Fe(s)$	0.44
$Hg(l)$	0.14
$Kr(g)$	0.25
$N_2(g)$	1.04
$CCl_4(g)$	0.86
$C_2H_5OH(l)$	2.46
$H_2O(l)$	4.18
$H_2O(s)$	2.00
$H_2O(g)$	2.00

Table 3.1: Specific Heats of Selected Substances

3.2-6. Specific Heat Exercise

EXERCISE 3.3:

How many kilojoules of heat are required to heat 17 g of ice from −22 °C to −10 °C?

The specific heat of ice is 2.0 J·g^{-1}·°C^{-1}.

The heat capacity of 17 g of ice is ____________ J·°C^{-1}

The temperature change is $\Delta T =$ ____________ °C

The amount of heat required is $q =$ ____________ kJ

3.2-7. Kinetic and Potential Energy

Energy can be kinetic or potential.

Energy is the capacity to do work or to transfer heat. It can be in the form of kinetic energy or potential energy.

- ***Kinetic energy*** is energy of motion. Any particle in motion has the capacity to do work and to transfer heat. For example, a moving truck can move another object (do work on it) by colliding with it. It can transfer its energy as heat through the brake drums and tires when the brakes are applied.
- ***Potential energy*** is energy of position. A stopped truck at the top of a hill has no kinetic energy, but its potential energy can be converted into kinetic energy by releasing the brake. The atoms in molecules have potential energy because of their positions relative to other atoms.

3.3 The First Law of Thermodynamics

Introduction

"Energy cannot be created or destroyed" is one of many statements of the First Law of Thermodynamics. In this section, we discuss how this law impacts the energy of a system.

Prerequisites

- (CAMS) 9.1 First Law of Thermodynamics

Objectives

- Use the expression, $\Delta E = q + w$, to determine how much of an energy flow is in the form of heat and how much is in the form of work.
- Define a state function.
- Calculate the amount of work associated with a change in the number of moles of gas in a reaction carried out at constant temperature and pressure.

3.3-1. First Law of Thermodynamics

Energy is conserved in all processes.

The ***First Law of Thermodynamics*** states that energy is conserved in all processes.

$$\Delta E_{\text{univ}} = 0 \qquad \text{Conservation of Energy} \tag{3.4}$$

However, the universe is the sum of the system and its surroundings, so we can write $\Delta E_{\text{univ}} = \Delta E + \Delta E_{\text{sur}} = 0$, which leads to the following statement of the first law:

$$\Delta E = -\Delta E_{\text{sur}} \qquad \text{Energy can only be transferred.} \tag{3.5}$$

The above shows that, although it cannot be created or destroyed, energy can be transferred between a system and its surroundings. Heat and work are the two most common ways of transferring energy. Thus, the energy of a system is increased when the surroundings transfers heat into the system and/or does work on it. The energy of the system decreases when it transfers heat to the surroundings or does work on them. This relationship is expressed mathematically in the following, which is **another statement of the First Law of Thermodynamics**:

$$\Delta E = q + w \qquad \text{Energy is transferred by heat and work.} \tag{3.6}$$

3.3-2. First Law Exercise

EXERCISE 3.4:

What energy change is experienced by a system that absorbs 358 J of heat and does 412 J of work?

$\Delta E =$ ________________ J

3.3-3. Partitioning Energy Changes

Energy change can be partitioned into heat and work.

The potential energy of a system (blue block in the following animation) decreases when it drops from a height, but the energy of the universe must be conserved in the process. The energy loss, which is transferred to the surroundings, is partitioned into heat and work ($\Delta E = q + w$) in the following animation by transferring the energy to the thermal and mechanical surroundings:

- The ***mechanical surroundings*** is that portion of the surroundings that exchanges energy with the system in the form of work. In the following, the system can lift another block. In doing so, the system does work on the lifted block, so some of the energy change of the system is transferred as work.
- The ***thermal surroundings*** is that portion of the surroundings that exchanges energy with the system in the form of heat. In the following, the falling system is stopped by friction, which converts the kinetic energy of the system into heat that is transferred to the thermal surroundings.

As the energy transferred to the mechanical surroundings increases, the amount transferred to the thermal surroundings decreases. Consequently, the speed with which the system drops decreases with the mass of the lifted block.

A video or simulation is available online.

3.3-4. State Functions

In the experiments described in the previous animation, we examined the transition between the same initial and final states by three different thermodynamic paths that differed in their distributions of q and w. ΔE was the same for each path because ΔE depends only upon the initial and final states—not on how they were achieved: $\Delta E = E_{\text{final}} - E_{\text{initial}}$. Properties, like energy, that depend only upon the state of the system are called ***state functions***. The fact that energy is a state function means that ΔE for a chemical process depends only upon the states of the reactants and products, not on the manner in which they react! This is an important property because it allows us to determine ΔE for a reaction using any path—even one that is unreasonable—as long as the reactants and products remain the same. Both q and w are path dependent, so they are not state functions. q and w for a reaction depend not only on the reactants and products; they also depend on how the reaction is carried out.

3.3-5. Changing the Number of Moles of Gas in a Reaction

Δn_{g} is the change in the number of moles of gas.

Most reactions carried out in a chemistry laboratory start and end at the same temperature and pressure, so $\Delta T = 0$ and $\Delta P = 0$. These conditions are very common and they simplify the thermodynamics, so we limit our discussions to processes run at constant temperature and pressure.

Almost all reactions exchange energy with the thermal surroundings, but those involving gases can also exchange energy with the mechanical surroundings, and we now show how to partition the energy change of a reaction involving gases into heat and work. We begin by expressing the ideal gas law for a mixture as the following:

$$PV = n_{\mathrm{g}}RT$$

n_{g} is the total number of moles of gas in the mixture, but n_{g} can change during a reaction as gases are consumed or created. Under conditions of constant temperature and pressure, P, R, and T are all constant, so the volume of the container must also change if n_{g} changes. The relationship is expressed as follows:

$$P\Delta V = \Delta n_{\mathrm{g}}RT \qquad \text{Volume Change in Chemical Reactions} \qquad (3.7)$$

ΔV is the volume change, and Δn_{g} is the change in the total number of moles of gas. The change in the number of moles of gas in a reaction would be determined as follows:

$$\Delta n_{\mathrm{g}} = \text{moles of gas phase products} - \text{moles of gas phase reactants} \qquad (3.8)$$

EXAMPLE:

Δn_{g} would be determined from the chemical equation 2 $H_2(g)$ + $O_2(g) \rightarrow$ 2 $H_2O(g)$ as $\Delta n_{\mathrm{g}} = 2$ moles gaseous product $-$ 3 moles gaseous reactants $= -1$ mole gas, but that is -1 mole of gas for every two moles of H_2O that are produced. However, if the reaction actually produced 0.5 mol H_2O, then Δn_{g} would be determined as follows:

$$\Delta n_{\mathrm{g}} = 0.5 \text{ mol } H_2O \times \frac{-1 \text{ mol gas}}{2 \text{ mol } H_2O} = -0.25 \text{ mol gas}$$

3.3-6. Change in Moles Exercise

EXERCISE 3.5:

Determine the value of Δn_{g} for each of the following processes.

$N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$

$\Delta n_{\mathrm{g}} =$ ____________ mol

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

$\Delta n_{\mathrm{g}} =$ ____________ mol

$H_2O(l) \rightarrow H_2O(g)$

$\Delta n_{\mathrm{g}} =$ ____________ mol

$NH_4Cl(s) \rightarrow NH_3(g) + HCl(g)$

$\Delta n_{\mathrm{g}} =$ ____________ mol

3.3-7. Volume Change Example

Work is done whenever gases are produced or consumed in a reaction.

Consider the following reaction carried out at constant T and P.

$$2\ NH_3(g) \rightarrow N_2(g) + 3\ H_2(g)$$

$$\Delta n_{\mathrm{g}} = 4 \text{ mol} - 2 \text{ mol} = 2 \text{ moles of gas}$$

The number of moles of gas in the container increases by 2 mol for every 2 mol of NH_3 that react. However, the reaction takes place at constant T and P, so the volume of the container must change. We can use the ideal gas equation to relate the volume change to Δn_g as follows.

$$P\Delta V = \Delta n_g RT$$

The volume change is demonstrated by the animation.

A video or simulation is available online.

3.3-8. *PV* Work

The piston moves as the volume changes in the animation above, so work was done when the number of moles of gas changed. We now determine how much work was done. The work done **by** an object is the force exerted by the object times the distance moved, Fd. However, w is defined as the work done **on** the object, so $w = -Fd$. A force is exerted by the expanding gas because it must push back the atmosphere, which is exerting a pressure on the cylinder. We will call this pressure the opposing pressure, P_{op}. The force that must be overcome by the expanding gas is then $P_{op}A$, where A is the cross-sectional area of the piston. Consequently, we can write that $w = -P_{op}Ad$, but the product of the cross-sectional area of the piston times the distance that it moves is the volume change that the gas undergoes ($Ad = \Delta V$), so we can express the work done on the gas as

$$w = -P_{op}\Delta V \qquad PV\text{ Work} \tag{3.9}$$

Recall that $P\Delta V = \Delta n_g RT$ for processes at constant temperature and pressure, so we can also express the work done on the gases in a reaction as

$$w = -\Delta n_g RT \qquad \text{Work Due to a Change in the Number of Moles of Gas} \tag{3.10}$$

A video or simulation is available online.

3.3-9. Expansion Work Exercise

EXERCISE 3.6:

How much work is done when 12 g of water evaporates at 25 °C?

$\Delta n_g =$ ______________ mol H_2O $RT =$ ______________ J/mol

$w =$ ______________ J

Is the work done "on" or "by" the water?

on
by

3.3-10. *PV* Work Exercise

EXERCISE 3.7:

What is the energy change of a gas that absorbs 432 J of heat and expands from 0.932 L to 1.684 L against an opposing pressure of 4.46 atm?

First determine the amount of energy exchanged with the thermal surroundings.

$q =$ ______________ J

Next, use Equation 3.9 to determine the amount exchanged with the mechanical surroundings.

$\Delta V =$ ______________ L $\qquad w = -P\Delta V =$ ______________ L·atm

Use the fact that 1 L·atm = 101.3 J to convert w from L·atm to J.

$w =$ ______________ J

Use q and w to determine the energy change.

$\Delta E =$ ______________ J

3.3-11. Work in Combustion Exercise

EXERCISE 3.8:

How much work is done by the gases when 5.000 g of butane is combusted at 25 °C and 1 atm?

$$C_4H_{10}(g) + 13/2\ O_2(g) \rightarrow 4\ CO_2(g) + 5\ H_2O(l)$$

Δn_g for the reaction shown above = ______________ mol

This results in work being done ______________ the system.
on
by

The number of moles of butane that react is ______________ mol

Δn_g for the combustion of 5.000 g of butane = ______________ mol

w for the combustion of 5.000 g of butane = ______________ J

3.4 Enthalpy

Introduction

In the last section, we saw that some of the energy change ($\Delta n_g RT$) of a reaction carried out at constant pressure is in the form of work as escaping gases push back the atmosphere. This portion of the energy is lost and not available to do other work. Thus, it is only the heat that is absorbed or given off by a reaction that is important in processes carried out at constant pressure. Thus, ΔE does not represent the energy that is important in constant pressure processes. In this section, we define a new thermodynamic function that is more appropriate for these processes.

Prerequisites

- (CAMS) 9.2 Enthalpy
- (CAMS) 9.3 Enthalpies of Combustion

Objectives

- Define the enthalpy of reaction and distinguish between it and the energy change of a reaction in terms of the heat absorbed at constant pressure or volume.
- Calculate the enthalpy of reaction from the energy change of the reaction and vice versa.

3.4-1. ΔH vs. ΔE

ΔH is the heat absorbed at constant pressure, while ΔE is the heat absorbed at constant volume.

We have seen that the First Law of Thermodynamics can be expressed in the following manner:

$$\Delta E = q + w$$

For chemical processes, w is the work done by gases as they react or are produced. We now examine this statement under two different conditions: constant volume and temperature and constant pressure and temperature.

Constant Volume Processes: Nothing moves if the volume does not change, so no work is done ($w = 0$) and the first law expression can be written as the following:

$$\Delta E = q_\text{V} + w = q_\text{V} + 0 = q_\text{V}$$

where q_V is the heat absorbed at constant volume. Based on the above, we conclude that **ΔE is the heat absorbed in a process carried out at constant volume and temperature.**

Constant Pressure Processes: The volume changes to maintain a constant pressure as gases are produced or consumed, so work can be done and the first law expression is

$$\Delta E = q_\text{P} + P\Delta V$$

where q_P is the heat absorbed at constant pressure and $P\Delta V$ is the work done by the gases. Solving this expression for the heat absorbed at constant pressure we obtain

$$q_\text{P} = \Delta E - P\Delta V$$

q_P is the difference between two state functions, so it too must be a state function, which is called the ***enthalpy of reaction*** and given the symbol ΔH. Thus, **ΔH is the heat absorbed by the reaction carried out at constant pressure and temperature**. Substitution of ΔH for q_P and $\Delta n_\text{g}RT$ for the work into the first law expression for a constant pressure process yields the following:

$$\Delta E = \Delta H - \Delta n_\text{g}RT \qquad \Delta H \text{ and } \Delta E \text{ Related} \tag{3.11}$$

which can be read ***the heat absorbed by a process carried out at constant volume (ΔE) equals the heat absorbed by the process when carried out at constant pressure (ΔH) plus the work done by changing the number of moles of gas.***

3.4-2. Enthalpy-Energy Exercise

EXERCISE 3.9:

The enthalpy of vaporization of water at 25 °C is 44.0 kJ·mol^{-1}. What is ΔE for the vaporization of a mole of water at 25 °C?

$$\text{H}_2\text{O}(l, 25\ {}^\circ\text{C}) \rightarrow \text{H}_2\text{O}(g, 25\ {}^\circ\text{C}) \qquad \Delta H = 44.0 \text{ kJ}$$

$\Delta n_\text{g} =$ ________________ mol

$\Delta n_\text{g}RT =$ ________________ kJ

$\Delta E =$ ________________ kJ

Note that the energy difference between a mole of liquid and a mole of gas is less than the amount of energy that must be supplied to vaporize a mole of liquid because some energy is used by the escaping gases to "push back the atmosphere."

3.4-3. Enthalpy-Energy Exercise

EXERCISE 3.10:

Determine ΔH_{comb} for butane given that $\Delta E = -244.9$ kJ for the combustion of 5.000 g of butane at 25 °C.

Method:

1. Write the chemical equation for the combustion reaction.

$$C_4H_{10}(g) + 13/2\ O_2(g) \rightarrow 4\ CO_2(g) + 5\ H_2O(l)$$

2. Determine the number of moles of butane that react. ($M_m = 58.12$ g/mol)

$n =$ ______________ mol

3. Use the given values to determine ΔE for combustion of one mole of butane.

$\Delta E_{\text{comb}} =$ ______________ kJ/mol

4. Determine Δn_g for the combustion of one mole of butane.

$\Delta n_g =$ ______________ mol

5. Determine the amount of energy that is in the form of work.

$\Delta n_g RT =$ ______________ kJ/mol

6. Use Equation 3.11 to determine the heat of combustion.

$\Delta H_{\text{comb}} =$ ______________ kJ/mol

3.5 Standard States and Properties of Enthalpy Changes

Introduction

The enthalpy of a reaction depends upon the states of the reactants (solid, liquid, gas, or solution) and upon the amounts of each of the substances. Thus, thermodynamic data are tabulated at reference states and apply to specific chemical equations. In this section, we discuss these reference states and how the enthalpy is dependent upon how the chemical equation is balanced.

Objectives

- Identify the standard state of a substance.

3.5-1. Standard States

The standard state is defined by a pressure (1 atm), but there is no standard temperature.

The enthalpy change of a reaction depends upon the concentrations and states of the substances. Consequently, most tabulated data refer to the situation in which all substances are in a specified state, called the ***standard state***.

- The standard state of a pure substance is the most stable state at 1 atm pressure and the specified temperature. Solids and liquids are assumed to be pure unless specified otherwise.
- The standard state of a gas is a partial pressure of 1 atm.
- The standard state of a solute is a concentration of 1 *M*.

When considering standard states, 1 atm is the standard pressure, but there is no standard temperature. If no temperature is given, assume exactly 25 °C (298.15 K), which is the most common temperature used for tabulated data. The standard state of water is

- a solid at −10 °C
- a liquid at 25 °C

- a gas at 1 atm pressure at 110 °C

Most thermochemical data pertain to the reaction in which all of the products and reactants are in their standard states. These quantities are distinguished from their non-standard values with the use of a superscript. Thus, $\Delta H°$ is the standard enthalpy of reaction. Consider the following thermochemical equation:

$$\mathrm{Fe_2O_3}(s) + 2\ \mathrm{Al}(s) \rightarrow\ \mathrm{Al_2O_3}(s) + 2\ \mathrm{Fe}(s) \qquad \Delta H° = -852\mathrm{kJ}$$

No temperature is reported, so we assume a temperature of 298.15 K. The solid state is the standard state for each substance at 298.15 K, so the enthalpy change is the standard enthalpy of reaction as indicated by the superscript zero.

3.5-2. Properties of Enthalpy

The enthalpy change also depends upon the amount of reactant that reacts or product that is formed. For example, consider the following reaction:

$$\mathrm{Fe_2O_3}(s) + 2\ \mathrm{Al}(s) \rightarrow \mathrm{Al_2O_3}(s) + 2\ \mathrm{Fe}(s) \qquad \Delta H° = -852\ \mathrm{kJ}$$

$\Delta H° = -852$ kJ in the above reaction as it is written. This means that 852 kJ are released for each mole of Fe_2O_3 or every two moles of Al that react or every 2 mol Fe or 1 mole Al_2O_3 that are produced. Thus, the following factors can be used to determine the amount of heat liberated from the amount of reactant consumed or product formed:

$$\frac{-852\ \mathrm{kJ}}{1\ \mathrm{mol\ Fe_2O_3\ reacting}};\ \frac{-852\ \mathrm{kJ}}{2\ \mathrm{mol\ Al\ reacting}};\ \frac{-852\ \mathrm{kJ}}{1\ \mathrm{mol\ Al_2O_3\ produced}};\ \frac{-852\ \mathrm{kJ}}{2\ \mathrm{mol\ Fe\ produced}}$$

Enthalpy is a state function, so reversing the initial and final states simply changes the sign. Thus, 852 kJ would be *absorbed* when 1 mol of Al_2O_3 reacts with 2 mol Fe to produce 1 mol Fe_2O_3 and 2 mol Al.

The properties of the enthalpy change of a reaction can be summarized as the following:

- If a reaction is multiplied by some number, then the enthalpy change must be multiplied by the same number.
- If a reaction is reversed, the sign of its enthalpy change is reversed.

3.5-3. Balanced Chemical Equation and Enthalpy Change Exercise

EXERCISE 3.11:

The thermochemical equation for the thermite reaction is:

$$\mathrm{Fe_2O_3}(s) + 2\ \mathrm{Al}(s) \rightarrow \mathrm{Al_2O_3}(s) + 2\ \mathrm{Fe}(s) \qquad \Delta H° = -852\ \mathrm{kJ}$$

What is the standard enthalpy for the reaction of 1.00 mol of Al with an excess of Fe_2O_3?

$\Delta H° =$ ______________ kJ

What is the standard enthalpy for the reaction of 2.00 mol of Fe with an excess of Al_2O_3?

$\Delta H° =$ ______________ kJ

3.6 Hess's Law of Heat Summation

Introduction

Enthalpy is a state function, so the enthalpy change of a process is independent of the path used to convert the initial state into the final state. This means that the enthalpy change of a process can be determined by breaking the process into a series of smaller processes whose enthalpy changes are known. The steps we choose don't even have to be realistic; they only have to move the system from the initial to the final state.

Objectives

- Apply Hess's Law of Heat Summation to determine the enthalpy of reaction.

3.6-1. Hess's Law

We will frequently use the fact that enthalpy is a state function to deduce its value from other known enthalpies with the use of Hess's Law of Heat Summation.

Hess's Law of Heat Summation:

- If a process can be expressed as the sum of several steps, then the enthalpy change of the process is the sum of the enthalpy changes of the steps.

3.6-2. A Heating Curve

Adding heat to a substance results in either a temperature change or a phase change. For example, consider the heating curve for heating water from 25 °C to 150 °C shown in Figure 3.3. Initially, the heat results only in a temperature change until the boiling point is reached. There is no temperature change as heat is added at the boiling point because all of the heat is used to vaporize the liquid. Once all of the liquid is vaporized, additional heat again causes the temperature to rise. The amount of heat required in each step is determined as follows:

- Temperature change: Combining Equation 3.2 and Equation 3.1, we see that the heat required to raise the temperature of m grams of a substance by ΔT degrees is $\Delta H = ms\Delta T$.
- Phase change: Enthalpies of phase change are usually given in kJ·mol^{-1}, so the enthalpy change required to change the phase of n moles is $\Delta H = n\Delta H_{\text{phase change}}$.

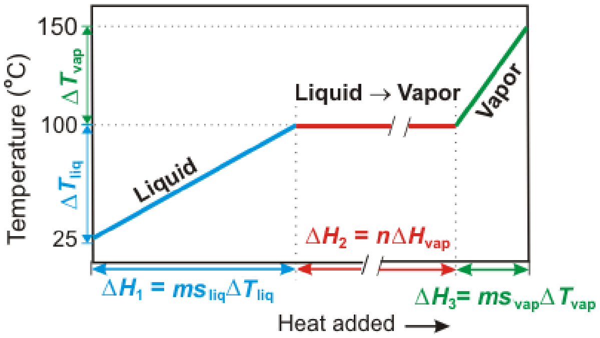


Figure 3.3: Heating Curve for Water from 25 °C to 150 °C

3.6-3. Hess's Law Example

Hess's Law, coupled with the fact that enthalpy change is path independent, allows us to determine enthalpy changes for complicated processes by considering simpler ones. Consider the process of heating water from 25 °C to 150 °C that was discussed above. To determine the heat required for the overall process, we would first break the process down into smaller processes (chemical equations) for which we can readily determine individual enthalpies. The processes are chosen so that they involve only one change, either temperature or phase, but not both.

Process	Chemical Equation
Heat the liquid from 25 °C to its boiling point.	$\mathbf{H_2O(\mathit{l}, 298\ K)} \rightarrow H_2O(l, 373\ K)$
Vaporize the liquid at its boiling point.	$H_2O(l, 373\ K) \rightarrow H_2O(g, 373\ K)$
Heat the steam to 150 °C.	$H_2O(g, 373\ K) \rightarrow \mathbf{H_2O(\mathit{g}, 423\ K)}$

Table 3.2

Note that the final state of each process is the same as the initial state of the following process, so these two states cancel when the three processes are added to leave only the initial state of the first process and the final state of the last process (the two states in bold):

$$H_2O(l, 298\text{ K}) \rightarrow \; H_2O(g, 423\text{ K})$$

Since the process can be represented as the sum of three processes, the enthalpy change for the overall process is the sum of the three enthalpy changes. The enthalpy changes are determined for an expanded problem in the following section.

3.6-4. State Change Exercise

<u>EXERCISE 3.12</u>:

Use the following table for the thermal properties of water to determine how much heat is required to convert 1.00 mole of ice at −20. °C to steam at 120. °C.

	Specific Heats $\mathbf{J{\cdot}g^{-1}{\cdot}{}^\circ C}$
solid	2.0
liquid	4.18
gas	2.0
	Enthalpies ($\mathbf{kJ{\cdot}mol^{-1}}$)
fusion	6.01
vaporization	40.7

Table 3.3: Some Thermal Properties of Water

First, break the overall process down into a series of smaller processes and determine the value of ΔH for each of the simple processes. Note: the enthalpy units must be the same for each process in order to add them. In this example, we determine the enthalpies in kJ.

Process	**ΔH (kJ/mol)**
$H_2O(s, 253\text{ K}) \rightarrow H_2O(s, 273\text{ K})$	
$H_2O(s, 273\text{ K}) \rightarrow H_2O(l, 273\text{ K})$	
$H_2O(l, 273\text{ K}) \rightarrow H_2O(l, 373\text{ K})$	
$H_2O(l, 373\text{ K}) \rightarrow H_2O(g, 373\text{ K})$	
$H_2O(g, 373\text{ K}) \rightarrow H_2O(g, 393\text{ K})$	

Use the above values and Hess's Law to determine ΔH for the entire process.

Process	ΔH (kJ/mol)
$H_2O(s, 253\text{ K}) \rightarrow H_2O(g, 393\text{ K})$	

3.6-5. Any Path Will Do

Although some ice may sublime, and some of the water vaporizes prior to the boiling point, the processes used in the preceding example follow closely those that actually occur during the heating process. However, enthalpy is a state function, so we are free to choose any path, even one that is totally unrelated to the overall process under consideration. As long as the sum of the processes in the path chosen sum to the overall process, we can use Hess's Law. One path that we can sometimes use is to combust all of the reactants and then let the products of the combustion recombine to produce the desired products. To do this, we use heats of combustion, which are defined as follows:

- ***Enthalpy of combustion*** is the heat absorbed when one mole of a substance reacts with oxygen.

Tables of heats (enthalpies) of combustion are common. In the following example, we determine the enthalpy of a reaction from the enthalpies of combustion of the reactants and products.

3.6-6. Using Heats of Combustion in the Path

EXERCISE 3.13:

Given the following combustion reactions:

1 $CH_4 + 2\ O_2 \rightarrow 2\ H_2O + CO_2$ $\Delta H_1 = -890.$ kJ

2 $C_2H_6 + 7/2\ O_2 \rightarrow 3\ H_2O + 2\ CO_2$ $\Delta H_2 = -54$ kJ

3 $H_2 + 1/2\ O_2 \rightarrow H_2O$ $\Delta H_3 = -142$ kJ

Determine the enthalpy change for the following reaction:

$$2\ CH_4(g) \rightarrow\ C_2H_6(g) +\ H_2(g)$$

We must rearrange the given chemical equations (multiply each by a number and/or reverse the reaction) so that the sum of the resulting equations produces the desired equation. Reversing the direction of a reaction changes its sign, so **use a minus sign with the multiplier to indicate that the reaction must be reversed**.

Each reactant and product appears in only one of the given reactions, so we can construct the desired reaction from the individual molecules.

Two molecules of CH_4 appear on the reactant side of the desired reaction, and one molecule appears on the reactant side of Equation 1.

The multiplier that should be applied to Equation 1 is ____________

The resulting chemical equation is the following. (Denote any subscripts with an underscore. For example, NH_3 for NH_3. Place a single space between the coeffient and the compound. Omit any coefficients of 1.)

Eq A = ☐ + ☐ → ☐ + ☐

The enthalpy change is $\Delta H_A =$ ____________ kJ

One molecule of C_2H_6 is required on the product side, and one molecule of C_2H_6 appears on the reactant side of Equation 2.

The multiplier that should be applied to Equation 2 is ____________

The resulting chemical equation is the following. (Denote any subscripts with an underscore. For example, NH_3 for NH_3. Place a single space between the coeffient and the compound. Omit any coefficients of 1.)

Eq B = ☐ + ☐ → ☐ + ☐

The enthalpy change is $\Delta H_B =$ ____________ kJ

One molecule of H_2 appears on the product side of the desired equation, and one molecule appears as a reactant in Equation 3.

The multiplier that should be applied to Equation 3 is ________

The resulting chemical equation is the following. (Denote any subscripts with an underscore. For example, NH_3 for NH_3. Place a single space between the coeffient and the compound. Omit any coefficients of 1.)

Eq C = ________ → ________ + ________

The enthalpy change is $\Delta H_C =$ ________ kJ

The chemical equation produced by the sum of equations A, B, and C is the following. (Denote any subscripts with an underscore. For example, NH_3 for NH_3. Place a single space between the coeffient and the compound. Omit any coefficients of 1.)

________ → ________ + ________

The enthalpy change for the above reaction is $\Delta H =$ ________ kJ

3.6-7. Heats of Combustion Summary

We saw in the preceding example that the enthalpy of the reaction

$$2\ CH_4 \rightarrow C_2H_6 + H_2$$

can be determined from the heats of combustion of the reactants and products as

$$\Delta H = 2\Delta H_{\text{comb}}(CH_4) - \Delta H_{\text{comb}}(C_2H_6) - \Delta H_{\text{comb}}(H_2)$$

In other words, the enthalpy of this reaction can be determined as the heats of combustion of the reactants minus the heats of combustion of the products, where each heat of combustion is multiplied by the coefficient in the balanced equation.

3.7 Enthalpies (or Heats) of Formation

Introduction

In the previous section, we saw that the enthalpy of a reaction can be determined from the heats of combustion of the reactants and products. This would be an excellent method to use to determine enthalpies of reactions, but it is limited to reactions in which all reactants and products react with oxygen, and not all compounds do. Thus, another, more general, reaction needs to be used. The reaction that is used is the formation reaction; not all compounds combust, but they all form.

Objectives

- Determine the enthalpy of reaction given the heats of formation of the reactants and products.
- Determine the enthalpy of formation of one of the reactants or products of a reaction given the ΔH of the reaction and the heats of formation of all other participants in the reaction.

3.7-1. Definition

The ***standard heat of formation***, ΔH_f°, of a compound is the heat absorbed when one mole of the compound is formed from its elements in their standard states. For example, saying that "the heat of formation of hydrogen chloride is −92.3 kJ/mol" implies the following thermochemical equation.

$$1/2\ \mathrm{H_2}(g) + 1/2\ \mathrm{Cl_2}(g) \rightarrow \mathrm{HCl}(g) \qquad \Delta H^\circ = -92.3\ \mathrm{kJ}$$

The equation obtained by multiplying the above by 2 to eliminate the fractions corresponds to twice the heat of formation of HCl because it involves the production of 2 mol HCl.

The heat of formation of an element in its standard state is zero because there is no reaction required to produce an element from its elements. For example, consider the formation reaction for elemental oxygen:

$$\mathrm{O_2}(g) \rightarrow \mathrm{O_2}(g) \qquad \Delta H^\circ = 0$$

The enthalpy change for the above reaction is zero because the final and initial states are the same.

3.7-2. Writing Formation Reaction Exercise

EXERCISE 3.14:

Write the formation reaction for each of the following. Order the elements in the same order they appear in the given compound. Denote any subscripts with an underscore. For example, NH_3 for NH_3. Place a single space between the coeffient and the compound. Omit any coefficients of 1. Be sure to indicate the state of each substance as (s), (l), or (g) and express non-integer coefficients as fractions.

$C_{12}H_{22}O_{11}(s)$

☐ + ☐ + ☐ → ☐

$Na_2O(s)$

☐ + ☐ → ☐

$NH_3(g)$

☐ + ☐ → ☐

$(NH_4)_2Cr_2O_7(s)$

☐ + ☐ + ☐ + ☐ → ☐

3.7-3. Using Heats of Formation

The path that is assumed when heats of formation are used involves breaking up the reactant molecules into their elements, then combining the elements that were produced to form the products. The application of Hess's Law to the process can be summarized as follows:

- The enthalpy of any reaction can be determined as the sum of the enthalpies of formation of the products, each multiplied by its coefficient in the balanced equation, minus the sum of the enthalpies of formation of the reactants, each multiplied by its coefficient in the balanced equation.

$$\Delta H^\circ = \sum c_\mathrm{P}(\Delta H_\mathrm{f}^\circ)_\mathrm{P} - \sum c_\mathrm{R}(\Delta H_\mathrm{f}^\circ)_\mathrm{R} \tag{3.12}$$

- $(\Delta H_\mathrm{f}^\circ)_\mathrm{P}$ is the standard heat of formation of the product whose coefficient in the balanced equation is c_P.
- $(\Delta H_\mathrm{f}^\circ)_\mathrm{R}$ is the standard heat of formation of the reactant whose coefficient in the balanced equation is c_R.

For example, the enthalpy for the reaction $Al_2O_3(s) + 3\ CO(g) \rightarrow 2\ Al(s) + 3\ CO_2(g)$ could be determined as

$$\Delta H^\circ = 2\Delta H_\mathrm{f}^\circ(\mathrm{Al}) + 3\Delta H_\mathrm{f}^\circ(\mathrm{CO_2}) - \Delta H_\mathrm{f}^\circ(\mathrm{Al_2O_3}) - 3\Delta H_\mathrm{f}^\circ(\mathrm{CO})$$

Heats of formation are available in tables (See Thermodynamic Properties in the Resources). Substitution of the tabulated values yields

$$\Delta H^\circ = 2(0) + 3(-393.51) - (-1676) - 3(-110.52) = 827\text{ kJ}$$

3.7-4. Heat of Combustion from Heats of Formation Exercise

EXERCISE 3.15:

Determine the standard heat of combustion of ethanol, $C_2H_5OH(l)$, at 298 K.

First, write the combustion reaction for $C_2H_5OH(l)$. The carbon and hydrogen atoms are oxidized to carbon dioxide and water, respectively. At 298 K, the water is a liquid. Denote any subscripts with an underscore. For example, NH_3 for NH_3. Place a single space between the coeffient and the compound. Omit any coefficients of 1. When writing the reaction, be sure to include the states of matter and express noninteger coefficients as fractions.

______ + ______ → ______ + ______

Next, use the resource titled Thermodynamic Properties to determine the heat of formation of each product and reactant.

$C_2H_5OH(l)$ ______ kJ/mol $O_2(g)$ ______ kJ/mol

$CO_2(g)$ ______ kJ/mol $H_2O(l)$ ______ kJ/mol

Finally, use Equation 3.12 to determine the enthalpy of combustion of ethanol.

$\Delta H_{\text{comb}} =$ ______ kJ/mol

3.7-5. Heats of Formation from Heat of Combustion Exercise

Heats of formation are not always determined from direct measurement. For example, when $C(s)$ and $H_2(g)$ react, a number of different compounds will be produced. Consequently, the heat of formation of something like C_6H_6 cannot be determined directly. Instead, the heat of reaction for a different reaction is measured and used with known heats of formation to determine the unknown heat of formation. The heat of formation of octane is determined from its heat of combustion in the following example.

3.7-6. Exercise

EXERCISE 3.16:

The enthalpy of combustion of octane (C_8H_{18} is -5494 kJ/mol). What is the heat of formation of octane?

First, write the combustion reaction for $C_8H_{18}(l)$. The carbon and hydrogen atoms are all oxidized to carbon dioxide and water. At 298 K, the water is a liquid. Denote any subscripts with an underscore. For example, NH_3 for NH_3. Place a single space between the coeffient and the compound. Omit any coefficients of 1. Express all noninteger coefficients as fractions and include the states of matter.

______ + ______ → ______ + ______

Next, use the resource titled Thermodynamic Properties to determine the heat of formation of each of the other compounds in the reaction.

$O_2(g)$ ______________ kJ/mol $CO_2(g)$ ______________ kJ/mol

$H_2O(l)$ ______________ kJ/mol

Write the expression for the heat of combustion in terms of the heats of formation and solve it for the heat of formation of octane.

$\Delta H_\text{f} =$ ______________ kJ/mol

3.8 Bond Dissociation Energies

Introduction

Although tables of heats of formation are extensive, there are still many compounds whose heats of formation are unknown. However, all chemical reactions involve breaking and forming bonds and the enthalpy of a reaction can be approximated from the energies of the broken and formed bonds. In this section, we define the bond or dissociation energy, show how bond energies can be determined from heats of formation, and finally show how bond energies can be used to approximate the enthalpy of any reaction.

Prerequisites

- (CAMS) 9.4 Bond Energies

Objectives

- Determine the enthalpy of atomization of a molecule and the average bond energy of its bonds when all of the bonds are between the same pair of atoms.
- Use bond energies to estimate enthalpies of gas-phase reactions.

3.8-1. Definition

The ***bond energy*** or ***dissociation energy***, D, is the energy required to break a mole of bonds in the gas phase. When all of the bonds in a gas phase molecule are broken to produce the constituent atoms in the gas phase, the molecule is said to be atomized and the energy required to atomize a mole of molecules is called the ***atomization energy***, ΔH_atom. Note that *the atoms, not the elements in their standard states, are the products of atomization.* The chemical equation for the atomization of CH_4 is

$$CH_4(g) \rightarrow\ C(g) + 4\ H(g)$$

The atomization energy is the sum of the bond energies of all of the broken bonds, but it can also be determined from the heats of formation of the products and reactants. We next combine both methods for the above process.

$$\Delta H_\text{atom} = \Delta H_\text{f}(\text{C}) + 4\Delta H_\text{f}(\text{H}) - \Delta H_\text{f}(\text{CH}_4) = 4D_\text{C-H}$$

The atomization of CH_4 requires breaking the four C–H bonds, so $D_\text{C–H}$, which is the average C–H bond energy in CH_4, can be determined as $\Delta H_\text{atom}/4$. Atomization energies are often used to estimate bond energies.

3.8-2. Determining a Bond Energy Exercise

EXERCISE 3.17:

What is the average N–O bond energy in NO_2?

Our strategy is to determine the atomization energy from heats of formation and then relate that to the N–O bond energy.

Write the atomization reaction for NO_2. (Denote any subscripts with an underscore. For example, NH_3 for NH_3. Place a single space between the coeffient and the compound. Omit any coefficients of 1. Include states of matter.)

______ → ______ + ______

Look up the required heats of formation (Thermodynamic Properties).

NO_2 ______ kJ/mol

N ______ kJ/mol

O ______ kJ/mol

Use the heats of formation to determine the atomization energy of NO_2.

$\Delta H_{\text{atom}} =$ ______ kJ/mol

Determine the average bond strength given that two N–O bonds must be broken to atomize the molecule.

$D_{\text{N–O}} =$ ______ kJ/mol

3.8-3. Determining a Bond Energy Exercise

EXERCISE 3.18:

Determine the average C–F bond energy in CHF_3 from the following data.

- Enthalpies of formation: C = 717; F = 79; H = 218; $CHF_3 = -695$ kJ/mol
- C–H bond energy = 413 kJ/mol

Write the atomization reaction for CHF_3. (Denote any subscripts with an underscore. For example, NH_3 for NH_3. Place a single space between the coeffient and the compound. Omit any coefficients of 1. Include states of matter.)

______ → ______ + ______ + ______

Determine the atomization energy of CHF_3.

$\Delta H_{\text{atom}} =$ ______ kJ/mol

Use the given bond energy to determine the energy of three C–F bonds.

$3D_{\text{C–F}} =$ ______

Determine the average C–F bond energy in CHF_3.

$D_{\text{C–F}} =$ ______ kJ/mol

3.8-4. Enthalpies of Reaction from Bond Energies

Reactions involve breaking and forming bonds, so enthalpies of reaction can be estimated with bond energies. The path assumed for a reaction when bond energies are used involves breaking all of the relevant reactant bonds to produce fragments and then combining the fragments so as to produce the desired products. Application of Hess's Law to the process can again be summarized in a simple fashion.

- The enthalpy of a reaction can be *estimated* as the energy required to break the reactant bonds minus the energy released when the product bonds are formed.

$$\Delta H \approx \sum(D_{\text{broken bonds}}) - \sum(D_{\text{formed bonds}}) \tag{3.13}$$

The above is only an approximation because the energy of a bond depends on its environment (the other atoms attached to the bound atoms). In addition, bond energies are sometimes used to estimate enthalpies in solution, but the tabulated values are average values for gas phase bonds only, so such approximations should be treated with care.

3.8-5. Bond Energy Table

Bond energies are a convenient way to estimate reaction enthalpies, and a table of bond energies of common bonds can be found in the resource titled Bond Energies. For completeness, it is also given below.

C–H	413
C–F	485
C–Cl	328
C–Br	276
C–I	234

N–H	391
N–F	272
N–Cl	200
N–Br	243

O–H	463
O–F	190
O–Cl	203
O–Br	235
O–I	234

H–H	436
H–F	565
H–Cl	431
H–Br	366
H–I	299

F–F	159
Cl–Cl	243
Br–Br	193
I–I	151

C–C	347
C=C	612
C≡C	820

N–N	163
N=N	418
N≡N	941

N–O	201
N=O	607

C–N	293
C=N	615
C≡N	891

C–O	358
C=O	799
C≡O	1072

O–O	146
O=O	495

Table 3.4: Common Bond Energies (kJ·mol^{-1})

3.8-6. Using Bond Energies Exercise

EXERCISE 3.19:

Use bond energies to estimate the heat of formation of NH_3.

1) Write the chemical equation (no states needed) for the formation reaction. (Express all noninteger coefficients as fractions.)

N_2 + H_2 → NH_3

2) Draw Lewis structures for each compound to identify multiple bonds.

3) Use a table of bond energies (Bond Energies) to determine the energy of the reactant bonds.

Energy Reactant Bonds ______ kJ/mol

4) Use a table of bond energies (Bond Energies) to determine the energy of the produced bonds.

Energy Required to Break Reactant Bonds ______ kJ/mol

Use the results of 3 and 4 to determine the enthalpy of formation.

ΔH_f = ______________ kJ/mol

3.8-7. Using Bond Energies in Reactions that Involve a Simple Solid or Liquid

Bond energies should be applied directly only when all substances in a reaction are gases. However, they can be combined with other thermodynamic quantities to produce valid results for reactions that involve a simple solid or liquid. This is done by applying Hess's Law of Heat Summation to the enthalpy of reaction determined with bond energies and the energy required to convert the solid or liquid into a gas. Consider the example where the heat of combustion of butane at 298 K is determined from bond energies.

EXAMPLE:

Bond energies apply only to molecules in the gas phase, so using bond energies alone we would obtain the enthalpy of the following reaction.

$$C_4H_{10}(g) + 13/2\ O_2(g) \rightarrow 4\ CO_2(g) + 5\ H_2O(g) \qquad (1)$$

Using a table of bond energies (Bond Energies), we can determine the enthalpy of Reaction 1 as follows.

$$\begin{aligned}\Delta H &= 3D_{\mathrm{C-C}} + 10D_{\mathrm{C-H}} + 6.5D_{\mathrm{O=O}} - 8D_{\mathrm{C=O}} - 10D_{\mathrm{O-H}}\\ &= 3(347) + 10(413) + 6.5(495) - 8(799) - 10(463)\\ &= -2634\ \mathrm{kJ}\end{aligned}$$

However, water is a liquid at 298 K, not a gas, so the heat of vaporization of water must be combined with Reaction 1 to convert the gas to a liquid. Five moles of H_2O are produced, so we use the following:

$$5\ H_2O(g) \rightarrow 5\ H_2O(l) \Delta H = -5\Delta H_{\mathrm{vap}} = -5(44.0) = -220.\ \mathrm{kJ} \qquad (2)$$

Adding Reactions 1 and 2 provides the chemical equation for the combustion as the 5 $H_2O(g)$ cancels in the addition. Adding their enthalpy changes provides the heat of combustion.

$$\begin{aligned}C_4H_{10}(g) + 13/2\ O_2(g) \rightarrow 4\ CO_2(g) + 5\ H_2O(l) \Delta H_{\mathrm{comb}} &= -2634 - 220.\\ &= -2854\ \mathrm{kJ}\end{aligned}$$

3.8-8. Using Bond Energies for a Reaction with a Solid Exercise

EXERCISE 3.20:

Use bond energies to estimate the heat of formation of ethene (C_2H_4).

Write the balanced chemical equation for the formation as determined solely from bond energies. (Denote any subscripts with an underscore. For example, NH_3 for NH_3. Place a single space between the coeffient and the compound. Omit any coefficients of 1. Include states of matter.)

Reaction 1: ______ + ______ → ______

Draw Lewis structures and use bond energies to determine the enthalpy for Reaction 1:

ΔH_1 = ______________ kJ

The standard state of carbon is graphite. What equation must be added to the above to convert C(g) to C(s)? (Denote any subscripts with an underscore. For example, NH_3 for NH_3. Place a single space between the coeffient and the compound. Omit any coefficients of 1. Include states of matter.)

Reaction 2: ______ → ______

What is the enthalpy of Reaction 2?

$\Delta H_2 =$ ______ kJ

The enthalpy of formation of ethene is:

$\Delta H_f =$ ______ kJ

3.9 Calorimetry

Introduction

Heats of formation, heats of combustion, and bond energies are all available in tables and can be used to determine or approximate the enthalpy change of other reactions. However, these tabulated numbers are based on experimental values. In this section, we discuss how those values are obtained. Measuring the amount of heat absorbed or liberated in a process is called calorimetry.

Objectives

- Calculate the heat of a reaction from the temperature change it causes in a calorimeter with known heat capacity, and decide whether the heat is an enthalpy change or a change in the energy of the system.

3.9-1. A Calorimeter

Calorimetry is the measurement of the heat flow of a process, and a schematic of a simple calorimeter is shown in Figure 3.4. The calorimeter consists of a thermally insulated container, a thermometer, and a carefully measured amount of water. The thermal insulation can range from styrofoam as found in insulated cups to evacuated jackets as found in Thermos bottles. A heat source or sink, which is often a reaction, is then placed in the calorimeter, and the temperature change of the calorimeter is measured.

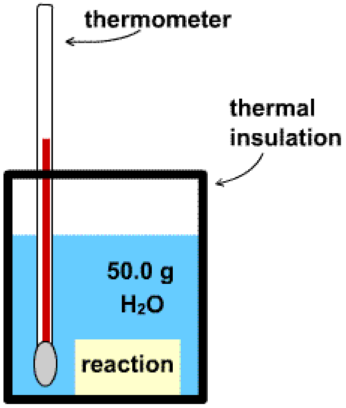


Figure 3.4 The amount of heat that is released or absorbed in a reaction is determined experimentally in a ***calorimeter***. The reaction is usually carried out in a container that is submerged in the water, so the heat flow is determined by measuring the temperature change in the water.

3.9-2. The Calorimetry Equations

Since the water and the reaction are in a thermally insulated container, no heat can enter or leave the system; i.e., $q_{\text{rxn}} + q_{\text{cal}} = 0$, which can be rearranged to the following:

$$q_{\text{rxn}} = -q_{\text{cal}} \qquad \text{Calorimetry Equation 1} \qquad (3.14)$$

The heat of the reaction causes only a temperature change in the calorimeter, so we can express q_{cal} as

$$q_{\text{cal}} = C_{\text{cal}}\Delta T_{\text{cal}}$$

Substituting this expression into Calorimetry Equation 1, we obtain

$$q_{\text{rxn}} = -C_{\text{cal}}\Delta T_{\text{cal}} \qquad \text{Calorimetry Equation 2} \qquad (3.15)$$

Almost all of the heat that is absorbed by the calorimeter is absorbed by the water, so we can make the following approximation:

$$C_{\text{cal}} \approx m_{\text{water}}s_{\text{water}}$$

Substitution of the above into Calorimetry Equation 2 yields a commonly used approximation that relates the heat of reaction to the mass and temperature change of the water in the calorimeter.

$$q_{\text{rxn}} = -m_{\text{water}}s_{\text{water}}\Delta T_{\text{water}} \qquad \text{Calorimetry Equation 3} \qquad (3.16)$$

3.9-3. Using a Calorimeter Exercise

EXERCISE 3.21:

When the reaction in the simulation online is the reaction of 0.0225 mol X, the temperature of the 50.0 g of water rises from 22.5 °C to 26.4 °C and there is no volume change.
A video or simulation is available online.

The reaction is ________________.
  exothermic
  endothermic

$\Delta T_{\text{water}} =$ ________________ °C

$s_{\text{water}} = 4.18\ \text{J·g}^{-1}{}^\circ\text{C}^{-1}$

$q_{\text{cal}} =$ ________________ J

$q_{\text{rxn}} =$ ________________ J

$\Delta H =$ ________________ kJ/mol

3.9-4. Determining Specific Heat Exercise

EXERCISE 3.22:

9.0 g of Al at 100.0 °C are placed in 20.0 mL of water at 20.0 °C contained in a Styrofoam cup. At thermal equilibrium, the temperature of the water and aluminum is 27.1 °C. What is the specific heat of aluminum?

The heat absorbed by the water:

$m_{\text{water}} = \underline{\qquad\qquad\qquad}$ g

$s_{\text{water}} = 4.18\ \text{J}\cdot\text{g}^{-1}\cdot{}^{\circ}\text{C}^{-1}$

$\Delta T_{\text{water}} = \underline{\qquad\qquad\qquad}$ °C

$q_{\text{water}} = \underline{\qquad\qquad\qquad}$ J

The specific heat of Al:

$q_{\text{Al}} = \underline{\qquad\qquad\qquad}$ J

$m_{\text{Al}} = \underline{\qquad\qquad\qquad}$ g

$\Delta T_{\text{Al}} = \underline{\qquad\qquad\qquad}$ °C

$s_{\text{Al}} = \underline{\qquad\qquad\qquad}\ \text{J}\cdot\text{g}^{-1}\cdot{}^{\circ}\text{C}^{-1}$

3.9-5. Energy or Enthalpy

The heat of reaction determined in a bomb calorimeter is ΔE, but the heat determined in an open calorimeter is ΔH.

The state function assigned to q_{rxn} depends upon how the reaction is carried out.

- No gases are involved in the reaction or the number of moles of gas does not change. Under these conditions, no $P\Delta V$ work can be done. This is the case in most reactions that occur in solution.
  - $q_{\text{rxn}} = \Delta E = \Delta H$
- The number of moles of gas does change. Under these conditions, some $P\Delta V$ work can be done.
  - **at constant pressure**: $q_{\text{rxn}} = \Delta H$ because $P\Delta V$ work can be done. Any reaction open to the atmosphere or carried out in a piston/cylinder is carried out at constant pressure.
  - **at constant volume**: $q_{\text{rxn}} = \Delta E$ because no $P\Delta V$ work can be done. This is the case in a **bomb calorimeter**, where the reaction is carried out in a steel vessel with a cap that is screwed on so no volume change (no work) can take place.

3.9-6. Bomb Calorimeter Exercise

EXERCISE 3.23:

What temperature rise would occur in a bomb calorimeter with a heat capacity of 4.877 kJ/°C when 0.00750 mol C_4H_{10} is burned at 25 °C?

First, decide which thermodynamic property should be used to determine q_{rxn}.

$\Delta H_{\text{comb}} = -2856$ kJ/mol
$\Delta E_{\text{comb}} = -2847$ kJ/mol

Next, determine q_{rxn} for the combustion of 0.00750 mol C_4H_{10}.

$q_{\text{rxn}} = \underline{\qquad\qquad\qquad}$ kJ

Finally, solve Equation 3.15 for ΔT.

$\Delta T = \underline{\qquad\qquad\qquad}$ °C

3.9-7. Heat of Formation from Calorimetry Exercise

EXERCISE 3.24:

Combustion of 1.00 g of sucrose ($C_{12}H_{22}O_{11}$) causes the temperature in a bomb calorimeter with a heat capacity of 4.90 kJ/°C to rise from 24.92 to 28.33 °C. What is the standard heat of formation of sucrose? The heats of formation of $CO_2(g)$ and $H_2O(l)$ are −393.5 kJ/mol and −285.8 kJ/mol, respectively.

The combustion reaction:

$$C_{12}H_{22}O_{11}(s) + 12\ O_2(g) \rightarrow 12\ CO_2(g) + 11\ H_2O(l)$$

heat of reaction in calorimeter $q_{\text{rxn}} =$ ______________ kJ

moles of sucrose reacting $n =$ ______________ mol $C_{12}H_{22}O_{11}$

energy change for combustion (reaction is carried out in a bomb) $\Delta E_{\text{comb}} =$ ______________ kJ/mol

change in number of moles of gas in balanced equation $\Delta n_{\text{g}} =$ ______________ mol

heat of combustion of sucrose $\Delta H_{\text{comb}} =$ ______________ kJ/mol

heat of formation of sucrose $\Delta H_{\text{comb}} =$ ______________ kJ/mol

3.10 Combustion: Food as Fuel

Introduction

The energy that is derived from the metabolism of carbohydrates and fats is essentially the same as is produced by their combustion in a calorimeter. Thus, the calorie content used in nutrition is the same as that derived from calorimetry.

3.10-1. Nutrition Labels

In the last example of the previous section, we showed that the heat of combustion of 1 g of $C_{12}H_{22}O_{11}$, a carbohydrate, is 17 kJ. Indeed, the heat of combustion of most carbohydrates is 17 kJ/g. The heats of combustion of proteins are also 17 kJ/g, while those of fats are 38 kJ/g. These are approximately the same values derived from their metabolism in the body.

A dietary calorie (Cal, upper case "C") is actually a kcal of energy and 1 kcal = 4.18 kJ. We can summarize the heats of combustion as follows:

Substance	**ΔH_{comb} (kJ/g)**	**ΔH_{comb} (Cal/g)**
carbohydrates	17	4
proteins	17	4
fats	38	9

Table 3.5

3.10-2. Nutrition Label Exercise

EXERCISE 3.25:

Use the heats of combustion given above to determine the number of calories derived from each substance and the total number of calories in one serving of a can of soup with the following nutrition information on one serving.

- Total Fat 1 g
- Total Carbohydrates 31 g
- Total Protein 7 g

Calories from Fat __________ Cal

Calories from Carbohydrates __________ Cal

Calories from Protein __________ Cal

Total Calories __________ Cal

3.11 Exercises and Solutions

Links to view either the end-of-chapter exercises or the solutions to the odd exercises are available in the HTML version of the chapter.

CHAPTER 4 – THERMODYNAMICS AND EQUILIBRIUM

Introduction

Thus far, we have assumed that the limiting reactant is always consumed completely in a reaction, but this is not always the case because many reactions reach equilibrium with substantial amounts of reactant still present. Recall that a reaction at equilibrium is a dynamic process in which the reaction continues but with no net change in the amount of product because the product is consumed at the same rate at which it is formed. To emphasize the dynamic nature of the process, equilibria are represented with double arrows. $\mathrm{A} \rightleftharpoons \mathrm{B}$ implies that, not only is A producing B, but B is also producing A.

The preceding discussion is a review of the kinetic definition of equilibrium, but this chapter focuses on its thermodynamic basis, $\Delta G = 0$. Indeed, we will show how equilibrium constants can be determined from thermodynamic data.

4.1 Entropy

Introduction

In CAMS Section 9.6, we described entropy as a measure of the number of ways over which the energy of a system could be dispersed. We now explain the basis for the previous treatment.

Prerequisites

- CAMS 9.6 Second Law of Thermodynamics

Objectives

- Explain entropy.
- Name the different degrees of freedom.
- Relate entropy to the extent of the restrictions on the motion of the particles.
- Define "Density of States" and explain how it is related to entropy.
- Explain how the relative disorder of two systems can be used to determine relative entropies.
- Explain why systems with higher entropies are favored over those with lower entropies.
- Distinguish between translations, rotations, and vibrations.
- Describe the degrees of freedom of a diatomic molecule.
- Explain how the energy of a molecule is stored in its degrees of freedom.
- Explain how the energy of a system depends upon the energy of its molecules.
- Explain how the relative order of a system can be used to predict its relative entropy.
- Relate the sign of ΔS for a process to the change in the number of moles of gas it causes.
- Determine whether the entropy of reaction is positive, negative, or very small.
- Indicate the effects on the entropy of a system caused by adding heat and how the effect is dependent upon the temperature at which the heat is added.

4.1-1. Degrees of Freedom

The energy of a molecule is distributed in the relative motions of its atoms, which are called the ***degrees of freedom*** of the molecule. The motion of each atom can be described as a combination of three directions (x, y, and z), so each atom has three degrees of freedom, and a molecule with N atoms has 3N degrees of freedom. The degrees of freedom are:

- ***Translational degrees of freedom*** involve straight line motion of the center of mass. Translations in molecules result when all of the atoms move in the same direction.
- ***Rotational degrees of freedom*** involve rotations of the molecule about an axis through the center of mass of the molecule.
- ***Vibrational degrees of freedom*** are derived from the relative motion of the atoms within the molecule. Vibrations involve small changes in the bond lengths and angles, which oscillate about the equilibrium geometry.

Figure 4.1 shows the six degrees of freedom of a diatomic molecule. The motions can be broken down into three translations, two rotations, and one vibration. Click on each image to start or stop an animation of that degree of freedom.

A video or simulation is available online.

4.1-2. The Energy of a Molecule versus the Energy of a System of Molecules

The energy of a molecule is the sum of its translational, rotational, and vibrational energies.

The energy of a degree of freedom is quantized just as the energy of an electron in an atom or molecule is quantized. Thus, there are translational, rotational, and vibrational quantum numbers and energy levels. The speed with which a molecule translates, the frequency with which it rotates, and the speed with which its atoms move relative to one another as it vibrates are all dictated by its translational, rotational, and vibrational quantum numbers. The energy of the m^{th} molecule in a system composed of many molecules can be expressed as a sum of the energies of each of its degrees of freedom as follows:

$$E_{\text{m}} = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} \qquad (4.1)$$

Partitioning the Energy of a Molecule into its Degrees of Freedom

The energy of a system of molecules is the sum of the energies of all of the molecules in the system.

$$E_{\text{total}} = \sum_{\text{m}} E_{\text{m}} \qquad (4.2)$$

System Energy is the Sum of Molecular Energies

where E_{m} is the energy of the m^{th} molecule as defined in Equation 4.1, and the sum is over all of the molecules (m) in the system.

We will discuss molecular energies in this section, which are very small. We therefore use a generic 'U' to indicate an arbitrary unit of energy, so read 6 U as six units of energy. For example, if a molecule has 4 U of translational energy, 2 U of rotational energy, and 0 U of vibrational energy, then Equation 4.1 allows us to determine that its total energy is $E_{\text{m}} = 4 + 2 + 0 = 6$ U. If a system contains three molecules with 6, 3, and 3 U of energy each, then Equation 4.2 can be used to determine that the total energy of the system is $E_{\text{total}} = 6 + 3 + 3 = 12$ U.

4.1-3. Representing Molecular Energies

Molecules have allowed energies, just as electrons in atoms, and we can draw energy level diagrams for them just as we did for electrons in atoms. Consider particle X that has energy levels at 0, 3, 6, 9, ... U shown in Figure 4.2. The allowed energy levels of X particles in the energy range of the figure are shown as dotted lines, while the energy of a particular particle, which is 3 U for the particle in the figure, is shown by the blue circle lying on the line at 3 U.

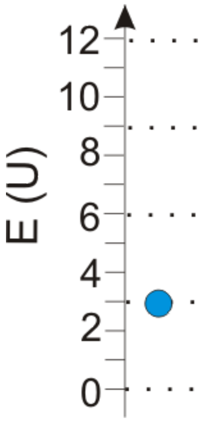


Figure 4.2: Allowed Energy Levels of X

4.1-4. Energy Configurations

If the temperature of a collection of three X particles is such that $E_{\text{total}} = 6$ U, and the allowed energy levels of each X particle are only at 0, 3, 6, 9, and 12 U, then there are only two combinations, called *energy configurations*, that produce 6 U:

1 $E_{\text{total}} = 6 + 0 + 0$

2 $E_{\text{total}} = 3 + 3 + 0$

So either one X particle has 6 U and the other two have none, or two particles have 3 U each and the third has none. The energy configuration that the system is actually in at any given time will vary as the molecules collide. For example, a particle with 6 U might collide with one that has no energy to produce two particles with 3 U of energy each. However, as long as the temperature (total energy) remains the same, the molecules would always be in one of these two configurations. Recall that thermal energy is the average kinetic energy of the molecules; some have more energy and others have less.

The energy of an electron configuration is the energy of the system and can be written as given in Equation 4.2, but we can also sum over the energy levels rather than the individual molecules as given in Equation 4.3, below.

$$E_{\text{total}} = \sum_{\text{i}} n_{\text{i}} E_{\text{i}} \qquad \text{System Energy in terms of Energy Levels and their Population} \qquad (4.3)$$

i is the number of the energy level, E_{i} is the energy of the level, and n_{i} is the number of particles in that level. Thus, instead of writing $E = 6 + 0 + 0$, we could write $E = 6 + 2(0)$ to indicate that one particle has 6 U of energy and two particles have no energy. Similarly, $E = 3 + 3 + 0$ could be written $E = 2(3) + 0$.

4.1-5. The Weight of a Configuration

The number of ways in which a configuration can be achieved is called the ***configuration weight*** of the configuration and given the symbol W. The weight of a configuration can be determined with Equation 4.4.

$$W = \frac{N!}{\prod_{\text{i}} n_{\text{i}}!} \qquad \text{Weight of an Energy Configuration} \qquad (4.4)$$

N is the number of particles in the system, n_{i} is the number of particles that are in the E_{i} energy level. ! = factorial. $4! = 4 \cdot 3 \cdot 2 \cdot 1 = 24$. By definition, $0! = 1$.

For example, consider a system with 14 particles. One particle has 0 U of energy, five particles have 2 U, two particles have 4 U, three particles have 6 U, and three particles have 8 U. Using Equation 4.3, we determine the total energy as follows: $E_{\text{total}} = 1(0) + 5(2) + 2(4) + 3(6) + 3(8) = 60$ U, where the numbers in parentheses are the E_{i} and their multipliers are the n_{i}. Using the n_{i} and $N = 14$, we determine the weight of this configuration to be

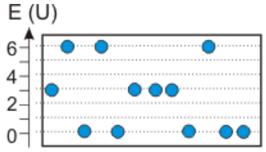
$$W = \frac{14!}{1!5!2!3!3!} = \frac{14 \cdot 13 \cdot 12 \cdot 11 \cdot 10 \cdot 9 \cdot 8 \cdot 7 \cdot 6 \cdot 5 \cdot 4 \cdot 3 \cdot 2 \cdot 1}{1 \cdot (5 \cdot 4 \cdot 3 \cdot 2 \cdot 1) \cdot (2 \cdot 1) \cdot (3 \cdot 2 \cdot 1)(3 \cdot 2 \cdot 1)} = 1,009,008$$

There are over one million ways in which this configuration can be achieved! They differ only in which particle has no energy, which five particles have 2 U, which two particles have 4 U, etc.

4.1-6. Determining Weight Exercise

EXERCISE 4.1:

What is the total energy of the system shown in the figure, and what is the weight of the configuration?



$E_{\text{total}} =$ _______________ U

$N =$ _______________ particles

$W =$ _______________ ways to achieve energy with this configuration

4.1-7. Distributing Energy into Three X particles

We now examine the different ways in which three X particles can be distributed in a system with a total energy of 6 U. Recall that the individual X particles have energy levels only at 0, 3, and 6 U. As shown in Figure 4.3, there are only two configurations that yield a total energy of 6 U: 1(6) + 2(0) and 2(3) + 1(0), which are represented by the a and b figures. There are three particles, so there are clearly three different ways in which one particle can have 6 U of energy, so the weight of the configuration in Figure a is $W_{\text{a}} = 3$. Similarly, there are three different ways in which one particle can have zero energy, so $W_{\text{b}} = 3$ for the distribution of Figure b. However, we can arrive at these weights using Equation 4.4, the fact that $N = 3$, and the n_{i} given in the energy expressions.

$$W_{\text{a}} = \frac{3!}{1!2!} = 3; \quad W_{\text{b}} = \frac{3!}{2!1!} = 3$$

Thus, there are just six allowed energy states for this system. The six ways to distribute the energy in these two configurations are shown graphically in the figure.

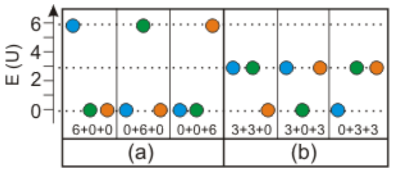


Figure 4.3: Six ways of Distributing 6 U of Energy into for Three X Particles

4.1-8. Distributing Energy into Three Y Particles

Equation 4.4 shows that the W increases when the number of particles (N) increases or the number of particles in each energy level (each n_{i}) decreases. The number of particles in any one level decreases as the number of available levels increases. We now demonstrate this affect by again considering a system of three particles with a total energy of 6 U. However, this time the system is composed of Y molecules with energy levels that are separated by only one energy unit. The energy levels available to each Y molecule in a system with a total energy of 6 U are 0, 1, 2, 3, 4, 5, or 6 U. The fact that each Y molecule has more levels available to it in this energy range than does each X molecule means that there are more ways to distribute the energy in the Y molecules. Indeed, Figure 4.4 shows that there are seven possible energy configurations. The weight of each configuration is determined in the figure. Summing the weights of the seven configuration, we obtain 3 + 6 + 6 + 3 + 6 + 3 + 1 = 28 different ways for Y particles to distribute 6 U of energy, while there were only six states of X molecules with 6 U of energy. The number of states available in this energy range is greater for Y molecules, so we say that Y has a greater ***density of states***. The density of states is greater for Y molecules because the energy separation between allowed levels in individual Y molecules is smaller; i.e., there are more energy levels available.

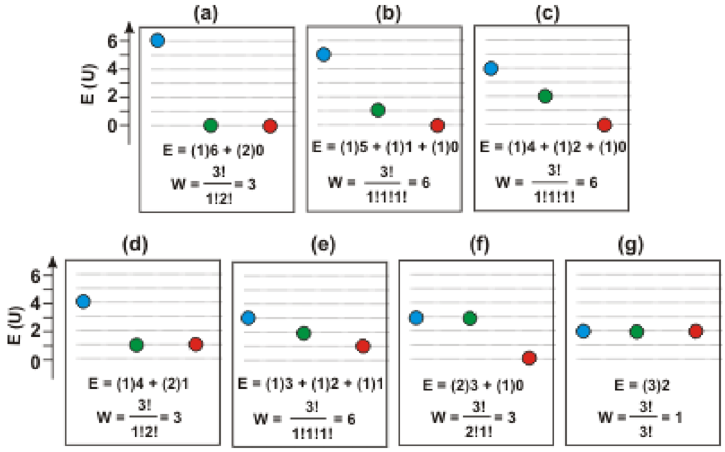


Figure 4.4: Seven Configurations of Y Particles that Produce 6 U of Energy

4.1-9. Increasing Energy and the Number of Ways to Distribute Energy

<u>EXERCISE 4.2</u>:

In how many ways can a system of three X particles (energy levels at 0, 3, 6, 9, ... U) distribute 9 U of energy?

The number of possible configurations with 9 U of energy: ____________

The weight of the configuration in which one particle has 9 U: ____________

The weight of the configuration in which one particle has 6 U: ____________

The weight of the configuration in which no particle has either 6 U or 9 U: ____________

The number of ways in which three X particles can distribute 9 U of energy: ____________

4.1-10. Distributions and Temperature

We have seen that there are only six ways for three X particles to distribute 6 U of energy, but, as shown in the figure below, there are ten ways in which they can distriubute 9 U. Thus, increasing the energy of a system increases the number of ways in which it can distribute the energy. Since the energy of a system is dictated by its temperature, we conclude that

Increasing the temperature of a system always increases the number of ways in which it can distribute its energy.

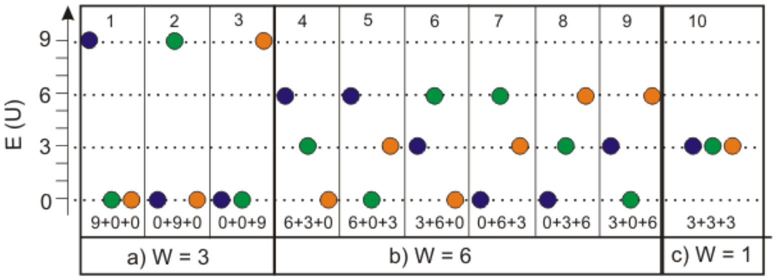


Figure 4.5: Distributions of 10 U of Energy by Three X Particles

4.1-11. Entropy Defined

Now consider the process in which 3 X molecules are converted into 3 Y molecules: 3 X → 3 Y.

We assume that $\Delta H \sim 0$, so the enthalpy change is not a factor in the reaction. If the temperature is such that the energy of the reaction mixture is 6 U, then there are 28 states over which three Y molecules can distribute the energy but only 6 states over which three X molecules can distribute it, which is represented in Figure 4.6. Consequently, energy is more likely to be found on Y molecules than on X molecules. For this purely statistical reason, the number of Y molecules at equilibrium will be greater than the number of X molecules, i.e., the reaction is extensive. The number of ways in which a system can distribute energy is an important property of the system, and a thermodynamic property of the system, called **entropy** (S), is used to measure it. The entropy (S) of a system is related to the number of ways in which it can distribute its energy (W) by the Boltzmann formula given in Equation 4.5.

$$S = k\ln W \qquad \text{Boltzmann Formula for Entropy} \tag{4.5}$$

k is the Boltzmann constant, which equals the ideal gas constant divided by Avogadro's number: $k = R/N_\mathrm{a} = 8.314/6.023 \times 10^{23} = 1.381 \times 10^{-23}$ J·K^{-1}.

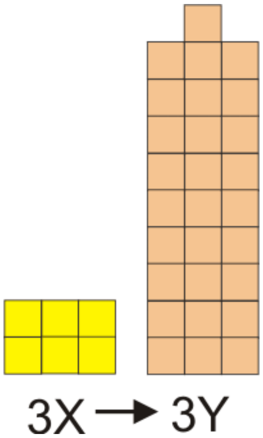


Figure 4.6: Energy States Available for 3X and 3Y Each box represents an allowed energy state. 3Y has over four times as many states as 3X, so energy is over four times as likely to be found on 3Y as on 3X, so 3X → 3Y is extensive if ΔH ~ 0.

4.1-12. Two Driving Forces

Systems with high entropies are favored over those with low entropies because systems with high entropies can distribute energy over more states. The entropy of Y(S_Y) is greater than the entropy of X (S_X) because Y can store energy in more ways than X. The entropy change for the process X → Y is $\Delta S = S_\mathrm{Y} - S_\mathrm{X}$, so $\Delta S > 0$ for the process, and the process is extensive so long as $\Delta H \sim 0$ because the product can disperse energy better than the reactant. Thus, systems strive to maximize the number of ways they can distribute their energy, but they also strive to minimize their potential energy. We conclude that the two driving forces behind a process are:

1 the tendency of systems to minimize their potential energy (ΔH)

2 the tendency of systems to maximize the dispersion of their energy (ΔS)

These two forces can operate in concert or in opposition.

4.1-13. Entropy and Constraints

The entropy of a less constrained system is greater than the entropy of a more constrained system.

The spacing between the energy levels of a degree of freedom depends upon the extent to which the particles are constrained (confined or restricted) during the motion. As shown in Figure 4.7, the more restricted the motion of a particle is, the more restricted the number of energy levels that are available to it is. If there are no constraints on the motion of a particle (a free particle), then there are no constraints on the energies it can have. However, as soon as a particle is constrained to a small region, its movement becomes quantized and the number of available energies decreases. As the particle's motion becomes more restricted, the available energies also become more restricted. In other words, the density of states of a motion increases as its constraints are reduced. The entropy of a system depends upon the density of states of the system, so less constrained systems have higher entropies than do more constrained systems.

This behavior is illustrated nicely by an electron. The gap between levels in a molecule in which the bonding electrons are localized into one bond is very large, but when the electrons are delocalized over a number of orbitals, the gap decreases. In the case of a metal, where the electrons are spread out into orbitals involving millions of atoms the energy gap between levels goes almost to zero as an energy band is formed. In the limit of a free electron, one that is not constrained to the region around an atom or a bond, there are no energy levels, so any energy is available to the electron.

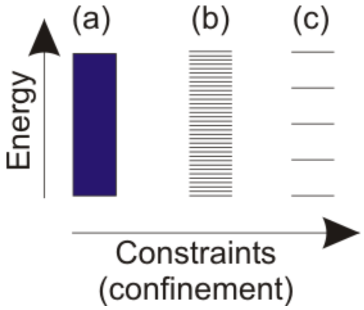


Figure 4.7: Density of States is Greater for Less Constrained Systems. (a) A free particle can have any energy. (b) The energy of a constrained particle is quantized. (c) The separation between energy levels increases (density of states decreases) as the constraints on the motion are increased.

4.1-14. Entropy and States of Matter

The entropy of a gas is much greater than that of a liquid or a solid.

We now compare the entropies of a substance in the gas and solid states. The differences in entropy between the two states of matter result from differences in the restrictions on the degrees of freedom. However, the major constraints on vibrational motion are due to the bonds, which are similar in the solid and gas phase, so vibrations are very similar in the solid and the gas and have little impact on entropy differences between the two states. Thus, it is differences in the translational and rotational degrees of freedom that result in large differences in entropies for the two states. Click on each image in Figure 4.8 to compare a translation and rotation in the solid and gas phases.

Translation in a gas	Molecules in the gas are confined to the relatively large volume of a flask, so the motion is not very constrained. Consequently, the density of states for translational motion is very high in the gas phase.
Translation in a solid	Translational motion in a solid is constrained to an oscillation about the molecule's equilibrium position in the lattice. Increasing the restriction on the motion decreases the density of translational states, i.e., the translational energy levels are much farther apart in the solid than in the gas.
Rotation in a gas	Rotational levels in the gas are relatively close together because the rotation is not constrained.
Rotation in a solid	Rotational energy levels are much farther apart in the solid because other molecules in the solid constrain the rotation to a back-and-forth oscillation about the equilibrium position.

Table 4.1

Translational and rotational motion in the liquid state are also very constrained, but they not quite as restricted as in the solid. We conclude that translational and rotational motion is much more restricted in the liquid and solid states, so the density of states is much greater in the gas. Consequently, the relative entropies of a substance in the three states of matter follow the following trend:

- $S_{\text{gas}} >> S_{\text{liquid}} > S_{\text{solid}}$

A video or simulation is available online.

4.1-15. Disorder as a Guide to Entropy

Disorder is often used as an indicator of entropy. A more disordered system almost always has a higher entropy than a more ordered one.

We have now shown that the entropy of a system decreases as the constraints on the particles in the system are increased. However, increasing the constraints on a system ordinarily introduces order into the system. For example, constraining gas phase molecules sufficiently moves them from a very disordered collection of molecules undergoing random motion into a very ordered collection of molecules in the solid state that undergo organized motion. Indeed, entropy is often defined as a measure of the amount of disorder in a system—highly disordered systems have high entropies. Although, entropy is actually a measure of the number of energy states available to the system, disorder is a good indicator because disordered systems like the gas phase have higher densities of states than do ordered ones. Therefore, we will occasionally use the relative disorder in two systems as an indicator of their relative entropies.

4.1-16. Entropy and the Change in the Number of Moles of Gas

Processes that increase the number of moles of gas have large, positive entropy changes.

$S_{\text{gas}} >> S_{\text{liquid}} > S_{\text{solid}}$, so entropy changes for processes that increase the number of molecules in the gas phase increase the entropy of the system, while processes that decrease the number of molecules in the gas phase decrease the entropy of the system. Entropy changes in processes that do not change the number of moles of gas are usually much smaller than those that do. In these cases, enthalpy changes dominate.

Entropy changes drive vaporization.

The entropy of vaporization ($\Delta S_{\text{vap}} = S_{\text{gas}} - S_{\text{liquid}}$) is always large and positive because vaporization increases the number of moles of gas, which is the driving force behind the vaporization of a liquid even though vaporization is endothermic.

4.1-17. Example

The entropy change of a reaction is proportional to the change in the number of moles of gas caused by the reaction.

Although entropy is an important factor in some processes, such as evaporation, it is more often the case that lowering the enthalpy of the system is far more important. Consequently, we need to be able to determine whether the entropy change of a process is large and negative ($\Delta S < 0$), large and positive ($\Delta S > 0$), or small enough to be neglected ($\Delta S \sim 0$). Use the following facts to predict the sign of ΔS for a reaction.

- $\Delta S > 0$ for reactions that produce gas.
- $\Delta S < 0$ for reactions that consume gas.
- $\Delta S \sim 0$ (is usually negligibly small) for reactions that do not involve gas phase molecules.

EXERCISE 4.3:

Predict the sign of $\Delta S°$ for each of the following reactions:

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
  $\Delta S < 0$
  $\Delta S > 0$
  $\Delta S \sim 0$
$Ag(s) + NaCl(s) \rightarrow AgCl(s) + Na(s)$
  $\Delta S < 0$
  $\Delta S > 0$
  $\Delta S \sim 0$
$H_2O(l)$ at 25 °C → $H_2O(l)$ at 5 °C
  $\Delta S < 0$
  $\Delta S > 0$
  $\Delta S \sim 0$
$3H_2(g) + N_2(g) \rightarrow 2NH_3(g)$
  $\Delta S < 0$
  $\Delta S > 0$
  $\Delta S \sim 0$
$H_2O(l) \rightarrow H_2O(g)$
  $\Delta S < 0$
  $\Delta S > 0$
  $\Delta S \sim 0$

4.1-18. Effects of Heat and Temperature on Entropy

The entropy of a system increases as the total energy increases. For example, recall that, when the energy of the system of X molecules was raised from 6 to 9 units, the number of possible ways to distribute the energy increased from 6 to 10, and dispersing the energy in 10 ways rather than 6 means an increase in the entropy of the system. The energy of a system depends upon its temperature, so the entropy of a system always increases with temperature. One way to increase the energy of a system is to add heat. However, the addition of a fixed amount of heat to a system has a much larger impact on the system when the system entropy is low because increasing the number of accessible states has more impact when there are only a few states to start with. The system entropy is low when its temperature is low, so we can say that the effect of heating is reduced as the temperature at which it is heated is raised.

Using disorder as an indicator of entropy, we can better understand this relationship by considering the effect on the change in order of a room that results when a book is casually dropped in it. The probability is very high that the book will NOT drop into its allotted location on the bookshelf, so the dropped book will increase the disorder (entropy) of the system. In a neat room (representing a more ordered, lower temperature system), the effect of the out-of-place book is dramatic. However, its effect on a messy room (representing a higher temperature, less ordered system) is negligible as the out-of-place book is hardly noticeable. Similarly, adding 1 J of heat to a solid at 5 K (very ordered, low entropy) has a much more dramatic effect on the entropy than adding 1 J to the vapor at 500 K (disordered, high entropy).

The relationship between the change in entropy caused by the addition of heat at some temperature is given in Equation 4.6.

$$\Delta S = \frac{\text{heat added reversibly}}{\text{temperature at which the heat is added}} = \frac{q_{\text{rev}}}{T}\text{J/K} \tag{4.6}$$

q_{rev} is used to indicate that the heat must be added reversibly, which means that it must be added so slowly that the slightest change could reverse the direction of heat flow. Note that the units of entropy from the above are $J{\cdot}K^{-1}$, and that $T\Delta S$ has units of J, so it is an energy term.

4.1-19. Entropy Exercise

EXERCISE 4.4:

Indicate which process in each of the following pairs increases the entropy of the system more:

adding 10 J of heat to neon at 300 K
adding 50 J of heat to neon at 300 K

adding 50 J of heat to neon at 800 K
adding 10 J of heat to neon at 300 K

adding 10 J of heat to neon at 300 K
adding 10 J of heat to neon at 800 K

melting 1 g of neon at its melting point
evaporating 1 g of neon at its boiling point

4.2 The Second and Third Laws of Thermodynamics

Introduction

Our discussions of entropy have been restricted to changes in the system, but processes impact the entropy of both the system and its surroundings. In this section, we extend our studies to changes in the universe.

Prerequisites

- CAMS 9.6 Second Law of Thermodynamics

Objectives

- Predict whether a reaction is spontaneous from ΔG.
- Determine ΔG from the values of ΔH and ΔS.
- State the second law of thermodynamics.

4.2-1. The Second Law of Thermodynamics

Recall that a spontaneous process is one that occurs without intervention, so you may be asking "If the dispersal of energy is so important, why isn't entropy alone sufficient to predict spontaneity?" The short answer is: systems interact with their surroundings, so it is the entropy of the universe not just the system that dictates spontaneity. This important difference is stated in the second law of thermodynamics.

- ***Second Law of Thermodynamics***: the entropy of the universe increases ($\Delta S_{\text{univ}} > 0$) for all spontaneous processes

In other words, a spontaneous process is one that increases the number of states over which the energy of the universe is dispersed.

4.2-2. Heat Flows from Hot to Cold

The fact that heat flows from a hot source to a cold one is a consequence of the second law. For example, consider the heat flow between two systems at different temperatures as shown in the figure. We assume that the two thermal reservoirs, which are at temperatures T_1 and T_2, are brought into contact in an insulated container (represented by the black border in the figure). The conditions under which heat flows spontaneously from T_1 to T_2 are determined by the second law as follows:

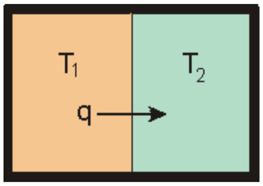


Figure 4.8

1	Determine ΔS_{univ}	According to the second law, heat flows spontaneously in the direction in which $\Delta S_{\text{univ}} > 0$. The two reservoirs are insulated, so the two reservoirs constitute a thermodynamic universe (no heat can pass through the insulation). Consequently, $\Delta S_{\text{univ}} = \Delta S_1 + \Delta S_2 > 0$
2	Determine ΔS	q joules flow *out of* system 1 and into system 2, so $\Delta S_1 = -q/t_1$ and $\Delta S_2 = +q/T_2$. The sign of ΔS indicates the direction of the heat flow.
3	Conclusion	$\Delta S_{\text{univ}} = \Delta S_1 + \Delta S_2 = -q/T_1 + q/T_2 = q(1/T_2 - 1/T_1) > 0$ which is true only if $T_1 > T_2$. Consequently, *heat flows spontaneously from a hot source to a cold one* as a consequence of the second law of thermodynamics.

Table 4.2

4.2-3. The Third Law

Thermodynamic tables give values for ΔH_f° rather than simply H because only relative enthalpies (ΔH's) can be determined. However, tabulated values of S° are known because there is a known reference point for entropy. This reference point is established by the third law of thermodynamics. To establish the third law, we define a perfect crystal as one in which all lattice sites are occupied by the correct particles, which differs from a real crystal in which some sites may not be occupied or may be occupied by impurities. We must also recognize that all molecules at 0 K are in their lowest energy levels. Thus, there is just one way in which the energy of a perfect crystal at 0 K can be distributed; i.e., $W = 1$ for a perfect crystal at 0 K. Applying Equation 4.5, we obtain $S = k\ \ln(1) = 0$. This conclusion is stated in the third law of thermodynamics.

- **Third Law of Thermodynamics**: The entropy of a perfect crystal at 0 K is zero.

The third law gives us a reference point for entropy that we do not have for enthalpy or free energy. We can determine differences in enthalpy (ΔH) and free energy (ΔG) but not absolute values (H and G). We can determine the entropy difference between a substance at 0 K and at 298 K, $\Delta S = S_{298} - S_0$, and because we know that $S_0 = 0$, we know the absolute value of the entropy at 298 K. Consequently, there is no Δ preceding the S in the heading of entropy tables. Note that *the entropy of an element in its standard state at 298 K is not zero* because every substance with nonzero thermal energy must have entropy.

4.2-4. Factors Influencing Absolute Entropies

The factors that influence the entropy of a substance are: its state of matter, its temperature, and the number and nature of its bonds.

- The entropy of a substance increases in going from solid to liquid to gas ($S_{\text{solid}} < S_{\text{liquid}} << S_{\text{gas}}$). For example, the absolute entropy of liquid water at 298 K is 69.91 $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$while that of water vapor at 298 K is 188.7 $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$.
- The entropy of a substance always increases with temperature.
- The entropy of a substance increases as the number of atoms it contains increases. This is because additional atoms provide more ways in which it can move (rotate and vibrate about the bonds), and the more ways it can move, the more disorder it has. For example, the entropy at 298 K of O atoms is 160.95 $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ while that of O_2 molecules is 205.03 $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ and that of O_3 molecules is 237.6 $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$.

4.2-5. Predicting Relative Entropies Exercise

EXERCISE 4.5:

Indicate the substance with the greater entropy in each case.

CO(g) at 300 K	CO(g) at 250 K	CO(g) at 300 K
CO_2(g) at 300 K	CO(g) at 350 K	I_2(s) at 300 K

4.3 Determining Entropy Changes

Introduction

As with enthalpies, tabulated values of entropy are normally the standard state values and represented as $S°$. Everything we have discussed to this point applies to both standard or nonstandard conditions, and the superscript was unnecessary. However, tabulated thermodynamic properties are almost always standard state values, so the thermodynamic values we obtain from them are also for reactions at standard conditions. Consequently, we will use the superscript zero on our entropy changes, $\Delta S°$, to indicate that the tabulated values of absolute entropies are all standard state values.

Objectives

- Calculate the entropy change of a reaction from tabulated values of the absolute entropies of the reactants and the products.

4.3-1. Method

The entropy change accompanying a process is the entropy of the final state minus the entropy of the initial state: $\Delta S = S_\mathrm{f} - S_\mathrm{i}$. In a chemical reaction, the final entropy is the entropy of the products and the initial entropy is the entropy of the reactants. Consequently, the following expression can be used to determine $\Delta S°$ from tabulated values of standard state entropies:

$$\Delta S° = \sum c_\mathrm{P} \times S°_\mathrm{P} - \sum c_\mathrm{R} \times S°_\mathrm{R}$$

Standard Entropy Change from Absolute Entropies of Products and Reactants (4.7)

- c_P is the coefficient in the balanced chemical equation of the **product** whose standard entropy is $S°_\mathrm{P}$.
- c_R is the coefficient in the balanced chemical equation of the **reactant** whose standard entropy is $S°_\mathrm{R}$.

If the standard entropies of all of the products and reactants are known, the standard entropy change of a reaction can be determined.

4.3-2. Example

EXERCISE 4.6:

Determine the entropy change for each process at 298 K and 1 atm.

$H_2O(l) \rightarrow H_2O(g)$

First, look up the absolute entropy for each substance in the resource titled Thermodynamic Properties.

Substance	**$H_2O(l)$**	$\rightarrow$	**$H_2O(l)$**
$S°$	J·mol^{-1}·K^{-1}		J·mol^{-1}·K^{-1}

Next, use Equation 4.7 to determine $\Delta S°$.

$\Delta S° =$ ______________ J·mol^{-1}·K^{-1}

$H_2(g) + I_2(g) \rightarrow 2\ HI(g)$

First, look up the absolute entropy for each substance in the resource titled Thermodynamic Properties.

Substance	**$H_2(g)$**	+	**$I_2(g)$**	$\rightarrow$	**2 $HI(g)$**	
$S°$						J·mol^{-1}·K^{-1}

Next, use Equation 4.7 to determine $\Delta S°$.

$\Delta S° =$ ______________ J·mol^{-1}·K^{-1}

$N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$

First, look up the absolute entropy for each substance in the resource titled Thermodynamic Properties.

Substance	**$N_2(g)$**	+	**3 $H_2(g)$**	$\rightarrow$	**2 $NH_3(g)$**	
$S°$						J·mol^{-1}·K^{-1}

Next, use Equation 4.7 to determine $\Delta S°$.

$\Delta S° =$ ______________ J·mol^{-1}·K^{-1}

4.4 Free Energy

Introduction

Like enthalpy but unlike entropy, free energy is not absolute, so tables of $G°$ do not exist. Consequently, free energies of formation are tabulated. The method used to determine the standard free energy of a reaction at 298 K is identical to that used to determine the standard enthalpy of a reaction from enthalpies of formation. However, the standard free energy can also be determined from enthalpies of formation and absolute entropies. We discuss both methods in this section.

Prerequisites

- CAMS 9.7 Free Energy

Objectives

- Determine free energy of a reaction from tabulated free energies of formation.
- Define *Gibbs free energy* and explain why it is important.
- Describe the two driving forces behind the free energy change and write the expression that shows how they are related to the free energy.

4.4-1. Free Energy

A spontaneous process at constant T and P is one in which $\Delta G < 0$.

Entropy changes in the universe can be broken down into the changes in the system and its surroundings:

$$\Delta S_{\text{univ}} = \Delta S + \Delta S_{\text{sur}}$$

During the process, heat can be exchanged between the system and the surroundings, which changes the entropy of the surroundings. For a reaction carried out at constant T & P, the amount of heat that is transferred from the system to the surroundings is $q_{\text{sur}} = -\Delta H$, so $\Delta S_{\text{sur}} = -\Delta H/T$. Thus, an exothermic reaction releases heat into the surroundings, which increases the entropy of the surroundings, while an endothermic reaction absorbs heat from the surroundings, which decreases the entropy of the universe. The entropy change in the universe resulting from a reaction carried out at constant temperature and pressure can then be expressed as follows:

$$\Delta S_{\text{univ}} = \Delta S - \Delta H/T$$

Multiplying both sides by $-T$, we obtain $-T\Delta S_{\text{univ}} = \Delta H - T\Delta S$. This system quantity is the ***Gibbs free energy change***, ΔG.

$$\Delta G = \Delta H - T\Delta S = -T\Delta S_{\text{univ}}$$

Definition of Free Energy at constant T and P (4.8)

The Second Law states that $\Delta S_{\text{univ}} > 0$ for a spontaneous processes, so a reaction at constant temperature and pressure is spontaneous when $\Delta G < 0$. Thus, the equation above shows driving forces behind a process carried out at constant T and P.

- ΔG is the change in free energy. It dictates the spontaneous direction of the reaction. Reactions proceed spontaneously in the direction in which $\Delta G < 0$.
- ΔH is the change in potential energy that results from breaking and forming interactions. Reactions that lower their potential energy ($\Delta H < 0$) reduce the free energy, which is favorable.
- $T\Delta S$ is the change in free energy caused by changing the number of ways energy can be dispersed in the system. Using order as our indicator for entropy, we would say that $T\Delta S$ is the energy change associated with the change in order of the system. Thus, processes for which $\Delta S > 0$ are favored because they lower the free energy of the system by introducing disorder.

As shown in Figure 4.9 (a), exothermic reactions release energy. They are spontaneous if the entropy change is small or positive. Any energy that is not used to overcome a negative entropy change is free energy. Endothermic reactions as shown in Figure 4.9 (b) cannot occur without an input of energy, so they can be spontaneous only if $T\Delta S > \Delta\text{H}$.

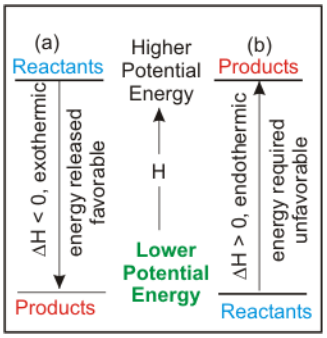


Figure 4.9: Enthalpy

Processes for which $\Delta S > 0$ in Figure 4.10 (a) release energy that can be used to drive reactions uphill in enthalpy, but any $T\Delta S$ energy that is not used in this manner is released as free energy. Processes for which $\Delta S < 0$ in Figure 4.10 (b) require energy, which must be supplied from ΔH if the process is to be spontaneous.

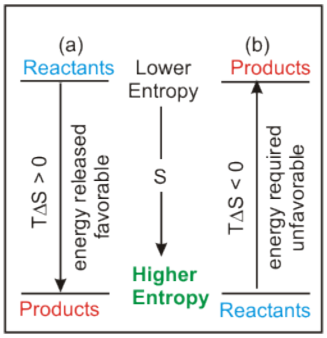


Figure 4.10: Entropy

4.4-2. Free Energy is Free to do Work

It is the free energy released in a reaction that is free to do work.

Not all energy released as ΔH can be harnessed to do work in reactions in which $\Delta S < 0$, and not all of the energy contained in $T\Delta S$ when $\Delta S > 0$ can be used to do work if some must be used to overcome $\Delta H > 0$. It is the net reduction in energy of the system that can be used to do work, which is the free energy of the reaction. Indeed, ΔG is referred to as the free energy because it is the energy that is free to do work; i.e., it the maximum amount of work that can be obtained from a reaction.

$$\text{maximum work available from a reaction} = -w = -\Delta G$$

Free Energy and Work (4.9)

The above equation states that the maximum work that can be done by the system equals the amount of free energy that is released by the system. The negative signs in Equation 4.9 are required because:

- w is defined as the work done on the system, but we are interested in the work done by the system
- ΔG is defined as the free energy that is absorbed, but free energy must be released to do work.

For example, if $\Delta G = -50$ kJ then up to 50 kJ of work can be done by the process. Processes for which $\Delta G = 0$ or $\Delta G > 0$ are not spontaneous and cannot do work. However, such processes can sometimes be forced uphill in free energy by doing work on them. Thus, a process for which $\Delta G = +50$ kJ can sometimes be accomplished by an input of over 50 kJ of work.

4.4-3. Standard Free Energy Equation

Most of our calculations will be for the standard state, so we apply Equation 4.8 to the standard state to obtain the standard free energy of reaction,

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad \text{Standard Gibbs Free Energy} \tag{4.10}$$

ΔG° is the free energy of a reaction when all reactants and products are in their standard state, so its sign indicates the spontaneous direction under this specific set of conditions. Consider the reaction A(g) → B(g). ΔG° is the value of ΔG when both A and B are in their standard states, which is a partial pressure of 1 atm for each gas. If $\Delta G^\circ < 0$, the spontaneous direction is A → B. If A is consumed and B is formed when they are at equal pressures, then B will be present in the greater amount when the reaction is complete; i.e., the reaction is extensive because there is more product than reactant at completion. If $\Delta G^\circ > 0$, the spontaneous process is A ← B when they are at equal pressures, so more A than B will be present at completion and the reaction is not extensive. We conclude that

- The sign of ΔG° indicates the side of the reaction that is favored at equilibrium. If $\Delta G^\circ > 0$, the reactants are favored, but if $\Delta G^\circ < 0$, the products are favored.

4.5 Determining Free Energy Changes

Objectives

- Determine standard state free energy changes for a reaction from either standard free energies of formation or standard enthalpies of formation and standard entropies.

4.5-1. Method

Values of standard free energies of formation ($\Delta G_\mathrm{f}^\circ$) can be found in the Resources titled Thermodynamic Properties. We again employ Hess's law of heat summation along with the free energies of formation to obtain free energies of reactions:

$$\Delta G^\circ = \sum c_\mathrm{P}(\Delta G_\mathrm{f}^\circ)_\mathrm{P} - \sum c_\mathrm{R}(\Delta G_\mathrm{f}^\circ)_\mathrm{R}$$

Free Energy of Reaction from Free Energies of Formation of Reactants and Products (4.11)

- $(\Delta G_\mathrm{f}^\circ)_\mathrm{P}$ is the standard free energy of formation of the product whose coefficient in the balanced equation is c_P
- $(\Delta G_\mathrm{f}^\circ)_\mathrm{R}$ is the standard free energy of formation of the reactant whose coefficient in the balanced equation is c_R

The result obtained in this manner is the same as would be obtained by determining the ΔH° and ΔS° of the reaction and applying Equation 4.8.

As with enthalpies, the units of free energies of formation are kJ·mol^{-1}, but multiplication by the number of moles of each substance in the balanced equation produces units of kJ for free energy changes in thermochemical equations.

4.5-2. Determining ΔG° Exercise

EXERCISE 4.7:

Determine the standard free energy of reaction at 298 K and 1 atm for each process from free energies of formation and from enthalpies of formation and absolute entropies.

$H_2O(l) \rightarrow H_2O(g)$

	$H_2O(l)$	→	$H_2O(g)$	
ΔG_f°	−237.2		−228.59	kJ/mol
ΔH_f°	−285.83		−241.82	kJ/mol
S°	69.91		188.7	J/mol · K

ΔG° from (ΔG_f°)

$\Delta G^\circ =$ ______________ kJ

ΔG° from standard enthalpies and entropies

$H_2(g) + I_2(g) \rightarrow 2\ HI(g)$

$\Delta H^\circ =$ ______________ kJ
$\Delta S^\circ =$ ______________ J/mol·K
$\Delta G^\circ =$ ______________ kJ

	$H_2(g)$	+	$I_2(g)$	→	2 $HI(g)$	
ΔG_f°	0		19.36		1.71	kJ/mol
ΔH_f°	0		62.438		26.5	kJ/mol
S°	130.57		260.6		206.48	J/mol · K

ΔG° from (ΔG_f°)

$\Delta G^\circ =$ ______________ kJ

ΔG° from standard enthalpies and entropies

$\Delta H^\circ =$ ______________ kJ
$\Delta S^\circ =$ ______________ J/mol·K
$\Delta G^\circ =$ ______________ kJ

$N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$

	$N_2(g)$	+	3 $H_2(g)$	→	2 $NH_3(g)$	
ΔG_f°	0		0		−16.5	kJ/mol
ΔH_f°	0		0		−46.11	kJ/mol
S°	191.5		130.57		192.3	J/mol · K

ΔG° from (ΔG_f°)

$\Delta G^\circ =$ ______________ kJ

ΔG° from standard enthalpies and entropies

$\Delta H^\circ =$ ______________ kJ
$\Delta S^\circ =$ ______________ J/mol·K
$\Delta G^\circ =$ ______________ kJ

4.5-3. Free Energy and the Balanced Equation

As with enthalpy, the entropy and free energy of reaction change signs when the direction of the reaction is reversed. If a chemical equation is multiplied by a number, then the values of ΔS and ΔG must also be multiplied by that number. For example, consider the thermochemical equations below.

Reaction	ΔH° kJ/mol	ΔH° kJ/mol	ΔH° kJ/mol
A: $N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$	-92.2	-33.0	-198.6
B: $1/2\ N_2(g) + 3/2\ H_2(g) \rightarrow NH_3(g)$	-46.1	-16.5	-99.3
C: $2\ NH_3(g) \rightarrow N_2(g) + 3\ H_2(g)$	92.2	33.0	198.6

Table 4.3: Thermodynamic Properties as a Function of How the Reaction Is Written

Reaction A is the reaction considered in the previous example. In Reaction B, the reaction has been multiplied by 1/2 as have all of the thermodynamic properties. Reaction C is the reverse of Reaction A, and the signs of the thermodynamic properties have all been changed. Note that Reaction B is the formation reaction used to determine thermodynamic properties because one mole of ammonia is formed from its elements in their standard states. The values of ΔH° and ΔG° are the same values listed for ammonia in Thermodynamic Properties. However, ΔS° is different from the value for S° in the table. ΔS° in Reaction B is the standard entropy of formation of ammonia; but, as pointed out previously, the tables list the absolute entropies, not the entropies of formation.

4.6 Standard Free Energy and Equilibrium

Introduction

At a given temperature, ΔG° is a constant for a reaction, but ΔG varies with the concentrations of the reactants and products. In this section, we present the thermodynamic definitions of two important quantities: the equilibrium constant, which shows the fixed nature of ΔG°, and the reaction quotient, which expresses the variability of ΔG.

Objectives

- Calculate the reaction quotient of a reaction given the activities of the reactants and the products.
- Calculate the equilibrium constant of a reaction from the standard free energy of the reaction and vice versa.
- Indicate the instantaneous direction of a reaction from the relative values of Q and K.

4.6-1. Free Energy and Activity

The free energy of a substance deviates from its standard free energy by the relationship shown in Equation 4.12.

$$G = G^\circ + RT\ \ln(a) \qquad \text{Free Energy and Activity} \qquad (4.12)$$

a in the above is called the ***activity*** of the substance. It indicates the extent to which the substance deviates from standard conditions. It is defined as the ratio of the concentration of the species to its concentration in its standard state, so it is unitless. The activity of substance A depends upon its state of matter as shown below.

- $a = 1$ for solids and liquids because they are in their standard states
- $a = [\mathrm{A}]/1$ M when A is a solute because the standard state of a solute is a concentration 1 M
- $a = P_\mathrm{A}/1$ atm when A is a gas because the standard state of a gas is a partial pressure of 1 atm

Since the activities of solutes and gases are numerically equal to their concentrations or partial pressures, their activities are represented by their molar concentrations and partial pressures in atmospheres, respectively.

4.6-2. Free energy and the reaction quotient

An absolute free energy cannot be determined from Equation 4.12 because the value of G° is not known, but the change in the standard free energy of a process can be determined because the difference in the standard free energy is frequently known. As an example, consider the variation of ΔG in the following reaction:

$$Cu(s) + 2Fe^{3+}(aq) \rightarrow Cu^{2+}(aq) + 2Fe^{2+}(aq)$$

The free energy change of the reaction is the free energy of the products minus the free energy of the reactants:

$$\Delta G = \{G_{\mathrm{Cu}^{2+}} + 2\ G_{\mathrm{Fe}^{2+}}\} + \{G_{\mathrm{Cu}} + 2\ G_{\mathrm{Fe}^{3+}}\}$$

The ions are all solutes in aqueous solution, so their activities are represented by their molar concentrations. The activity of the solid is unity. Applying Equation 4.12 we obtain the following:

$$\begin{aligned}\Delta G \quad = \quad & \{G^{\circ}_{\mathrm{Cu}^{2+}} + RT\ \ln[\mathrm{Cu}^{2+}]\} + 2\{G^{\circ}_{\mathrm{Fe}^{2+}} + RT\ \ln[\mathrm{Fe}^{2+}]\} - \{G^{\circ}_{\mathrm{Cu}} + RT\ \ln(1)\} - \\ & 2\{G^{\circ}_{\mathrm{Fe}^{3+}} + RT\ \ln[\mathrm{Fe}^{3+}]\}\end{aligned}$$

We use the relationship that ($n\ \ln\ x = \ln\ x^n$) and gather terms to obtain

$$\begin{aligned}\Delta G \quad = \quad & \Delta G^{\circ}_{\mathrm{Cu}^{2+}} + 2\Delta G^{\circ}_{\mathrm{Fe}^{2+}} - \Delta G^{\circ}_{\mathrm{Cu}} - 2\Delta G^{\circ}_{\mathrm{Fe}^{3+}} + RT\ \ln[\mathrm{Cu}^{2+}] + RT\ \ln[\mathrm{Fe}^{2+}]^2 - \\ & RT\ \ln(1) - RT\ \ln[\mathrm{Fe}^{3+}]^2\end{aligned}$$

Next, we combine the first three terms by realizing that they represent ΔG° for the reaction and the last three terms by applying the relationship that $\ln\ x - \ln\ y - \ln\ z = \ln(x/yz)$.

$$\Delta G = \Delta G^{\circ} + RT\ \ln\left(\frac{[\mathrm{Cu}^{2+}][\mathrm{Fe}^{2+}]^2}{(1)[\mathrm{Fe}^{3}]^2}\right)$$

Finally, we define the term in parentheses as the ***reaction quotient***, which is represented by the symbol Q. Substitution of Q yields the result shown in Equation 4.13.

$$\Delta G = \Delta G^{\circ} + RT\ \ln\ Q \qquad \text{Free Energy and the Reaction Quotient} \qquad (4.13)$$

Note that different activities must sometimes be mixed in the reaction quotient. For example, consider the reaction: $2\mathrm{H}^{1+}(aq) + \mathrm{Fe}(s) \rightarrow \mathrm{H}_2(g) + \mathrm{Fe}^{2+}(aq)$. It involves two solutes in aqueous solution, a solid, and a gas, so the reaction quotient is

$$Q = \frac{P_{\mathrm{H}_2}[\mathrm{Fe}^{2+}]}{[\mathrm{H}^{1+}]^2(1)} = \frac{P_{\mathrm{H}_2}[\mathrm{Fe}^{2+}]}{[\mathrm{H}^{1+}]^2}$$

4.6-3. The Standard Free Energy and the Equilibrium Constant

The value of Q for any reaction is obtained by raising the activity (pressure or concentration) of each substance to an exponent equal to its coefficient in the balanced chemical equation and then multiplying the results for the products and dividing by the results for the reactants. The reaction quotient can have any non-negative value. Indeed, it increases in a typical reaction because the numerator (product activity) is increasing and the denominator (reactant activity) is decreasing. However, it always has the same value at equilibrium. Its equilibrium value is called the equilibrium constant, K. Thus, **Q and K are calculated using the same expression, but Q is a variable that changes as the reaction proceeds, while K is a constant for the reaction at a specified temperature**. Consequently, $\Delta G = 0$ and $Q = K$ at equilibrium. Rewriting Equation 4.13 for these equilibrium conditions, we obtain $0 = \Delta G^{\circ} + RT\ \ln\ K$, which leads to Equation 4.14.

$$\Delta G^{\circ} = -RT\ \ln K \qquad \text{Standard Free Energy from the Equilibrium Constant} \qquad (4.14)$$

Solving the above for the equilibrium constant, we obtain Equation 4.15.

$$K = \exp\left(-\frac{\Delta G^{\circ}}{RT}\right) \qquad \text{Equilibrium Constant from the Standard Free Energy} \qquad (4.15)$$

ΔG° indicates the extent of reaction.

- If $\Delta G^{\circ} < 0$ then $K > 1$, so the products dominate the equilirium.
- If $\Delta G^{\circ} > 0$ then $K < 1$, so reactants dominate the equilibrium and the reaction is not extensive.
- If $\Delta G^{\circ} = 0$ then $K = 1$, and the amounts of reatants and products are comparable at equilibrium.

4.6-4. Standard Free Energy to Equilibrium Constant Exercise

EXERCISE 4.8:

Use the given standard free energies and Equation 4.15 to determine the values of K at 298, where RT = (8.314e−03 kJ/mol·K)(298 K) = 2.48 kJ/mol.

Reaction	**ΔG° kJ/mol**	**K**
$H_2O(l) \rightarrow H_2O(g)$	8.6	
$H_2(g) + I_2(g) \rightarrow 2\ HI(g)$	−15.9	
$N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$	−33.0	

4.6-5. Equilibrium Constant to Standard Free Energy Exercise

EXERCISE 4.9:

The vapor pressure of CH_3OH (methanol or wood alcohol) is 132 torr at 25 °C. What is the standard free energy of vaporization of methanol?

The activity of a gas is defined as its partial pressure in atm, so first convert the vapor pressure from torr into atm.

$P^\circ =$ ______________ atm

Next, use the vapor pressure to determine the equilibrium constant.

$K =$ ______________

Finally, use Equation 4.14 to convert the equilibrium constant into the standard free energy of reaction.

$\Delta G^\circ =$ ______________ kJ·mol^{-1}

4.6-6. The Q/K ratio

The spontaneous direction of a reaction depends upon the relative values of Q and K, which is given by the sign of ΔG.

Substitution of the expression for ΔG° given in Equation 4.14 into Equation 4.13 yields,

$$\Delta G = -RT \ln K + RTlnQ$$

Application of the identity, $\ln x - \ln y = \ln(x/y)$, to the preceding yields Equation 4.16.

$$\Delta G = RT \ln\left(\frac{Q}{K}\right) \qquad \text{Free Energy, the Equilibrium Constant, and the Reaction Quotient} \qquad (4.16)$$

Thus, the sign of ΔG is dictated by the relative magnitudes of Q and K. The second law states that the spontaneous direction of a reaction at constant pressure and temperature is that direction for which $\Delta G < 0$. Consequently, **the sign of ΔG (relative values of Q and K) indicates the spontaneous direction of the reaction**. The following summarizes the possibilities.

- If $Q < K$ then $\Delta G < 0$ and the reaction is proceeding to the right (→).
- If $Q = K$ then $\Delta G = 0$ and the reaction is at equilibrium ($\rightleftharpoons$).

- If $Q > K$ then $\Delta G > 0$ and the reaction is proceeding to the left (←).

4.6-7. Graphical View of Q, K, ΔG, and $\Delta G°$

The standard free energy and the equilibrium constant for a reaction are functions of temperature only, but the free energy and reaction quotient are functions of concentrations as well.

Consider the following figure, which shows the variation of the free energy of the reaction $\mathrm{A}(g) \rightarrow \mathrm{B}(g)$ at 300 K as a function of the partial pressures of A (bottom axis) and B (top axis).

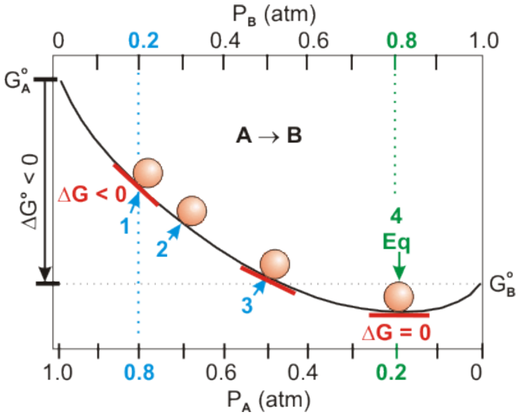


Figure 4.11: Free Energy for A → B The spheres represent the position (composition) of the reaction as it "rolls" toward the minimum. The red lines at points 1, 3, and 4 represent the tangents to the curve at those points.

$\Delta G°$ and K are constants for this reaction at this temperature. Equilibrium lies at the minimum in the curve (Point 4), so the equilibrium pressures are $P_{\mathrm{A}} = 0.20$ atm (bottom scale) and $P_{\mathrm{B}} = 0.80$ atm (top scale). The equilibrium constant is

$$K = \frac{P_B}{P_A} = \frac{0.80}{0.20} = 4.0$$

$\Delta G° = G_{\mathrm{B}}°$ - $G_{\mathrm{A}}°$ can be determined from the value of K with Equation 4.14.

$$\Delta G = -RT = -(0.008314)(300) = -3.5 \text{ kJ} \cdot \text{mol}^{-1}$$

ΔG and Q vary as the reaction proceeds. The sphere on the curve represents reaction progress as it spontaneously moves toward the minimum. As it moves, the pressures of A and B change, which causes $Q = P_{\mathrm{B}}/P_{\mathrm{A}}$ to change. Changes in Q are reflected in changes in ΔG as given by Equation 4.16. Note that ΔG is related to the slope of the tangent at each point. At Point 1, the slope of the tangent is negative, so $G < 0$ and the reaction is spontaneous from left to right. The following table summarizes the points in the figure.

Point	P_{A}	P_{B}	Q	$\Delta G = RT \ln (Q/K)(\text{kJ} \cdot \text{mol}^{-1})$
1	0.80	0.20	0.25	−6.9
2	0.70	0.30	0.43	−5.6
3	0.50	0.50	1.0	−3.5
4	0.20	0.80	4.0	0

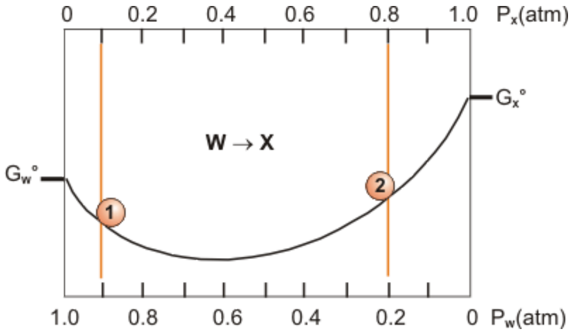
Table 4.4

Note that as the reaction proceeds, Q gets larger and ΔG gets less negative. At Point 4, movement in either direction requires energy ($\Delta G = 0$), so the reaction proceeds no further as equilibrium is established.

4.6-8. Graphical Exercise

EXERCISE 4.10:

Use the accompanying diagram for the reaction W(g) → X(g) at 500 K.



(a) What is the sign of $\Delta G°$?

+
−
0

(b) Calculate K.

____

(c) Calculate $\Delta G°$.

_______________ kJ·mol^{-1}

(d) Is the reaction consuming or producing X.

At point 1:	At point 2:
consuming	consuming
producing	producing

(e) What are the values of Q and ΔG?

at point 1:

$Q_1 =$ _______________

$\Delta G_1 =$ _______________ kJ·mol^{-1}

at point 2:

$Q_2 =$ _______________

$\Delta G_2 =$ _______________ kJ·mol^{-1}

4.6-9. Using Q and K Exercise

EXERCISE 4.11:

Consider the following reaction: $H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$ $K = 623$

Determine Q, the sign of ΔG, and the direction in which the reaction is proceeding at the following partial pressures.

$H_2 = 0.122$ atm, $I_2 = 0.025$ atm, HI = 1.77 atm

$Q =$ ______________

ΔG:
- +
- −
- ~ 0

Direction:
- left
- right
- at equilibrium

$H_2 = 0.362$ atm, $I_2 = 0.188$ atm, HI = 6.51 atm

$Q =$ ______________

ΔG:
- +
- −
- ~ 0

Direction:
- left
- right
- at equilibrium

4.6-10. ΔG vs. $\Delta G°$

Consider the following process:

$$H_2O(l) \rightarrow H_2O(g) \quad \Delta G^\circ_{vap} = +8.6 \text{ kJ/mol at } 25\ ^\circ C$$

The above is often misinterpreted to mean that the evaporation is not spontaneous at this temperature. However, water can evaporate spontaneously at 25 °C. The problem with the misinterpretation is that spontaneity is based on ΔG not on $\Delta G°$. The standard state of water vapor is 1 atm pressure, so the fact that $\Delta G > 0$ simply means water vapor would condense (reaction would go left to right) if its pressure were 1 atm at 25 °C. The equilibrium pressure (vapor pressure) of water at this temperature is only 23.8 torr, which means that it will never evaporate spontaneously to a pressure greater than 23.8 torr at 25 °C. This difference is examined in the next example.

4.6-11. Signs of ΔG and ΔG° Exercise

EXERCISE 4.12:

The temperature of an equilibrium mixture of liquid and vapor water is changed very quickly to 75 °C. Immediately after the change, the pressure of vapor in the container is 375 torr. The vapor pressure of water at 75 °C is 289 torr.

Qualitative treatment of ΔG and ΔG°

What is the sign of ΔG for the process $H_2O(l) \rightarrow H_2O(g)$ under these conditions?
+
−
~0
What is the sign of ΔG° for the process $H_2O(l) \rightarrow H_2O(g)$ under these conditions?
+
−
~0

Quantitative treatment of ΔG and ΔG°

$RT =$ ______________ kJ/mol

$Q =$ ______________

$K =$ ______________

$\Delta G =$ ______________ kJ/mol

$\Delta G^\circ =$ ______________ kJ/mol

4.7 Temperature Dependence of ΔG, ΔG°, and K

Introduction

Although the absolute entropy of a substance is temperature dependent, ΔS° often varies only slightly with temperature because the entropies of the reactants and products vary in the same direction. Similar considerations apply to the enthalpy. In this section, we examine the temperature dependence of both the standard free energy and the equilibrium constant of a chemical reaction by assuming that both the enthalpy and entropy terms do not vary.

Objectives

- Estimate the value of ΔG° at temperatures other than 298 K from ΔH° and ΔS° values.
- Estimate the boiling point of a liquid from thermodynamic data.
- Determine the equilibrium constant at one temperature given the equilibrium at another temperature and the enthalpy of reaction.

4.7-1. Linear Relationship of ΔG vs K

The variation of ΔG with temperature can be seen by rewriting Equation 4.8 in the form of a linear equation ($y = mx + b$).

$$\Delta G = (-\Delta S)T + \Delta H$$

Thus, a plot of ΔG versus T is a straight line with a slope of $-\Delta S$ and an intercept of ΔH. $\Delta G = 0 = \Delta H - T\Delta S$ where the two driving forces are equal and opposed; i.e., where $\Delta H = T\Delta S$. The temperature where they are equal is obtained by solving for T.

$$\Delta T = \frac{\Delta H}{\Delta S} \qquad \text{Temperature at which } \Delta G = 0 \tag{4.17}$$

4.7-2. The Graph of ΔG vs. T

Consider the variation of the free energy with temperature for Processes A - E shown in Figure 4.12.

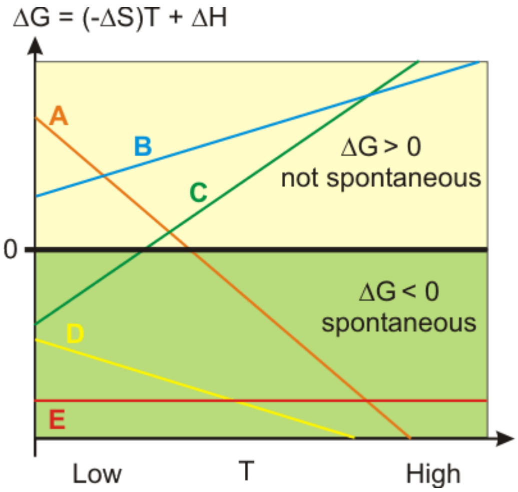


Figure 4.12: Temperature Variation of the Free Energy

Line A: $\Delta H > 0$, $\Delta S > 0$: A positive intercept means that $\Delta G > 0$ at low temperature, but the negative slope means that it becomes less positive with increasing temperature. Thus, the process is not spontaneous at low temperature because there is not enough $T\Delta S$ energy released to overcome the positive ΔH. However, at high temperature, sufficient $T\Delta S$ energy is available and the process becomes spontaneous.

Line B: $\Delta H > 0$, $\Delta S < 0$: Both driving forces are unfavorable, so both require energy. In the absence of energy from an outside source, this process cannot occur; i.e., the process is not spontaneous at any temperature.

Line C: $\Delta H < 0$, $\Delta S < 0$: At low T, there is sufficient energy liberated by the ΔH term to drive the unfavorable $T\Delta S$ term. However, as the temperature increases, the $T\Delta S$ term becomes more important. Eventually, $-T\Delta S > \Delta H$ and the reaction is no longer spontaneous. The temperature at which the $T\Delta S$ and ΔH terms are the same can be found with Equation 4.17.

Line D: $\Delta H < 0$, $\Delta S > 0$: Both terms are favorable, so this process is spontaneous at all T.

Line E: $\Delta H < 0$, $S \sim 0$: It is often the case that $\Delta S \sim 0$ compared to ΔH. When that occurs, the spontaneity is dictated solely by ΔH. In line E, $\Delta S \sim 0$, while $H < 0$, so this process is always spontaneous.

4.7-3. Temperature and Spontaneity Table

ΔH	ΔS	Spontaneity	T where $\Delta G = 0$
$+$	$+$	Not at low T, but it is at high T	If we assume that $\Delta H = +10$ kJ and $\Delta S = +20\text{J}\cdot\text{K}^{-1}$, we can use Equation 4.17 to determine that $T = (10\text{ kJ})/(0.02\text{ kJ})\cdot\text{K}^{-1} = 500$ K. Reaction is not spontaneous below 500 K, but it is above 500 K.
$+$	$-$	Both terms are unfavorable, so this process is never spontaneous.	No T
$-$	$-$	At low T, but not at high T	If we assume that $\Delta H = -50\text{ kJ}, \Delta S = -50\text{J}\cdot\text{K}^{-1}$, we can use Equation 4.17 to determine that $T = (-50\text{ kJ})/(-0.05\text{ kJ}\cdot\text{K}^{-1}) = 1000$ K. Reaction is spontaneous below 1000 K, but not above.
$-$	$+$	Both terms are favorable, so this process is always spontaneous.	All T

Table 4.5: Predicting Reaction Spontaneity

4.7-4. ΔG° vs T

The variation of ΔG° with temperature is given by $\Delta G^\circ = (-\Delta S^\circ)T + \Delta H^\circ$. Thus, a plot of ΔG° versus T is a straight line with a slope of $-\Delta S^\circ$ and an intercept of ΔH°. Such a plot is shown in Figure 4.13. It is identical to Figure 4.12. except that superscripts have been added to all thermodynamic quantities and 'spontaneous' has been replaced with 'extensive' to reflect the difference between ΔG and ΔG°.

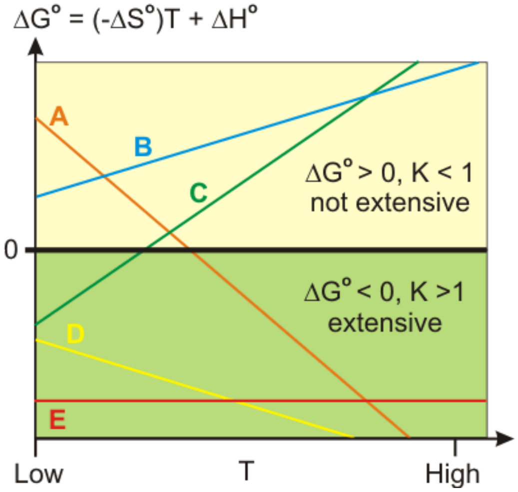


Figure 4.13: Temperature Variation of the Standard Free Energy

ΔH	ΔS	Extent
+	+	Not extensive at low T, but the extent does increase with temperature.
+	–	Both terms are unfavorable, so this process is never extensive. It becomes less extensive with temperature increases.
–	–	Extensive at low T, but the extent decreases with increasing temperature
–	+	Both terms are favorable, so this process is always extensive.

Table 4.6: Predicting Extent of Reaction

4.7-5. ΔG° and K at Temperatures other than 298 K Exercise

EXERCISE 4.13:

Assume that $\Delta H^\circ = -92.22$ kJ and $\Delta S^\circ = -198.6$ J·K^{-1} are temperature independent to estimate ΔG° at 435 K and 635 K for the reaction $N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$.

435 K

$\Delta G^\circ =$ ______________ kJ

$K =$ ______________

635 K

$\Delta G^\circ =$ ______________ kJ

$K =$ ______________

4.7-6. Boiling Points

A boiling point can be estimated from the heat and entropy of vaporization.

The (normal) boiling point is defined as the temperature at which the vapor pressure is 1 atm, and vapor pressure is the pressure of the vapor in equilibrium with the liquid at a given temperature. Thus, the (normal) boiling point is the temperature at which the equilibrium pressure of the vapor is 1 atm. It is an equilibrium process, so the free energy of vaporization, ΔG_{vap}, is zero. In addition, the pressure of the vapor is 1 atm, so it is an equilibrium at standard conditions, and we may write that $\Delta G^\circ_{\text{vap}}$ at the (normal) boiling point (T_{bp}). Substituting zero for $\Delta G^\circ_{\text{vap}}$ in Equation 4.8 yields

$$0 = \Delta H^\circ_{\text{vap}} - T_{\text{bp}}\Delta S^\circ_{\text{vap}}$$

or

$$\Delta H^\circ_{\text{vap}} = T_{\text{bp}}\Delta S^\circ_{\text{vap}}$$

Solving for T, the boiling point in Kelvins, we obtain Equation 4.18:

$$T_{\text{bp}} = \frac{\Delta H^\circ_{\text{vap}}}{\Delta S^\circ_{\text{vap}}} \qquad \text{Boiling Points} \qquad (4.18)$$

4.7-7. Boiling Point Exercise

EXERCISE 4.14:

Given that $\Delta H^\circ_{\text{vap}} - 44.01$ kJ/mol and $\Delta S^\circ_{\text{vap}} 118.8\ \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ for water, estimate the normal boiling point of water to the nearest degree Celsius.

$T =$ ______________ °C

4.7-8. *T* Dependence of *K*

Enthalpy is the source of the temperature dependence of the equilibrium constant.

The temperature dependence of the equilibrium constant can be obtained by combining Equation 4.8 and Equation 4.14.

$$\Delta G^\circ = -RT \ln K = \Delta H^\circ - T\Delta S^\circ$$

Dividing both sides by $-RT$ leads to the following:

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \qquad \ln K \text{ as a Function of Temperature} \qquad (4.19)$$

$\ln K$ increases with T when $\Delta H^\circ > 0$ (endothermic reactions), but decreases with T when $\Delta H^\circ < 0$ (exothermic reactions). If ΔS° and ΔH° are temperature independent, then a plot of the $\ln K$ versus $1/T$ should be a straight line with a slope of $\Delta S^\circ/R$ and an intercept of $-\Delta H^\circ/R$. Such plots are commonly used to determine ΔH° and ΔS°.

4.7-9. Determining *K* at a *T* Given Its Value at Another *T*

If the enthalpy and entropy of reaction are assumed to be temperature independent, we can write the equilibrium constants at two different temperatures as

$$\ln(K_1) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT_1} \text{ and } \ln(K_2) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT_2}$$

Subtracting the two expressions above to obtain $\ln(K_2) - \ln(K_1)$ and solving the resulting expression for $\ln(K_2)$, we obtain the desired result shown in Equation 4.20.

$$\ln(K_2) = \ln(K_1) + \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad K \text{ at Different Temperatures} \qquad (4.20)$$

Thus, if the enthalpy of reaction at one temperature (K_1 at T_1) is known, then the equilibrium constant can be determined at another temperature if ΔH° is also known.

4.7-10. Exercise

EXERCISE 4.15:

Estimate ΔG° at 0 °C and estimate K for 2 $NO_2(g) \rightarrow N_2O_4(g)$ using both Equation 4.15 and Equation 4.20.

$\Delta H^\circ_{298} = -58.02 \text{ kJ} \cdot \text{mol}^{-1}, \Delta S^\circ_{298} = -0.1766 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, and $K_{298} = 8.8$.

ΔG° at 0 °C = ____________ kJ/mol

$K = \exp(-\Delta G^\circ/RT) =$ ____________

K from Equation 4.20 = ____________

4.7-11. Another Exercise

EXERCISE 4.16:

Estimate K_{500} for $N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$ given $K_{298} = 6.1 \times 10^5$ and $\Delta H^\circ_{298} = -92.22 \text{ kJ} \cdot \text{mol}^{-1}$.

$K_{500} =$ ____________

4.8 Coupled Reactions

Introduction

A thermodynamically unfavorable reaction can be driven by a thermodynamically favorable one that is *coupled* to it. In this section, we consider two important examples: the smelting of iron ore and the use of adenosine triphosphate (ATP) in biological systems.

Objectives

- Calculate the free energy of reaction from the free energies of two reactions that can be coupled to produce the desired reaction.

4.8-1. Smelting of Iron Ore

The largest source of iron is the ore hematite (Fe_2O_3) but to get the iron from direct decomposition is thermodynamically unfavorable by a substantial amount (*Reaction 1*).

$$Fe_2O_3(s) \rightarrow 2\ Fe(s) + 3/2\ O_2(g) \quad \Delta G^\circ = +742.2 \text{ kJ} \qquad \text{Reaction 1}$$

There must be an input energy to drive *Reaction 1* in the unfavorable direction, and CO is used to supply the energy in a blast furnace because the oxidation of CO liberates free energy as shown in *Reaction 2.*

$$CO(g) + 1/2\ O_2(g) \rightarrow CO_2(g) \quad \Delta G^\circ = -257.2 \text{ kJ} \qquad \text{Reaction 2}$$

Reactions 1 and 2 are coupled in a blast furnace. Hess's law of heat summation can be used to determine ΔG° of the overall reaction. In order to cancel the 3/2 O_2 formed in *Reaction 1*, we multiply *Reaction 2* by 3. The two coupled reactions are

$$Fe_2O_3(s) \rightarrow 2\ Fe(s) + 3/2\ O_2(g) \quad \Delta G^\circ = 742.2 \text{ kJ}$$

$$3\ CO(g) + 3/2\ O_2(g) \rightarrow 3\ CO_2(g) \quad \Delta G^\circ = 3(-257.2) = -771.6 \text{ kJ}$$

Summing the two coupled reactions and their standard free energies yields the net thermochemical reaction for the smelting of iron ore shown in *Reaction 3.*

$Fe_2O_3(s) + 3\ CO(g) \rightarrow 2\ Fe(s) + 3\ CO_2(g) \quad \Delta G^\circ = 742.2 - 771.6 = -29.4$ kJ Reaction 3

The negative value of ΔG° means that the reaction is extensive at 298 K.

4.8-2. ATP

The human body couples the reactions of high-energy molecules that undergo exothermic reactions with thermodynamically unfavorable reactions to produce favorable ones. The most important of these energy containing molecules is *adenosine triphosphate*, which exists in the body as a 4− ion and is abbreviated as ATP^{4-} or simply ATP.

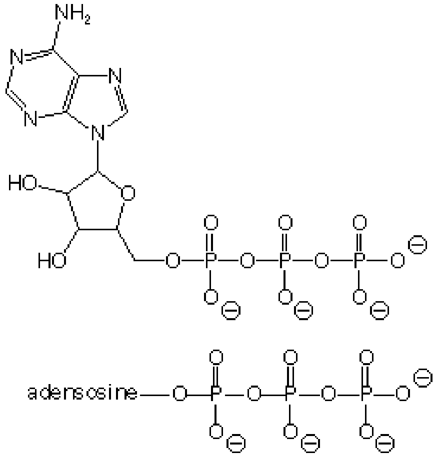


Figure 4.14: Adenosine Triphosphate (ATP)

4.8-3. ATP to ADP Conversion

The repulsion of the three negatively charged phosphate groups makes the P-O-P bonds very weak, which makes ATP an energy-rich ion. As shown in *Reaction 4* and Figure 4.15, the terminal phosphate group is readily removed by water to form *adenosine diphosphate* (ADP^{3-} or ADP). The 30.5 kJ/mol of free energy that is released in this reaction is used by all living organisms to drive non-spontaneous reactions.

$$ATP^{4-} + H_2O \rightarrow ADP^{3-} + HPO_4^{2-} + H^{1+} \qquad \text{Reaction 4}$$

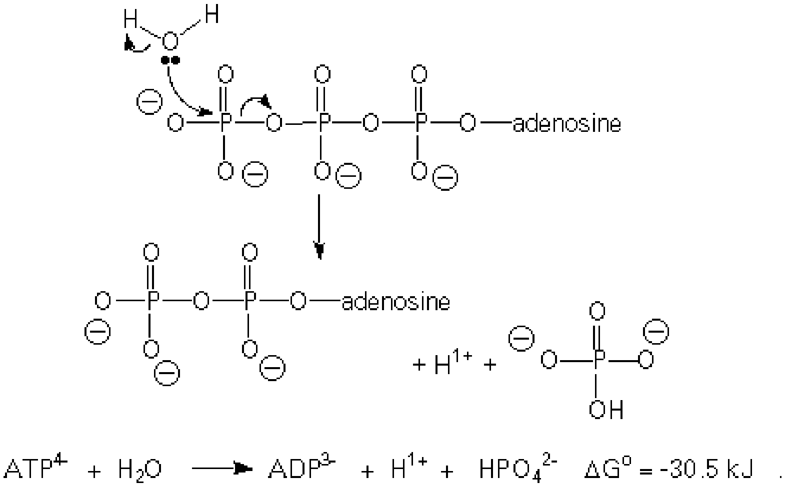


Figure 4.15: ATP to ADP

4.8-4. Combustion of Glucose Thermodynamics

As another very important example of coupled reactions, consider the combustion of glucose, which is the primary source of energy in all oxygen-using organisms.

$$C_6H_{12}O_6(s) + 6\ O_2(g) \rightarrow 6\ CO_2(g) + 6\ H_2O(l) \quad \Delta G^\circ = -2880\ \text{kJ}$$

The release of such a large amount of energy in an uncontrolled reaction would be wasteful and destroy cells. Consequently the body extracts the energy in sequential chemical reactions that allow it to harvest the energy a little at a time. Part of the energy is released in the form of heat, which helps maintain the body temperature. Part of the overall reaction for the combustion of glucose in the body is

$$C_6H_{12}O_6 + 6\ O_2 + 36\ \text{ADP} + 36\ H_3PO_4 \rightarrow 6\ CO_2 + 36\ \text{ATP} + 42\ H_2O$$

Much of the energy of the above reaction is stored in the 36 molecules of ATP that are produced.

4.8-5. Mechanism of Glucose Combustion

The process shown in Figure 4.16 (a) is not extensive ($\Delta G^\circ = +13.8$ kJ) in the absence of ATP due to the strength of the P-O bond that must be broken. However, placing a phosphate on glucose can be made extensive ($\Delta G^\circ = -16.7$ kJ) by coupling it with the ATP $\rightleftharpoons$ ADP conversion shown in Figure 4.15 to produce the extensive reaction shown in Figure 4.16 (b) with $\Delta G^\circ = -16.7$ kJ. The coupled reaction is much more extensive because the P-O bond that is broken is much weaker in the highly energetic ATP ion than in the HPO_4^{2-} ion.

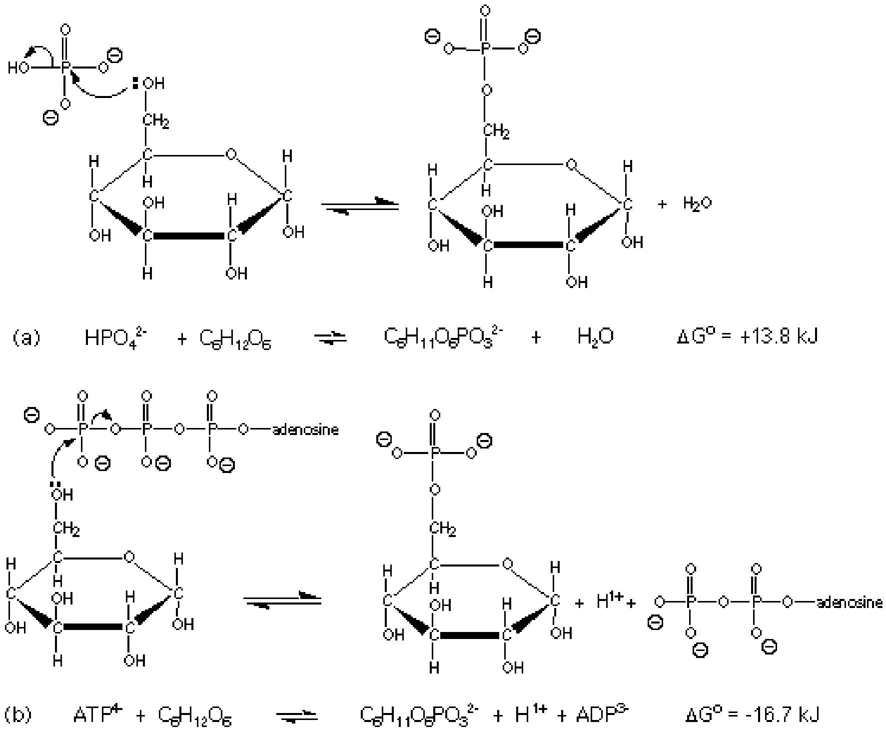


Figure 4.16: Formation of Glucose Phosphate from Glucose

Most of the remaining steps in the glucose oxidation are down hill in free energy, and much of the energy is used to convert ADP back into ATP. ATP is a short-lived species in the cell as it is usually consumed within a minute of being formed. During strenuous activity, ATP can be used at a rate of up to 0.5 kg/min.

4.9 Exercises and Solutions

Links to view either the end-of-chapter exercises or the solutions to the odd exercises are available in the HTML version of the chapter.

CHAPTER 5 – CHEMICAL EQUILIBRIUM

Introduction

The equilibrium constant was defined in Chapter 4, and calculations were done to establish the relationship between it and the standard free energy change of the reaction. However, the equilibrium constant is most valuable because it lets us predict the composition of an equilibrium mixture or to adjust the reactant concentrations so as to obtain an equilibrium mixture with the desired composition. These calculations are so important that they form the basis of this chapter and much of Chapters 6, 7, and 8, where the principles established in this chapter are applied to proton transfer, solubility, and electron transfer processes, respectively.

5.1 The Equilibrium Constant

Introduction

The thermodynamic equilibrium constant discussed in Chapter 4 is unitless because it is defined in terms of unitless activities. However, equilibrium constants can be defined in terms of partial pressures or molar concentrations. These equilibrium constants typically, but not always, have units. In this section, we introduce both types of equilibrium constants, show how to convert from one to the other, and demonstrate some of their properties.

Objectives

- Determine the value of K for a reaction given the value of K for a related reaction that differs only by a multiple or in direction.
- Determine the equilibrium constant of a reaction that is the sum of several other reactions.
- Convert between K_p and K_c.

K_p Versus K_c

5.1-1. K_p and K_c Defined

An equilibrium constant in which partial pressures are used for activities is called K_p, while one in which molar concentrations are used for activites is called K_c. For a reaction that involves only gases, K_p equals K (the thermodynamic equilibrium constant that has no units) if the partial pressures are in atmospheres because the activity of a gas is numerically equal to its partial pressure in atmospheres. For a reaction that involves only solutes in a liquid solution, K_c equals K because the activity of a solute is numerically equal to its molar concentration.

Consider the following equilibrium:

$$\mathrm{N_2 + 3\ H_2 \rightleftharpoons 2\ NH_3}$$

The units of K_p would be determined as follows:

$$K_\mathrm{p} = \frac{(P_{\mathrm{NH_3}})^2\ \mathrm{atm}^2}{(P_{\mathrm{N_2}})\ \mathrm{atm} \cdot (P_{\mathrm{H_2}})^3\ \mathrm{atm}^3}$$

which would have units of atm^{-2}. The exponent of the units equals the sum of exponents in the numerator minus the sum of exponents in the denominator or the number of moles of products minus the number of moles of reactants, which is Δn_g. This is true for any equilibrium, so we can state that for a gas phase equilibrium,

- the units of K_p are $\mathrm{atm}^{\Delta n_\mathrm{g}}$
- the units of K_c are $M^{\Delta n_\mathrm{g}}$

For solution equilibria, the units of K_c are $M^{\Delta n}$, where $\Delta n =$ the number of moles of solute products minus the number of moles of solute reactants.

5.1-2. Converting Between K_p and K_c

Since the thermodynamic K equals K_p for gas phase equilibria, K_p values are a common way to discuss their equilibria. However, there are times when it is more convenient to consider gas phase equilibria in terms of molar concentrations; i.e., in terms of K_c. In such cases, the K_p would have to be converted into a K_c. The conversion involves converting the partial pressures of the gases into molar concentrations, which is done with the ideal gas law. We first express the partial pressure of gas A in terms of its pressure as follows:

$$P_A = \frac{n_A RT}{V} = \frac{n_A}{V} \times RT$$

where P_A is the partial pressure of A, n_A is the number of moles of gas A. n_A/V is the number of moles of A per liter of gas, which is [A], the molar concentration of A. Substitution of $n_A/V = [A]$ into the above equation yields Equation 5.1, which relates the concentration of a gas to its partial pressure.

$$P_A = [A]RT \qquad \text{Pressure-Concentration Relationship} \qquad (5.1)$$

Substitution of $[A]RT$ for P_A into a K_p expression converts the expression from one of pressures to one of concentrations; i.e., it converts the K_p into a K_c. Equation 5.2 summarizes the relationship.

$$\begin{aligned} K_p &= K_c \times (RT)^{+\Delta n_g} \\ K_c &= K_p \times (RT)^{-\Delta n_g} \end{aligned} \qquad \text{Relationship of } K_p \text{ and } K_c \qquad (5.2)$$

5.1-3. Converting with the Factor Label Method

If remembering which sign of Δn_g to use is a problem, then $K_p \rightleftharpoons K_c$ conversions can be done as factor label conversions in which units of ($\text{atm}^{\Delta n_g}$) are converted into units of ($M^{\Delta n_g}$) using RT as the conversion factor. R, which is the ideal gas law constant, equals 0.08206 $\text{L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. However, it can be made more useful for converting between atm and M by recognizing that $\text{L}\cdot\text{mol}^{-1} = M^{-1}$, so the units of R can be expressed as $\text{atm}\cdot\text{K}^{-1}\cdot M^{-1}$, so

- RT has units of $\text{atm}\cdot M^{-1} = \text{atm}/M$.

EXAMPLE:

If $\Delta n_g = -2$, then K_p has units of atm^{-2}, so the conversion would be

$$K_c = \frac{K_p}{\text{atm}^2} \times \frac{(RT)^2\ \text{atm}^2}{M^2} = \frac{K_p(RT)^2}{M^2} = K_p(RT)^2 M^{-2}$$

Thus, $K_c = K_p(RT)^2 = K_p(RT)^{-\Delta n_g}$, consistent with Equation 5.2.

Finally, note that when $\Delta n_g = 0$, $K_c = K_p = K$. Thus, using either molarities or partial pressures in the equilibrium constant expression of a reaction consisting only of gases yields the same value of K, which is unitless and numerically equal to the thermodynamic equilibrium constant, so long as the number of moles of gas phase products equals the number of moles of gas phase reactants.

5.1-4. Thermodynamics and K Exercise

EXERCISE 5.1:

What are K, K_p, and K_c for the following at 298 K if $\Delta G° = -31.0$ kJ?

$$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$$

Δn_g = ______________

	Value	Units
K		
K_p		
K_c		

5.1-5. Exercise

EXERCISE 5.2:

Convert the given K_p to K_c at 298 K.

	Reaction	K_p
(a)	$H_2O(l) \rightleftharpoons H_2O(g)$	0.031 atm
(b)	$H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$	622
(c)	$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$	6.1e5 atm^{-2}

RT = ______________ atm·M^{-1}

	Δn_g	K_c
(a)	mol	M
(b)	mol	
(c)	mol	M^{-2}

Properties of the Equilibrium Constant

5.1-6. Properties

We will use the following two aqueous equilibria for our discussions of the properties of the equilibrium constant:

$$A(aq) \rightleftharpoons B(aq) \qquad K_1 = \frac{[B]}{[A]} = 5 \qquad \text{(Equilibrium 1)}$$

$$B(aq) \rightleftharpoons C(aq) \qquad K_2 = \frac{[C]}{[B]} = 0.3 \qquad \text{(Equilibrium 2)}$$

- If the coefficients of a chemical equation are all multiplied by some number n, then the equilibrium constant of the resulting chemical equation equals the original equilibrium constant raised to the n^th power: $K' = K^\mathrm{n}$. For example, multiplying Equilibrium 1 by 3, we obtain

$$3\ \mathrm{A}(aq) \rightleftharpoons 3\ \mathrm{B}(aq) \qquad K = K_1^3 = \frac{[\mathrm{B}]^3}{[\mathrm{A}]^3} = 5^3 = 125$$

- If the direction of the equation is reversed, then the equilibrium constant of the resulting equation is the reciprocal of the original equilibrium constant: $K' = 1/K$. For example, reversing Equilibrium 1, we obtain

$$\mathrm{B}(aq) \rightleftharpoons \mathrm{A}(aq) \qquad K = K_1^{-1} = \frac{[\mathrm{A}]}{[\mathrm{B}]} = 5^{-1} = 0.2$$

- If two chemical equations are added, then the equilibrium constant of the resulting equation is the product of the two original equilibrium constants. For example, adding Equilibria 1 and 2, we obtain $\mathrm{A}(aq) \rightleftharpoons \mathrm{C}(aq)$, and the equilibrium constant is then determined as follows:

$$\mathrm{A}(aq) \rightleftharpoons \mathrm{C}(aq) \qquad K = K_1K_2 = \frac{[\mathrm{B}]}{[\mathrm{A}]} \times \frac{[\mathrm{C}]}{[\mathrm{B}]} = \frac{[\mathrm{C}]}{[\mathrm{A}]} = (5)(0.3) = 1.5$$

5.1-7. Exercise

EXERCISE 5.3:

Given the following equilibrium constants,

	Reaction	***K***
1	$\mathrm{HF}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{F^{1-}}(aq) + \mathrm{H_3O^{1+}}(aq)$	7.2e−4
2	$\mathrm{HNO_2}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NO_2^{1-}}(aq) + \mathrm{H_3O^{1+}}(aq)$	4.0e−4

Determine the value of the equilibrium constants of the following.

Reaction	***K***
$\mathrm{F^{1-}}(aq) + \mathrm{H_3O^{1+}}(aq) \rightleftharpoons \mathrm{HF}(aq) + \mathrm{H_2O}(l)$	
$\mathrm{F^{1-}}(aq) + \mathrm{HNO_2}(aq) \rightleftharpoons \mathrm{HF}(aq) + \mathrm{NO_2^{1-}}(aq)$	

5.1-8. Exercise

EXERCISE 5.4:

Given the following equilibrium constants,

1 $\mathrm{HF}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{F^{1-}}(aq) + \mathrm{H_3O^{1+}}(aq) \qquad K_1 = 7.2\mathrm{e}{-4}$

2 $\mathrm{CaF_2}(s) \rightleftharpoons \mathrm{Ca^{2+}}(aq) + 2\ \mathrm{F^{1-}}(aq) \qquad K_2 = 3.9\mathrm{e}{-11}$

Determine the equilibrium constant for the following reaction.

$$\mathrm{CaF_2}(s) + 2\ \mathrm{H_3O^{1+}}(aq) \rightleftharpoons \mathrm{Ca^{2+}}(aq) + 2\ \mathrm{HF}(aq) + 2\ \mathrm{H_2O}(l)$$

First determine how to sum Equations 1 and 2 to obtain the desired equation.

Which chemical equation must be reversed?

Equation 1
Equation 2

Equation 1 must be multiplied by what integer?

____

Equation 2 must be multiplied by what integer?

____

K = _______________

5.2 Le Châtelier's Principle

Introduction

In Chapter 4, the spontaneous direction of a reaction was predicted from known concentrations by using the fact that a reaction proceeds from left to right when $Q < K$ and from right to left when $Q > K$. We also saw that a temperature rise causes the equilibrium constants of endothermic reactions to increase and the equilibrium constants of exothermic reactions to decrease. However, the same conclusions can be drawn without calculation by applying Le Châtelier's Principle. In this section, we apply this important principle to three types of disturbances:

- changing an amount of a reactant or product
- changing the volume
- changing the temperature

Objectives

- Explain how Le Châtelier's Principle is a summary of the relationship between Q and K of the reaction.
- Use Le Châtelier's Principle and considerations of the reaction quotient and the equilibrium constant to predict the direction of the shift in equilibrium caused by stress placed on the equilibrium.

5.2-1. Statement of Le Châtelier's Principle

Le Châtelier's Principle

- If a system at equilibrium is disturbed, then the system reacts so as to counteract the disturbance.

If a substance is added, then equilibrium shifts to remove it. If a substance is removed, then equilibrium shifts to replace it. If an equilibrium is heated, then it shifts so as to remove heat. If the volume is increased, then the equilibrium shifts to produce gas to fill the increased volume.

5.2-2. Changing the Amount of a Substance

Consider Figures 5.1a–c, which show the effect of changing one concentration in an equilibrium mixture of $\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C} + \mathrm{D}$.

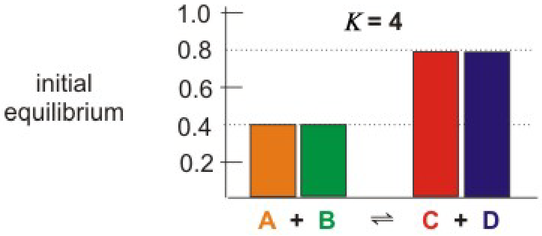


Figure 5.1a: Effect of Adding and Removing Substances from an Equilibrium Mixture

The colored rectangles represent the concentrations of each of the substances.

Figure 5.1a shows the original equilibrium in which [A] = [B] = 0.40 M and [C] = [D] = 0.80 M, so

$$K = \frac{[\mathrm{C}][\mathrm{D}]}{[\mathrm{A}][\mathrm{B}]} = \frac{(0.80)(0.80)}{(0.40)(0.40)} = 4.0$$

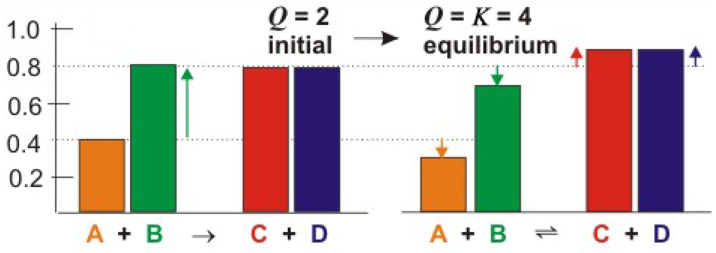


Figure 5.1b: Effect of Adding and Removing Substances from an Equilibrium Mixture
The colored rectangles represent the concentrations of each of the substances. Figures on the left correspond to the concentrations immediately after the change occurs, while those on the right represent the resulting equilibrium concentrations.

In Figure 5.1b, the concentration of B is increased to 0.800 M. Le Châtelier's Principle predicts that the equilibrium should shift so as to reduce the effect of the additional B by reducing its concentration. Alternatively, we determine that $Q = (0.80)^2/(0.40)(\mathbf{0.80}) = 2.0$ after the addition, so $Q < K$, and the reaction proceeds to the right, which has the effect of reducing [B] as predicted by Le Châtelier's Principle. Thus, B reacts with A to produce C and D. The changes in concentration resulting from the reaction cause Q to increase, which it does until it equals K and equlibrium is re-established. We use the symbol Δ for the changes in concentration; i.e., [A] and [B] each decrease by Δ, while [C] and [D] each increase by Δ. The magnitude of Δ is given by the arrows on the right side of the figure. We will show how to determine the value of Δ in the following section, but now we simply state that a $\Delta = 0.105\ M$ is required to restore equilibrium, so the new concentrations would be the following:

- $[A] = 0.400 - \Delta = 0.40 - 0.105 = 0.295\ M$
- $[B] = 0.800 - \Delta = 0.80 - 0.105 = 0.695\ M$
- $[C] = [D] = 0.800 + \Delta = 0.80 + 0.105 = 0.905\ M$

Note that we carry an extra decimal place in the concentrations to avoid rounding errors. Placing these concentrations back into the equation for Q, we obtain

$$Q = \frac{(0.905)^2}{(0.295)(0.695)} = 4.0 = K$$

Thus, $Q = K$ at these concentrations, so the system is back to equilibrium.

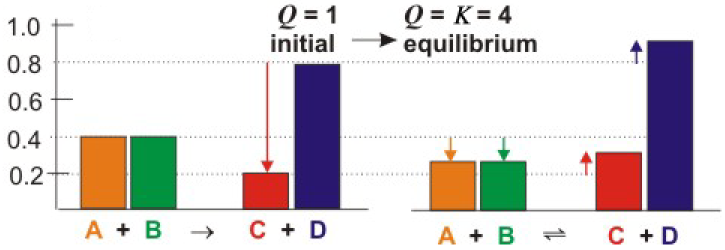


Figure 5.1c: Effect of Adding and Removing Substances from an Equilibrium Mixture
The colored rectangles represent the concentrations of each of the substances. Figures on the left correspond to the concentrations immediately after the change occurs, while those on the right represent the resulting equilibrium concentrations.

In Figure 5.1c, the concentration of C is reduced to 0.20 M, so equilibrium should shift so as to replace some of the C; i.e., A and B must react in order to replace some of the removed C. The original conditions result in $Q = (\mathbf{0.20})(0.80)/(0.40)^2 = 1.0$. $Q < K$, so again the reaction proceeds to the right and Q increases again until $Q = K$ and equilibrium is re-established. Again the extent of reaction, Δ, is represented by the arrows on the right side of the figure. In this case, $\Delta = 0.125\ M$, which produces the following concentrations:

- $[A] = [B] = 0.400 - \Delta = 0.400 - 0.125 = 0.275\ M$
- $[C] = 0.200 + \Delta = 0.200 + 0.125 = 0.325\ M$
- $[D] = 0.800 + \Delta = 0.800 + 0.125 = 0.925\ M$

$$Q = \frac{(0.325)(0.925)}{(0.275)^2} = 4.0 = K$$

$Q = K$, so the new concentrations are indeed equilibrium concentrations.

5.2-3. Changing the Volume

Changing the volume changes the pressures of the gases, and Le Châtelier's Principle states that an equilibrium mixture reacts to counteract the change. At constant temperature, the only way to change the pressure is to change the number of moles of gas. Consequently, equilibrium mixtures react so as to increase the number of moles of gas when the volume of the mixture is increased or decrease the number of moles of gas when the volume is decreased.

Changing the volume changes both the pressures and the concentrations of the gases, which changes Q. The change in Q depends upon Δn_g in such a way that the same conclusions are drawn from Q and K considerations as with Le Châtelier's Principle.

5.2-4. Changing the Temperature

Changing the temperature at constant pressure changes K not Q, and Le Châtelier's Principle summarizes the effect that temperature has on the equilibrium constant. Heat can be viewed as a product of an exothermic reaction and as a reactant in an endothermic reaction. Heating an exothermic reaction is the same as adding a product, which shifts the reaction toward the reactant side (←). The shift increases the equilibrium concentrations of the reactants and decreases the equilibrium concentrations of the products. The result is that the value of K is decreased in agreement with the conclusion reached using the equation $\ln(K_2) = \ln(K_1) + \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$.

5.2-5. Exercises

EXERCISE 5.5:

Consider the following equilibrium:

$$3\ H_2(g) + N_2(g) \rightleftharpoons 2\ NH_3(g) \qquad \Delta H^\circ = -46\ \text{kJ}$$

Apply Le Châtelier's Principle to determine the effect on the equilibrium pressure of N_2.

Adding H_2:
- increase
- decrease
- no change

Increasing the volume:
- increase
- decrease
- no change

Removing NH_3:
- increase
- decrease
- no change

Increasing the temperature:
- increase
- decrease
- no change

EXERCISE 5.6:

Consider the following equilibrium:

$$\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag}^{1+}(aq) + \mathrm{Cl}^{1-}(aq) \qquad \Delta H^\circ = 66\ \mathrm{kJ}$$

Indicate the effect on the equilibrium concentration of Ag^{1+} caused by the following.

Dissolving solid $AgNO_3$ in the solution:
- increase
- decrease
- no change

Increasing the temperature:
- increase
- decrease
- no change

Adding solid AgCl to the solution:
- increase
- decrease
- no change

Adding water:
- increase
- decrease
- no change

EXERCISE 5.7:

Consider the equilibrium:

$$\mathrm{HSO}_4^{1-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O}^{1+}(aq) + \mathrm{SO}_4^{2-}(aq) \qquad \Delta H^\circ < 0$$

Indicate the effect on the hydrogen sulfate ion concentration of the following.

Adding $Pb(NO_3)_2(aq)$, which precipitates $PbSO_4$ from the solution:
- increase
- decrease
- no change

Warming the solution:
- increase
- decrease
- no change

Adding hydrochloric acid to increase $[H_3O^{1+}]$:
- increase
- decrease
- no change

5.3 Using the Equilibrium Constant

Introduction

The stoichiometry problems of Chapter 1 all assumed that the limiting reactant disappeared completely during reaction. However, this assumes that the equilibrium constant is very large. In this section, we address problems in which the equilibrium constant is not very large, so the limiting reactant does not disappear completely. We will again use a reaction table as introduced in Chapter 1. The reaction table consists of three lines: the initial, change, and final. In equilibrium problems, the unknown can lie on any one of these lines or it can require filling in the table to determine the value of the equilibrium constant. In this section we show how to solve equilibrium problems.

Objectives

- Calculate the concentrations of one substance in an equilibrium mixture from the other concentrations and the equilibrium constant.
- Determine the equilibrium constant for a reaction given the initial amounts and one equilibrium amount.
- Determine the equilibrium composition from the initial composition and the equilibrium constant.
- Calculate the amount of one reactant required to react with a given amount of another reactant to produce a given amount of product.
- Determine the extent of the change caused by the addition of known amounts of reactants or products to an equilibrium mixture, given K and the initial equilibrium concentrations.

- Calculate the amount of one substance that would have to be added to an equilibrium to change the concentration of another substance in the equilibrium by a given amount.

Solving for One Concentration when K and the Other Concentrations are Known

5.3-1. Determining an Unknown Concentration

We begin with the easiest of equilibrium problems: determining an unknown concentration when all other concentrations and the equilibrium constant are known. Solving this type of problem involves setting up the equilibrium constant expression, solving it for the unknown, and substituting the known values into the resulting expression. The next two exercises demonstrate the process.

5.3-2. Exercise

EXERCISE 5.8:

What is the acetate ion concentration in a solution in which $[\mathrm{CH_3COOH}] = 0.10\ M$ and $[\mathrm{H_3O^{1+}}] = 1.0\text{e}{-5}\ M$? Recall that K_a is the equilibrium constant for the reaction of an acid with water and is referred to as the acid dissociation constant.

$$\mathrm{CH_3COOH}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{CH_3COO^{1-}}(aq) + \mathrm{H_3O^{1+}}(aq) \qquad K_\mathrm{a} = 1.8\text{e}{-5}$$

$[\mathrm{CH_3COO^{1-}}] =$ ______________ M

5.3-3. Exercise

EXERCISE 5.9:

What is the maximum calcium ion concentration that can exist in equilibrium with $[\mathrm{H_3O^{1+}}] = 0.10\ M$ and $[\mathrm{HF}] = 0.20\ M$?

$$\mathrm{CaF_2}(s) + 2\ \mathrm{H_3O^{1+}}(aq) \rightleftharpoons \mathrm{Ca^{2+}}(aq) + 2\ \mathrm{HF}(aq) + 2\ \mathrm{H_2O}(l) \qquad K = 7.5\text{e}{-5}$$

$[\mathrm{Ca^{2+}}] =$ ______________

Using Reaction Tables in Equilibrium Problems

5.3-4. Filling in the Reaction Table

The amount of a substance present in an equilibrium mixture is determined from the concentrations of all reactants and products, not just a single limiting reactant, and the reaction table is again the best way to track the changes. However, the label of the last line is changed from “final” to “eq” to emphasize that equilibrium is established. The Δ line represents the amount of each substance that must form or react in order to change from initial to equilibrium concentrations. When making entries into it, remember the following:

- It is the only line to which stoichiometry applies. If one entry on the Δ line is known, then all other entries can be determined by stoichiometry.
- If the initial system must shift to the right ($\rightarrow$, $Q < K$), the concentrations of everything on the right (product) side of the reaction must increase ($\Delta > 0$), while all concentrations on the left side must decrease ($\Delta < 0$).
- If the shift is to the left ($\leftarrow$, $Q > K$), the concentrations of everything on the left side must increase ($\Delta > 0$), while the concentrations of everything on the right side must decrease ($\Delta < 0$).

5.3-5. Types of Equilibrium Problems

We will be doing equilibrium problems in most of the remaining chapters as we examine acid-base, solubility, and redox equilibria. However, there are only three different kinds of equilibrium problems:

1 Determine K from the equilibrium concentrations. If K is the unknown, then the reaction table can contain no unknowns.

2 Determine the equilibrium concentrations from K and a set of initial concentrations. The unknown is in the Δ line and therefore also in the equilibrium line. We will use x as our unknown identifier.

3 Determine the amount of substance that must be added (removed) to (from) a known amount of another reactant to produce a desired equilibrium concentration. The unknown is in the initial line.

You should realize that the methods set forward in the remainder of this chapter will be used repeatedly in subsequent chapters. We examine each of these types in the following exercises.

Determining *K*

5.3-6. Method

In order to determine K, you must be given sufficient information to determine the equilibrium concentrations. This information can be given directly, but many times only the initial concentrations and the final concentration of just one of the substances are given. Setting up a reaction table is the easiest way to establish the other concentrations.

In these cases, use the following method:

1 Enter the given concentrations into the reaction table.

2 Determine the entry on the Δ line of the substance whose final concentration is given by subtracting the initial concentration from the equilibrium concentration: $\Delta = \text{eq} - \text{initial}$.

3 Determine the other entries on the Δ line by applying stoichiometry to the entry determined in Step 2.

4 Determine the other equilibrium concentrations by adding the initial and Δ lines.

5 Use the equilibrium concentrations determined in Step 4 to determine K.

5.3-7. K_c for a Gas Phase Reaction

EXERCISE 5.10:

At some temperature, 6.0 moles of hydrogen and 4.0 moles of nitrogen are added to a 10.0 L flask and allowed to react. At equilibrium, there is 1.0 mole of hydrogen remaining. What is the value of K_c for the following reaction at this temperature? Fill in the reaction table in molar concentrations, then determine K. **Include the signs in the Δ line, even when positive.**

	$N_2(g)$	+	$3\ H_2(g)$	$\rightleftharpoons$	$2\ NH_3(g)$	
initial						M
Δ						M
eq						M

K_c = ______________ M^{-2}

5.3-8. Aqueous Reaction

EXERCISE 5.11:

10. mmol of NH_4Cl and 15 mmol of KCN are dissolved in enough water to make 200. mL of solution. What is the value of the equilibrium constant of the following reaction if $[NH_4^{1+}] = 0.018\ M$ at equilibrium? Fill in the reaction table and then use the equilibrium values to determine K. The entries in the Δ line must include the sign.

	$NH_4^{1+}(aq)$	+	$CN^{1-}(aq)$	$\rightleftharpoons$	$NH_3(aq)$	+	$HCN(aq)$	
initial								M
Δ								M
eq								M

$K =$ ______________

Determining Equilibrium Amounts

5.3-9. Method

If you are asked for an equilibrium concentration or pressure, you must be given the value of K and the initial conditions. The unknown (x) is in the reaction table. To find equilibrium concentrations or pressures given the equilibrium constant and the initial concentrations, use the following method.

1 Put the initial quantities in the reaction table.

2 If both reactants and products are present, calculate Q and determine the direction in which the reaction is proceeding by comparing Q and K. This will help you decide upon the signs to use with the entries on the Δ line.

3 Use x's to complete the Δ line. To simplify stoichiometry considerations, the coefficient of x in each entry should be the same as the coefficient in the balanced equation for that substance. Be sure to include the proper sign.

4 Add the initial and final lines to get the equilibrium line.

5 Substitute the equilibrium line entries into the equilibrium constant expression and solve for x.

6 Use the value of x determined in Step 5 and the expressions for the equilibrium concentrations to determine the equilibrium concentrations or pressures.

5.3-10. Hints to Simplify the Problems

Equilibrium problems involving gas phase reactions in which $\Delta n_\mathrm{g} = 0$ can be done in moles rather than molarities because the volumes cancel.

K_c depends upon the equilibrium concentrations, which depend upon the volume of the container and the number of moles of each species present. However, if $\Delta n_\mathrm{g} = 0$, the volumes in the numerator and denominator cancel, so K_c depends only upon the number of moles. In other words, equilibrium problems on gas phase reactions in which $\Delta n_\mathrm{g} = 0$ can be done in moles rather than molarities. However, if Δn_g is not zero, you must convert to molarities in order to use a K_c.

Taking the square root of both sides of the equilibrium expression will often simplify the algebra.

Solving an equilibrium expression can be very difficult because many expressions contain high order terms. However, the problems in this course have been constructed to simplify the algebra, so you can focus on the equilibrium.

Many of the problems involve squares and can be solved with the quadratic equation, but most of these can be simplified because the equilibrium expression is a perfect square. In these cases, take the square root of both sides of the equation before solving for x.

5.3-11. Equilibrium Moles

EXERCISE 5.12:

0.80 mol N_2 and 0.80 mol O_2 are mixed and allowed to react in a 10 L vessel at 2500 °C. How many moles of nitric oxide would be present when the equilibrium is established? Use x as the unknown identifier.

Hint: You are given moles and are asked for moles, and $\Delta n_g = 0$, so the problem can be done in moles with the given equilibrium constant.

	N_2	+	O_2	$\rightleftharpoons$	2 NO	K = 2.1e−3
initial						mol
Δ						mol
eq						mol

The equilibrium constant expression is a perfect square, so take the square root of both sides and solve for x.

$x =$ ______________ mol moles of NO = ______________ mol

5.3-12. Determining Equilibrium Pressures

EXERCISE 5.13:

What are the equilibrium pressures in a mixture if the initial pressures of CO and H_2O are each 0.200 atm?

	$CO(g)$	+	$H_2O(g)$	$\rightleftharpoons$	$CO_2(g)$	+	$H_2(g)$	$K = 10.0$
initial								atm
Δ								atm
eq								atm

The equilibrium constant expression is a perfect square, so take the square root of both sides and solve for x.

$x =$ ______________ atm

$P_{CO} = P_{H_2O} =$ ______________ atm $P_{CO_2} = P_{H_2} =$ ______________ atm

5.3-13. Re-establishing Equilibrium After an Addition

EXERCISE 5.14:

At a temperature near 450 °C, an equilibrium mixture in a 1.0 L flask contains 0.70 mol of HI(g) and 0.10 mol each of $I_2(g)$ and $H_2(g)$. If 0.30 mol of H_2, 0.30 mol of I_2, and 0.10 mol of HI are injected into this equilibrium mixture, how many moles of each gas will be present when equilibrium is re-established?

	H_2	+	I_2	$\rightleftharpoons$	2 HI		
initial equilibrium						mol	$K =$
injected						mol	
initial						mol	$Q =$
Δ						mol	
eq						mol	

The equilibrium constant expression is a perfect square, so take the square root of both sides and solve for x.

$x =$ ______________ mol

moles of HI = ______________ mol

moles of H_2 = moles of I_2 = ______________ mol

Determining the Amount to Add or Remove

5.3-14. Method

Another important calculation involves determining how much of one substance to add or remove in order to get a desired amount of one of the substances. In these cases, the unknown lies in the initial line. Sometimes, you add or remove the substance from an equilibrium mixture, but the equilibrium mixture cannot be the initial line because nothing would happen if it were at equilibrium. However, adding or removing a substance from an equilibrium line makes it an initial line. Remember that you will have only one unknown in each problem, so there are no other unknowns if one is already in the initial line.

5.3-15. Percent Yield

EXERCISE 5.15:

At 700 K, the equilibrium constant for $H_2 + I_2 \rightleftharpoons 2\ HI$ is 49.0. How many moles of H_2 would have to be added to 1.00 mol I_2 in a 1.00 L flask to get a 90.0% yield? Use x for the number of moles to be added.

	H_2	+	I_2	$\rightleftharpoons$	2 HI	$K = 49.0$
initial						mol
Δ						mol
eq						mol

$x =$ ______________ mol H_2 must be added

5.3-16. Adding Reactants to Shift Equilibrium to Desired Position

<u>EXERCISE 5.16</u>:

An equilibrium mixture in a 1.00 L flask at some temperature was found to contain 0.0500 mol of SO_2, 0.0250 mol of O_2, and 0.0180 mol of SO_3. How many moles of O_2 should be added to this equilibrium mixture to double the number of moles of SO_3 at equilibrium?

Note that Δn_g does not equal zero, so the problem must be done in molarity. However, the reaction takes place in a 1.00 L flask, so the molarity of each gas equals the number of moles.

	$2\ SO_2$	+	O_2	$\rightleftharpoons$	$2\ SO_3$	
initial						M
Δ						M
eq						M

$K_c =$ ______________ M^{-1}

The number of moles of O_2 that must be added = ______________ mol

Putting it Together

5.3-17. Mixing an Acid and a Base

<u>EXERCISE 5.17</u>:

100. mL of a 0.10 M solution of KF and 100. mL of a 0.10 M solution of HNO_2 are mixed.

What are the equilibrium concentrations in the final solution?

	$F^{1-}(aq)$	+	$HNO_2(aq)$	$\rightleftharpoons$	$HF(aq)$	+	$NO_2^{1-}(g)$	$K = 0.56$
initial								M
Δ								M
eq								M

The equilibrium constant expression is a perfect square, so take the square root of both sides and solve for x.

$x =$ ______________ M

$[F^{1-}] = [HNO_2] =$ ______________ M $\qquad$ $[HF] = [NO_2^{1-}] =$ ______________ M

EXERCISE 5.18:

The equilibrium mixture in the previous exercise was $[F^{1-}] = [HNO_2] = 0.029\ M$ and $[HF] = [NO_2^{1-}] = 0.021\ M$. By how much should the fluoride ion concentration be increased to increase the HF concentration to 0.040 M?

	$F^{1-}(aq)$	+	$HNO_2(aq)$	$\rightleftharpoons$	$HF(aq)$	+	$NO_2^{1-}(g)$	$K = 0.56$
initial								M
Δ								M
eq								M

Solve the equilibrium expression for x.

$x =$ ______________ mol/L fluoride ion must be added

5.4 Exercises and Solutions

Links to view either the end-of-chapter exercises or the solutions to the odd exercises are available in the HTML version of the chapter.

CHAPTER 6 – ACIDS AND BASES

Introduction

Brønsted acid-base reactions are proton transfer reactions. Acids donate protons to bases. In the process, the acid is converted into its conjugate base and the base into its conjugate acid. A conjugate acid-base pair differ by one and only one proton. The relative strength of an acid is given by its ***acid dissociation constant***, K_{a}, which is the equilibrium constant for the reaction of the acid with the weak base water. In this chapter, we show how to use the K_{a} expression to determine equilibrium concentrations in solutions of acids and bases.

6.1 Autoionization of Water

Introduction

All of the acid-base reactions we will discuss occur in water, so it is important to understand the acid-base properties of water. Water is said to be ***amphiprotic*** because it can behave as either an acid or a base. In fact, the acidity of an aqueous solution is the extent to which water reacts with an acid to produce its conjugate acid H_3O^{1+}, the hydronium ion. Similarly, the basicity of a solution is the extent to which water reacts with a base to produce its conjugate base, OH^{1-}. In this section, we examine the relationship between the hydronium and hydroxide ion concentrations in aqueous solutions.

Objectives

- Convert between $[H_3O^{1+}]$ and $[OH^{1-}]$ in an aqueous solution.

6.1-1. Review of Acids and Bases

The following is a brief review of the more thorough treatment of acid-base chemistry which can be found in CAMS Chapter 12. You should refer to that chapter for a more in-depth discussion. The material in this and the following chapter assumes a knowledge of how to write chemical equations for acid-base reactions, so viewing the video in CAMS Section 12.8-1. would be especially helpful.

A Lewis base is a substance that contains a lone pair that can be used in a coordinate covalent bond, and a Lewis acid is a substance that has an empty orbital that can be used to share the lone pair in the bond. A Lewis acid-base reaction is the formation of the bond between the acid and the base. The Lewis acid-base reaction between ammonia and acetic acid is represented in Figure 6.1a. In it, the lone pair on ammonia is used to form a covalent bond to a hydrogen atom on the acetic acid. Ammonia contains the lone pair, so it is the base, and acetic acid accepts the lone pair, so it is the acid. In the reverse reaction a lone pair on the acetate ion attacks a proton of the ammonium ion in another Lewis acid-base reaction. This very broad classification allows us to treat many reactions as acid-base reactions. However, the reaction in the figure can also be viewed has a proton transfer from the acid to the base. Although proton transfer reactions can be viewed as Lewis acid-base reactions, a different acid-base theory was developed for this very important branch of chemistry.

In Brønsted-Lowery or simply Brønsted theory, an acid is a proton donor and a base is a proton acceptor. Acetic acid has a proton that it can transfer, so it is an acid, while ammonia can accept a proton, so it is a base. The loss of a proton converts the acid into its conjugate base, and the gain of the proton converts the base into its conjugate acid. An acid and a base differ by one proton only and are said to be a conjugate acid-base pair. The only reactants and products present in a Brønsted acid-base reaction are an acid, a base, and their conjugate base and acid. The brackets in Figure 6.1b identify the conjugate acid-base pairs in the reaction of acetic acid and ammonia.

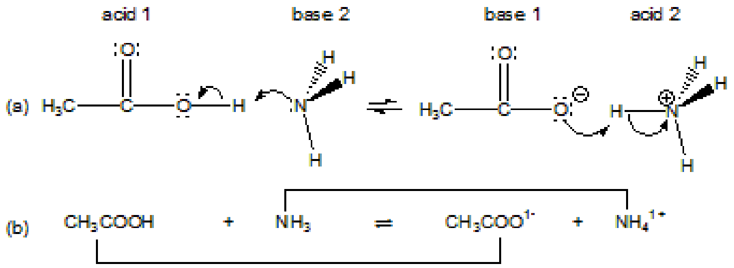


Figure 6.1: Acid-Base Reaction Between Acetic Acid and Ammonia (a) Lewis formalism (b) Brønsted formalism. The brackets connect conjugate acid-base pairs in the Brønsted formalism.

6.1-2. Ion Product Constant

K_w must be satisfied in all aqueous solutions.

Since water is both an acid and a base, it can react with itself in a process called ***autoionization***.

$$\mathrm{H_2O}(l) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^{1+}}(aq) + \mathrm{OH^{1-}}(aq)$$

The equilibrium constant expression for the autoionization, which is given in Equation 6.1, is called the ***ion product constant of water*** and given the symbol K_w. Water is the solvent, so it is treated as a pure liquid with an activity of unity, so it does not appear in the equilibrium constant expression.

$$\begin{aligned} K_\mathrm{w} &= [\mathrm{H_3O^{1+}}][\mathrm{OH^{1-}}] \\ &= 1.0\times 10^{-14} \text{ at } 25\ ^\circ\mathrm{C} \end{aligned} \qquad \text{Ion Product Constant for Water} \qquad (6.1)$$

The subscript 'w' simply indicates 'water'. It is called an ion product constant because it involves only the product of the concentrations of two ions. K_w must be satisfied in all aqueous solutions, regardless of what other substances may be dissolved. Thus, the hydronium and hydroxide ion concentrations in ALL aqueous solutions are related by Equation 6.1.

6.1-3. Acidity and Basicity

If water is the only source of $\mathrm{H_3O^{1+}}$ and $\mathrm{OH^{1-}}$ ions, then their concentrations must be equal because they are produced in a 1:1 ratio. However, addition of an acid to an aqueous solution increases $[\mathrm{H_3O^{1+}}]$ and decreases $[\mathrm{OH^{1-}}]$ so that the resulting concentrations obey Equation 6.1. Addition of a base has the opposite effect of increasing $[\mathrm{OH^{1-}}]$ and decreasing $[\mathrm{H_3O^{1+}}]$. Consequently, aqueous solutions can be classified as one of the following types.

- **Neutral Solution**: $[\mathrm{H_3O^{1+}}] = [\mathrm{OH^{1-}}]$
- **Acidic Solutions**: $[\mathrm{H_3O^{1+}}] > [\mathrm{OH^{1-}}]$
- **Basic Solutions**: $[\mathrm{H_3O^{1+}}] < [\mathrm{OH^{1-}}]$

However, Equation 6.1 is obeyed in all three types.

6.1-4. Exercise

EXERCISE: 6.1

What are the hydronium and hydroxide ion concentrations in pure water at 25 °C?

$[H_3O^{1+}] = [OH^{1-}] =$ ______________ M

HCl is added to water until $[H_3O^{1+}] = 0.042$ M. What is the concentration of the hydroxide ion in the resulting solution at 25 °C?

$[OH^{1-}] =$ ______________ M

What is $[H_3O^{1+}]$ in a solution that is 0.50 M in hydroxide ion?

$[H_3O^{1+}] =$ ______________ M

6.2 The p-Scale

Introduction

Many of the numbers used in this chapter are very small, so they are often expressed on the p-scale to avoid the use of negative exponents or preceding zeroes.

Objective

- Determine $[H_3O^{1+}]$, $[OH^{1-}]$, pH, and pOH of a solution of a strong acid or strong base of known concentration.

6.2-1. Method for Converting to the p-Scale

The p-scale is defined in Equation 6.2. A ‘p’ placed before a concentration or a constant means that the number is the negative log of the concentration or constant.

$$\mathrm{pX} = -\log(\mathrm{X}) \qquad \text{Converting a Number to the p-Scale} \qquad (6.2)$$

For example, ***pH*** $= -\log\,[H_3O^{1+}]$ and $\mathrm{p}K_\mathrm{a} = -\log\, K_\mathrm{a}$.

Taking the antilogarithm of both sides of Equation 6.2 gives the expression for converting the p-scale to the concentration or constant.

$$\mathrm{X} = (10)^{-\mathrm{pX}} \qquad \text{Converting from the p-Scale Back to the Number} \qquad (6.3)$$

The hydronium ion concentration in a solution with pH = 3.20 is $[H_3O^{1+}] = 10^{-\mathrm{pH}} = 10^{-3.20} = 6.3\mathrm{e}{-04}$ and an acid with a $\mathrm{p}K_\mathrm{a} = 5.62$ has a $K_\mathrm{a} = 10^{-5.62} = 2.4\mathrm{e}{-06}$.

It might appear that the $[H_3O^{1+}]$ and K_a do not have the correct number of significant figures. After all, the pH has three, while the $[H_3O^{1+}]$ and K_a each have only two. The difference arises because the numbers to the left of the decimal in a logarithm indicate the exponent, not the significant figures. This is due to the way negative exponents are handled. An exponent of -3.20 is expressed as $0.80 - 4$, so $10^{-3.20} = (10^{0.80})(10^{-4}) = (6.3)(10^{-4})$. Thus, the significant figure, 6.3, is determined from 0.80, which comes from the 0.20 in the pH. The exponent, -4, is dictated by the number to the left of the decimal.

We conclude that significant figures can be lost when converting from pX to X, while they can be gained in going from X to pX. This is the reason that $\mathrm{p}K_\mathrm{a}$ values are usually reported to three significant figures, while K_a values have only two.

The following are common uses of the p-scale.

$\text{pH} = -\log\,[\text{H}_3\text{O}^{1+}]$	$[\text{H}_3\text{O}^{1+}] = 10^{-\text{pH}}$
$\text{pOH} = -\log\,[\text{OH}^{1-}]$	$[\text{OH}^{1-}] = 10^{-\text{pOH}}$
$\text{p}K_\text{w} = -\log(K_\text{w}) = -\log(1.0 \times 10^{-14}) = 14.00$	$K_\text{w} = 10^{-\text{p}K_\text{w}} = 10^{-14}$
$\text{p}K_\text{a} = -\log(K_\text{a})$	$K_\text{a} = 10^{-\text{p}K_\text{a}}$

Table 6.1

6.2-2. pK_w, pH, and pOH

We now express the ion product for water (Equation 6.1) in terms of pH and pOH.

$$K_\text{w} = [\text{H}_3\text{O}^{1+}][\text{OH}^{1-}]$$

Taking the negative logarithm of both sides, we obtain the following.

$$-\log\,K_\text{w} = -\log\,[\text{H}_3\text{O}^{1+}] - \log\,[\text{OH}^{1-}]$$

Substitution of the p-scale definitions results in the relationship between pH, pOH, and pK_w.

$$\text{p}K_\text{w} = \text{pH} + \text{pOH} = 14.00 \text{ at } 25\ ^\circ\text{C} \qquad \text{p}K_\text{w} \tag{6.4}$$

Equation 6.4 is an important relationship that we will use to convert between the pH and pOH of aqueous solutions. It is important to realize that pK_w = 14.00 only at 25 °C, but values at some selected temperatures are given in the following table.

T (°C)	pK_w	K_w
0	14.94	1.15e−15
25	14.00	1.00e−14
50	13.28	5.25e−15
75	12.71	1.95e−13
100	12.26	5.50e−13

Table 6.2: pK_w at Selected Temperatures

6.2-3. pH, Acidity, Basicity, and Neutrality

Acidic solutions: $[\text{H}_3\text{O}^{1+}] > 1.0 \times 10^{-7}$. Taking the negative logarithm of both sides of this inequality produces pH < 7.00 for acidic solutions. A solution in which $[\text{H}_3\text{O}^{1+}] = 1.0\ M$ (pH = 0.0) is fairly acidic solution, so most pH values for acidic solutions lie between 0 and 7. However, H_3O^{1+} concentrations greater than 1.0 M are possible. We conclude that **the pH of a solution decreases as the acidity increases, and the pH of most acidic solutions lies between 0 and 7, but negative values are possible.**

Basic Solutions: $[\text{OH}^{1-}] > 1.0 \times 10^{-7}$, so $[\text{H}_3\text{O}^{1+}] < 1.0 \times 10^{-7}$. Taking the negative logarithm of both sides yields pOH < 7 or pH > 7 for basic solutions. A solution in which $[\text{OH}^{1-}] = 1.0\ M$ has a pOH = −log(1.0) = 0.0, which gives it a pH = 14.0 − 0.0 = 14.0, which is a very basic solution. However, solutions in which $[\text{OH}^{1-}] > 1\ M$ are not uncommon. We conclude that **the pH of a solution increases as the basicity increases, and the pH of most basic solutions lie between 7 and 14, but values higher than 14 are possible.**

Neutral Solutions: $[\text{H}_3\text{O}^{1+}] = [\text{OH}^{1-}] = 1.0 \times 10^{-7}$, so pH = pOH = 7.00 (at 25 °C). Thus, **a neutral solution at 25 °C is one with pH = 7.00.**

These conclusions are summarized in the following figure.

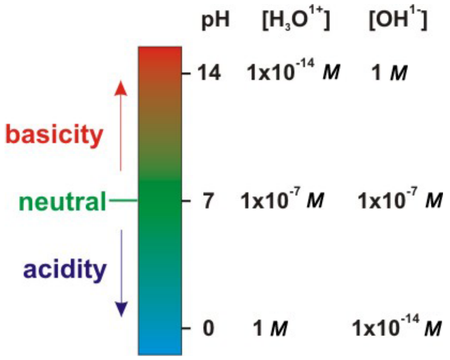


Figure 6.2: pH and Solution Type at 25 °C Pictured above is the relationship between pH, acidity, and basicity.

6.2-4. Converting to the p-Scale Exercises

<u>EXERCISE 6.2</u>:

Determine the pH and pOH of the following solutions.

Concentration	pH	pOH
$[H_3O^{1+}] = 1.0e{-}07\ M$		
$[H_3O^{1+}] = 0.042\ M$		
$[OH^{1-}] = 0.50\ M$		

6.2-5. Exercise

<u>EXERCISE 6.3</u>:

What are $[H_3O^{1+}]$ and $[OH^{1-}]$ in a solution with a pH of 8.62?

$[H_3O^{1+}] =$ ________________ M $[OH^{1-}] =$ ________________ M

pOH = ________________

6.2-6. Exercise

<u>EXERCISE 6.4</u>:

The pH of a sample of lemon juice is found to be 2.32. What are the hydronium and hydroxide ion concentrations?

$[H_3O^{1+}] =$ ________________ M $[OH^{1-}] =$ ________________ M

pOH = ________________

6.2-7. Exercise

EXERCISE 6.5:

The hydroxide ion concentration in a bottle of household ammonia is 0.0083 *M*. Determine the pH, pOH, and the hydronium ion concentration of the solution.

pOH = ______________

$[H_3O^{1+}]$ = ______________ *M*

pH = ______________

6.3 Strong Acids

Introduction

The common strong acids are $HClO_4$, HCl, HBr, HI, HNO_3, and H_2SO_4. In this section, we discuss how the pH of a strong acid solution is determined.

Objective

- Calculate the pH of the solutions of strong acids and of strong bases.

6.3-1. Strong Acid Video

A video or simulation is available online.

6.3-2. Strong Acid Solutions

Hydrochloric acid is a strong acid, so essentially all of the HCl reacts. The reaction is so extensive that it is usually represented with a single arrow.

	HCl	+	$\mathbf{H_2O}$	→	$\mathbf{H_3O^{1+}}$	+	$\mathbf{Cl^{1-}}$
initial	c_o				0		0
Δ	$-c_o$				$+c_o$		c_o
eq	0				c_o		c_o

In the reaction table above, c_o is the *makeup* concentration of the acid, which is the concentration given on the acid bottle. For strong, monoprotic acids, the hydronium ion concentration is given by the makeup concentration because all of the acid reacts. The case of H_2SO_4 is a little more complicated because only the first proton is strongly acidic. We will consider sulfuric acid in more detail in the section on polyprotic acids.

6.3-3. Exercises

EXERCISE 6.6:

What is the pH of a 0.16 *M* solution of hydrochloric acid?

pH = ______________

6.4 Weak Acids

Introduction

Weak acids react only slightly with water, so the hydronium ion concentration in a solution of a weak acid does not equal the makeup concentration. In this section, we show how to determine the concentrations of all of the species in a solution of a weak acid.

Objectives

- Write the K_a expression for a weak acid.
- Determine the equilibrium concentrations of all species present in and the pH of solutions of weak acids.
- Determine the pH, K_a, or initial concentration of a weak acid solution given the other two.
- Calculate the percent ionization of a weak acid.
- Convert between pK_a and K_a.

6.4-1. Weak Acid Video

A video or simulation is available online.

6.4-2. Weak Acid-Water Reaction Table

The equilibrium constant for the reaction of an acid and water is called the acid dissociation constant, K_a. K_a is so large for strong acids that all of the acid reacts to produce hydronium ion and the conjugate base of the acid. K_a is small for weak acids, so only a portion of a weak acid reacts with water. Thus, the Δ line entries of the reaction table are unknown. Consider the reaction of a generic weak acid HA with water.

	$\mathbf{HA}$	$+$	$\mathbf{H_2O}$	$\rightleftharpoons$	$\mathbf{H_3O^{1+}}$	$+$	$\mathbf{A^{1-}}$
initial	c_o				0		0
Δ	$-x$				x		x
initial	$c_o - x$				x		x

Water is the solvent, so it is treated as a pure liquid (activity = 1), so the K_a expression is the following.

$$K_\text{a} = \frac{[\text{H}_3\text{O}^{1+}][\text{A}^{1-}]}{[\text{HA}]} = \frac{(x)(x)}{c_o - x} = \frac{x^2}{c_o - x} \qquad \text{Acid Dissociation Expression} \qquad (6.5)$$

The values of K_a and pK_a for several acids are given in the Acid-Base Table with pK_a.

6.4-3. Solving the K_a Expression

We must solve Equation 6.5 for x to obtain the equilibrium concentrations in an aqueous solution of the weak acid HA.

$$K_\text{a} = \frac{x^2}{c_o - x}$$

where $x = [\text{H}_3\text{O}^{1+}] = [\text{A}^{1-}]$ and $c_o - x = [\text{HA}]$. The equation is a quadratic that could be solved by gathering terms and using the quadratic formula. However, it can be solved more simply if x is negligible compared to c_o, i.e., if $c_o - x \sim c_o$. In other words, if so little of the acid reacts that the acid concentration is essentially unchanged. Making this substitution, we obtain the following expression for a weak acid

$$K_\text{a} = \frac{x^2}{c_o}$$

which can be solved for x, the concentration of the hydronium ion or the conjugate base (A^{1-}), with Equation 6.6.

$$[\text{H}_3\text{O}^{1+}] = [\text{A}^{1-}] = \sqrt{K_\text{a} c_o} \qquad \text{Concentrations in an Aqueous Solution of HA} \quad (6.6)$$

Although neglecting x in the $c_o - x$ term is acceptable most of the time, there are times (K_a is large or c_o is small) when x is not negligible. Consequently, you should use the above expression only when solving for the squared term, and you should always check your result to see if it is indeed negligible. An easy way to determine whether the approximation is valid is given next.

6.4-4. Five Percent Rule

Equation 6.6 is an easy way to determine the concentrations in a solution of a weak acid, but the approximation used to derive it is not always valid, so the answer should always be checked. There are two ways to check whether x is negligible:

- Inspection: The value of x calculated with Equation 6.6 is often so small that it is obviously negligible compared to c_o. For example, if $c_o = 0.100\ M$ and $x = 0.0000001\ M$ then $c_o - x = 0.100\ M$ and the assumption is good.
- **5% Rule**: If x is less than 5% of c_o, then approximating c_o for $c_o - x$ will produce the same answer as the quadratic formula. For example, substitution of $c_o = 0.100$ and $K_\mathrm{a} = 1.6\mathrm{e}{-04}$ into Equation 6.6 gives $x = 0.004\ M$. In this case, $c_o - x = 0.100 - 0.004 = 0.096$, which is not equal to c_o. However, $(x/c_o) = 0.04$, which is 4%. Thus, x is less than 5%, so using the quadratic formula would result in the same answer for x.

6.4-5. Solving Without Approximation

If the answer produced by Equation 6.6 is greater than 5% of c_o, the terms in Equation 6.5 must be gathered in the form of a quadratic equation ($ax^2 + bx + c = 0$) and solved with the quadratic formula given below.

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

However, Equation 6.6 is so easy to use, that it is usually simpler to use it and check to be certain that x is within the 5% limit. This is especially true since most of the acids and concentrations we deal with in this course are so weak that the 5% rule is usually obeyed. However, for the stronger of the weak acids or for very dilute solutions, more than 5% of the acid may react, so always check.

6.4-6. Method for Weak Acid Problems

Equations 6.5 and 6.6 indicate that three terms (c_o, x, and K_a) are required to establish a weak acid equilibrium. Consequently, there are three different types of problems that are solved using these equations. The three differ in the identity of the unknown.

- x: What is the pH, $[\mathrm{H_3O^{1+}}]$, or $[\mathrm{A^{1-}}]$? Given: K_a (or the identity of the acid so you can look it up) and the makeup concentration. Method: Use Equation 6.6 to solve for the unknown then check that x is indeed small enough to neglect. If x is not small enough, rearrange the expression so that it is in the form of a quadratic equation and use the quadratic formula to solve for the unknown concentration.
- K_a: What is the value of K_a? Given: x as the pH, $[\mathrm{H_3O^{1+}}]$, or $[\mathrm{A^{1-}}]$ and the makeup concentration. Method: Substitute the known values into Equation 6.5. Since x and c_o are known, there is no reason to make the neglect-x approximation, so make the subtraction.
- c_o: How much acid must be used to make a solution? Given: x as pH, $[\mathrm{H_3O^{1+}}]$, or $[\mathrm{A^{1-}}]$, and K_a (or the identity of the acid so you can look it up). Method: Solve Equation 6.5 for the equilibrium concentration of the weak acid ($c_o - x$), then solve for c_o using the given value of x.

6.4-7. Determining the pH Exercise

EXERCISE 6.7:

What is the pH of a 0.10-M solution of acetic acid?

$$CH_3COOH + H_2O \rightleftharpoons H_3O^{1+} + CH_3COO^{1-}$$

First, look up the K_a of acetic acid in the resource titled Acid-Base Table with pK_a.

$K_a =$ _______________

Then use Equation 6.6 with the K_a and the given initial concentration to determine $x = [H_3O^{1+}]$.

$[H_3O^{1+}] =$ _______________ M

Finally, convert $[H_3O^{1+}]$ into pH.

pH = _______________

6.4-8. Determining the pH Exercise

EXERCISE 6.8:

What is the pH of a 0.080-M solution of ammonium nitrate? Ammonium ion is a weak acid.

$$NH_4^{1+} + H_2O \rightleftharpoons H_3O^{1+} + NH_3$$

(The relevant pK_a can be found in the Acid-Base Table with pK_a.)

$K_a =$ _______________

pH = _______________

$[H_3O^{1+}] =$ _______________ M

6.4-9. Determining K_a Exercise

EXERCISE 6.9:

If a 0.0750-M solution of formic acid has a pH of 2.447, what is the K_a of formic acid?

$$CHOOH + H_2O \rightleftharpoons CHOO^{1-} + H_3O^{1+}$$

The equilibrium concentrations are as follows.

$[H_3O^{1+}] =$ _______________ M

$[CHOOH] =$ _______________ M

$[CHOO^{1-}] =$ _______________ M

$K_a =$ _______________

6.4-10. Determining the Makeup Concentration Exercise

EXERCISE 6.10:

What initial concentration of a $KHSO_4$ solution would be required to make a pH = 2.00 solution?

$$HSO_4^{1-} + H_2O \rightleftharpoons SO_4^{2-} + H_3O^{1+}$$

(The relevant pK_a can be found in the Acid-Base Table with pK_a.)

K_a = ______________

The equilibrium concentrations are as follows.

$[H_3O^{1+}]$ = ______________ M

$[HSO_4{}^{1-}]$ = ______________ M

$[SO_4{}^{2-}]$ = ______________ M

c_o = ______________

6.4-11. Percent Ionization

We now show that the fraction of an acid that reacts depends upon both its concentration and its acid dissociation constant. We start by reproducing the equilibrium line in the reaction table for a weak acid reacting with water.

$$\begin{array}{lcccccc} & \mathbf{HA} & + & \mathbf{H_2O} & \rightleftharpoons & \mathbf{H_3O^{1+}} & \mathbf{A^{1-}} \\ \mathbf{eq} & c_o - x & & & & x & x \end{array}$$

Of the initial concentration c_o, x mol/L react, so the fraction that reacts is x/c_o. If we assume that the amount that reacts is negligible ($c_o - x = c_o$), we can use Equation 6.6 to determine x as $(c_o K_a)^{1/2}$. Substitution of this value of x into the expression for the fraction that reacts produces the following.

$$\text{fraction dissociating} = \frac{x}{c_o} = \frac{\sqrt{K_a c_o}}{c_o} = \sqrt{\frac{K_a}{c_o}}$$

Multiplication of the above by 100% gives us the percent ionization (reaction) of a weak acid.

$$\text{percent ionization} = \sqrt{\frac{K_a}{c_o}} \times 100\% \qquad \text{Percent Ionization of a Weak Acid} \qquad (6.7)$$

Note that the percent that reacts depends upon both K_a and c_o. Thus, the 5% rule is obeyed by acids with low K_a values and relatively high concentrations. Consider the following table that compares the percent ionization of nitrous (K_a = 4.0e−4), acetic (K_a = 1.8e−5), and hypochlorous (K_a = 3.5e−8) acids as a function of their concentrations.

Molarity	$\mathbf{HNO_2}$	$\mathbf{CH_3COOH}$	**HOCl**
1.0	2.0%	0.42%	0.019%
0.10	6.1%*	1.3%	0.059%
0.010	18%*	4.2%	0.19%
0.00010	83%*	34%*	1.9%

Table 6.3: Percent Ionization of Selected Acids

*The percent ionization exceeds 5% in these cases, so the quadratic formula was used to determine x.

6.4-12. Percent Ionization Exercise

EXERCISE 6.11:

What is the percent ionization and pH of 0.026 *M* HF? (The relevant pK_a can be found in the Acid-Base Table with pK_a.)

$$HF + H_2O \rightleftharpoons F^{1-} + H_3O^{1+}$$

K_a = ______________

% dissociation using Equation 6.7 = ______________ %

Is Equation 6.7 valid for this solution?
Yes
No

$[H_3O^{1+}]$ using the quadratic formula = ______________ *M*

% dissociation = ______________ %

pH = ______________

6.5 Polyprotic Acids

Introduction

Polyprotic acids contain two or more protons. For example, H_2S is diprotic and H_3PO_4 is triprotic. There are some polyprotic acids that contain more than three protons, but we will not consider any of these acids. The conjugate base of a polyprotic acid is also an acid, and the solution of a polyprotic acid is really a solution of more than one acid. Although it might seem that this would make the treatment of these acids very difficult, determining the concentrations of the species present in a polyprotic acid is not much different than determining the concentrations in a solution of a monoprotic acid.

Objective

- Determine the concentrations of all species in a solution of a polyprotic acid of known concentration.

6.5-1. Phosphoric Acid Overview

We examine a 0.10-*M* solution of phosphoric acid as an example because it contains three protons and is the most complicated. The three deprotonation steps are the following.

$H_3PO_4 + H_2O \rightleftharpoons H_2PO_4^{1-} + H_3O^{1+}$	$K_1 = 7.5 \times 10^{-5}$
$H_2PO_4^{1-} + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^{1+}$	$K_2 = 6.2 \times 10^{-8}$
$HPO_4^{2-} + H_2O \rightleftharpoons PO_4^{3-} + H_3O^{1+}$	$K_3 = 4.8 \times 10^{-13}$

Note that each K value is over 1,000 times smaller than the preceding value. This is the case for most polyprotic acids, and it is why polyprotic acids can be treated in a relatively simple manner. The large decrease in K means that a negligible amount of each acid reacts in each step, so the concentration of any species is the concentration determined in the first step in which it is produced. The method we will use to find the concentrations of all species is the following:

1. Determine $[H_3O^{1+}]$, $[H_2PO_4{}^{1-}]$, and $[H_3PO_4]$ from the first acid dissociation. These concentrations are not affected by subsequent steps because the subsequent equilibrium constants are so small.

2 Set up the reaction table for the second reaction using the $[H_3O^{1+}]$ and $[H_2PO_4{}^{1-}]$ determined in step 1 as the initial conditions. Solve the equilibrium problem for $[HPO_4{}^{2-}]$, which will be shown to equal K_2.

3 Set up the reaction table for the third reaction using $[H_3O^{1+}]$ and $[HPO_4{}^{2-}]$ determined in steps 1 and 2 as initial concentrations. Solve the equilibrium problem for $[PO_4{}^{3-}]$.

We next examine each of these steps more closely.

6.5-2. Phosphoric Acid Step 1

Essentially all of the hydronium ion in a solution of a polyprotic acid is produced in the first deprotonation step.

The reaction table for the first step in the deprotonation of 0.10 M H_3PO_4 is as follows.

	$\mathbf{H_3PO_4}$	+	$\mathbf{H_2O}$	$\rightleftharpoons$	$\mathbf{H_2PO_4^{1-}}$	+	$\mathbf{H_3O^{1+}}$	$\boldsymbol{K_1 = 7.5 \times 10^{-3}}$
initial	0.10				0		0	M
Δ	$-x$				$+x$		$+x$	M
eq	$0.10 - x$				x		x	M

H_3PO_4 is about five hundred times stronger than acetic acid so x is probably not negligible in a 0.10 M solution, but we try the approximation to be sure.

$$x = (c_o K_\text{a})^{1/2} = (0.10)(7.5\text{e}{-3})^{1/2} = 0.027\ M$$

The result represents a 27% dissociation, which is well above the 5% limit. The approximation cannot be used, so we must solve for x with the quadratic formula as follows:

1 Set up the K_a expression.

$$7.5\text{e}{-3} = \frac{x^2}{0.10 - x}$$

2 Multiply both sides by $(0.10 - x)$ to get x out of the denominator.

$$(7.5\text{e}{-3})(0.10 - x) = x^2$$

3 Carry out the multiplication on the left side.

$$7.5\text{e}{-4} - 7.5\text{e}{-3}x = x^2$$

4 Gather terms in the form of a quadratic equation.

$$x^2 + 7.5\text{e}{-3}x - 7.5\text{e}{-4} = 0$$

5 Compare the above to the quadratic equation to obtain the following.

$$a = 1, b = 7.5\text{e}{-3},\ \text{and}\ c = -7.5\text{e}{-4}$$

6 Use these values in quadratic formula to obtain the following.

$$x = [H_3O^{1+}] = [H_2PO_4^{1-}] = 0.024\ M$$

7 Use $[H_3PO_4] = c_o - x$ to obtain the following.

$$[H_3PO_4] = 0.10 - 0.02 = 0.08\ M$$

Next we use these concentrations in the second deprotonation.

6.5-3. Phosphoric Acid Step 2

The reaction table for the second deprotonation step is the same as that for the dissociation of 0.024 M $H_2PO_4{}^{1-}$ except that the initial concentration of $[H_3O^{1+}]$ is also 0.024 M as a result of the dissociation of H_3PO_4.

	$\mathbf{H_2PO_4^{1-}}$	+	$\mathbf{H_2O}$	$\rightleftharpoons$	$\mathbf{HPO_4^{2-}}$	+	$\mathbf{[H_3O^{1+}]}$	$\boldsymbol{K_2 = 6.2 \times 10^{-8}}$
initial	0.024				0		0.024	M
Δ	$-x$				0		$+x$	M
eq	$0.024 - x$				x		$0.024 + x$	M

Set up the equilibrium constant expression.

$$K_\mathrm{a} = \frac{[\mathrm{HPO_4^{2-}}][\mathrm{H_3O^{1+}}]}{[\mathrm{H_2PO_4^{1-}}]}$$

Substitute the given K_a and the entries in the equilibrium line.

$$6.2\mathrm{e}{-8} = \frac{x(0.024 + x)}{0.024 - x}$$

If x is negligible then $0.024 + x = 0.024 - x$ and the two terms cancel in the K_2 expression to yield $[\mathrm{HPO_4}^{2-}] = K_2 = 6.2\mathrm{e}{-8}$, which is certainly negligible compared to 0.024.

We conclude the following.

The concentration of the ion produced in the second deprotonation of a polyprotic acid equals K_2, the equilibrium constant for the deprotonation.

6.5-4. Phosphoric Acid Step 3

The reaction table for the third deprotonation step is the same as dissociation of $\mathrm{HPO_4}^{2-}$ except that the initial concentration of $[\mathrm{H_3O^{1+}}]$ is 0.024 M from the first step and that of $\mathrm{H_2PO_4}^{1-}$ is $6.2\mathrm{e}{-8}$ M as a result of the second step.

	$\mathbf{HPO_4^{2-}}$	+	$\mathbf{H_2O}$	$\rightleftharpoons$	$\mathbf{PO_4^{3-}}$	+	$\mathbf{[H_3O^{1+}]}$	$\boldsymbol{K_3 = 4.8 \times 10^{-13}}$
initial	$6.2\mathrm{e}{-8}$				0		0.024	M
Δ	$-x$				$+x$		$+x$	M
eq	$6.2\mathrm{e}{-8}$				x		0.024	M

x has been assumed to be negligible compared to the initial concentrations. Set up the equilibrium constant expression.

$$K_3 = \frac{[\mathrm{PO_4^{3-}}][\mathrm{H_3O^{1+}}]}{[\mathrm{HPO_4^{2-}}]}$$

Substitute the given K_a and the entries in the equilibrium line.

$$4.8\mathrm{e}{-13} = \frac{x(0.024)}{(6.2\mathrm{e}{-8})}$$

Solve for $x = [\mathrm{PO_4}^{3-}]$ to obtain

$$[\mathrm{PO_4^{3-}}] = \frac{(4.8\mathrm{e}{-13})(6.2\mathrm{e}{-8})}{(0.024)} = 1.2\mathrm{e}{-18}\ M$$

which is negligible. Indeed, there is hardly any phosphate ion present in 0.1 M phosphoric acid. In summary, the concentrations of the phosphorus containing species are as follows.

- $[\mathrm{H_3PO_4}] = 0.08\ M$
- $[\mathrm{H_2PO_4}^{1-}] = 0.024\ M$
- $[\mathrm{HPO_4}^{2-}] = 6.2\mathrm{e}{-8}\ M$
- $[\mathrm{PO_4}^{3-}] = 1.2\mathrm{e}{-18}\ M$

Note that the sum of the concentrations should be 0.10 *M*, the make-up concentration of H_3PO_4. The fact that the sum, 0.08 + 0.024 = 0.104 *M*, does not equal the total added initially is due to the number of significant figures; i.e., the final digit in the sum is not significant.

6.5-5. Hydrogen Sulfide Exercise

EXERCISE 6.12:

A saturated solution of hydrogen sulfide is 0.10 *M* at 1 atm and 25 °C. What are the concentrations of all species present in a saturated H_2S solution? (K_1 = 1.0e-7 and K_2 = 1.3e-13.)

First, determine the concentrations of the species involved in the first reaction. **Use ”x” as the unknown identifier, and assume that it is negligible compared to 0.10 *M* on the “eq” line.**

	H_2S	+	H_2O	$\rightleftharpoons$	HS^{1-}	+	H_3O^{1+}	$K_1 = 1.0e{-}07$
initial								*M*
Δ								*M*
eq								*M*

$[HS^{1-}] =$ ______________ *M*

$[H_3O^{1+}] =$ ______________ *M*

$[H_2S] =$ ______________ *M*

Next, determine the concentration of the species formed in the second reaction. **Use ”y“ as the unknown identifier, and assume it is negligible on the ”eq” line.**

	HS^{1-}	+	H_2O	$\rightleftharpoons$	S^{2-}	+	H_3O^{1+}	$K_2 = 1.3e{-}13$
initial								*M*
Δ								*M*
eq								*M*

$[S^{2-}] =$ ______________ *M*

6.5-6. Carbonic Acid Exercise

EXERCISE 6.13:

Determine the pH and the concentrations of all carbon containing species in 0.18 *M* H_2CO_3 solution.

$$H_2CO_3 + H_2O \rightleftharpoons HCO_3^{1-} + H_3O^{1+} \quad K_1 = 4.3e{-}7$$

$$HCO_3^{1-} + H_2O \rightleftharpoons CO_3^{2-} + H_3O^{1+} \quad K_2 = 4.7e{-}11$$

$[H_2CO_3] =$ ______________ *M*

$[HCO_3{}^{1-}] =$ ______________ *M*

$[H_3O^{1+}] =$ ______________ *M*

pH = ______________

$[CO_3{}^{2-}] =$ ______________ *M*

6.5-7. Sulfuric Acid Exercise

EXERCISE 6.14:

What are the H_3O^{1+}, $HSO_4{}^{1-}$, and $SO_4{}^{2-}$ concentrations in 0.10 *M* sulfuric acid?

Sulfuric acid is a strong acid and its conjugate base (hydrogen sulfate ion) is one of the strongest weak acids, so this exercise is a little different.

$$H_2SO_4 + H_2O \rightarrow HSO_4^{1-} + H_3O^{1+} \quad \text{extensive}$$

$$HSO_4^{1-} + H_2O \rightleftharpoons SO_4^{2-} + H_3O^{1+} \quad K = 0.012$$

After the extensive deprotonation of H_2SO_4:

$[H_3O^{1+}] =$ ______________ *M*

$[HSO_4{}^{1-}] =$ ______________ *M*

Assume the amount of $HSO_4{}^{1-}$ that reacts in the second step is negligible.

$SO_4{}^{2-} =$ ______________ *M*

However, that would require a 12% reaction, so the amount that reacts is not negligible. Use the quadratic formula to obtain the equilibrium concentrations.

$[SO_4{}^{2-}] =$ ______________ *M*

$[H_3O^{1+}] =$ ______________ *M*

$[HSO_4{}^{1-}] =$ ______________ *M*

6.6 Strong Bases

Introduction

The solutions of strong bases are usually made by dissolving metal hydroxides in water. In this section, we discuss how the pH of a strong base solution is determined.

Objective

- Calculate the pH of the solutions of strong bases.

6.6-1. Strong Base Solutions

Dissolving a metal hydroxide in water is represented by the following chemical equation.

$$M(OH)_n \rightarrow M^{n+} + nOH^{1-}$$

$[OH^{1-}] = nc_o$ in such a solution. However, most metal hydroxides are only sparingly soluble, so the metal is normally a Group 1 metal ion ($n = 1$) or Ba^{2+} ($n = 2$) in solutions with appreciable hydroxide ion concentrations.

6.6-2. Exercise

EXERCISE 6.15:

What is the pH of a solution labeled 0.16 M $Ba(OH)_2$ at 25 °C? pH cannot be determined directly for a base, so we can either convert the hydroxide ion concentration to a hydronium concentration and then determine the pH, or we can convert the hydroxide ion concentration to a pOH and then to a pH. We choose the latter.

OH^{1-} = ______________ M pH = ______________

pOH = ______________

6.7 Weak Bases

Introduction

Weak bases are treated in a manner identical to that used for weak acids.

Objectives

- Write the K_b expression for a weak base.
- Determine the equilibrium concentrations of all species present in and the pH of solutions of weak bases.
- Determine the pH, K_b, or initial concentration of a weak base solution given the other two.
- Convert between pK_b and K_b.
- Convert between the K_a and K_b of a conjugate acid-base pair.

6.7-1. Weak Base-Water Reaction

The equilibrium constant for the reaction of a base and water has the symbol, K_b. K_b is small for weak bases, so only a portion of a weak base reacts with water. Thus, the Δ line entries of the reaction table are unknown. Consider the reaction of a generic weak base A^{1-} with water.

	$\mathbf{A^{1-}}$	+	$\mathbf{H_2O}$	→	$\mathbf{OH^{1-}}$	+	**HA**
initial	c_o				0		0
Δ	$-x$				x		x
initial	$c_o - x$				x		x

Water is the solvent, so it is treated as a pure liquid (activity = 1), so the K_b expression is the following.

$$K_\mathrm{b} = \frac{[OH^{1-}][HA]}{A^{1-}} = \frac{(x)(x)}{c_o - x} \qquad \text{Weak Base Equilibrium Constant} \qquad (6.8)$$

If we assume that the extent of reaction of the weak base is negligible, i.e., $c_o - x = c_o$, we can express the K_b expression as follows.

$$K_\mathrm{b} = \frac{x^2}{c_o}$$

which can be solved for x, the concentration of the hydroxide ion or the conjugate acid (HA).

$$[OH^{-1}] = [HA] = \sqrt{K_\mathrm{b} c_o} \qquad \text{Solving the } K_\mathrm{b} \text{ Expression} \qquad (6.9)$$

6.7-2. Relating K_a and K_b

Consider the product of the K_a of HA (a weak acid) and the K_b of A^{1-} (its conjugate base).

$$(K_\mathrm{a})(K_\mathrm{b}) = \frac{[\mathrm{H_3O^{1+}}][\mathrm{A^{1-}}]}{[\mathrm{HA}]} \times \frac{[\mathrm{OH^{1-}}][\mathrm{HA}]}{[\mathrm{A^{1-}}]}$$

Note that $[\mathrm{A^{1-}}]$ appears in the numerator of K_a and in the denominator of K_b, so the two terms cancel. Similarly, [HA] appears in the denominator of K_a and in the numerator of K_b, so these two terms cancel as well. Canceling these terms results in the following.

$$(K_\mathrm{a})(K_\mathrm{b}) = [\mathrm{H_3O^{1+}}][\mathrm{OH^{1-}}]$$

Substitution of K_w for $[\mathrm{H_3O^{1+}}][\mathrm{OH^{1-}}]$ produces Equation 6.10.

$$K_\mathrm{a}K_\mathrm{b} = K_\mathrm{w} \qquad \text{Relating } K_\mathrm{a} \text{ and } K_\mathrm{b} \text{ of a Conjugate Acid-Base Pair} \qquad (6.10)$$

The Acid-Base Table with pK_a gives only K_a and pK_a, so Equation 6.10 must be used to determine the K_b of the conjugate base. At 25 °C, K_w = 1.0e−14, so the following can be used to determine the K_b at 25 °C.

$$K_\mathrm{b} = \frac{1.0 \times 10^{-14}}{K_\mathrm{a}} \qquad K_\mathrm{b} \text{ from } K_\mathrm{a} \text{ at 25 °C} \qquad (6.11)$$

6.7-3. Weak Base pH Exercise

EXERCISE 6.16:

What is the pH of a solution that is 0.12 *M* in $\mathrm{NO_2}^{1-}$? (The relevant pK_a can be found in the Acid-Base Table with pK_a.)

K_b = ______________

pOH = ______________

$[\mathrm{OH^{-1}}]$ = ______________ *M*

pH = ______________

6.7-4. pK_a and pK_b

Acid and base constants are frequently given on the p-scale as follows.

$$\begin{aligned} \mathrm{p}K_\mathrm{a} &= -\log(K_\mathrm{a}) \\ \mathrm{p}K_\mathrm{b} &= -\log(K_\mathrm{b}) \end{aligned} \qquad \mathrm{p}K_\mathrm{a} \text{ and } \mathrm{p}K_\mathrm{b} \text{ Definitions} \qquad (6.12)$$

Due to the minus sign in the definition, a higher pK_a or pK_b indicates a weaker acid or base. Taking the negative logarithm of both sides of Equation 6.10 produces the following relationship.

$$\mathrm{p}K_\mathrm{a} + \mathrm{p}K_\mathrm{b} = \mathrm{p}K_\mathrm{w} = 14.00 \text{ at 25 °C} \qquad \mathrm{p}K_\mathrm{a} \text{ and } \mathrm{p}K_\mathrm{b} \text{ Relationship} \qquad (6.13)$$

6.7-5. Determining K_b Exercise

EXERCISE 6.17:

The pH of a 0.085-*M* solution of methylamine is 11.77. What are the K_b of methylamine ($\mathrm{CH_3NH_2}$) and the pK_a of $\mathrm{CH_3NH_3}^{1+}$, its conjugate acid?

$[\mathrm{OH^{1-}}]$ = ______________ *M*

K_b = ______________

$[\mathrm{CH_3NH_3}^{1+}]$ = ______________ *M*

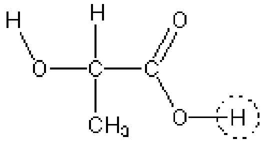
pK_a of $\mathrm{CH_3NH_3}^{1+}$ = ______________

$[\mathrm{CH_3NH_2}]$ = ______________ *M*

6.7-6. pK_a, pK_b, K_a, and K_b Exercise

EXERCISE 6.18:

Lactic acid is usually prepared by fermentation of starch, cane sugar, or whey. Large amounts of lactic acid in muscle lead to fatigue and can cause cramps. Lactic acid, generated in milk by fermentation of lactose, causes milk to sour. Lactic acid is used in the preparation of cheese, soft drinks, and other food products. Its stucture is given below. The proton with a circle around it is the acidic proton.



The pK_a of lactic acid is 3.89.

K_a of lactic acid = ______________ K_b of lactate ion = ______________

pK_b of lactate ion = ______________

6.7-7. Bases of Polyprotic Acids

Bases that can accept more than one proton are treated much the same way as polyprotic acids. Consider the case of the sulfide ion, which can accept two protons.

1 $S^{2-} + H_2O \rightleftharpoons HS^{1-} + OH^{1-} \quad K_1 = 0.077$

2 $HS^{1-} + H_2O \rightleftharpoons H_2S + OH^{1-} \quad K_2 = 1.0 \times 10^{-7}$

Note that the two K_b values differ by a factor of about a million. Thus, the hydroxide produced in the second step is negligible compared to that produced in the first step. Consequently, the hydroxide ion concentration in an aqueous solution of a base that can accept more than one proton can usually be determined by considering only the first step.

6.7-8. Base of a Polyprotic Acid Exercise

EXERCISE 6.19:

What is the pH of 0.064 *M* sulfide ion? (The relevant pK_a can be found in the Acid-Base Table with pK_a.)

K_b = ______________

$[OH^{1-}]$ = ______________ using Equation 6.9. Check 5% assumption.

$[OH^{1-}]$ = ______________ using quadratic formula if assumption is not valid.

pOH = ______________

pH = ______________

6.8 Salts of Weak Acids and Bases

Introduction

Salts are ionic compounds that are produced in acid-base reactions. The anion of the salt is the conjugate base of the reacting acid, and the cation is usually a metal ion that was associated with the reacting base. For example, the reaction between NaOH and HCl is the acid-base reaction between H_3O^{1+} and OH^{1-}. Na^{1+} ion, the metal ion associated with the reacting base and Cl^{1-}, the conjugate base of the reacting acid serve as spectator ions. Combination of the spectator ions produces a salt, NaCl. Salts can be acidic, basic, or neutral depending upon the relative acidity/basicity of the cation and anion. In this section, we discuss the acid-base properties of salts.

Objective

- Define the term salt and predict whether a salt is neutral, basic, or acidic.

6.8-1. Acid-Base Properties of Cations and Anions

Small, highly-charged metal cations have orbitals available to accept electron pairs to form covalent bonds, so they are Lewis acidic. However, the available orbitals of the 1A metal ions are so high in energy that these ions are not acidic in aqueous solutions. Thus, 1A metal ions do not impact the acidity or basicity of a salt. For simplicity, we will limit our use of metal ions to 1A metal ions. The only other common cation is ${NH_4}^{1+}$, which is acidic.

Most anions readily accept the positive charge of a proton, so anions are usually good bases. The exceptions are the conjugate bases of the strong acids (${ClO_4}^{1-}$, Cl^{1-}, Br^{1-}, I^{1-}, and ${NO_3}^{1-}$), which are neutral, and the protonated anions (${HSO_4}^{1-}$, ${HSO_3}^{1-}$ and ${H_2PO_4}^{1-}$), which are acidic.

6.8-2. Acid-Base Properties of Salts

A salt can be acidic, basic, or neutral depending upon the relative acid and base strengths of the cation and anion.

1 ***Neutral Salts***: The reaction of a strong acid and a strong base produces a neutral salt. The cation in such reactions is a 1A metal and the anion is the conjugate base of a strong acid. Thus, both ions are neutral, which produces a neutral salt. The salt of a weak acid and a weak base can be neutral only when the K_a of the cation equals the K_b of the anion. Ammonium acetate is a neutral salt formed in the reaction of acetic acid and ammonia. It is neutral because the K_a of the ammonium ion equals the K_b of the acetate ion.

2 ***Basic Salts***: Basic Salts are produced in the reaction between a weak acid and a strong base. For example, NaCN is a basic salt that is produced by the reaction of HCN and NaOH. It is basic because sodium ion does not impact the acid-base properties, while the cyanide ion is a basic anion. Basic salts are produced in the reaction between a weak acid and a weak base if the K_b of the base is greater than the K_a of the acid. Ammonium sulfide is a basic salt because the K_b of the sulfide ion is greater than the K_a of the ammonium ion. Basic salts are the most common source of weak bases.

3 ***Acidic salts***: The reaction of a strong acid and a weak base produces acidic salts. NH_4Cl is an acidic salt produced by the reaction between HCl and NH_3. It is acidic because the ammonium ion is a weak acid, but chloride ion is the conjugate base of a strong acid, so it is not basic. Ammonium fluoride is acidic because the K_a of ammonium ion is greater than the K_b of the fluoride ion.

6.8-3. Predicting Salt Basicity and Acidity Exercise

EXERCISE 6.20:

Indicate whether a solution of each of the following salts is acidic, basic, or neutral.

$KClO_4$
- acidic
- basic
- neutral

Na_2S
- acidic
- basic
- neutral

NH_4NO_2
- acidic
- basic
- neutral

$(NH_4)_3PO_4$
- acidic
- basic
- neutral

$NH_4C_2H_3O_2$
- acidic
- basic
- neutral

6.8-4. Determining the pH of a Salt Exercise

EXERCISE 6.21:

What is the pH of a solution prepared by dissolving 3.5 g of KF ($M_m = 58.1$ g·mol^{-1}) in sufficient water to make 150 mL of solution? (The relevant pK_a can be found in the Acid-Base Table with pK_a.)

K_b for F^{1-} = ______________

mol F^{1-} = ______________ mol

$[F^{1-}]$ = ______________ M

$[OH^{1-}]$ = ______________ M

pOH = ______________

pH = ______________

6.9 Amphiprotic Salts

Introduction

Amphiprotic salts are both acids and bases, so their aqueous equilibria are slightly more complicated than those of weak acids or bases. In this section, we discuss the equilibria and give a simple expression for determining their pH.

Objective

- Determine the pH of a solution of an amphiprotic salt.

6.9-1. Acid Equilibrium

As shown in the figure, $HCO_3{}^{1-}$ is an amphiprotic substance because it can behave as both an acid and a base.

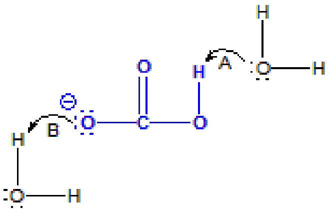


Figure 6.3: Amphiprotic Substances are Both Acids and Bases $HCO_3{}^{1-}$ is amphiprotic because its acidic proton can be lost (arrow A) or a lone pair on the oxygen with negative formal charge can accept a proton (arrow B).

It produces hydronium ion through its K_{a} reaction.

$$\mathrm{HCO_3^{1-} + H_2O \rightleftharpoons CO_3^{2-} + H_3O^{1+}} \quad K_{\mathrm{a2}} = \frac{[\mathrm{CO_3^{2-}}][\mathrm{H_3O^{1+}}]}{[\mathrm{HCO_3^{1-}}]} = 4.7\mathrm{e}{-11}$$

For every mole of hydronium produced, a mole of carbonate ion is also produced; i.e.,

$$[\mathrm{OH^{1-}}]_{\mathrm{produced}} = [\mathrm{CO_3^{2-}}]$$

The concentration of hydronium ion produced in this step equals the equilibrium concentration of its conjugate base, carbonate ion.

However, $\mathrm{HCO_3}^{1-}$ also produces hydroxide ion through its K_{b} reaction.

$$\mathrm{HCO_3^{1-} + H_2O \rightleftharpoons H_2CO_3 + OH^{1-}} \quad K_{\mathrm{b1}} = \frac{[\mathrm{H_2CO_3}][\mathrm{OH^{1-}}]}{[\mathrm{HCO_3^{1-}}]} = 2.3\mathrm{e}{-8}$$

For every mole of hydroxide ion produced, a mole of carbonic acid is also produced; i.e.,

$$[\mathrm{OH^{1-}}]_{\mathrm{produced}} = [\mathrm{H_2CO_3}]$$

Each mole of hydroxide ion that is produced consumes a mole of hydronium ion ($\mathrm{H_3O^{1+}} + \mathrm{OH^{1-}} \rightarrow 2\ \mathrm{H_2O}$). Thus, the following is true.

$$[\mathrm{OH^{1-}}]_{\mathrm{produced}} = [\mathrm{H_3O^{1+}}]_{\mathrm{consumed}} = [\mathrm{H_2CO_3}]$$

The equilibrium hydronium ion concentration is the following.

$$[\mathrm{H_3O^{1+}}] = [\mathrm{H_3O^{1+}}]_{\mathrm{produced}} - [\mathrm{H_3O^{1+}}]_{\mathrm{consumed}} = [\mathrm{CO_3^{2-}}] - [\mathrm{H_2CO_3}]$$

The concentrations of $\mathrm{CO_3}^{2-}$ and $\mathrm{H_2CO_3}$ can be obtained from K_{a2} and K_{b1}. After some algebra and the assumption that $[\mathrm{HCO_3}^{1-}] >> K_{\mathrm{a1}}$, we arrive at the result below.

$$\mathrm{pH} = \frac{1}{2}(\mathrm{p}K_1 + \mathrm{p}K_2) \qquad \text{pH of an Amphiprotic Salt} \qquad (6.13)$$

The pH of an amphiprotic substance is half-way between its pK_{a} (pK_2) and that of its conjugate acid (pK_1) so long as its concentration is much larger than the K_{a} of its conjugate acid, K_{a1}.

6.10 Exercises and Solutions

Links to view either the end-of-chapter exercises or the solutions to the odd exercises are available in the HTML version of the chapter.

CHAPTER 7 – MIXTURES OF ACIDS AND BASES

Introduction

In Chapter 6, we examined the equilibrium concentrations in solutions of acids and solutions of bases. In this chapter, we continue our discussion of acids and bases by focusing on the equilibrium concentrations of solutions formed by mixing acids and bases.

7.1. The Common-Ion Effect

Introduction

Predicting the effect on an equilibrium mixture caused by the presence of an ion that appears in the equilibrium but is introduced from a separate source is something we will need to do frequently. Qualitative predictions of this type are frequently made with the use of the common ion effect, the topic of this section.

Objectives

- Explain the common-ion effect and predict the effect of a common ion on an equilibrium mixture.

7.1-1. Definition

When solutions are prepared in such a way that there are two or more separate sources of an ion in an equilibrium, then that ion is referred to as a ***common ion***. In this and the following chapters, we will have the occasion to deal with the effect on an equilibrium mixture caused by the addition of a common ion. The effect of a common ion can readily be predicted with Le Châtelier's principle, which predicts that the composition of the mixture shifts to counteract the addition. Consequently, the common ion effect is summarized as the following:

- **Common Ion Effect**: The addition of a common ion to an equilibrium mixture shifts the equilibrium away from the side of the common ion.

Thus, the concentrations of those substances on the same side of the common ion decrease while those on the opposite side increase.

7.1-2. Mixture of a Weak Acid and a Strong Acid

We examine the effect that the presence of a strong acid has on the dissociation of a weak acid by considering the dissociation of 0.10 M HClO in water and then in a 0.05 M solution of a strong acid.

$$\mathrm{HClO + H_2O \rightleftharpoons ClO^{1-} + H_3O^{1+}} \quad K_\mathrm{a} = 3.5\mathrm{e}{-8}$$

We use Equation 6.6 to determine that $[\mathrm{ClO^{1-}}] = \{(0.10)(3.5\mathrm{e}{-8})\}^{1/2} = 5.9\mathrm{e}{-5}$ M, which is a measure of the extent of the dissociation of HClO in water. We now consider the dissociation of HClO in 0.05 M HCl. $\mathrm{H_3O^{1+}}$ is a common ion because it appears in the HClO equilibrium, but it has a separate source, the HCl. The common ion effect predicts that the presence of the common ion would reduce the concentrations of those substances on the same side of the equilibrium, so $[\mathrm{ClO^{1-}}]$ should drop, while it increases the concentrations of those substances on the opposite side, so [HClO] should increase. The solution is 0.10 M in HClO and 0.05 M in $\mathrm{H_3O^{1+}}$ initially, so the reaction table takes the following form:

	HClO	+	**$\mathrm{H_2O}$**	$\rightleftharpoons$	**$\mathrm{ClO^{1-}}$**	+	**$\mathrm{H_3O^{1+}}$**
initial	0.10				0		0.05
Δ	$-x$				$+x$		$+x$
equilibrium	$0.10 - x$				x		$0.05 + x$

The equilibrium constant expression is

$$K_\mathrm{a} = \frac{[\mathrm{ClO^{1-}}][\mathrm{H_3O^{1+}}]}{[\mathrm{HClO}]} = \frac{x(0.05 + x)}{(0.10 - x)}$$

$[ClO^{1-}]$ was 5.9e−5 M in water, and it will be less than that in the presence of acid, so we can assume that x is negligible in both the addition and the subtraction, and the equilibrium constant expression can be written as follows.

$$3.5\text{e}{-8} = \frac{x(0.05)}{(0.10)}$$

Solving the above leads to $x = [ClO^{1-}] = 7.0\text{e}{-8}\ M$, which is almost 1000 times less than in pure water. Furthermore, $[H_3O^{1+}] = 0.05 + x = 0.05\ M$, i.e., the hydronium ion concentration in a solution of a strong acid and a weak acid equals the concentration of the strong acid. We conclude the following.

The presence of a strong acid suppresses the dissociation of a weak acid to the point where the strong acid is essentially the sole source of hydronium ions.

7.1-3. Mixture of a Weak Base and a Strong Base

We examine the effect that the presence of a strong base has on the dissociation of a weak base by determining the concentration of HClO in 0.10 M KClO that has been dissolved in water and then in a 0.05 M solution of a strong base.

$$ClO^{1-} + H_2O \rightleftharpoons HClO + OH^{1-} \qquad K_\text{b} = 2.9\text{e}{-7}$$

We use Equation 6.9 to determine that $[HClO] = \{(0.10)(2.9\text{e}{-7})\}^{1/2} = 1.7\text{e}{-4}\ M$, which is a measure of the extent of the reaction in water. We now look at the reaction in 0.05 M NaOH. The common ion effect predicts that the presence of additional OH^{1-}, the common ion, will reduce [HClO] and increase $[ClO^{1-}]$. The solution is 0.10 M in ClO^{1-} and 0.05 M in OH^{1-} initially, so the reaction table takes the following form.

	$\mathbf{ClO^{1-}}$	+	$\mathbf{H_2O}$	$\rightleftharpoons$	**HClO**	+	$\mathbf{OH^{1-}}$
initial	0.10				0		0.05
Δ	$-x$				$+x$		$+x$
equilibrium	$0.10 - x$				x		$0.05 + x$

The equilibrium constant expression is

$$K_b = \frac{[HClO][OH^{1-}]}{[ClO^{1-}]} = \frac{x(0.05 + x)}{(0.10 - x)}$$

[HClO] was 1.7e−4 M in water, and it will be less than that in the presence of base, so we can assume that x is negligible in both the addition and the subtraction. The equilibrium constant expression is then the following.

$$2.9\text{e}{-7} = \frac{x(0.05)}{(0.10)}$$

Solving the above leads to $x = [HClO] = 5.8\text{e}{-7}\ M$, which is almost 1000 times less than in pure water. Furthermore $[OH^{1-}] = 0.05 + x = 0.05\ M$, i.e., the hydroxide ion concentration in a solution of a strong base and a weak base equals the concentration of the strong base. We conclude the following.

The presence of a strong base suppresses the dissociation of a weak base to the point where the strong base is essentially the sole source of hydroxide ions.

7.2. Buffers

Introduction

In Chapter 6, we discussed four types of acid-base solutions in some detail: strong acid, strong base, weak acid, and weak base. We now discuss buffers, the last type of acid-base solution to be considered. A buffer is defined in the dictionary as a "device that softens the shock of a blow." A chemical buffer serves much the same purpose: it softens the pH change resulting from the addition of a strong acid or base. For example, aspirin is an acid that can upset the stomach, but Bufferin® contains buffers to reduce the pH changes that ordinarily accompany the addition of an acid. Much of the maintenance involved in the upkeep of an aquarium involves maintaining proper buffer levels in the water to assure that the pH stays in a range that is safe for the fish. Blood is also buffered, which is why it maintains a pH of about 7.4 even though many acid-base reactions take place in it. In this section, we discuss the action of buffers.

Objectives

- Define a buffer and explain how it works.
- Choose an appropriate conjugate acid-base pair to use in the preparation of a buffer of a known pH.
- Determine the base to acid ratio required to produce a buffer of given pH.
- Determine the pH of a buffer given the amounts of acid and base present.
- Calculate the change in pH expected when a strong acid or base is added to a buffered solution.

7.2-1. Introduction to Buffers Video

A video or simulation is available online.

7.2-2. Definition

A ***buffer*** is a solution of a weak acid and its conjugate base in *comparable* and *appreciable* amounts. They are able to minimize changes in pH because they contain both a weak acid and a weak base. Thus, if a strong acid is added to a buffered solution, it reacts with the weak base component of the buffer, and if a strong base is added to a buffered solution, it reacts with the weak acid component of the buffer. Either way, the effect of the addition of hydroxide or hydronium ion on the solution is dramatically reduced because these strong acids and bases are converted to much weaker acids and bases by the action of the buffer.

7.2-3. Hydronium Ion Concentrations in Buffer Solutions

A buffer contains both the weak acid and the weak base, so both K_a and K_b must be satisfied, and either can be used to determine the composition of the equilibrium mixture. However, because pH is more common than pOH, we use the acid dissociation reaction to discuss buffered solutions because it contains the hydronium ion directly. Consider a hypochlorous acid/hypochlorite ion buffer in which the initial concentrations of the acid (c_a) and the base (c_b) are comparable. The reaction table for the acid dissociation of acid in the presence of the base has the following form:

	$\mathbf{HClO}$	+	$\mathbf{H_2O}$	$\rightleftharpoons$	$\mathbf{ClO^{1-}}$	+	$\mathbf{H_3O^{1+}}$
initial	c_a				c_b		0
$\boldsymbol{\Delta}$	$-x$				$+x$		$+x$
equilibrium	$c_\mathrm{a} - x$				$c_\mathrm{b} + x$		x

The equilibrium constant expression for the reaction is:

$$K_\mathrm{a} = \frac{[\mathrm{ClO^{1-}}][\mathrm{H_3O^{1+}}]}{[\mathrm{HClO}]} = \frac{(c_\mathrm{b} + x)x}{(c_\mathrm{a} - x)}$$

The presence of the conjugate base suppresses the dissociation of the acid, so x is negligible in both the addition and the subtraction. Consequently, the equilibrium constant expression can be written as the following:

$$K_\mathrm{a} = \frac{c_\mathrm{b} x}{c_\mathrm{a}}$$

Solving for the above for hydronium ion concentration (x), we obtain Equation 7.1.

$$[\mathrm{H_3O^{1+}}] = x = K_\mathrm{a}\frac{c_\mathrm{a}}{c_\mathrm{b}} = K_\mathrm{a}\frac{n_\mathrm{a}}{n_\mathrm{b}}$$

Hydronium ion Concentration in a Buffer Solution (7.1)

$c_\mathrm{a} = n_\mathrm{a}/V$ and $c_\mathrm{b} = n_\mathrm{b}/V$, and the volumes cancel in the ratio $c_\mathrm{a}/c_\mathrm{b}$. Thus, $c_\mathrm{a}/c_\mathrm{b} = n_\mathrm{a}/n_\mathrm{b}$, i.e., the ratio of the concentrations equals the ratio of the numbers of moles.

Taking the negative logarithms of both sides of Equation 7.1 we obtain the equation that is known as the Henderson-Hasselbalch equation,

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\left(\frac{c_\mathrm{b}}{c_\mathrm{a}}\right) = \mathrm{p}K_\mathrm{a} + \log\left(\frac{n_\mathrm{b}}{n_\mathrm{a}}\right)$$

Henderson-Hasselbalch Equation (7.2)

where the identity $\log(x/y) = -\log(y/x)$ has been used. Equation 7.2 is the most common method for determining the pH of a buffer.

7.2-4. Buffer pH Exercise

EXERCISE 7.1:

What is the pH of a solution that is 0.600 M potassium acetate and 0.750 M acetic acid?

(Refer to the Acid-Base Table with pK_a and Equation 7.2.)

pK_a = ______________

c_a = ______________ M

c_b = ______________ M

pH = ______________

7.2-5. Buffer Action Video

A video or simulation is available online.

7.2-6. Buffer Action Against Addition of Base

Buffers act to protect the solution from drastic pH changes resulting from the addition of hydronium or hydroxide ions. They do so by reacting with the added acid or base. However, **in order for the buffer to function properly, it must be the excess reactant**. Consider the case where x mmol OH^{1-} ion are added to a buffer solution that contains n_a mmol HClO and n_b mmol ClO^{1-}. The strong base reacts extensively with the weak acid in the buffer, so, as long as HClO is in excess, all of the hydroxide reacts. The reaction table has the following form:

	HClO	+	$\mathbf{OH^{1-}}$	$\rightleftharpoons$	$\mathbf{ClO^{1-}}$	+	$\mathbf{H_2O}$
initial	n_a		x		n_b		0
Δ	$-x$		$-x$		$+x$		$+x$
equilibrium	$n_\mathrm{a} - x$		~ 0		$n_\mathrm{b} + x$		x

Of course $[OH^{1-}]$ cannot be zero, which is why the approximate sign is used, but it will be very small compared to the weak base concentration. The above reaction table is valid, and the solution is a buffer only so long as there is sufficient acid to react with the base. In other words, an **appreciable amount of acid is required**. The resulting solution is a solution of a weak acid and its conjugate base, so it is still a buffer solution, and Equation 7.2 can still be used to determine its pH.

7.2-7. Strong Base–Buffer Worked Example

A video or simulation is available online.

7.2-8. Buffer Action with Strong Base Exercise

EXERCISE 7.2:

In a previous exercise, we determined that the pH of a buffer that is 0.600 *M* potassium acetate and 0.750 *M* acetic acid is 4.64.

What is the pH of a solution prepared by adding 10. mL of 6.0 M NaOH to 200. mL of this buffer?

First, complete the reaction table for the reaction of the weak acid with the strong base. Note that all entries are in mmol. (Refer to the Acid-Base Table with pK_a and Equation 7.2.)

	Reacting Acid	+	Reacting Base	→	Produced Base	+	Produced Acid	
		+		→		+		
initial								mmol
Δ								mmol
equilibrium								mmol

pH = ________________

7.2-9. Buffer Action Against Addition of Acid

Consider the case where x mmol of H_3O^{1+} ions are added to a buffer solution that contains n_a mmol HClO and n_b mmol ClO^{1-}. The strong acid reacts extensively with the weak base in the buffer, so, as long as ClO^{1-} is in excess, all of the hydronium reacts. The reaction table has the following form:

	ClO^{1-}	+	H_3O^{1+}	$\rightleftharpoons$	HClO	+	H_2O
initial	n_b		x		n_a		0
Δ	$-x$				$+x$		$+x$
equilibrium	$n_b - x$		~ 0		$n_a + x$		x

$[H_3O^{1+}]$ cannot be zero, which is why the approximate sign is used, but it will be very small compared to the weak acid concentration. The above reaction table is valid, and the solution is a buffer only so long as there is sufficient base to react with the acid. In other words, **an appreciable amount of base is required.** The resulting solution is a solution of a weak acid and its conjugate base, so it is still a buffer solution, and Equation 7.2 can still be used to determine its pH.

7.2-10. Buffer Action with Strong Acid Exercise

EXERCISE 7.3:

What is the pH of a solution prepared by adding 10. mL of 6.0 *M* HCl to 200. mL of the buffer?

Complete the reaction table for the reaction of the weak base with the strong acid in millimoles. (Refer to the Acid-Base Table with pK_a and Equation 7.2.)

	Reacting Base	+	Reacting Acid	→	Produced Acid	+	Produced Base	
		+		→		+		
initial								mmol
Δ								mmol
equilibrium								mmol

pH = ______________

7.2-11. Buffer Exercise

EXERCISE 7.4:

A buffer is prepared by dissolving 23.5 g of KNO_2 (M_m = 85.1 g·mol^{-1}) in 1.25 L of 0.0882 *M* HNO_2.

(a) What is the pH of the buffer?

n_a = ______________ mol

pK_a = ______________

n_b = ______________ mol

pH = ______________

(b) What would be the pH of the buffer solution after the addition of 22.8 mL of 1.45 *M* NaOH?

	Reacting Acid	+	Reacting Base	→	Produced Base	+	Produced Acid	
		+		→		+		
initial								mol
Δ								mol
equilibrium								mol

Use Equation 7.2 to determine the pH.

pH = ______________

7-2.12. Buffer Capacity

There must be appreciable amounts of the acid and its conjugate base in a buffer to assure that it has acceptable ***buffer capacity***, which is the amount of acid or base that can be added without destroying the effectiveness of the buffer. Thus, a buffer solution has a large buffer capacity if it contains a large number of moles of the weak acid and of the weak base.

7.2-13. Buffer Range

A buffer functions well when the addition of large amounts of acid or base result in only small pH changes. The pH range over which the buffer is effective is called the ***buffer range***. Figure 7.1 shows the relationship between pH of an acetic acid/acetate ion buffer and the mole fractions of the acid and the base. The buffer range is the pH range over which the mole fractions change most dramatically with pH (highlighted by the box in the figure).

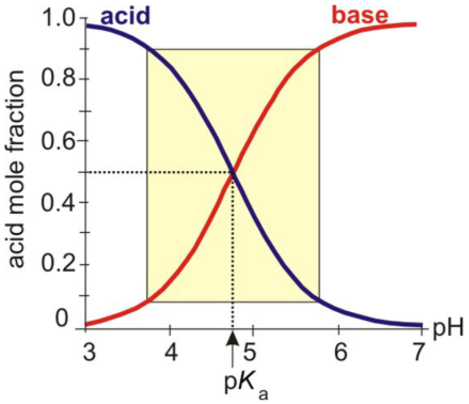


Figure 7.1: Effective Buffer Range The mole fractions of acetic acid and its conjugate base as a function of pH. The effective buffer range is indicated by the box. The pH of a buffer solution in which the two mole fractions are equal is equal to the pK_a of the acid.

The center of the buffer range is where the two mole fractions (or concentrations) are equal ($c_A/c_B = 1$). Application of Equation 7.2 and log 1 = 0 to the midpoint indicates that pH = pK_a. Thus, buffers are most effective at pH values near their pK_a.

As shown in Figure 7.1, buffers operate acceptably in the range where the mole fraction of the acid or base is in the range of 0.1 to 0.9, which means that $0.1 < c_a/c_b < 10$.

We conclude that a buffer is effective at a pH that is within one pH unit of its pK_a.

7.2-14. Preparing a pH = 7 Buffer Exercise

EXERCISE 7.5:

How would you prepare a pH = 7.00 buffer?

First, select the best buffer system for this pH.

$H_3PO_4/H_2PO_4^{1-}$ p$K_a = 2.12$
HNO_2/NO_2^{1-} p$K_a = 3.40$
$H_2PO_4^{1-}/HPO_4^{2-}$ p$K_a = 7.21$
NH_4^{1+}/NH_3 p$K_a = 9.25$
HPO_4^{2-}/PO_4^{3-} p$K_a = 12.32$

Next, use Equation 7.2 to determine $\log(n_b/n_a)$.

$\log(n_b/n_a) =$ ______________

Take the antilog to obtain the ratio.

$n_b/n_a =$ ______________

Assume you have 1.50 L of a 0.840 *M* solution of the acid and determine the number of moles of base that would have to be added to produce the buffer.

moles of acid present = ______________ mol

moles of base present = ______________ mol

7.2-15. Preparing a pH = 9.8 Buffer Exercise

EXERCISE 7.6:

How many moles of base should be added to 500. mL of 0.222 *M* acid to prepare a pH = 9.80 buffer solution?

First, select the best buffer system for this pH.

$H_3PO_4/H_2PO_4^{1-}$ $pK_a = 2.12$
HNO_2/NO_2^{1-} $pK_a = 3.40$
$H_2PO_4^{1-}/HPO_4^{2-}$ $pK_a = 7.21$
NH_4^{1+}/NH_3 $pK_a = 9.25$
HPO_4^{2-}/PO_4^{3-} $pK_a = 12.32$

Next, use Equation 7.2 to determine $\log(n_b/n_a)$.

$\log(n_b/n_a) =$ ______________

Take the antilog to obtain the ratio.

$n_b/n_a =$ ______________

Determine the number of moles of base that would have to be added to the acid.

moles of acid = ______________ mol

moles of base = ______________ mol

7.3. Acid-Base Composition from Reactant Amounts

Introduction

We have now treated five different types of acid-base solutions and shown how to determine $[H_3O^{1+}]$, $[OH^{1-}]$, and pH of each:

1 **Strong acid**: Strong acids dissociate completely, so $[H_3O^{1+}] = c_o$.

2 **Strong base**: Strong bases ($M(OH)_n$) dissociate completely, so $[OH^{1-}] = nc_o$.

3 **Weak acid**: Solve the K_a expression for $[H_3O^{1+}]$ using Equation 6.6.

4 **Weak base**: Solve the K_b expression for $[OH^{1-}]$ using Equation 6.9.

5 **Buffers**: Solve the K_a expression for $[H_3O^{1+}]$ using Equation 7.1 or solve directly for pH using Equation 7.2.

Thus, there are four types of acid-base reactions. (When buffers react, they do so as the weak acid or the weak base.)

1 weak acid–weak base

2 strong acid–strong base

3 weak acid–strong base

4 strong acid–weak base

In this section, we examine acid-base properties of the solutions that result from these reactions.

Objectives

- Write acid-base reactions and determine their equilibrium constants from the K_a's of the reacting and produced acids.
- Determine the concentrations of all species in a solution prepared by mixing a strong acid (or base) with a strong base (or acid) or a weak base (or acid).

Weak Acid–Weak Base Reactions

7.3-1. The Equilibrium Constant

Consider the following reaction.

$$\mathrm{HF} + \mathrm{OCl^{1-}} \rightarrow \mathrm{F^{1-}} + \mathrm{HOCl}$$

The equilibrium constant expression for the reaction is

$$K = \frac{[\mathrm{F^{1-}}][\mathrm{HOCl}]}{[\mathrm{HF}][\mathrm{OCl^{1-}}]}$$

Compare that with the expression obtained by dividing the K_a expression of the reacting acid (HF) by that of the produced acid (HOCl).

$$\frac{K_\mathrm{a}\ (\mathrm{HF})}{K_\mathrm{a}\ (\mathrm{HOCl})} = \frac{[\mathrm{H_3O^{1+}}][\mathrm{F^{1-}}]}{[\mathrm{HF}]} \times \frac{[\mathrm{HOCl}]}{[\mathrm{H_3O^{1+}}][\mathrm{OCl^{1-}}]} = \frac{[\mathrm{F^{1-}}][\mathrm{HOCl}]}{[\mathrm{HF}][\mathrm{OCl^{1-}}]}$$

Note that the hydronium ion concentrations cancel to produce the K_a expression, which is identical to the equilibrium expression for the reaction of HF with $\mathrm{OCl^{1-}}$ ion. Thus, the equilibrium constant for the reaction can be determined as shown below.

$$K = \frac{K_\mathrm{a}\ \text{of reacting acid HF}}{K_\mathrm{a}\ \text{of produced acid HOCl}} = \frac{7.2\mathrm{e}{-4}}{3.5\mathrm{e}{-8}} = 2.1\mathrm{e}{+4}$$

We conclude that the equilibrium constant for an acid-base reaction can be determined from the acid dissociation constants of the reacting and produced acids as follows.

$$K = \frac{K_\mathrm{a}\ (\text{reacting acid})}{K_\mathrm{a}\ (\text{produced acid})} \qquad \text{Equilibrium Constant for an Acid-Base Reaction} \qquad (7.3)$$

The produced acid is the conjugate acid of the reacting base. The strength of an acid is inversely proportional to the strength of its conjugate base, so the above expression indicates that the value of K depends upon the relative strengths of the reacting acid and base. If both are relatively strong, then both K_a (reacting acid) and K_b (reacting base) are large. However, if K_b (reacting base) is large, then K_a (produced acid) must be small, which makes the equilibrium constant of the reaction large.

7.3-2. Determining K Exercise

EXERCISE 7.7:

Determine the value of K for the following aqueous weak acid–weak base reactions.

Reaction	K_a (reacting acid)	K_a (produced acid)	K
$HNO_2 + F^{1-} \rightleftharpoons NO_2^{1-} + HF$			
$HCN + CH_3COO^{1-} \rightleftharpoons CN^{1-} + CH_3COOH$			
$NH_3 + HSO_4^{1-} \rightleftharpoons NH_4^{1+} + SO_4^{2-}$			

7.3-3. Mixing Exercise

EXERCISE 7.8:

What is the ${NO_2}^{1-}$ ion concentration in a solution prepared by mixing 75 mL of 0.10 M HNO_2 and 75 mL of 0.10 M KF? Fill in the reaction table with molar concentration, and use x to indicate the final concentration of ${NO_2}^{1-}$.

Use the Acid-Base Table with pK_a to determine the value of the equilibrium constant.

$K =$ ______________

The reaction table:

	Reacting Acid	+	Reacting Base	→	Produced Base	+	Produced Acid	
		+		→		+		
initial								mol
Δ								mol
equilibrium								mol

Set up the equilibrium constant expression. It is a perfect square, so take the square root of both sides to determine the answer.

$[NO_2^{1-}] =$ ______________ M

7.3-4. Overview of Extensive Reactions

The remainder of the acid-base reaction types all involve a strong acid and/or a strong base, so they are all extensive. Consequently, the limiting reactant is assumed to disappear completely, which means that there are no unknowns in the reaction table. We will use the following method in each case:

1 Write the chemical equation and construct the reaction table. We will use millimoles in the reaction table because the volumes are all given in milliliters, but molarities can also be used.

2 Identify the type of solution that results from the mixing based upon the equilibrium entries.

- Strong acid if the entry under $[H_3O^{1+}]$ is not zero. There can be no base present if there is some H_3O^{1+} because they would react, and a weak acid can be ignored in the presence of a strong acid.

  - Strong base if the entry under OH^{1-} is not zero. There can be no acid present if there is some OH^{1-} because they would react, and a weak base can be ignored in the presence of a strong one.
  - Weak acid if the only nonzero entry lies under a weak acid.
  - Weak base if the only nonzero entry lies under a weak base.
  - Buffer if the entries under both the weak acid and its conjugate base are nonzero.

3 Determine $[H_3O^{1+}]$, $[OH^{1-}]$, pH, or pOH using the equation appropriate to the solution type above.

We will apply the above method to each of the reaction types in the following sections.

7.3-5. Titration Curves

Recall from Section 2.4-5. that the equivalence point in an acid-base titration is that point where the number of moles of analyte in the initial flask equals the number of moles of titrant that are added, which is summarized as follows.

- **Equivalence Point:** moles acid = moles base, so $M_{\text{acid}} V_{\text{acid}} = M_{\text{base}} V_{\text{base}}$

The above expression was then used to determine M_{acid} from a known M_{base} and the known volumes.

We now examine the pH of the acid solution as a function of the volume of base that is added to generate the titration curve for the titration. A ***titration curve*** is a plot of the pH of the solution as a function of the volume of a titrant. The shape of the curve depends on the nature of both the acid and base, and we start by examining the titration of a strong acid with a strong base in the following video.

Strong Acid–Strong Base Reactions

7.3-6. Strong Acid–Strong Base Titration Video

A video or simulation is available online.

7.3-7. Method

Our first titration curve is for the titration of a strong acid with a strong base. We start out with n_a moles of acid and determine the pH after n_b moles of base have been added. The reaction is extensive, so there is essentially no limiting reactant present at equilibrium and the solution type is dictated solely by the reactant in excess. The solution type depends upon the relative values of n_a and n_b, and the following reaction table shows the case where the base is the limiting reactant:

	$\mathbf{H_3O^{1+}}$	**+**	$\mathbf{OH^{1-}}$	**→**	$\mathbf{H_2O}$	**+**	$\mathbf{H_2O}$
initial	n_a		n_b				
$\mathbf{\Delta}$	$-n_b$		$-n_b$				
equilibrium	$n_a - n_b$		~ 0				

The equilibrium solution is a strong acid that contains $n_a - n_b$ mol of acid in a total volume $V_{\text{total}} = V_{\text{acid}} + V_{\text{base}}$, so $[H_3O^{1+}] = (n_a - n_b)/V_{\text{total}}$.

At the equivalence point, $[H_3O^{1+}] = [OH^{1-}]$, so pH = 7.0 at 25 °C. Beyond the equivalence point, OH^{1-} is in excess and the equilibrium solution is one of a strong base. The following table summarizes these conclusions:

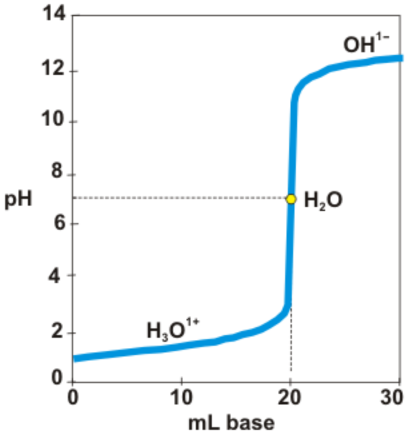
Moles	Solution Type	Moles of Excess Reactant	
$n_a > n_b$	strong acid	$n_a - n_b$ mol H_3O^{1+}	$pH = -\log[H_3O^{1+}]$
$n_a = n_b$	neutral	no excess reactant	$pH = 7.00$
$n_a < n_b$	strong base	$n_a - n_b$ mol OH^{1-}	$pOH = -\log[OH^{1-}]$

Table 7.1: Solution Types Resulting From Mixing a Strong Acid and a Strong Base
Solution type resulting from the reaction of n_a moles of a *strong acid* with n_b moles of a *strong base*.

7.3-8. SA–SB Titration Curve Exercise

EXERCISE 7.9:

A strong acid–strong base titration curve is shown below. The equivalence point (yellow circle) in a strong acid–strong base titration is pure water, so the pH is 7.00.



Determine the pH after the addition of 10.0 mL, 20.0 mL, and 30.0 mL of base in the titration of 20.0 mL of 0.100 *M* HCl with 0.100 *M* NaOH.

Put the number of millimoles of excess reactant present at equilibrium in the "xs" line or 0 if neither reactant is in excess.

	10.0 mL base	20.0 mL base	30.0 mL base	
n_a				mmol
n_b				mmol
xs				mmol
total volume				mL
xs concentration				*M*
pH				mmol

Weak Acid–Strong Base Reactions

7.3-9. Weak Acid–Strong Base Titration Video

A video or simulation is available online.

7.3-10. Weak Acid–Strong Base Titration Calculations

We now examine the titration curve for the titration of n_a moles of a weak acid HA with hydroxide ion.

Initially the solution is one of the weak acid HA, so if less than 5% of the acid reacts, we can write

$$[H_3O^{1+}] = (cK_a)^{1/2}$$

where c is the concentration of HA.

OH^{1-} is limiting reactant. The reaction table has the following form:

	HA	+	**OH^{1-}**	→	**A^{1-}**	+	**H_2O**
initial	n_a		n_b		0		
Δ	$-n_b$		$-n_b$		$+n_b$		
equilibrium	$n_a - n_b$		~ 0		n_b		

The equilibrium line contains both a weak acid and its conjugate base, so it is a buffer solution, and we can use the Henderson-Hasselbalch equation to determine the pH.

$$\text{pH} = \text{p}K_a + \log \frac{n_b}{n_a - n_b}$$

A special case in this region occurs at the **midpoint of the titration**; i.e., when $n_b = n_a/2$. In this special case the table would be

	HA	+	**OH^{1-}**	→	**A^{1-}**	+	**H_2O**
initial	n_a		$n_a/2$		0		
Δ	$-n_a/2$		$-n_a/2$		$+n_a/2$		
equilibrium	$n_a/2$		~ 0		$n_a/2$		

Thus, the resulting solution is still a buffer, but at the midpoint of the titration the number of moles of HA and A^{1-} are equal. The ratio $(n_b/n_a) = 1$ and $\log(1) = 0$, so the Henderson-Hasselbalch equation becomes,

$$\text{pH} = \text{p}K_a + \log(1) = \text{p}K_a$$

The pH at the midpoint of a titration of a weak acid with a strong base is equal to the pK_a of the acid.

At the **equivalence point**, $n_a = n_b = n$, so the reaction table would be

	HA	+	**OH^{1-}**	→	**A^{1-}**	+	H_2**O**
initial	n		n		0		
Δ	$-n$		$-n$		$+n$		
equilibrium	~ 0		~ 0		n		

The only equilibrium entry that is not zero is under the weak base, so the solution is a weak base solution that contains n mol of the weak base. The $[OH^{1-}]$ of this weak acid solution would be determined as follows:

$$[A^{1-}] = c_b = n/V_{\text{total}}$$
$$K_b = 1.0\text{e}{-14}/K_a$$
$$[OH^{1-}] = (c_b K_b)^{1/2}$$

Note that in the titration of a weak acid with a strong base, the solution at the equivalence point is that of a weak base, so pH > 7.

When **HA is the limiting reactant**, the reaction table is given as the following:

	HA	+	**OH^{1-}**	→	**A^{1-}**	+	**H_2O**
initial	n_a		n_b		0		
Δ	$-n_a$		$-n_a$		$+n_a$		
equilibrium	~ 0		$n_b - n_a$		n_a		

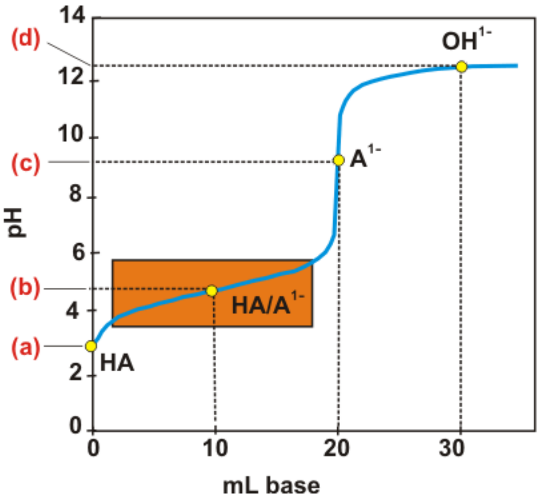
The equilibrium entry under OH^{1-} is not zero, so the solution is a strong base that contains $n_b - n_a$ mol of base. The presence of the weak base does not impact the pH of the solution due to the common ion effect, so we can write

$$[OH^{1-}] = \frac{n_b - n_a}{V_{\text{total}}}$$

7.3-11. WA–SB Titration Curve Exercise

EXERCISE 7.10:

Determine the pH at **points (a)–(d)** in the titration curve of 20.0 mL of 0.100 M $HC_2H_3O_2$ with 0.100 M NaOH shown below. The orange rectangle outlines the buffer region.



$n_a =$ __________ mmol acid initially

point (a) 0 mL ($n_b = 0$ – weak acid)

$[H_3O^{1+}] =$ __________ M pH = __________

point (b) 10.0 mL ($0 < n_b < n_a$: buffer)

$n_b =$ __________ mmol base added weak base produced = __________ mmol

weak acid remaining = __________ mmol pH = __________

point (c) 20.0 mL ($n_b = n_a$: equivalence point, weak base)

$n_b =$ __________ mmol base added $[CH_3COO^{1-}] =$ __________ M

weak acid remaining = __________ mmol $[OH^{1-}] =$ __________ M

weak base produced = __________ mmol pH = __________

point (d) 30.0 mL ($n_b > n_a$: strong base)

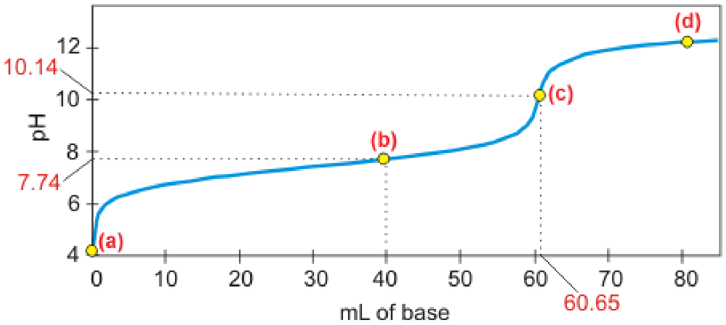
$n_b =$ __________ mmol base added $[OH^{1-}] =$ __________ M

excess $OH^{1-} =$ __________ mmol pH = __________

7.3-12. Using a Titration Curve Exercise

EXERCISE 7.11:

Consider the titration curve for the titration of 50.00 mL of an unknown weak acid with 0.122 *M* NaOH that is shown below.



Determine the concentration of the weak acid and its pK_a.

volume of base at the equivalence point: ____________ mL

mmol base added at equivalence point: ____________ mmol

mmol acid present initially: ____________ mmol

concentration of original acid: ____________

The solution type at **point (b)** is which of the following?

weak acid
strong base
weak base
buffer

mmol of hydroxide added at **point (b)** = ____________ mmol

equilibrium mmol weak acid at **point (b)** = ____________ mmol

equilibrium mmol conjugate base at **point (b)** = ____________ mmol

pK_a = ____________

7.3-13. The Shape of an Acid-Strong Base Titration Curve

The general shape of a titration curve consists of a sharp rise in pH in the vicinity of the equivalence point, but how steep the slope of the rise is depends upon the strength of the acid. Compare the titration curves for the titrations of 0.1 *M* HCl, 0.1 *M* $HC_2H_3O_2$, and 0.1 *M* HCN. In each case, the final pH approaches the pH of the strong base, which would be 13.0 in the case of 0.1 *M* NaOH. However, the pH at the midpoint of the titration varies with the acid strength. Thus, the pH is about 1.5 at the midpoint in the titration of 0.10 *M* HCl, but it equals the pK_a of the acid for a weak acid, which is 4.74 for $HC_2H_3O_2$ and 9.40 for HCN. Thus, the rise of the curve in the case of a strong acid is about 12 pH units, but it is only about 8 pH units for $HC_2H_3O_2$ and about 3 pH units for HCN. The less dramatic change in pH associated with very weak acids can make it difficult to get as a precise determination of the equivalence point.

7.3-14. Mixing Exercise

EXERCISE 7.12:

What is the pH of a solution prepared by mixing 34.0 mL of 0.250 M NaOH and 16.5 mL of 0.515 M $KHSO_4$?

The reaction table:

	$HSO_4{}^{1-}$	+	OH^{1-}	$\rightleftharpoons$	$SO_4{}^{2-}$	+	H_2O	
initial								mmol
Δ								mmol
equilibrium								mmol

The resulting solution type is which of the following?

weak acid
strong base
weak base
buffer

$[SO_4^{2-}] =$ ______________ M

$[OH^{1-}] =$ ______________ M

$K_b =$ ______________

pH = ______________

7.3-15. Polyprotic Acid–Strong Base Titration Video

A video or simulation is available online.

7.3-16. Polyprotic Acid–Strong Base

Polyprotic acids dissociate one proton at a time, and they are deprotonated by OH^{1-} ion one proton at a time. The loss of each proton gives rise to one equivalence point. The equilibrium constants for the individual dissociations are usually very different, so only one or two species usually have non-negligible concentrations in polyprotic acid solutions. Indeed, their equilibria are identical to those of monoprotic acids except that the base may be amphiprotic. Consider the titration of H_2A with a strong base. The following reaction table covers the reaction up to the first equivalence point.

	$\mathbf{H_2A}$	+	$\mathbf{OH^{1-}}$	$\rightarrow$	$\mathbf{HA^{1-}}$	+	$\mathbf{H_2O}$	
initial	n_a		n_b		0			mmol
Δ	$-n_b$		$-n_b$		$+n_b$			mmol
equilibrium	$n_a - n_b$		~ 0		$+n_b$			mmol

Thus, adding hydroxide to H_2A produces a solution that can be treated as an H_2A/HA^{1-} buffer. At the first equivalence point, the solution is that of an amphiprotic substance, so we can use Equation 6.13, which is shown below, to determine its pH.

$$\text{pH} = 1/2(\text{p}K_1 + \text{p}K_2)$$

The following reaction table then covers the reaction between the first and second equivalence points. Note that the first titration creates n_a mmol of HA^{1-}, so we use that for the initial amount of weak acid. n_b is the number of mmoles of base added after the first equivalence point.

	$\mathbf{HA^{1-}}$	$+$	$\mathbf{OH^{1-}}$	$\rightarrow$	$\mathbf{A^{2-}}$	$+$	$\mathbf{H_2O}$	
initial	n_a		n_b		0			mmol
$\boldsymbol{\Delta}$	$-n_\mathrm{b}$		$-n_\mathrm{b}$		$+n_\mathrm{b}$			mmol
equilibrium	$n_\mathrm{a} - n_\mathrm{b}$		~ 0		$+n_\mathrm{b}$			mmol

Adding hydroxide to HA^{1-} produces a solution that can be treated as an HA^{1-}/A^{2-} buffer. At the second equivalence point, the solution is that of the weak base A^{2-}. After the second equivalence point the solution is a strong base. The resulting titration curve is shown in Figure 7.2.

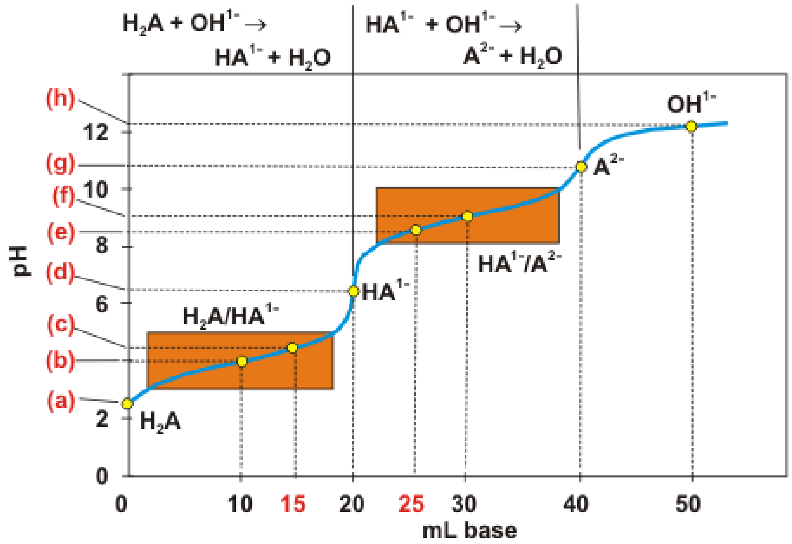


Figure 7.2: Diprotic acid–Strong base Titration Curve The rectangles outline the two buffer ranges. The points on the graph represent the following: **(a)** weak acid H_2A; **(b)** 1st midpoint so $pH = pK_1$; **(c)** H_2A/HA^{1-} buffer; **(d)** 1st equivalence point, amphiprotic HA^{1-}; **(e)** HA^{1-}/A^{2-} buffer; **(f)** 2nd midpoint so $pH = pK_2$; **(g)** 2nd equivalence point, weak base A^{2-}; and **(h)** strong base solution.

7.3-17. Polyprotic Titration Curve Exercise

EXERCISE 7.13:

Determine the pH at various points in the titration curve for the titration of 20.0 mL of 0.100 *M* H_2A (pK_1 = 4.00, pK_2 = 9.00) with 0.100 *M* NaOH. The titration curve is shown in Figure 7.2. You should construct a reaction table at each point, determine the solution type, and then the pH.

$n_a =$ ______________ mmol

point (b) 10.0 mL (midway to first equivalence point)

pH = ______________

point (c) 15.0 mL (buffer region of first equivalence point)

$n_b =$ ______________ mmol

eq mmol $H_2A =$ ______________ mmol

eq mmol $HA^{1-} =$ ______________ mmol

pH = ______________

point (d) 20.0 mL (solution of amphiprotic substance HA^{1-})

pH = ______________

point (e) 25.0 mL (buffer region of second equivalence point)

$n_b =$ ______________ mmol from first eq point

eq mmol $HA^{1-} =$ ______________ mmol

eq mmol $A^{2-} =$ ______________ mmol

pH = ______________

point (f) 30.0 mL (midway to second equivalence point)

pH = ______________

Strong Acid–Weak Base Reactions

7.3-18. Summary of Strong Acid–Weak Base Reactions

The reaction between a strong acid and a weak base is treated analogously with that between a weak acid and a strong base. The nature of the resulting solution depends upon the relative number of moles of acid (n_a) and base (n_b).

$\boldsymbol{n_a < n_b}$**:** acid is limiting reactant

	H_3O^{1+}	+	A^{1-}	→	HA	+	H_2O	
equilibrium	~ 0		$n_b - n_a$		n_a			**Buffer**

$\boldsymbol{n_a = n_b = n}$**:** acid and base in stoichiometric amounts

$$\begin{array}{lccccccccl} & \mathbf{H_3O^{1+}} & + & \mathbf{A^{1-}} & \rightarrow & \mathbf{HA} & + & \mathbf{H_2O} & & \\ \textbf{equilibrium} & \sim 0 & & \sim 0 & & n & & & & \textbf{Weak Acid} \end{array}$$

$\boldsymbol{n_a > n_b}$**:** base is limiting reactant

$$\begin{array}{lccccccccl} & \mathbf{H_3O^{1+}} & + & \mathbf{A^{1-}} & \rightarrow & \mathbf{HA} & + & \mathbf{H_2O} & & \\ \textbf{equilibrium} & n_a - n_b & & \sim 0 & & n_a & & & & \textbf{Strong Acid} \end{array}$$

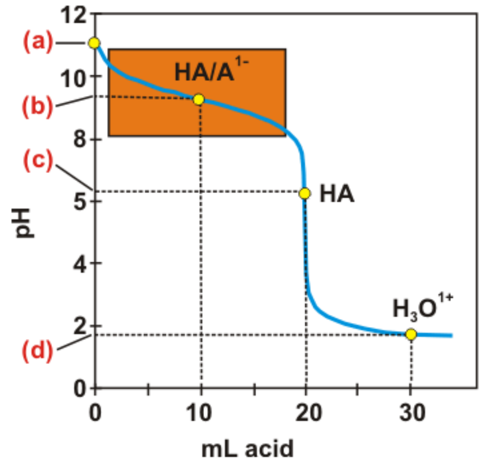
7.3-19. Strong Acid–Weak Base Titration

A video or simulation is available online.

7.3-20. Strong Acid–Weak Base Titration Curve

EXERCISE 7.14:

Determine the pH at each of the following points in the titration curve for the titration of 20.0 mL of 0.100 *M* NH_3 with 0.100 *M* HCl.



- **(a)** $n_a = 0$: a solution of the weak base NH_3.
- **(b)** $n_a < n_b$: a buffer solution. pH = pK_a at **point (b)**.
- **(c)** $n_a = n_b$: the equivalence point is a solution of the weak acid HA.
- **(d)** $n_a > n_b$: excess H_3O^{1+} makes the solution a strong acid.

initial mmoles of weak base, $n_b =$ ______________ mmol

point (a) 0.0 mL (weak base) pH = ______________

point (b) 10.0 mL (buffer) pH = ______________

point (c) 20.0 mL (equivalence point, weak acid) pH = ______________

point (d) 30.0 mL (strong acid) pH = ______________

Making Buffers by Reaction

7.3-21. Three Ways to Make Buffers

We have now seen three ways in which buffers can be made:

1 mixing the acid and its conjugate base directly in the appropriate ratio to achieve the required pH
2 adding a strong acid to an excess of weak base until the required pH is achieved
3 adding a strong base to an excess of weak acid until the required pH is achieved

Examples of the first method were presented in CAQS Section 7.2, and an example of the second method is presented in the following section.

7.3-22. Preparing a Buffer with a Strong Acid and a Weak Base

EXERCISE 7.15:

How many mL of 0.26 M HCl must be added to 500. mL of 0.12 M NH_3 to make a pH = 10.00 buffer?

First, construct the reaction table using x for the number of mmols of H_3O^{1+} that are required.

Answer the following questions about the pH = 10.00 solution to obtain the volume of acid that would be needed.

pK_a (Acid-Base Table with pK_a) ________

mmol NH_3 in initial solution ________

$\log\left(\dfrac{\text{mmol NH}_3}{\text{mmol NH}_4^{1+}}\right)$ ________

$\dfrac{\text{mmol NH}_3}{\text{mmol NH}_4^{1+}}$ ________

mmol ${NH_4}^{1+}$ (in terms of x) in equilibrium mixture ________

mmol NH_3 (in terms of x) in equilibrium mixture ________

Use the ratio and mmols to solve for x. ________ mmol H_3O^{1+}

volume of 0.26 M HCl required ________ mL

7.4. Acid-Base Composition from Equilibrium pH

Introduction

Solutions are frequently prepared by adjusting the solution pH to a desired level rather than adding a known volume of acid or base. For example, the easiest way to make a buffer of a desired pH is to decide on the proper acid-base pair, make a solution that contains an appreciable amount of the acid or base and then add a strong base or acid until the solution has the required pH. The question then becomes: Once you have attained the appropriate pH, what are the concentrations of the acid(s) and base(s) in the solution? We answer that question in this section.

7.4-1. Method

One equation is required for each unknown concentration in a solution, so determining $[H_2X]$, $[HX^{1-}]$, and $[X^{2-}]$ in a solution of a diprotic acid involves three equations and three unknowns. The equilibrium constant expressions for K_1 and K_2 are two of the equations. The third equation is mass balance, which is based on the fact that even though reaction may take place in solution, the total amount of X does not change; i.e., $c_o = [H_2X] + [HX^{1-}] +$

$[X^{2-}]$. Fortunately, chemistry can often be used to simplify the algebra because only one or two of the concentrations are usually appreciable at any pH. Once the one or two appreciable concentrations have been determined at a given pH, the other concentrations can be readily determined from the given K values, c_o, and pH. Thus, our first task is to identify these one or two species that dominate the concentration. We do so by assuming that the concentration of a substance is negligible if it is less than 1% of the concentration of either its conjugate acid or base, so

- the acid concentration is negligible if $[\text{base}]/[\text{acid}] > 100$, and
- the base concentration is negligible if $[\text{base}]/[\text{acid}] < 0.01$

We use the above conditions in the Henderson-Hasselbalch equation to conclude the following.

- the acid is negligible if $\text{pH} > \text{p}K_\text{a} + \log(100) = \text{p}K_\text{a} + 2$
- the base is negligible if $\text{pH} < \text{p}K_\text{a} + \log(0.01) = \text{p}K_\text{a} - 2$

The concentration of an acid and its conjugate base are both appreciable at pH's within 2 pH units of the pK_a of the acid, but only the acid can be appreciable below this pH range, and only the base can be appreciable above it.

7.4-2. Concentrations vs. pH

Monoprotic Acid: The concentrations of CH_3COOH and CH_3COO^{1-} as a function of pH are shown in Figure 7.3. The pK_a of CH_3COOH is 4.7, so $[CH_3COOH] = c_o$ if $\text{pH} < 2.7$ $(\text{pH} = 4.7 - 2)$, but $[CH_3COO^{1-}] = c_o$ if $\text{pH} > 6.7$ $(4.7 + 2)$. At intermediate pH values $(2.7 < \text{pH} < 6.7)$, neither concentration is negligible, so we use $[CH_3COOH] + [CH_3COO^{1-}] = c_o$. Thus, the solution is treated as a buffer in the yellow region of the figure, as an acetic acid solution at lower pH, and as an acetate ion solution at higher pH.

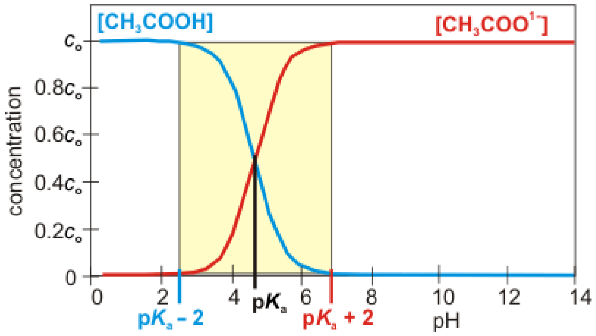


Figure 7.3: Concentrations of acetic acid and acetate ion as a function of pH. The [acid] $\sim c_o$ and [base] ~ 0 at pH's below $(\text{p}K_\text{a} - 2)$, but [acid] ~ 0 and [base] $\sim c_o$ at pH's above $(\text{p}K_\text{a} + 2)$. The concentrations of both substances are appreciable only in the yellow region. $\text{p}K_\text{a} = 4.74$

Diprotic Acid: The case of the diprotic acid H_2S $(\text{p}K_1 = 7.0,\ \text{p}K_2 = 12.9)$ is shown in Figure 7.4. The two yellow boxes represent the two pH ranges $(\text{p}K_\text{a} \pm 2)$ in which both the acid (H_2S or HS^{1-}) and its conjugate base (HS^{1-} or S^{2-}) are appreciable. Only one substance is appreciable at all other values of pH.

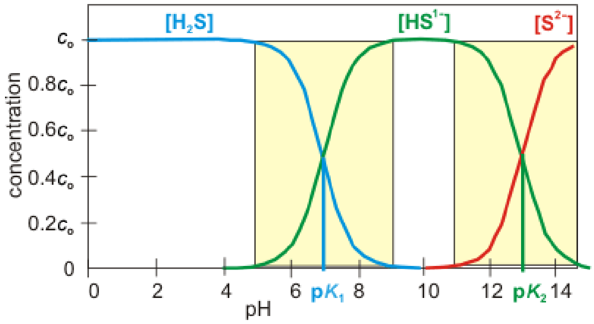


Figure 7.4: Concentrations of hydrosulfuric acid, hydrogen sulfide ion, and sulfide ion as a function of pH. The concentrations of two substances are comparable and appreciable in the yellow boxes, but only one component is appreciable outside. The pH ranges of the yellow boxes are from $\text{pH} = \text{p}K_\text{a} - 2$ to $\text{pH} = \text{p}K_\text{a} + 2$.

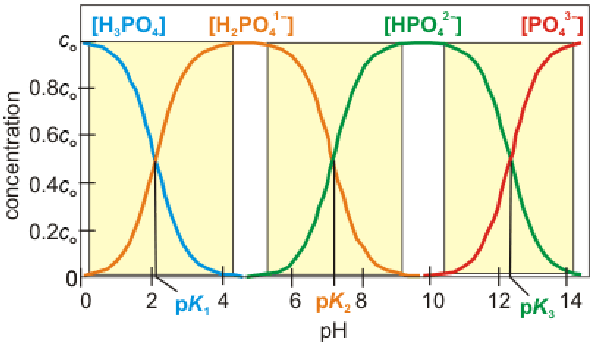
Triprotic Acid: The example of a triprotic acid, H_3PO_4, is considered in the following exercise. Even though there are four concentrations to determine, no more than two are appreciable at any pH.

7.4-3. Triprotic Exercise

<u>EXERCISE 7.16</u>:

Solid NaOH is dissolved in a 0.10 M H_3PO_4 solution. Assume no volume change and calculate the concentrations of the phosphorus containing species at each pH. Use the Acid-Base Table with pK_a to get the pK_a's.

p$K_1 =$ ________ p$K_2 =$ ________ p$K_3 =$ ________



pH = 7.00

The number of appreciable concentrations is ________

$[H_2PO_4^{1-}] =$ ________ M

$[H_3PO_4] =$ ________ M

$[HPO_4^{2-}] =$ ________ M

$[PO_4^{3-}] =$ ________ M

pH = 10.00

The number of appreciable concentrations is ________

$[HPO_4^{1-}] =$ ________ M

$[H_2PO_4^{1-}] =$ ________ M

$[PO_4^{3-}] =$ ________ M

$[H_3PO_4] =$ ________ M

7.4-4. Combining Equilibria

While the protons of a polyprotic acid are removed individually, the equilibria can be combined to eliminate concentrations of intermediate ions. For example, consider the dissociation equilibria of H_2S.

$$\begin{array}{ll} H_2S + H_2O \rightleftharpoons HS^{1-} + H_3O^{1+} & K_1 = 1.0 \times 10^{-7} \\ HS^{1-} + H_2O \rightleftharpoons S^{2-} + H_3O^{1+} & K_2 = 1.3 \times 10^{-13} \end{array}$$

Adding the above chemical equations results in the cancellation of the HS^{1-} ion concentration and eliminates it from the equilibrium constant expression. The equilibrium constant for the reaction that results from the addition of two equilibria equals the product of the two equilibrium constants, so we can write the following for the loss of both protons in one equation.

$$H_2S + 2H_2O \rightleftharpoons S^{2-} + 2H_3O^{1+} \quad K_{12} = \frac{[S^{2-}][H_3O^{1+}]^2}{[H_2S]} = K_1K_2 = 1.3 \times 10^{-20}$$

The above affords us a quick way to determine the concentration of sulfide ion in a solution where both the H_3O^{1+} and H_2S concentrations are known. However, the H_2S concentration is its equilibrium concentration, not its makeup concentration. Referring to Figure 7.4, we conclude that

- The above K_{12} expression is best used for solutions in which pH < 5, because above this pH, the H_2S concentration is no longer equal to the makeup concentration and would have to be determined with K_1.

7.4-5. Exercise

EXERCISE 7.17:

Sulfide ion is used to selectively precipitate metal ions from solution, but the concentration of the sulfide ion must be adjusted carefully to select which metals will precipitate. This is done by adjusting the pH of the solution.

(a) What is $[S^{2-}]$ in a saturated solution of H_2S (0.10 M) at a pH = 3.00?

$[S^{2-}]$ = ______________ M

(b) At what pH will the sulfide ion concentration be 1.0×10^{-12} M?

pH = ______________

7.5. Acid-Base Indicators

Introduction

Acid-base indicators change color in small ranges of pH change and indicate the endpoint of an acid-base titration, but they too are weak acids and bases.

7.5-1. Acid-Base Indicators

Acid-base ***indicators*** are organic dyes that are also weak acids. They function because the weak acid (HIn) and its conjugate base (In^{1-}) differ in color. Consider the K_a reaction of the indicator HIn.

$$HIn + H_2O \rightleftharpoons +In^{1-} + H_3O^{1+}$$

The K_a expression is

$$K_a = \frac{[In^{1-}][H_3O^{1+}]}{[HIn]}$$

Solving the above for the ratio of the concentrations of the base and the acid:

$$\frac{[In^{1-}]}{[HIn]} = \frac{K_a}{[H_3O^{1+}]}$$

The human eye perceives the color of In^{1-} when the ratio is greater than 10 and the color of HIn if the ratio is less than 0.1. In order to change the ratio from 0.1 to 10, the hydronium ion concentration must decrease by a factor of 100, which means that the pH must increase by 2 pH units. For this reason, most indicators have a useful range of about 2 pH units. Thus, a good indicator has a K_a that is close to the hydronium ion concentration at the equivalence point. Alternatively, **a good indicator has a pK_a that is close to the pH at the equivalence point of the titration.** The following table gives the useful range of some common acid-base indicators.

Indicator	**pH Range**	**Color Change**
Methyl violet	0.0 − 1.6	yellow → blue
Thymol blue	1.2 − 2.8	red → yellow
Methyl orange	3.2 − 4.4	red → yellow
Bromocresol green	3.8 − 5.4	yellow → blue
Alizarin	5.4 − 6.6	colorless → yellow
Bromothymol blue	6.0 − 7.6	yellow → blue
Phenolphthalein	8.2 − 10.0	colorless → pink
Alizarin yellow R	10.1 − 12.0	yellow → red

Table 7.2: Some Common Indicators The pH range and color change of selected acid-base indicators.

7.5-2. Titration Exercise

EXERCISE 7.18:

The titration of 25.00 mL of a weak monoprotic acid HA requires 35.22 mL of 0.1095 *M* NaOH to reach the equivalence point. The pH of the solution was 5.26 after the addition of 20.00 mL of the base.

What is the concentration of HA in the original solution?

base added at the equivalence point = ______________ mmol

HA in the original HA solution = ______________ mmol

[HA] = ______________ *M*

What is the pK_a of the acid?

A^{1-} present at the 20.00 mL point of the titration = ______________ mmol

HA present at the 20.00 mL point of the titration = ______________ mmol

if the pH at this point is 5.26, the pK_a = ______________

What is the pH at the equivalence point?

the concentration of A^{1-} at the equivalence point is $[\text{A}^{1-}]$ = ______________

the pK_b of A^{1-} is pK_b = ______________

the K_b of A^{1-} is K_b = ______________

the concentration of hydroxide at the equivalence point is $[\text{OH}^{1-}]$ = ______________ *M*

the pH at the equivalence point is pH = ______________

What indicator in Table 7.2 would be best to use for this titration? (Enter the first four letters.)

____

7.6. Exercises and Solutions

Links to view either the end-of-chapter exercises or the solutions to the odd exercises are available in the HTML version of the chapter.

CHAPTER 8 – EQUILIBRIA CONTAINING METAL IONS

Introduction

Several different equilibria must be considered when dealing with aqueous metal ions:

- Metal ions are Lewis acids, so they are involved in acid-base equilibria.
- As Lewis acids, they can react with other Lewis bases to form complex ions.
- Many metal ions form sparingly soluble salts, so solubility equilibria must also be considered.

In this chapter, all three of these types of equilibria are considered.

8.1 Acid-Base Equilibria

Introduction

While metal ions rarely have protons to donate as required by the Brønsted acid definition, they can accept electron pairs to form covalent bonds, which makes them acidic by the Lewis definition. Thus, an aqueous solution of iron(III) nitrate is acidic even though it contains no protons.

Objectives

- Explain the acidity of metal ions and write the acid-dissociation reaction associated with the acidity.

8.1-1. Metal Ions as Acids

Metal ions form acidic solutions because the positive charge on the metal ion weakens the O–H bonds of the bound water molecules.

$Fe(NO_3)_3$ is a strong electrolyte that dissociates completely into Fe^{3+} and ${NO_3}^{1-}$ ions. The small, highly charged iron(III) ion interacts with the surrounding water molecules in a Lewis acid-base reaction to produce ${Fe(H_2O)_6}^{3+}$, the octahedral ion in Figure 8.1. Ions, such as ${Fe(H_2O)_6}^{3+}$, that consist of a metal ion bound to several molecules or anions are called ***complex ions***, and the bound molecules or anions are referred to as ***ligands***. The positive charge of the central metal ion withdraws electron density from the O–H bonds, which weakens them and makes the water ligands stronger acids.

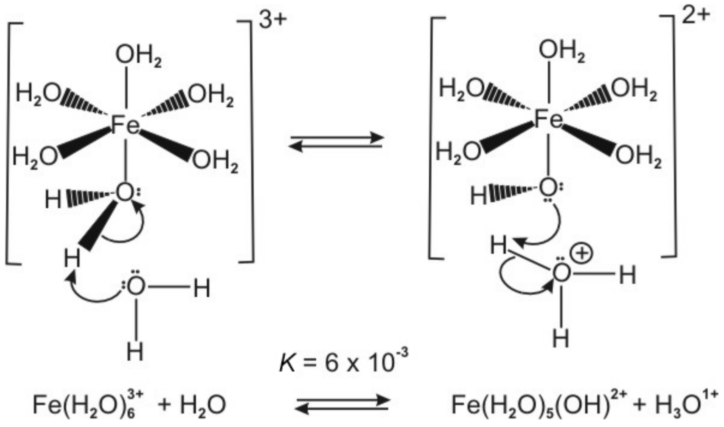


Figure 8.1: Acidity of Metal Ions

Thus, the acidity of Fe^{3+} ions arises from the following reaction:

$$Fe(H_2O)_6^{3+} + H_2O \rightleftharpoons [Fe(H_2O)_5OH]^{2+} + H_3O^{1+} \qquad K = 6e{-}03$$

which is the reaction of a weak acid with water, so the equilibrium constant is the K_a of the weak acid $\text{Fe(H}_2\text{O)}_6{}^{3+}$. Note that $\text{Fe(H}_2\text{O)}_6{}^{3+}$ is a stronger acid than acetic acid (K_a = 1.8e−05). The K_a values of several hydrated metal ions are listed in the table.

Hydrated Metal Ion	$\boldsymbol{K_\text{a}}$
$\text{Fe(H}_2\text{O)}_6^{3+}$	6e−03
$\text{Al(H}_2\text{O)}_6^{3+}$	1e−05
$\text{Cu(H}_2\text{O)}_6^{2+}$	3e−08
$\text{Zn(H}_2\text{O)}_6^{2+}$	1e−09
$\text{Ni(H}_2\text{O)}_6^{2+}$	1e−10

Table 8.1: Acid Dissociation Constants of Hydrated Metal Ions

8.2 Dissolution and the Solubility Product Constant

Introduction

Calcium carbonate (also known as limestone) is a slightly soluble salt that is responsible for scale in containers of hard water. In addition, caves and the unusual structures in them called stalactites and stalagmites are the result of dissociation and subsequent precipitation of calcium carbonate. This important dissociation process is represented in the following equilibrium:

$$\text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq) \qquad\qquad K = [\text{Ca}^{2+}][\text{CO}_3^{2-}]$$

This type of process, the equilibrium between a solid and its ions in solution, is an important one and forms the topic of this section.

Objectives

- Write the dissociation reaction of a slightly soluble salt.
- Write the expression for the solubility product constant, K_sp, of a given salt.
- Calculate the solubility of an ionic compound given its K_sp value, and vice versa.
- Calculate the solubility of an ionic compound in the presence of one of its ions.

8.2-1. The Solubility Product

The equilibrium between a solid and its solution is an important one. Indeed, it is so important that the equilibrium is given a special symbol and name: the ***solubility product constant*** (K_sp). Consider the equilibrium between solid silver chloride and its solution: $\text{AgCl} \rightleftharpoons \text{Ag}^{1+} + \text{Cl}^{1-}$. The activity of the solid is unity, so the form of the equilibrium constant, K_sp, for the reaction is $K_\text{sp} = [\text{Ag}^{1+}][\text{Cl}^{1-}]$. It is called the solubility product constant because it is simply a product of concentrations that indicates the solubility of the solid.

Most slightly soluble salts contain basic anions, which are involved in both acid-base equilibria with water and salt dissolution equilibria with metal ions. This can lead to a complicated set of equilibria in the case of fairly strong bases such as $\text{CO}_3{}^{2-}$ and $\text{PO}_4{}^{3-}$. Consequently, our discussions of solubility in water centers on the solubility of neutral or only weakly basic anions, such as Cl^{1-} and $\text{SO}_4{}^{2-}$. The reaction table for the dissociation of Ag_2SO_4 in water has the following form:

	$\mathbf{Ag_2SO_4}(s)$	$\rightleftharpoons$	$\mathbf{2\ Ag^{1+}}$	$+$	$\mathbf{SO_4^{2-}}$	$\boldsymbol{K_\text{sp} = 1.4 \times 10^{-5}}$
initial	enough		0		0	M
$\boldsymbol{\Delta}$			$+2x$		$+x$	M
equilibrium	some		$2x$		x	M

where x is the molar solubility of silver sulfate. The activity of a solid is unity, so it does not enter into the equilibrium constant expression. Consequently, the amount of solid is irrelevant so long as there is enough of the solid initially to assure that there is some solid present at equilibrium. The K_sp expression is

$$K_{\text{sp}} = 1.4 \times 10^{-5} = [\text{Ag}^{1+}]^2[\text{SO}_4^{2-}] = (2x)^2(x) = 4x^3$$

Solving the above expression for x, we obtain the molar solubility of silver sulfate and the ion concentrations in a saturated solution in terms of the solubility product constant.

$$x = \sqrt[3]{\frac{K_{\text{sp}}}{4}} = [\text{SO}_4^{2-}] = \frac{1}{2}[\text{Ag}^{1+}]$$

Substituting $1.4 \times 10^{-5} = K_{\text{sp}}$, we obtain the following:

- molar solubility of silver sulfate; $x = 0.015\ M$
- $[\text{SO}_4{}^{2-}] = x = 0.015\ M$
- $[\text{Ag}^{1+}] = 2x = 0.030\ M$

We can check our calculation by substituting concentrations back into the K_{sp} expression:

$$K_{\text{sp}} = [\text{Ag}^{1+}]^2[\text{SO}_4^{2-}] = (0.030)^2(0.015) = 1.4\text{e}{-05}$$

K_{sp} values can be found in Selected Solubility Product Constants in the Resources.

8.2-2. K_{sp} from Solubility Exercise

EXERCISE 8.1:

What is the K_{sp} of MgF_2 (M_m = 62.3 g/mol) if its solubility is 7.6 mg/100. mL?

The molar solubility of MgF_2 = ______________ M

$[\text{Mg}^{2+}]$ = ______________ M $[\text{F}^{1-}]$ = ______________ M K = ______________

8.2-3. K_{sp} from pH Exercise

EXERCISE 8.2:

What is the K_{sp} of Fe(OH)_2 if the pH of a saturated solution is 9.07? Watch out for rounding errors!

$[\text{OH}^{1-}]$ = ______________ M $[\text{Fe}^{2+}]$ = ______________ M K = ______________

8.2-4. Solubility from K_{sp} Exercise

EXERCISE 8.3:

The K_{sp} of AgI is 8.3e−17. What is its molar solubility?

Molar solubility = ______________ M

8.2-5. K_{sp} and Strong Bases

Let us now determine the solubility of the salt of Ag_3PO_4; $K_{\text{sp}} = 2.6 \times 10^{-18}$.

The reaction table for the dissolution has the following form:

	$\mathbf{Ag_3PO_4}(s)$	$\rightleftharpoons$	$\mathbf{3\ Ag^{1+}}$	$+$	$\mathbf{PO_4^{3-}}$
initial	enough		0		0
Δ			$+3x$		$+x$
equilibrium	some		$3x$		x

$$K_{\text{sp}} = [\text{Ag}^{1+}]^3[\text{PO}_4^{3-}] = (3x)^3(x) = 27x^4$$

Solving $27x^4 = 2.6 \times 10^{-18}$ for x, we obtain a solubility of 1.8×10^{-5} M.

However, the measured solubility is 1.5×10^{-4}. Thus, the actual solubility is over eight times greater than that determined with K_{sp}. The K_{sp} is correct, and it is still obeyed. However, $PO_4{}^{3-}$ is a fairly strong base, so some of the $PO_4{}^{3-}$ that is produced by the dissolution reacts with water to produce $HPO_4{}^{2-}$ and OH^{1-}. Therefore, $K_{\text{sp}} = [\text{Ag}^{1+}]^3[\text{PO}_4^{3-}]$ is still valid, but the loss of $PO_4{}^{3-}$ in the reaction with water means that the equality $3[\text{Ag}^{1+}] = [\text{PO}_4^{3-}]$ is no longer valid. This is why we restrict our discussion of solubility to neutral or weakly basic salts only. We treat the solubility of Ag_3PO_4 in more detail in Section 8.4.

8.2-6. Cation:Anion Ratios in K_{sp}

The preceding examples demonstrate that the form of the K_{sp} expression in terms of the molar solubility of the salt (x) depends only upon the cation:anion ratio in the salt. The K_{sp} expressions for the common ratios are given below.

Cation:Anion Ratio	K_{sp}
1:1	x^2
1:2 or 2:1	$4x^3$
1:3 or 3:1	$27x^4$
2:3 or 3:2	$108x^5$

Table 8.2: K_{sp} expressions in terms of molar solubilities (x) for salts with common cation:anion ratios

The relative solubilities of salts with the same cation:anion ratios can be obtained by simply looking at the magnitudes of their K_{sp}'s. However, when the ratios are different, you must determine the value of x.

8.2-7. Determining Relative Solubilities Exercise

EXERCISE 8.4:

List the following salts in order of increasing solubility.

$PbCl_2$	$K_{\text{sp}} = 1.7\text{e}{-5}$
AgCl	$K_{\text{sp}} = 1.2\text{e}{-10}$
TlCl	$K_{\text{sp}} = 1.9\text{e}{-4}$

Least soluble salt:	Intermediate salt:	Most soluble salt:
$PbCl_2$	$PbCl_2$	$PbCl_2$
AgCl	AgCl	AgCl
TlCl	TlCl	TlCl

8.2-8. Predicting the More Soluble Salt Exercise

EXERCISE 8.5:

Indicate the more soluble compound in each pair.

$PbSO_4$ (K_{sp} = 2e−8)
$CaSO_4$ (K_{sp} = 2e−5)

$BaCrO_4$ (K_{sp} = 2e−10)
Ag_2CrO_4 (K_{sp} = 3e−12)

BaF_2 (K_{sp} = 2e−6)
PbF_2 (K_{sp} = 4e−8)

Ag_3PO_4 (K_{sp} = 2e−18)
$Mg_3(PO_4)_2$ (K_{sp} = 5e−24)

8.2-9. Common-Ion Effect

Consider the dissolution of $Ag_2SO_4(s)$ in 1.0 M Na_2SO_4.

	$\mathbf{Ag_2SO_4(s)}$	$\rightleftharpoons$	$\mathbf{2\ Ag^{1+}}$	$+$	$\mathbf{SO_4^{2-}}$	$\mathbf{K_{sp} = 1.4 \times 10^{-5}}$
initial	enough		0		1.0	M
Δ			$+2x$		$+x$	M
equilibrium	some		$2x$		$0.10 + x$	M

$$K_{sp} = [Ag^{1+}]^2[SO_4^{2-}] = (2x)^2(1.0 + x)$$

which would involve solving a cubic equation. However, in the beginning of this section, we determined that the solubility of Ag_2SO_4 in water was 0.015 M, and the presence of the common ion (sulfate) will decrease the dissociation, so $x < 0.015$ M. If we assume that x is negligible in the addition ($1.0 + x \sim 1.0$), we can simplify the expression

$$K_{sp} = (2x)^2(1.0)$$

which is solved for x as follows:

$$x = \sqrt{\frac{K_{sp}}{4(1.0)}} = \sqrt{\frac{1.4 \times 10^{-5}}{4.0}} = 1.9 \times 10^{-3}\ M$$

Thus, the solubility drops from 0.015 M in water down to 0.0019 M (an 88% drop) in 1.0 M Na_2SO_4 due to the presence of the common ion.

8.2-10. Common-Ion Solubility from pH Exercise

EXERCISE 8.6:

Determine the solubility of $Sn(OH)_2$ in solutions buffered at the following pHs.

K_{sp} = ______________

pH = 9.00

The concentration of the common ion: $[OH^{1-}]$ = ______________ M

solubility ______________ M

pH = 2.00

The concentration of the common ion: $[OH^{1-}]$ = ______________ M

solubility ______________ M

8.2-11. Solubility of AgCl Exercise

EXERCISE 8.7:

$K_{\text{sp}} = 1.8\text{e}{-10}$ for AgCl. Determine the solubility of AgCl in the following:

water	0.10 M NaCl
solubility = ______________ M	solubility = ______________ M

8.3 Precipitation and Separation of Ions

Introduction

Our discussions thus far have focused on the amount of a slightly soluble salt that dissolves, but now we consider the reverse process; i.e., does a precipitate form under a given set of concentrations? We do this by considering the dissociation reaction from the reverse direction; that is, we examine the formation (precipitation) of the salt.

Objectives

- Predict whether a precipitation will occur given the concentrations of the ions and the K_{sp} of the salt.
- Determine the appropriate anion concentration to achieve maximum separation of two ions by the selective precipitation of one.

8.3-1. The Ion Product

Does a solid form under a given set of conditions, or what minimum concentration of one of the ions is required to produce a precipitate? These are two questions we will answer in this section. For example, consider a mixture that contains some solid $Ag_2SO_4(s)$ suspended in a solution that is 0.01 M in Ag^{1+} and 0.10 M in $[SO_4{}^{2-}]$. Under these conditions, does the solid dissolve or does it precipitate out of solution? To answer this question, we examine the direction in which the following reaction is proceeding under these conditions.

$$\begin{array}{lccccccc} & \mathbf{Ag_2SO_4}(\boldsymbol{s}) & \rightleftharpoons & \mathbf{2\ Ag^{1+}} & + & \mathbf{SO_4^{2-}} & \boldsymbol{K}_{\mathbf{sp}} \mathbf{= 1.4 \times 10^{-5}} \\ \textbf{initial} & ? & & 0.01 & & 0.10 & M \end{array}$$

The direction in which a reaction proceeds depends upon the relative values of the reaction quotient, Q, and the equilibrium constant K. The reaction quotient for dissociation is used so frequently that it is given a special name and symbol: the ***ion product***, Q_{ip}.

- Precipitation occurs (reaction proceeds ←) if $Q_{\text{ip}} > K_{\text{sp}}$
- The salt dissolves (reaction proceeds →) if $Q_{\text{ip}} < K_{\text{sp}}$

In this case, $Q_{\text{ip}} = [Ag^{1+}]^2[SO_4^{1-}] = (0.01)^2(0.10) = 1 \times 10^{-5}$ and $K_{\text{sp}} = 1.4 \times 10^{-5}$. $K_{\text{sp}} > Q_{\text{ip}}$, so some salt can still dissolve and no precipitate would form.

8.3-2. Identifying Precipitating Hydroxides Exercise

EXERCISE 8.8:

An acidic solution is made 0.01 *M* in Cu^{2+}, Mg^{2+}, Fe^{2+}, and Sn^{2+}. The pH of the solution is then adjusted by adding NaOH. Select all hydroxides that precipitate at each of the following pHs.

pH = 4

Q_{ip} = ______________

only $Sn(OH)_2$
$Sn(OH)_2$ and $Cu(OH)_2$
$Sn(OH)_2$, $Cu(OH)_2$, and $Fe(OH)_2$
All four hydroxides precipitate.

pH = 6

Q_{ip} = ______________

only $Sn(OH)_2$
$Sn(OH)_2$ and $Cu(OH)_2$
$Sn(OH)_2$, $Cu(OH)_2$, and $Fe(OH)_2$
All four hydroxides precipitate.

pH = 8

Q_{ip} = ______________

only $Sn(OH)_2$
$Sn(OH)_2$ and $Cu(OH)_2$
$Sn(OH)_2$, $Cu(OH)_2$, and $Fe(OH)_2$
All four hydroxides precipitate.

8.3-3. Identifying Precipitating Chlorides Exercise

EXERCISE 8.9:

Identify any precipitates that result when 5.0 mL of 0.010 *M* HCl is added to 20. mL of a solution in which $[Tl^{1+}] = 0.15$ *M* and $[Pb^{2+}] = 0.20$ *M*.

K_{sp} of TlCl = 1.9e−4

K_{sp} of $PbCl_2$ = 1.7e−5

Concentrations after mixing:

$[Cl1^{1-}]$ = ______________ *M*

$[Tl^{1+}]$ = ______________ *M*

$[Pb^{2+}]$ = ______________ *M*

Ion-products:

TlCl: ______________

$PbCl_2$: ______________

The precipitate is ______________.
TlCl
$PbCl_2$

8.3-4. Determining a Required Concentration

Precipitation occurs when the ion-product exceeds the solubility product, so the concentration of one reactant that is required to initiate precipitation can be determined if the concentration of the other reactant and the K_{sp} are known. To determine the minimum concentration required, we solve the K_{sp} expression for the unknown concentration, which is the maximum concentration at which no precipitation occurs. Thus, the calculation indicates both the minimum concentration required for precipitation or the maximum concentration allowed with no precipitation.

8.3-5. Determining pH at which Precipitate Forms Exercise

EXERCISE 8.10:

At what pH does $Mg(OH)_2$ ($K_{sp} = 1.8 \times 10^{-11}$) begin to precipitate from a solution that is 0.01 *M* in Mg^{2+}?

Use the given Mg^{2+} concentration to determine the hydroxide ion concentration at which $Q_{ip} = K_{sp}$.

$[OH^{1-}] =$ ______________ *M*

Convert the hydroxide ion concentration into a pOH.

pOH = ______________

Convert the pOH into a pH.

pH = ______________

8.3-6. Separations

Chemists frequently need to separate a mixture into its components. In the case of aqueous mixtures of ions, this can often be accomplished by selectively precipitating the ions from the solution. We demonstrate the method by separating Sn^{2+} and Mg^{2+} ions from a solution by selectively precipitating the less soluble hydroxide by adjusting the pH to a value that results in the precipitation of only one ion.

The K_{sp} of $Sn(OH)_2$ is much less that that of $Mg(OH)_2$, so we will choose to precipitate $Sn(OH)_2$ and leave Mg^{2+} ions in solution. We could determine the pH at which $Sn(OH)_2$ begins to precipitate, and adjust the pH to a slightly higher value to precipitate $Sn(OH)_2$. However, Sn^{2+} ions will remain in solution with the following concentration:

$$[Sn^{2+}] = \frac{K_{sp}}{[OH^{1-}]^2}$$

In an optimum separation, the remaining Sn^{2+} concentration in solution should be at a minimum. To minimize the Sn^{2+} concentration, the hydroxide ion concentration should be as high as possible without precipitating any Mg^{2+} ions. Thus, we determine the hydroxide ion concentration at which $Mg(OH)_2$ begins to precipitate and adjust the pH of the solution to just below that value. See the example in Exercise 8.11.

8.3-7. Optimum Separation Exercise

EXERCISE 8.11:

A solution is 0.010 *M* each in Sn^{2+} and Fe^{2+}. At what pH would optimum separation be achieved?
K_{sp} = 8.0e−16 for $Fe(OH)_2$ and 1.4e−28 for $Sn(OH)_2$.

Which metal ion should be precipitated?
- Sn^{2+}
- Fe^{2+}

Which of the following would be the best pH to use for the separation?
- 6
- 7
- 8
- 9
- 10
- 11

What are the concentrations of the metal ions in solution after precipitation?

$[Fe^{2+}]$ = ______________ *M*　　　　$[Sn^{2+}]$ = ______________ *M*

Note that the precipitated hydroxide could be redissolved in an acidic solution, so the solution of two metal ions could be separated into two solutions that each contain only one metal ion.

8.3-8. Reaction Table Exercise

EXERCISE: 8.12

Determine the mass of Ag_2CrO_4 (K_{sp} = 1.1e−12, M_m = 331.7 g/mol) that is formed and the concentrations of Ag^{1+} and $CrO_4{}^{2-}$ in the resulting solution when 50. mL of 0.10 *M* K_2CrO_4 and 50. mL of 0.10 *M* $AgNO_3$ are mixed.

The equilibrium constant for the precipitation is ~1e+12 (the reciprocal of K_{sp} because the reaction is the reverse of the dissociation reaction), so essentially all of the limiting reactant disappears.

Fill in the reaction table in millimoles.

	$2\ Ag^{1+}$	$+$	$CrO_4{}^{2-}$	$\rightleftharpoons$	$Ag_2CrO_4(s)$	
initial						mmol
Δ						mmol
equilibrium						mmol

mass (in grams) of Ag_2CrO_4 that precipitates = ______________ g

$[CrO_4{}^{2-}]$ = ______________ *M*

The stoichiometry of Chapter 1 can be used for all entries except the limiting reactant because the limiting reactant concentration cannot be zero if the K_{sp} is to be satisfied. Finding the concentration of the limiting reactant is the same as finding the solubility of the salt in the presence of a common ion (the excess reactant). Use the K_{sp} expression and the $[CrO_4{}^{2-}]$ determined above to find the limiting reactant concentration, which will be small but not zero.

$[Ag^{1+}]$ = ______________ *M*

8.3-9. Reaction Table Exercise

EXERCISE 8.13:

What is the concentration of lead ions in a solution formed by mixing 24 mL of 0.10 M $Pb(NO_3)_2$ and 50. mL of 0.12 M KF?

Be sure to include coefficients with the substances in the balanced equation.

	Cation		Anion		Product	
		+		→		
initial						mmol
Δ						mmol
equilibrium						mmol

$[F^{1-}]$ = ______________ M

$[Pb^{2+}]$ = ______________ M

8.4 Complex Ions

Introduction

Complex ions are ions in which a central metal ion is surrounded by molecular or anionic ligands. For example, the $[Fe(H_2O)_6]^{3+}$ ion discussed in Section 8.1 is a complex ion. The ligands and the metal are in equilibrium in much the same way that the protons and anion of a polyprotic acid are in equilibrium. That is, there is a series of equilibria in which the ligands are added or removed one at a time. However, in our treatment of complex-ion equilibria, we will consider only the overall process in which all of the ligands are added or removed in one step.

Objectives

- Write the formation reaction for a given complex ion.
- Write the formation constant expression for a given complex ion.

8.4-1. The Formation and Dissociation Constants

The equilibrium constant governing the one-step formation of a complex ion from its metal ion and ligands is called the ***formation constant***, K_f. Table 8.3 contains the formation constants at 25 °C for some common complex ions.

Complex Ion	K_f	K_d
$Ag(NH_3)_2^{1+}$	1.7e07	5.9e−08
$Ag(CN)_2^{1-}$	3.0e20	3.3e−21
$Cu(NH_3)_4^{2+}$	4.8e12	2.1e−13
$Fe(CN)_6^{4-}$	1.0e35	1.0e−35
$Fe(CN)_6^{3-}$	1.0e42	1.0e−42
$Ni(NH_3)_6^{2+}$	5.6e08	1.8e−09
$Zn(OH)_4^{2-}$	2.8e15	3.6e−16

Table 8.3: Formation and Dissociation Constants at 25 °C

As an example, consider formation of the complex ion ${Ag(NH_3)_2}^{1+}$.

$$\mathrm{Ag^{1+} + 2\ NH^3 \rightleftharpoons Ag(NH_3)_2^{1+}}$$

The equilibrium constant for the reaction is the formation constant of the $Ag(NH_3)_2{}^{1+}$ ion.

$$K_\mathrm{f} = \frac{[\mathrm{Ag(NH_3)_2^{1+}}]}{[\mathrm{Ag^{1+}}][\mathrm{NH_3}]^2} = 1.7 \times 10^7$$

Biochemists prefer the reverse of the formation reaction, so the ***dissociation constant***, K_d, is also common. However, the K_d of an ion is merely the reciprocal of its K_f. Table 8.3 shows both the dissociation and formation constants of selected complex ions.

8.4-2. Exercise

EXERCISE 8.14:

What is the concentration of free Cu^{2+} in a 0.26 *M* solution of $Cu(NH_3)_4{}^{2+}$ (K_d = 2.1 × 10^{-13})?

Use x for the amount of $Cu(NH_3)_4{}^{2+}$ that reacts and determine the equilibrium line for the reaction table.

	$Cu(NH_3)_4{}^{2+}$	$\rightleftharpoons$	Cu^{2+}	+	$4NH_3$	
equilibrium						*M*

Assume that x is negligible compared to the initial concentration of $Cu(NH_3)_4{}^{2+}$ to set up the equilibrium constant expression and solve for x ($[Cu^{2+}]$).

$[Cu^{2+}]$ = ______________ *M*

8.4-3. Separations with Sulfide Ion

Metal sulfides are very insoluble, so many metals can be separated by adjusting the sulfide ion concentration in solution. Recall from Section 7.4 that the two K_a equilibria of H_2S can be combined to eliminate HS^{1-} ion as follows:

$$\mathrm{H_2S + 2H_2O \rightleftharpoons S^{2-} + 2H_3O^{1+}} \qquad K_{12} = \frac{[\mathrm{S^{2-}}][\mathrm{H_3O^{1+}}]^2}{[\mathrm{H_2S}]} = K_1K_2 = 1.3 \times 10^{-20}$$

If $[H_2S]$ is known, K_{12} allows us to determine the pH required for a given $[S^{2-}]$ or to determine $[S^{2-}]$ from a given pH. H_2S is a gas, and its solubility in water at 25 °C is 0.10 *M*; thus, a solution with a desired sulfide ion concentration can be prepared by buffering a solution to a predetermined pH and then saturating it with H_2S. Both $[H_2S]$ and pH are known, so the sulfide ion concentration can be determined. However, as was also shown in Section 7.4, above pH = 5, the H_2S concentration can no longer be assumed to be 0.10 *M* because the HS^{1-} concentration can no longer be ignored.

8.4-4. Sulfide Separation Exercise

EXERCISE 8.15:

To what pH should a solution that is 0.010 M in each Fe^{2+} and Mn^{2+} be saturated with H_2S to achieve an optimum separation of ions?

- $K_{sp}(MnS) = 5.6e{-16}$
- $K_{sp}(FeS) = 6.3e{-18}$

The optimum separation is accomplished at the highest pH that does not precipitate the more soluble sulfide, so first determine the highest $[S^{2-}]$ allowed without precipitating the more soluble sulfide.

$[S^{2-}]$ = _______________ M

Use the K_{12} expression in the previous section to determine the $[H_3O^{1+}]$ required to deliver the above sulfide ion concentration.

$[H_3O^{1+}]$ = _______________ M

The optimum separation pH to the nearest 0.1 pH units is

pH = _______________

Assume the pH is adjusted to exactly the above pH; i.e., if the above answer is 4.2, assume a pH of 4.20 and calculate the ion concentrations at this pH.

$[S^{2-}]$ = _______________ M $[Mn^{2+}]$ = _______________ M $[Fe^{2+}]$ = _______________ M

Is this a good separation?

Yes
No

8.5 Competing or Simultaneous Equilibria

Introduction

As we have seen, metal ions can be involved in acid-base, solubility, and complex ion equilibria. Thus, several components of a solution containing a metal ion may compete with one another for the metal ion. These competing or simultaneous equilibria are the topic of this section.

Objectives

- Calculate the solubility of a slightly soluble salt in the presence of a substance that forms a complex ion with the metal.
- Write the reaction for the dissociation of a basic salt in acid.
- Determine the equilibrium constant for the dissociation of a basic salt in acid.

8.5-1. Silver Chloride Dissolves in Ammonia

Ag^{1+} ions react with both chloride ions and ammonia molecules, so two competing equilibria are established when AgCl is placed in an aqueous solution of NH_3 as both NH_3 and Cl^{1-} compete for Ag^{1+}.

$$AgCl(s) \rightleftharpoons Ag^{1+} + Cl^{1-} \qquad K_{sp} = 1.8 \times 10^{-10} \qquad \text{(Reaction 1)}$$

$$Ag^{1+} + 2\ NH_3 \rightleftharpoons Ag(NH_3)_2^{1+} \qquad K_f = 1.7 \times 10^{7} \qquad \text{(Reaction 2)}$$

To determine how much AgCl would dissolve in NH_3, we add *Reaction 1* and *Reaction 2* to obtain *Reaction 3*, which represents the dissolution of AgCl in NH_3. The equilibrium constant for the reaction would then be the product of the equilibrium constants of the summed chemical equations.

$$2\ NH_3 + AgCl(s) \rightleftharpoons Ag(NH_3)_2^{1+} + Cl^{1-} \qquad \text{(Reaction 3)}$$

$$K = K_{sp}K_f = (1.8\times10^{-10})(1.7\times10^{7}) = 3.1\times10^{-3}$$

$$K = 3.1\times10^{-3} = \frac{[Ag(NH_3)_2^{1+}][Cl^{1-}]}{[NH_3]^2}$$

Reaction 1 describes the solubility of AgCl in water, while *Reaction 3* describes its solubility in aqueous NH_3. We examine the solubility of AgCl in NH_3 in the following exercise.

8.5-2. AgCl in NH_3 Exercise

EXERCISE 8.16:

What is the solubility of AgCl in 1.0 M NH_3?

Use x as the solubility of AgCl (x mol/L of AgCl dissolve) to fill in the reaction table. Note that AgCl is a solid, so there are no entries under it. ($K = 3.1\times10^{-3}$ for the reaction below.)

	$2\ NH_3$	+	$AgCl(s)$	$\rightleftharpoons$	$Ag(NH_3)_2^{1+}$	+	Cl^{1-}	
initial								M
Δ								M
equilibrium								M

Set up the equilibrium constant expression using the equilibrium line entries. Take the square root of both sides and solve for x, the molar solubility.

solubility of AgCl = ______________ M

8.5-3. Acids and Bases Dissolve One Another

The solubility of AgCl is 4×10^3 times greater in 1 M ammonia than in water. In fact, it is a general principle that an insoluble salt can be dissolved by placing it into a solution of a Lewis base (OH^{1-}, CN^{1-}, or NH_3) with which the metal forms a complex ion. However, the metal goes into solution predominantly as the complex ion, not as the free metal ion. Dissolving an insoluble salt by forming a complex ion is a Lewis acid-base reaction. Ag^{1+} is a Lewis acid and Cl^{1-} and NH_3 are bases that can compete for the Lewis acid. In cases where the anion is a weak base, the insoluble salt can be dissolved by placing it in strong acid. For example, CN^{1-} is a base and Ag^{1+} and H_3O^{1+} are acids that can compete for the base. An example of this type is considered in the following exercise.

8.5-4. Determining *K* Exercise

EXERCISE 8.17:

F^{1-} ion is a weak base that can react with acids. In this exercise, we use the solubility of CaF_2 in a strong acid to examine the competition between H_3O^{1+} and Ca^{2+} for the F^{1-} ion.

What is the equilibrium constant for the dissociation of CaF_2 in strong acid?

$$CaF_2(s) + 2\ H_3O^{1+} \rightleftharpoons Ca^{2+} + 2\ HF + 2\ H_2O$$

- K_{sp} for $CaF_2 = 3.9 \times 10^{-11}$
- K_a for HF $= 7.2 \times 10^{-4}$

1. The chemical equation for the K_{sp} of CaF_2 is the following.

$\rightleftharpoons$ $+$

2. By what number should the above be multiplied? Use a negative sign to indicate that the direction of the reaction must be reversed from the defined direction.

multiply CaF_2 dissociation by ______________

3. The equilibrium constant for the reaction produced in Step 2: $K =$ ______________

4. The chemical equation for the K_a of HF is the following.

$+$ $\rightleftharpoons$ $+$

5. By what number should the above be multiplied? Use a negative sign to indicate that the direction of the reaction must be reversed from the defined direction.

multiply HF dissociation by ______________

6. The equilibrium constant for the reaction produced in Step 5:

$K =$ ______________

7. The equilibrium constant for dissolving CaF_2 in acid:

$K =$ ______________

8.5-5. Solubility of Ag_3PO_4

EXERCISE 8.18:

In Section 8.2-5., we saw that the solubility of Ag_3PO_4 in water was over eight times greater than that determined with K_{sp} due to a competition between Ag^{1+} and H_2O for $PO_4{}^{3-}$. We now revisit that solubility as a competing equilibria problem. We assume that the equilibrium can be determined with the following:

$$Ag_3PO_4(s) \rightleftharpoons 3\ Ag^{1+} + PO_4^{3-} \qquad K_{sp} = 2.6 \times 10^{-18}$$

$$PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^{1-} \qquad K_b = 0.021$$

Assume that the reaction is $Ag_3PO_4(s) + H_2O \rightleftharpoons 3\ Ag^{1+} + HPO_4{}^{2-} + OH^{1-}$ and determine the equilibrium constant for the solubility:

$K =$ ______________

If the pH of a saturated solution is 9.00, what is the solubility of Ag_3PO_4? As shown in Figure 7.3, all phosphate is in the form of $HPO_4{}^{2-}$ at pH = 9.00.

solubility = ______________

The observed solubility is 1.5×10^{-4} *M*, but that determined with K_{sp} alone is 1.8×10^{-5} *M*. Thus, it is competing equilibria like this that lead to such poor agreement between predicted and experimental solubilities for salts of relatively strong bases when only K_{sp} is used in the calculations.

8.6 Exercises and Solutions

Links to view either the end-of-chapter exercises or the solutions to the odd exercises are available in the HTML version of the chapter.

CHAPTER 9 – ELECTROCHEMISTRY

Introduction

Electron transfer, or redox, reactions form one of the broadest and most important classes of reactions in chemistry. All reactions involving oxygen, such as combustion and corrosion, are redox reactions. Photosynthesis, respiration, and the breakdown of food are biological processes that involve sequences of electron transfer reactions to transport and utilize energy from the sun. ***Electrochemistry*** is the marriage of electron transfer and electrical conductivity through a circuit, so all batteries are electrochemical devices. In this chapter, we review some of the topics introduced in Chapter 11 of CAMS, and extend our study of electron transfer to topics such as how concentrations affect cell potentials and how applied voltages can be used to plate one metal on another or to carry out non-spontaneous redox reactions.

9.1. Redox Review

Introduction

Electrochemistry was introduced in detail in CAMS Chapter 11, and a knowledge of that material is essential to the understanding of this chapter. While a brief summary is presented in this section, a more thorough background can be acquired by viewing the videos that can be found in the Sections of CAMS that are referenced in the following prerequisites. It is strongly recommended that you view these videos for a better review.

Prerequisites

- CAMS 11.1-1 Introduction to Electron Transfer and Redox Reactions
- CAMS 11.4-1 Standard Reduction Potentials
- CAMS 11.5-1 Reactivity and Standard Reduction Potentials
- CAMS 11.5-2 Writing Redox Chemical Equations

9.1-1. Definitions

- During a redox reaction, electrons are transferred from an electron **donor** to an electron **acceptor**.
- Donors lose electrons in a process known as **oxidation**, while the acceptors gain electrons in a process known as **reduction**.
- Reactions involving oxidation and reduction are called **redox reactions**.
- An acceptor cannot be reduced unless a donor is oxidized because electron transfer requires both a source and a destination for the transferred electrons.
- The reduction of an acceptor causes the oxidation of a donor, so acceptors are called **oxidizing agents** or **oxidants**.
- The oxidation of the donor causes the reduction of an acceptor, so donors are called **reducing agents** or **reductants**.
- Reductants lose electrons to become oxidants, and oxidants gain electrons to become reductants.
- A reducing agent and the oxidizing agent that it becomes when it is oxidized form a **redox couple**, which we will represent with the reduced form of the couple (RED) followed by a diagonal line then the oxidized form (OX) as in Cu/Cu^{2+}.

9.1-2. Proton and Electron Transfer Compared

There are many similarities between Brønsted acid-base reactions and electron transfer reactions. In acid-base reactions, protons (positive charges) are transferred from a proton donor (acid) to a proton acceptor (base), while in redox reactions, electrons (negative charges) are transferred from an electron donor to an electron acceptor. In an acid-base reaction, the reacting acid and the produced base are called a conjugate acid-base pair, and in a redox reaction, the reacting donor and produced acceptor are called a redox couple. Acid-base reactions are extensive when the reacting acid and base are stronger than the produced acid and base, and redox reactions are extensive when the reacting oxidizing and reducing agents are stronger than the produced oxidizing and reducing agents.

9.1-3. The Electron Transfer Process

Figure 9.1 represents the electron transfer from an isolated iron atom to an isolated copper(II) ion to produce an iron(II) ion and a copper atom. The electrons are on Fe initially, so it is the donor (reducing agent or reductant). The produced Fe^{2+} has empty redox orbitals, so it can function as an acceptor (oxidizing agent or oxidant). Thus, Fe is a donor, and Fe^{2+} is the produced acceptor, so Fe/Fe^{2+} is one redox couple in the reaction. The acceptor orbitals on Cu^{2+} are empty, but they are occupied in Cu. Thus, Cu^{2+} is the initial acceptor and Cu is the produced donor, so Cu/Cu^{2+} is the other redox couple in the reaction. The electrons are at higher energy on the donor (Fe) than on the acceptor (Cu), so the electron transfer is downhill in energy, exothermic, and spontaneous. The electron transfer from Cu to Fe^{2+} is uphill in energy, endothermic, and NOT spontaneous.

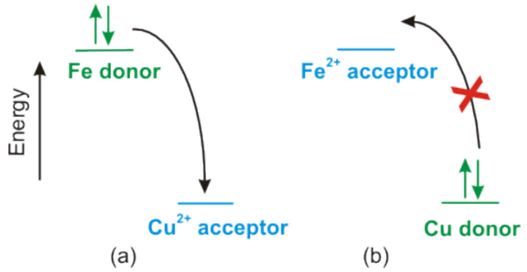


Figure 9.1: Electrons Transfer Spontaneously to Lower Energy

9.1-4. Process in Solution

We have considered electron transfer between isolated atoms and ions because the picture is far more complicated when metals and solutions are involved. Consider all that must occur when a piece of iron reacts with copper(II) ions in aqueous solution. Metallic bonds must be broken in the iron to produce an iron atom, the iron atom must lose two electrons to form Fe^{2+}, a cavity must be created in the water to accommodate the ion, and the Fe^{2+} ion must enter the cavity and be hydrated. Similar processes must occur in the reverse direction when the Cu^{2+} ion is reduced to copper metal. Thus, the situation in aqueous redox reactions is far more complicated. If the energy difference between the donor and acceptor orbitals is not large, then these other factors can dominate the energy of the redox process. Consequently, the simple tendency of electrons to move from an orbital at high-energy into one at lower energy is not sufficient if the orbital energies are not very different. As in all processes carried out at constant temperature and pressure, it is the free energy change, ΔG, that is the driving force behind redox reactions.

9.1-5. Galvanic Cell Review

When steel wool (Fe) is placed into a solution of Cu^{2+}, the electron transfer takes place sponteneously, and the energy released simply warms the solution. However, that energy can be harnessed by separating the two redox couples and connecting them into an electrical circuit. Such circuits are called **galvanic cells**, and the video below shows all of the processes that occur in a galvanic cell constructed with a Cu/Cu^{2+} couple as the cathode and a Fe/Fe^{2+} couple as the anode. By definition:

- The **cathode** is the compartment where reduction takes place, so it houses the Cu/Cu^{2+} couple.
- The **anode** is the compartment where oxidation takes place, so it houses the Fe/Fe^{2+} couple.

Click the "Cathode" or "Anode" button in the video to view the process that occurs in that compartment. You should note the following points:

- Electron movement is anode → cathode.
- The $CuSO_4$ solution loses its color as Cu^{2+} ions are consumed and the Cu electrode gets larger as Cu atoms are produced.
- The Fe electrode gets smaller as iron atoms are converted into Fe^{2+} ions that pass into solution.
- One K^{1+} ion enters the cathode for each electron that enters to maintain electrical neutrality.
- One Cl^{1-} ion enters the anode for each electron that leaves to maintain electrical neutrality.

The electrical circuit has three components:

1. charges (ions) migrate through the solution
2. electrons pass between the solution and the circuit at the surface of the electrodes, and
3. electrons move from the anode to the cathode in the external circuit.

A video or simulation is available online.

9.1-6. Cell Potential

The anode and cathode are each one-half of the redox process and are referred to as half-cells, and the cell potential is the potential difference between the two half-cells

$$\mathcal{E} = \mathcal{E}_{\text{cathode}} - \mathcal{E}_{\text{anode}} \qquad \text{The Cell Potential is the Difference Between the Half-cell potentials} \tag{9.1}$$

$\mathcal{E}_{\text{cathode}}$ and $\mathcal{E}_{\text{anode}}$ are known as the **half-cell potentials**. In a redox reaction, electrons must flow from the anode (donor) to the cathode (acceptor), but electrons are also negatively charged, so they also seek the more positive electical potential (charge). Thus, electrons transfer spontaneously to the cathode if it is at the higher electrical potential, but they must be forced to transfer if the cathode is at the lower electrical potential. A galvanic cell is a cell in which $\mathcal{E}_{\text{cathode}} > \mathcal{E}_{\text{anode}}$ ($\mathcal{E} > 0$), so redox reactions in galvanic cells are spontaneous ($\Delta G < 0$). The released free energy in a galvanic cell can be used to do work. Thus, we can conclude the following.

Galvanic cells convert chemical potential energy into electrical potential energy.

All batteries are galvanic cells. The cell potential of the electrochemical cell shown in Figure 9.2 is +0.78 V, so it is a galvanic cell, and the electron transfer from Fe to Cu^{2+} is spontaneous.

9.1-7. Electrolytic Cell

An electrolytic cell is a cell in which $\mathcal{E}_{\text{cathode}} < \mathcal{E}_{\text{anode}}$, so $\mathcal{E} < 0$, and $\Delta G > 0$. Consequently, the redox electrons must be forced to move to the more negative potential with an external power supply, so we can conclude the following.

An electrolytic cell converts electrical potential energy into chemical potential energy.

Recharging a battery and producing hydrogen and oxygen from water are two examples of the utility of electrolytic cells.

9.1-8. Standard Reduction Potentials

The criterion for spontaneous electron transfer is $\mathcal{E}_{\text{cathode}} > \mathcal{E}_{\text{anode}}$. Therefore, tables of half-cell potentials can be used to predict spontaneity in electron transfer reactions. However, the potential of only half of a cell cannot be measured as both a donor and an acceptor are required, so absolute half-cell potentials cannot be determined. To solve this problem, chemists chose the ***standard hydrogen electrode*** or SHE as the reference half-cell. The half-cell potential of the SHE is assigned a value of exactly zero. A SHE is represented as:

$$2\ \mathrm{H}^{1+}(\mathrm{aq}) + 2\ \mathrm{e}^{1-} \rightleftharpoons \mathrm{H}_2(g) \quad \mathcal{E}^o = 0\ \mathrm{V}$$

By convention, the cell potential is measured by connecting the 'lo' or (−) lead of the voltmeter to the SHE. This convention *assumes* that the SHE is the oxidation and the half-cell being measured is the reduction, so the potential of the cell at standard conditions is known as the **standard reduction potential** of the half-reaction connected to the SHE. Consider that, if the anode of the cell shown in Figure 9.2 had been a SHE instead of an Fe/Fe^{2+} half-cell, the cell potential would have been +0.34 V, which is the standard reduction potential of the Cu/Cu^{2+} couple. The positive sign implies that the electrical potential of the Cu/Cu^{2+} couple is 0.34 V higher than that of the SHE. A more positive electrical potential means that the redox orbitals of the Cu/Cu^{2+} couple are lower in energy. If the Fe/Fe^{2+} half-cell is attached to the 'hi' (+) side and the SHE to the 'lo' (−) side, the potential would be −0.44 V, which is the standard reduction potential of the Fe/Fe^{2+} couple. The negative sign indicates that the Fe/Fe^{2+} couple is at a more negative electrical potential than the SHE, so its orbital energy is higher.

9.1-9. Oxidizing Power and Reduction Potentials

The standard reduction potential of a redox couple is a measure of the electrical potential of the electron in the couple. Therefore, the standard cell potential can be determined from tabulated standard reduction potentials by rewriting Equation 9.1 for standard conditions.

$$\mathcal{E}^\circ = \mathcal{E}^\circ_{\text{cathode}} - \mathcal{E}^\circ_{\text{anode}}$$

$\mathcal{E}^\circ_{\text{cathode}}$ is the standard reduction potential of the redox couple in the cathode and $\mathcal{E}^\circ_{\text{anode}}$ is the standard reduction potential of the redox couple in the anode. For example, consider the reaction between Cu^{2+} and Fe in Figure 9.2. $\mathcal{E}^\circ_{\text{cathode}} = +0.34$ V (the standard reduction potential of the Cu/Cu^{2+} couple) and $\mathcal{E}^\circ_{\text{anode}} = -0.44$ V (the standard reduction potential of the Fe/Fe^{2+} couple). Using Equation 9.1, we determine that $\mathcal{E}^\circ = +0.34 - (-0.44) = +0.78$ V. $\mathcal{E}^\circ$ is positive (the reaction is extensive) when $\mathcal{E}^\circ_{\text{cathode}}$ is high and $\mathcal{E}^\circ_{\text{anode}}$ is low or negative. Therefore, we can conclude the following.

Good oxidizing agents have high standard reduction potentials and good reducing agents have low or negative standard reduction potentials.

9.2 Balancing Redox Reactions

Introduction

Redox reactions can be difficult to balance because the loss and gain of redox electrons must also be balanced, but there are two methods that simplify the task: the half-reaction method, which is readily applied to ionic equations; and the oxidation state change method, which is useful when balancing reactions that do not involve ions. Balancing redox reactions with these methods is something chemists do occasionally, but not frequently, so these tools are not presented here. All balanced redox reactions in this chapter are constructed from tabulated half-reactions.

Prerequisites

- CAMS 11.1 Electron Transfer or Redox Reactions (Explain the redox process and the common terms used to describe it.)
- CAMS 11.2 Half-Reactions (Write a balanced redox reaction given a table of reduction half-reactions.)
- CAMS 11.3 Galvanic Cells (Explain the workings of a galvanic cell.)
- CAMS 11.4 Standard Reduction Potentials (Explain what standard reduction potentials are and how they are used.)
- CAMS 11.5 Writing Redox Reactions (Use a table of standard reduction potentials to predict whether a redox reaction takes place when two substances are mixed.)

9.2-1. Method

Redox reactions are frequently balanced by using tabulated half-reactions like those given in the Resource titled Selected Standard Reduction Potentials at 298 K. To write the spontaneous reaction from two reduction half reactions:

1 Determine which half reaction has the less positive or more negative reduction potential and reverse it as it must serve as the oxidation half-reaction (anode).

2 Determine the number of electrons transferred in the balanced chemical equation. This is the lowest common multiple (LCM) of the number gained at the cathode and the number lost at the anode.

3 Multiply each half-reaction through by the integer required to make the number of electrons gained or lost in the half-reaction equal to the LCM determined in Step 2.

4 Add the resulting half-reactions to obtain the cell reaction. Note that the same substance cannot appear on both sides of the equation, so H_2O, H^{1+}, and OH^{1-} can often be canceled and not appear in the net equation.

5 Determine the cell potential as $\mathcal{E}^\circ_{\text{cell}} = \mathcal{E}^\circ_{\text{cathode}} - \mathcal{E}^\circ_{\text{anode}}$.

9.2-2. Half-cell Potentials and Balancing Equations

A standard reduction potential is a measure of the electrical potential or free energy of a redox electron, so it is independent of the number of electrons or the side of the half-reaction on which they are found. We conclude the following important fact.

The standard reduction potential of a half-reaction is not changed when the direction of the half-reaction is reversed or when it is is multiplied by an integer.

In other words, the fact that standard reduction potential for the Cu/Cu^{2+} couple is +0.34 V simply means that the electrical potential experienced by an electron in the Cu/Cu^{2+} couple is 0.34 V higher than that experienced by one in the H_2/H^{1+} couple. That fact is true whether the Cu is a reactant or a product or whether there are one, two, or three Cu atoms.

9.2-3. Exercise

EXERCISE 9.1:

Write the balanced chemical equation for the spontaneous process that involves the following half reactions and determine the standard cell potential.

$$\begin{array}{ll} VO_2^{1+} + 2\ H^{1+} + e^{1-} \rightleftharpoons VO^{2+} + H_2O & \mathcal{E}^\circ = +1.00\ \text{V} \\ Cr_2O_7^{2-} + 14\ H^{1+} + 6\ e^{1-} \rightleftharpoons 2\ Cr^{3+} + 7\ H_2O & \mathcal{E}^\circ = +1.33\ \text{V} \end{array}$$

1) Identify the reaction that must be reversed and serves as the anode.

$VO_2^{1+} + 2\ H^{1+} + e^{1-} \leftrightharpoons VO^{2+} + H_2O$

$Cr_2O_7^{2-} + 14\ H^{1+} + 6\ e^{1-} \leftrightharpoons 2\ Cr^{3+} + 7\ H_2O$

2) Determine the number of electrons that must be transferred in the reaction.

$n =$ ______________

3a) Determine the anode half reaction as it occurs in the overall reaction (after reversing and multiplying by the appropriate integer).

______ + ______ → ______ + ______ + ______ e^{1-}

3b) Determine the cathode half reaction as it occurs in the overall reaction (after multiplying by the appropriate integer).

______ + ______ + ______ e^{1-} → ______ + ______

4) Write the chemical equation ($Red_1 + Ox_2 + Other \rightarrow Ox_1 + Red_2 + Other$) for the spontaneous process.

______ + ______ + ______ → ______ + ______ + ______

5) What is the standard cell potential?

$\mathcal{E}^\circ =$ ______________ V

9.2-4. Exercise

EXERCISE 9.2:

Given the following half-reactions,

$$Au^3 + 3\ e^{1-} \rightleftharpoons Au$$
$$MnO_4^{1-} + 8\ H^{1+} + 5\ e^{1-} \rightleftharpoons Mn^{2+} + 4\ H_2O$$

write the overall reaction for the oxidation of gold by permanganate ion.

1) The lowest common multiple of electrons gained and lost is:

$n =$ ______________

2) Which half reaction must be reversed to an oxidation?

$Au^{3+} + 3\ e^{1-} \rightleftharpoons Au$
$MnO_4^{1-} + 8\ H^{1+} + 5\ e^{1-} \leftrightharpoons Mn^{2+} + 4\ H_2O$

3) The anode half reaction as it occurs in the overall reaction (after reversing and multiplying by the appropriate integer):

______ → ______ + ______ e^{1-}

4) The cathode half reaction as it occurs in the overall reaction (after multiplying by the appropriate integer):

______ + ______ + ______ e^{1-} → ______ + ______

5) Write the chemical equation (Red_1 + Ox_2 + Other → Ox_1 + Red_2 + Other) for the spontaneous process.

______ + ______ + ______ → ______ + ______ + ______

9.3 Free Energy and Electrochemical Cells

Introduction

We now continue our treatment of galvanic cells and begin our discussion of their thermodynamics.

Objectives

- Determine the anode and cathode reactions of the spontaneous cell given the standard reduction potentials of the two half-reactions.
- Express an electrochemical cell in the abbreviated form.
- Determine the free energy of a redox reaction from its cell potential, and vice versa.

9.3-1. Electrodes

Electron transfer reactions in electrochemical cells are known as electrochemical reactions. Electrochemical reactions occur at the surfaces of the two electrodes in the cell as electrons are injected into the external circuit at the anode as the donor is oxidized and withdrawn from the circuit at the cathode as the acceptor is reduced. Electrodes that take part in the electrochemical reactions are said to be ***active electrodes***. For example, the iron and copper electrodes in the galvanic cell discussed in the previous section are active electrodes because both are involved in the reaction. However, there are many instances where neither member of a redox couple is a conducting solid, but an electrode is still required to serve as the interface between the reaction and the circuit. In these cases, an inert metal is normally used as a ***passive electrode***. Passive electrodes do not participate in the reaction; they simply serve as a conducting surface through which electrons are injected into either the circuit or the reaction. For example, a Pt electrode is commonly used in a Standard Hydrogen Electrode (SHE) because there is no metal surface in the half-reaction ($2\ H^{1+} + 2\ e^{1-} \rightleftharpoons H_2$).

9.3-2. Electrochemical Cell Abbreviation

Electrochemical cells are quite common and are often represented in the following abbreviated form:

anode electrode | anode compartment ‖ cathode compartment | cathode electrode

A single vertical line represents a phase change (solid/solution), and a double vertical line represents a liquid junction (salt bridge).

The order in which components are listed is easily remembered if you remember your ABC's (Anode | Bridge | Cathode). As an example, the cell shown in Figure 9.2 is represented as

$$Fe \mid Fe^{2}+(1\ M) \parallel Cu^{2+}(1\ M) \mid Cu$$

and the cell in which the SHE is the anode and copper is the cathode is

$$Pt \mid H_2(1\ \text{atm}),\ H^{1+}(1\ M) \parallel Cu^{2+}(1\ M) \mid Cu$$

where a platinum wire serves as a passive electrode for the standard hydrogen electrode. Note that the order of components in a half-cell with a passive electrode is not specified, so the order in which H_2 and H^{1+} appear in the anode is not fixed.

9.3-3. Cell Abbreviation Exercise

EXERCISE 9.3:

Write the chemical equation for the following redox process:

$$Al \mid Al^{3+}(1\ M) \parallel Sn^{2+}(1\ M) \mid Sn$$

Lowest common multiple for electrons gained and lost.

$n =$ ______________

Write the chemical equation ($Red_1 + Ox_2 \rightarrow Ox_1 + Red_2$).

______________ + ______________ → ______________ + ______________

The standard reduction potentials of Al and Sn are −1.66 V and −0.14 V, respectively. What is the cell potential?

$\mathcal{E}^\circ =$ ______________ V

9.3-4. Free Energy

Recall from Equation 4.9 that the maximum amount of work that can be obtained from a process is the amount of free energy released during the process. Thus, the amount of work that can be done by the transferred electrons in a spontaneous redox reaction is:

$$\text{work done by electrons} = -\Delta G \qquad (9.2)$$

Work Done by the Electrons in terms of Free Energy Change

Historically, the work done by the transferred electrons was expressed in terms of charge and electrical potential difference, $\mathcal{E}$. The absolute value of the charge of one mole of electrons is called the ***faraday*** and given the symbol $\mathcal{F}$. The faraday is Avogadro's number times the absolute value of the charge on a single electron:

$$\mathcal{F} = 6.02214 \times 10^{23} \text{ electrons/mol } \times 1.60218 \times 10^{-19} \text{ C/electron } = 9.6485 \times 10^{4} \text{ C/mol}$$

Equation 9.3 expresses the work that can be done by the transfer of n moles of electrons through an electrical potential $\mathcal{E}$.

$$\text{work done by electrons} = n\mathcal{F}\mathcal{E} \qquad \text{Work is Charge times Electrical Potential} \qquad (9.3)$$

Equating the two expressions for the work done by the electrons in a redox reaction, we obtain the expressions for the free energy in terms of the cell potential given in Equation 9.4.

$$\Delta G = -n\mathcal{F}\mathcal{E} \qquad \text{Free Energy and Cell Potential} \qquad (9.4)$$

Of course superscript zeros can be added to the above for the electron transfer under standard conditions.

9.3-5. Free Energy from Cell Potential Exercise

EXERCISE 9.4:

Use Equation 9.4 to determine the standard free energy change for the following reaction:

$$3\ \text{Sn}^{2+} + 2\ \text{Al} \rightarrow 2\ \text{Al}^{3+} + 3\ \text{Sn} \quad \mathcal{E} = 1.52\ \text{V}$$

$\Delta G° =$ ______________ kJ

9.4 The Effect of Concentration on Cell Potential

Introduction

The cell potential is a measure of the chemical free energy of a redox reaction, and we now apply the relationships between the reaction quotient, the equilibrium constant, and the free energy of reaction presented in Chapter 4 to electrochemical processes. These relationships allow us to derive an expression for the effect of concentration on cell potential.

Objectives

- Determine the cell potential of a redox reaction given the standard cell potential and the concentrations of all reactants and products.

9.4-1. Nernst Equation

To determine the effect of concentrations on cell potentials, we start with Equation 4.13:

$$\Delta G = \Delta G° + RT \ln Q$$

Then use $\Delta G = -n\mathcal{F}\mathcal{E}$ to obtain the following:

$$-n\mathcal{F}\mathcal{E} = -n\mathcal{F}\mathcal{E}^\circ + RT \ln Q$$

Next, divide both sides by $-n\mathcal{F}$ to obtain an expression for the cell potential in terms of the standard cell potential and the reaction quotient.

$$\mathcal{E} = \mathcal{E}^\circ - \frac{RT}{n\mathcal{F}} \ln Q$$

Finally, use $\ln Q = 2.303 \log Q$ to convert to log base 10 and assume that $T = 298$ K to obtain the Nernst equation.

$$\mathcal{E} = \mathcal{E}^\circ - \frac{0.0592}{n} \log Q \qquad \text{Nernst Equation at 25 °C} \tag{9.5}$$

The Nernst equation allows us to determine the cell potential at 25 °C from the standard cell potential and the concentrations of the reactants and products (Q).

9.4-2. Determine Potential After Cell Discharge Exercise

EXERCISE 9.5:

Consider the following cell:

$$\text{Al} \mid \text{Al}^{3+}(1.00\ M) \parallel \text{Sn}^{2+}(1.00\ M) \mid \text{Sn} \quad \mathcal{E}^\circ = 1.52\ \text{V}$$

What is the cell potential if the cell is discharged from standard conditions to the point where $[\text{Sn}^{2+}] = 0.01\ M$? Assume that the volumes of the two half-cells are the same when determining Δ.

First, fill in the reaction table to determine the final concentration of Al^{3+}.

	2 Al	+	3 Sn^{2+}	→	2 Al^{3+}	+	3 Sn	
initial								M
Δ								M
final								M

The value of $Q =$ ______________

Use Equation 9.5 to determine the cell potential.

$\mathcal{E} =$ ______________ V

9.4-3. Cell Thermodynamics Exercise

EXERCISE 9.6:

Consider the following cell at 25 °C.

$$\mathrm{Pb} \mid \mathrm{Pb}^{2+}(0.12\ M) \parallel \mathrm{Cu}^{1+}(0.020\ M) \mid \mathrm{Cu} \quad \mathcal{E}^\circ = 0.58\ \mathrm{V}$$

Write the chemical equation for the cell reaction ($\mathrm{Red}_1 + \mathrm{Ox}_2 \rightarrow \mathrm{Ox}_1 + \mathrm{Red}_2$).

______ + ______ → ______ + ______

$n =$ ______ electrons transferred

$\Delta G =$ ______ kJ

$Q =$ ______

$\mathcal{E}^\circ =$ ______ V

$\Delta G^\circ =$ ______ kJ

Given that the standard reduction potential of Pb^{2+} is −0.13 V, determine the standard reduction potential of Cu^{1+}.

$\mathcal{E}^\circ =$ ______ V

9.4-4. pH from Cell Potential Exercise

EXERCISE 9.7:

A pH meter is an electrochemical cell whose voltage is pH dependent. This example shows how a pH meter could be constructed from a SHE and an Ag/AgCl couple. Of course, the SHE is far too cumbersome to be used in a real pH meter, but the principle is the same.

Determine the pH of the solution in the anode compartment of the following cell if the cell potential is 0.53 V.

$$\mathrm{Pt} \mid \mathrm{H}_2\ (1.00\ \mathrm{atm}),\ \mathrm{H}^{1+}\ (\mathrm{x}\ M) \parallel \mathrm{Cl}^{1-}\ (1.00\ M),\ \mathrm{AgCl} \mid \mathrm{Ag}$$

Determine the half-reactions, their standard reduction potentials, the chemical equation for the overall reaction ($\mathrm{Red}_1 + \mathrm{Ox}_2 \rightarrow \mathrm{Ox}_1 + \mathrm{Red}_2 + \mathrm{Other}$), and its standard cell potential. Write the half-reactions so that the electrons cancel in the sum. (Selected Standard Reduction Potentials at 298 K.)

	Reaction	$\mathcal{E}^\circ$
Anode	______ → ______ + ______ e^{1-}	______ V
Cathode	______ + ______ e^{1-} → ______ + ______	______ V
Cell	______ + ______ → ______ + ______ + ______	______ V

$n =$ ______ electrons transferred

$\log\ Q =$ ______

$\mathrm{pH} =$ ______ (Note: $\log\ [\mathrm{H}^{1+}]^2 = -2\ \mathrm{pH}$)

9.4-5. Qualitative Change in Cell Potential

Equation 9.5 indicates that $\mathcal{E}$ increases as log Q decreases, so any change that decreases Q (decreasing a product concentration or increasing a reactant concentration) increases the cell potential. Similarly, any change that increases Q (increasing a product concentration or decreasing a reactant concentration) decreases the cell potential.

This is the same direction that LeChâtelier's principle predicts for a product.

Cell potential is a *product* of a spontaneous redox reaction, so any change in the reaction that causes the equilibrium amount of product to increase will increase the cell potential, and any change that causes the amount of product to decrease will reduce the cell potential.

9.4-6. Effect of Changing Conditions on Cell Potential Exercise

EXERCISE 9.8:

Indicate the effect of each change on the cell potential of the following electrochemical cell.

$\text{Pt} \mid \text{H}_2, \text{H}^{1-} \parallel \text{Cu}^{2+} \mid \text{Cu}$

The balanced chemical equation ($\text{Red}_1 + \text{Ox}_2 \rightarrow \text{Ox}_1 + \text{Red}_2$) for the cell reaction is the following.

______ + ______ → ______ + ______

Note that ammonia is a good Lewis base, while Cu^{2+} and H^{1+} are both Lewis acids.

increasing the partial pressure of H_2
- increase
- decrease
- no change

adding NH_3 to the anode
- increase
- decrease
- no change

adding NH_3 to the cathode
- increase
- decrease
- no change

enlarging the copper electrode
- increase
- decrease
- no change

9.4-7. Changing Conditions Exercise

EXERCISE 9.9:

Predict the effect on the cell potential of the following cell.

$\text{Pb} \mid \text{Pb}^{2+}\ (0.12\ M) \parallel \text{Cu}^{1+}\ (0.020\ M) \mid \text{Cu}$

The balanced chemical equation ($\text{Red}_1 + \text{Ox}_2 \rightarrow \text{Ox}_1 + \text{Red}_2$) for the cell reaction is the following.

______ + ______ → ______ + ______

enlarging the lead electrode
- increase
- decrease
- no change

adding $Pb(NO_3)_2$ to the anode
- increase
- decrease
- no change

adding KCl to the anode to precipitate $PbCl_2$
- increase
- decrease
- no change

adding copper wire to the cathode
- increase
- decrease
- no change

evaporating some water from the cathode
- increase
- decrease
- no change

9.4-8. Equilibrium Constants and Standard Cell Potentials

At equilibrium, $Q = K$ and $\Delta G = 0$. However, $\Delta G = -\mathrm{n}\mathcal{F}\mathcal{E}$, so $\mathcal{E} = 0$ as well. Thus, batteries die when the reaction reaches equilibrium. Applying these equilibrium conditions to Equation 9.5, we obtain the following:

$$0 = \mathcal{E}^\circ - \frac{0.0592}{n}\log K$$

Solving the above for $\mathcal{E}^\circ$, we get Equation 9.6.

$$\mathcal{E}^\circ = \frac{0.0592}{n}\log K \qquad \text{Standard Cell Potential in Terms of log } K \tag{9.6}$$

Alternatively, we can solve for log K to get Equation 9.7.

$$\log K = \frac{n\mathcal{E}^\circ}{0.0592} = 16.9n\mathcal{E}^\circ \qquad \text{Log } K \text{ in Terms of the Standard Cell Potential} \tag{9.7}$$

Equation 9.7 indicates that log K increases as $\mathcal{E}^\circ$ increases. Thus, the extent of a redox reaction increases as its standard cell potential increases. The extent of a redox reaction is often referred to as the extent of electron transfer.

9.4-9. Determining K from Standard Cell Potential Exercise

EXERCISE 9.10:

What is the equilibrium constant for the following reaction?

$$3\ \mathrm{Sn}^{2+} + 2\ \mathrm{Al} \rightarrow 3\ \mathrm{Sn} + 2\ \mathrm{Al}^{3+} \quad \mathcal{E}^\circ = 1.52\ \mathrm{V}$$

$n =$ ______________

$\log K =$ ______________

$K =$ ______________

9.5 The Electrolytic Cell

Introduction

A second technological side of electrochemistry is based on the use of external electrical circuits to control the redox chemistry itself, including the ability to force electrons uphill in energy. The process of forcing electrons uphill in energy is called ***electrolysis***. An electrolysis reaction is one that converts electrical potential energy into chemical potential energy. Recharging batteries, electroplating, recovering elemental metals from ores, and making chemicals are some examples of electrolysis. The electrochemical cell that is used to do an electrolysis experiment is called an ***electrolytic cell***.

Prerequisites

- CAMS 11.8 Electrolytic Cells (Distinguish between electrolytic and galvanic cells.)
- CAMS 8.6 Fermi Level (Define a metallic band and the Fermi level.)

Objectives

- Describe how an electrolytic cell works.
- Determine the minimum voltage that must be applied in an electrolytic cell.

9.5-1. Electrodes

The voltage across two electrodes measures the energy difference in their Fermi levels.

Consider the figure of a power supply connected to two pieces of metal. The power supply removes electrons from the metal attached to the positive terminal and adds electrons to the metal attached to the negative terminal. The electrons added to one side occupy orbitals in the band of the metal and thus raise the Fermi level of that metal. The electrons that are removed from the other metal come from orbitals in the metallic band, so the Fermi level of that metal is lowered. The potential difference between the two pieces of metal that is caused by the power supply is the energy difference between the two Fermi levels.

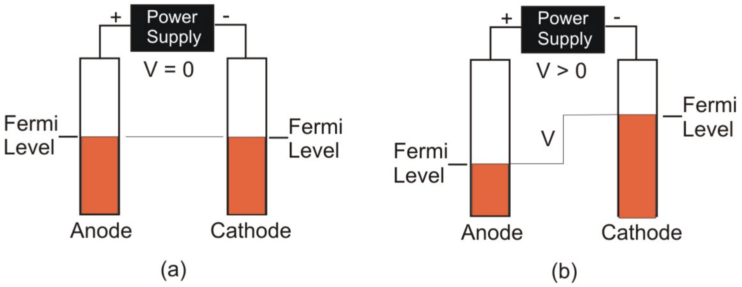


Figure 9.3: Applied Potential and Electrode Fermi Levels The orange rectangles represent the conduction band occupancies of two pieces of the same metal. (a) When no potential is applied to the metals, their band populations and therefore their Fermi levels are the same; i.e., there is no potential difference. (b) Application of an electrical potential causes the Fermi level of the anode to drop as electrons are removed and the Fermi level of the cathode to increase as electrons are added. The potential difference in the Fermi levels equals the applied potential

Recall that the cathode is the electrode where reduction takes place, so it is the electrode toward which the electrons move. In a galvanic cell they move spontaneously toward the positive electrode, which is the cathode. However, the power supply pushes the electrons toward the negative electrode in an electrolytic cell, so the negative electrode is the cathode and the reduction half reaction takes place there. Similarly, the positive electrode in an electrolytic cell is the anode, which is where oxidation takes place. Thus, **the signs of the electrodes in an electrolytic cell are opposite what they are in a galvanic cell.**

9.5-2. Ion Migration

Anions migrate toward electrodes at positive potential (anode), while cations migrate toward the electrode at negative potential (cathode).

Molten salts and aqueous solutions of electrolytes conduct electricity when a sufficient voltage is applied across two electrodes immersed in them because the ions (electrolytes) are mobile and migrate toward the electrodes. Cations move toward the cathode because it is at a negative potential, and anions move toward the anode because it is at a positive potential. Thus, the cathode is surrounded by cations, while the anode is surrounded by anions. Indeed, the names 'cation' and 'anion' derive from this behavior: anions move toward the anode and cations move toward the cathode.

A video or simulation is available online.

9.5-3. Potential Required for the Electrolysis of NaCl

When the cell potential is great enough, electrons can be forced from the cathode to the surrounding cations and to the anode from the surrounding anions. The resulting electron transfer reactions combine to produce a process called electrolysis. In an electrolysis experiment, which is carried out in an electrolytic cell, electrical potential is converted into chemical potential because the produced species are at a greater free energy than the reacting ones. We examine their function by studying the electrolysis of NaCl.

$$2\ \mathrm{NaCl} \rightarrow 2\ \mathrm{Na} + \mathrm{Cl_2} \quad \Delta G^\circ_{298} = +768\ \mathrm{kJ}$$

The reaction is not spontaneous at standard conditions and 298 K, but it can be made to occur by an input of energy sufficient to overcome the positive ΔG°. This energy can be supplied by a power supply in an electrolytic cell. We can estimate the cell voltage required from the value of ΔG° with Equation 9.4 as follows.

$$\mathcal{E}^\circ = \frac{\Delta G^\circ}{n\mathcal{F}} = \frac{768,000\ \text{J}}{(2\ \text{mol})(96,500\ \text{C/mol})} = -4\ \text{V}$$

The negative sign implies that 4 V must be applied to the cell. Alternatively, we could use the standard reduction potentials as follows.

cathode	$2\ \text{Na}^{1+} + 2\ \text{e}^{1-} \rightarrow 2\ \text{Na}$	$\mathcal{E}^\circ_{\text{cathode}} = -2.7$ V
anode	$2\ \text{Cl}^{1-} \rightarrow \text{Cl}_2 + 2\ \text{e}^{1-}$	$\mathcal{E}^\circ_{\text{anode}} = +1.4$ V
cell	$2\ \text{NaCl} \rightarrow 2\ \text{Na}^{1+} + 2\ \text{Cl}^{1-}$	$\mathcal{E}^\circ_{\text{cell}} = -2.7 - 1.4 = -4$ V

Both methods assume 298 K, and the half reactions represent aqueous solution. Our discussions are concerned with the molten salt, which must be heated to about 800 °C, so the applied voltage may differ from the 4 V calculated here. However, we will use 4 V for the discussion in the next section. Our conclusion is that NaCl can be electrolyzed to Na and Cl_2 by the application of over 4 V from an external power supply.

9.5-4. Electrolysis of NaCl

When the applied voltage is such that the energy of the electrons at the Fermi level of the cathode is higher than the empty valence orbitals on the oxidant (Na^{1+}), and the energy of unfilled orbitals at the Fermi level in the anode is less than the valence electrons on the reductant (Cl^{1-}), electrons flow through the circuit, and electricity is conducted through the melt. Conduction in an electrolytic cell is called ***electrolytic conduction***. Note that the direction of electron flow is from positive to negative as the power supply forces the electrons to lower (more negative) potential. Forcing electrons to move in this direction requires energy, which is stored in the higher free energy of the products. Thus,

- An electrolytic cell converts the electrical potential energy generated in the power supply into chemical potential energy, which is stored in the sodium metal and chlorine gas.

A video or simulation is available online.

9.5-5. Predicting the Required Voltage Exercise

EXERCISE 9.11:

What voltage must be applied to electrolyze water? The relevant half-reactions from Selected Standard Reduction Potentials at 298 K are:

$$2\ \text{H}_2\text{O} + 2\ \text{e}^{1-} \rightleftharpoons \text{H}_2 + 2\ \text{OH}^{1-} \quad \mathcal{E}^\circ = -0.41\ \text{V}$$
$$\text{O}_2 + 4\ \text{H}^{1+} + 4\ \text{e}^{1-} \rightleftharpoons 2\ \text{H}_2\text{O} \quad \mathcal{E}^\circ = +0.82\ \text{V}$$

Use the fact that $\text{H}^{1+} + \text{OH}^{1-} \rightarrow \text{H}_2\text{O}$ to write the cell reaction.

________ → ________ + ________

Required voltage = ________ V

9.5-6. Overpotential

The minimum voltage required to electrolyze water was determined to be 1.23 V in the previous exercise, but the rates of the two half-reactions are negligible at that potential because the activation energies of the two half-reactions are so high. To obtain reasonable reaction rates, the applied potential must be about 1 V higher than the predicted value.

- The amount by which the potential must be increased above the predicted value to obtain a reasonable rate of reaction is called the ***overpotential***.

The overpotential for each of the water half-reactions is about 0.5 volt. Overpotentials can be very difficult to predict because they depend not only upon the reaction, but also upon the electrode and the ions in solution.

9.6 Predicting the Products of Electrolysis

Introduction

The electrolysis of a mixture of several components *usually* produces only one product at each electrode. In this section we discuss some guidelines to use in predicting which product forms.

Objectives

- Predict the products of the electrolysis of a mixture.

9.6-1. Predicting the Products of Electrolysis

The predominant products formed in the electrolysis of a mixture are usually those from the components of the mixture that are most easily oxidized and reduced.

- The species that forms at the cathode is usually the reduced form of the best oxidant (most positive or least negative reduction potential).
- The species that forms at the anode is usually the oxidized form of the best reductant (least positive or most negative reduction potential).

We use the word ‘usually’ in the above because the situation can be complicated by high overpotentials. In these cases, reaction of the best oxidant or reductant may be negligibly slow at the predicted potential, and weaker oxidants or reductants with smaller overpotentials may react first. Many electrolysis experiments are performed in water, and water’s large overpotential can make predictions difficult. This is the case in the electrolysis of sea water, where chloride ion is oxidized to chlorine gas even though its reduction potential (+1.36 V) is more positive than that for the oxidation of water to oxygen gas (+0.88 V at pH = 7).

9.6-2. Predicting the Products Exercise

<u>**EXERCISE 9.12:**</u>

Predict the products of the electrolysis of the following.

a molten mixture of $FeCl_2$ and $NiBr_2$

- The molten mixture contains Fe^{2+}, Ni^{2+}, Cl^{1-}, and Br^{1-} ions, so the relevant half-reactions and standard reduction potentials are:

$$\begin{aligned}
&Fe^{2+} + 2\ e^{1-} \rightleftharpoons Fe && \mathcal{E}^\circ = -0.44\ V\\
&Ni^{2+} + 2\ e^{1-} \rightleftharpoons Ni && \mathcal{E}^\circ = -0.23\ V\\
&Br_2 + 2\ e^{1-} \rightleftharpoons 2\ Br^{1-} && \mathcal{E}^\circ = +1.09\ V\\
&Cl_2 + 2\ e^{1-} \rightleftharpoons 2\ Cl^{1-} && \mathcal{E}^\circ = +1.39\ V
\end{aligned}$$

product formed at cathode	product formed at anode
Fe	Fe
Ni	Ni
Br_2	Br_2
Cl_2	Cl_2

aqueous KI

- K^{1+} and I^{1-} are present and water can be oxidized and reduced, so there are four possible half-reactions.

$$\begin{aligned}
&K^{1+} + 1\ e^{1-} \rightleftharpoons K && \mathcal{E}^\circ = -2.92\ V\\
&2\ H_2O + 2\ e^{1-} \rightleftharpoons H_2 + 2\ OH^{1-} && \mathcal{E}^\circ = -0.41\ V\\
&I_2 + 2\ e^{1-} \rightleftharpoons 2\ I^{1-} && \mathcal{E}^\circ = +0.54\ V\\
&O_2 + 4\ H^{1+} + 4\ e^{1-} \rightleftharpoons 2\ H_2O && \mathcal{E}^\circ = +0.88\ V
\end{aligned}$$

product formed at cathode	product formed at anode
K	K
H_2	H_2
I_2	I_2
O_2	O_2

1 M $CuSO_4$ solution

- The solution contains H_2O, Cu^{2+}, and SO_4^{2-}, so the relevant half-reactions are:

$$\begin{aligned}
&2\ H_2O + 2\ e^{1-} \rightleftharpoons H_2 + 2\ OH^{1-} && \mathcal{E}^\circ = -0.41\ V\\
&Cu^{2+} + 2\ e^{1-} \rightleftharpoons Cu && \mathcal{E}^\circ = +0.34\ V\\
&O_2 + 4\ H^{1+} + 4\ e^{1-} \rightleftharpoons 2\ H_2O && \mathcal{E}^\circ = +0.88\ V\\
&S_2O_8^{2-} + 2\ e^{1-} \rightleftharpoons 2\ SO_4^{2-} && \mathcal{E}^\circ = +2.01\ V
\end{aligned}$$

product formed at cathode	product formed at anode
H_2	H_2
Cu	Cu
O_2	O_2
$S_2O_8^{2-}$	$S_2O_8^{2-}$

9.7 Stoichiometry of Electrochemistry

Introduction

By the 1830s, Michael Faraday had discovered that, when a chemical reaction was harnessed to an electrical current using an electrochemical cell, the amount of electricity produced or consumed corresponded directly to the amount of chemical reactant involved. In this section, we discuss these quantitative aspects of the electrochemical cell.

Objectives

- Determine the mass of product given the amount of charge that has flowed through the cell.
- Determine the number of coulombs of charge that are passed through a circuit given the current and the length of time the current flowed.
- Determine the mass of product given the current and the length of time the current flowed.
- Determine how long a given current must be applied in order to produce a given amount of product.

9.7-1. Relating the Charge Passed to the Mass formed

The electron is a reactant or a product in all half-reactions, so it is an integral part of the cell stoichiometry. However, we do not determine the mass or volume of electrons involved as we would with other reactants and products. Instead, we determine the charge in ***coulombs*** that passes during the reaction, which is measured with a coulometer. The number of coulombs that are transferred can then converted to moles of electrons with the use of the faraday, which is 96,500 C/1 mol electrons.

The number of moles of electrons is converted to moles of product by using the stoichiometry of the half-reaction that involves the given species. We do the following exercises in single steps, but the answer to each step is the starting point for the following step. Thus, the steps can be combined into a single factor-label exercise. This alternate method is shown in the feedback of the final answer in each problem.

9.7-2. Charge to Mass Exercise

EXERCISE 9.13:

What mass of copper is produced by passing 2.00×10^4 C through a solution of Cu^{2+}?

First, convert the charge to moles of electrons:

_______________ mol e^{1-}

Next, use the stoichiometric factor from the appropriate half-reaction to determine the moles of copper:

_______________ mol Cu

Finally, use the atomic mass of copper (63.5) to convert moles of copper to grams of copper.

_______________ g Cu

9.7-3. Electrical Current

1 amp = 1 C/s

Electrical current is the rate at which charge flows through the circuit. It is given the symbol i and has units of amperes (A or amps). One ampere is one coulomb per second (1 A = 1 C/s). Consequently, the charge in coulombs that flows during an electrochemical experiment carried out at a fixed current of i amperes for t seconds is given by Equation 9.8.

$$\text{charge} = i \times t \qquad \text{Charge is the product of current and time} \tag{9.8}$$

9.7-4. Mass of Product from Current and Time Exercise

EXERCISE 9.14:

What mass of gold would be plated on an earring by passing a current of 10. mA through a solution of $AuCl_3$ for 1.5 hours?

Note: the following steps can be combined into one series of multiplications. The order can be determined using the factor label method.

charge passed = ______________ C

moles of electrons passed = ______________ mol e^{1-}

moles of gold plated = ______________ mol Au

mass of gold plated in milligrams = ______________ mg Au

9.7-5. Time Required for Electrolysis Exercise

EXERCISE 9.15:

How long (in minutes) should a 5.0 A current be passed through a solution of $Ni(NO_3)_2$ in order to nickel plate a bathroom fixture with 0.85 g of nickel?

Time in minutes = ______________

9.8 Exercises and Solutions

Links to view either the end-of-chapter exercises or the solutions to the odd exercises are available in the HTML version of the chapter.

CHAPTER 10 – CHEMICAL KINETICS

Introduction

To this point in our study of chemistry, we have been concerned only with the composition of the equilibrium mixture, not the length of time required to obtain it. However, the time required is also an important consideration. If a reaction proceeds too slowly, it will not be useful no matter how large the equilibrium constant, and if a reaction proceeds too rapidly, it may not be possible to control it. Thermodynamics allows us to predict the extent of a reaction, but it tells us nothing about the speed of the reaction or how it occurs. These latter two considerations are the domain of kinetics, the study of the rates and mechanisms of chemical reactions.

10.1. Reaction Rates

Introduction

Rates are changes in one quantity with respect to another, and reaction rates are measured as changes in concentration with respect to time. They are the most important of the kinetic parameters, and we begin our study of kinetics with a treatment of reaction rates.

Objectives

- Express the relative rates of consumption of reactants and formation of products from the coefficients in a balanced chemical reaction.

10.1-1. Concentrations versus Time

It takes time for the concentrations of reactants and products to change from their initial to their equilibrium values, but once equilibrium is established, the concentrations no longer change. Kinetics studies the reaction during the time of change, while thermodynamics is concerned only with the initial and equilibrium conditions. Thus, the region of time in which the concentrations are changing is called the ***kinetic region***, while the region after equilibrium is established is called the ***thermodynamic region***.

Consider the decomposition of 0.020 M HI at 700 °C, $2\ \mathrm{HI}(g) \rightarrow \mathrm{H_2}(g) + \mathrm{I_2}(g)$. The concentrations of both reactants and products are shown in Figure 10.1a as a function of time in seconds. The concentration of HI decreases for about 10,000 seconds (about three hours) and then levels off at 0.015 M. During that time, the concentrations of H_2 and I_2 each rise from zero to about 0.0025 M. Once the concentrations are no longer changing, the system has reached equilibrium. Thus, approximately three hours are required to obtain an equilibrium mixture at this temperature. $\Delta n_\mathrm{g} = 0$ for the reaction, so the thermodynamic equilibrium constant for the reaction is equal to K_c, so it can be determined from the equilibrium concentrations,

$$K = \frac{[\mathrm{H_2}][\mathrm{I_2}]}{[\mathrm{HI}]^2} = \frac{(0.0025)(0.0025)}{(0.015)^2} = 0.028$$

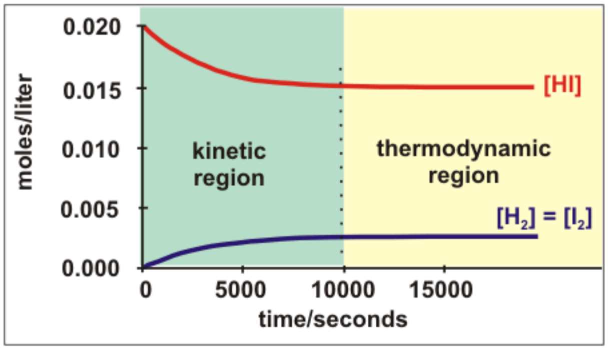


Figure 10.1a: Concentrations versus Time for the Decomposition of HI at 700 °C

If the reaction were extensive, 0.020 M HI would react to produce a mixture that was 0.010 M in each H_2 and I_2, and we now examine the reaction from the reverse direction by reacting 0.010 M H_2 with 0.010 M I_2 at 700 °C. The results are shown in Figure 10.1b. The HI concentration rises to its equilibrium value of 0.015 M, while the H_2 and I_2 concentrations each drop to their equilibrium value of 0.0025 M. Note that these are the same equilibrium concentrations obtained by the decomposition of HI shown in Figure 10.1a. We conclude that equilibrium concentrations, while dependent upon the initial concentrations, are independent of the direction from which they were obtained.

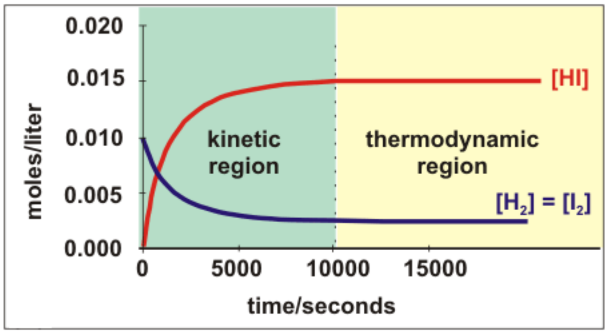


Figure 10.1b: Concentrations versus Time for the Decomposition of HI at 700 °C

10.1-2. Average Rates

Rates are changes in one quantity with respect to another. For example, speed is the rate of change of position with respect to time. The average speed is determined by dividing the distance traveled (the change in position) by the time required to travel it. Thus, a person traveling 300 kilometers in 4 hours has an average speed of 75 km·h^{-1} (~50 mph).

$$\frac{\text{change in position}}{\text{time interval}} = \frac{\Delta x}{\Delta t} = \frac{300\text{ km}}{4\text{ h}} = 75\text{ km}\cdot\text{h}^{-1}$$

The above is the average speed over the interval, but it is unlikely that the person traveled at a constant speed of 75 km·h^{-1} for the entire trip. The instantaneous speed (the speed given by the speedometer at any instant) for such a trip might vary from 0 to over 100 km·h^{-1}.

10.1-3. Average Rates of Formation of HI

Reaction rates are the most important of the kinetic parameters. They are measured as changes in concentration with respect to time. Products are formed during a reaction, so we refer to their ***rate of formation***. The average rate of formation of HI over a time interval Δt is given as the following.

$$\text{rate of formation of HI} = \frac{\Delta[\text{HI}]}{\Delta t}$$

Consider the following three points in the plot of HI concentration versus time at 700 °C for the reaction $H_2 + I_2 \rightarrow 2\text{ HI}$ shown in Figure 10.2.

time (s)	[HI] (M)
0	0.000
2000	0.011
5000	0.014

Table 10.1

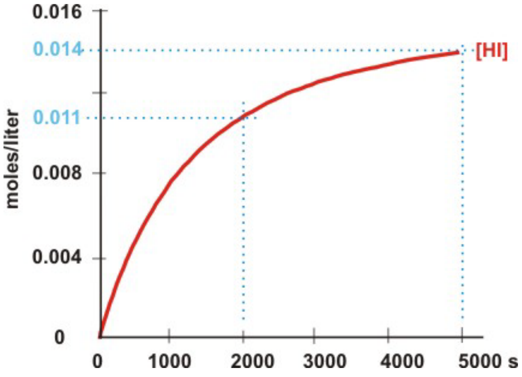


Figure 10.2

The average rate of formation of HI during the first 2000 s would be determined as

$$\frac{\Delta[\text{HI}]}{\Delta t} = \frac{0.010\,M - 0.000\,M}{2000\text{ s} - 0\text{ s}} = \frac{0.010\,M}{2000\text{ s} - 0\text{ s}} = 5.0 \times 10^{-6}\,M/\text{s}$$

and the average rate of formation in the interval 2000 to 5000 s would be

$$\frac{\Delta[\text{HI}]}{\Delta t} = \frac{0.014\,M - 0.010\,M}{5000\text{ s} - 2000\text{ s}} = \frac{0.004\,M}{3000\text{ s}} = 1 \times 10^{-6}\,M/\text{s}$$

Thus, the rate decreased by nearly 80%. Indeed, the rate of formation continues to decrease as it approaches 0 at equilibrium. Thus, rates of reaction vary with time.

10.1-4. Graphical Determination of a Rate of Formation

It is not the average rate of change that is important in kinetics studies. Rather it is the instantaneous rate of change; i.e., the rate at which the concentration is changing at a given time. The instantaneous rate at a given time is given by the slope of the tangent to the concentration versus time curve at that instant. We will assume that anytime a rate is given, that it is the instantaneous rate unless it is specified to be the average rate.

We now determine the rate of formation of HI 2130 s into the reaction. Consider the graph shown in Figure 10.3, which shows the variation of the HI concentration with time in more detail than in Figure 10.1a. The rate of formation of HI at this point equals the slope of the tangent (shown as a green line). The slope is determined by taking two points on the tangent line and determining the change in concentration by the time interval between the two points. We use the two points at the ends of the line to determine the slope and therefore the rate of formation at that time as follows.

$$\text{rate of formation of HI at 2130 s} = \frac{\Delta[\text{HI}]}{\Delta t} = \frac{+0.008\,M}{4000\text{ s}} = 2 \times 10^{-6}\,M/\text{s}$$

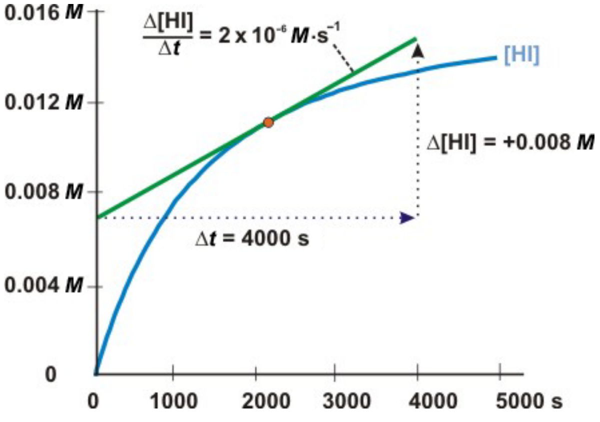


Figure 10.3: Graphical Determination of the Rate of Formation of HI at 2130 s

10.1-5. Graphical Determination of a Rate of Disappearance

Reactant concentrations decrease with time, so they are disappearing. Consequently, it is usually the ***rate of disappearance*** of reactants that is given. The rate of disappearance of H_2 is given as

$$\text{rate of disappearance of } H_2 = -\frac{\Delta[H_2]}{\Delta t}$$

Note that the rate at which $[H_2]$ is changing is negative, so its rate of *disappearance* is positive.

The rates of disappearance of H_2 and I_2 at 2130 s into the reaction is determined graphically in Figure 10.4. Note that the slope of the tangent is negative, which indicates a disappearance. Thus, the rates of disappearance of H_2 and I_2 are each $1 \times 10^{-6}\ M\cdot s^{-1}$. Note that the rates of disappearance of H_2 and I_2 are one-half of the rate of formation of HI, consistent with the fact that 2 HI are formed for each H_2 and I_2 that react.

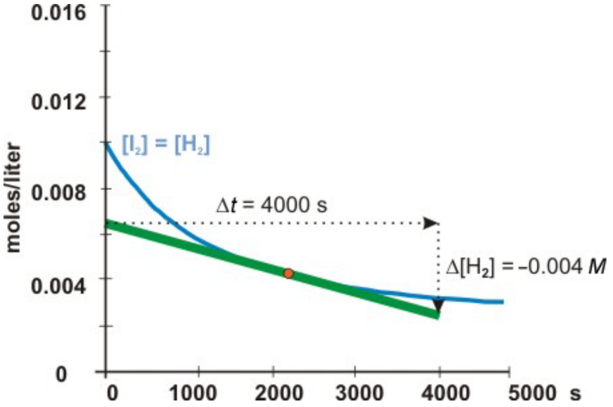


Figure 10.4: Graphical Determination of the Rates of disappearance of H_2 and I_2 at 2130 s

10.1-6. Rate of Reaction

The rate of formation of HI at any instant is exactly twice the rate of disappearance of H_2 or I_2 as dictated by the stoichiometry of the reaction (2 mol HI form for each mole of H_2 or I_2 that react). The rates of appearance of products and the rates of disappearance of reactants are often different, so what is meant by the term rate of reaction? To answer that question, we construct the reaction table to determine how much reaction takes place during some time interval Δt.

	H_2	+	I_2	→	2 HI
t	c		c		c'
Δt	$-\Delta x$		$-\Delta x$		$+2\Delta x$
$t+\Delta t$	$c-\Delta x$		$c-\Delta x$		$c'+2\Delta x$

In the reaction table, Δx is the change in concentration of any species whose coefficient in the balanced chemical equation is unity. In the reaction above, $\Delta x = -\Delta[H_2] = -\Delta[I_2] = \Delta[HI]/2$. The ***rate of reaction*** of the above reaction is defined as

$$\text{rate of reaction} = \frac{\Delta x}{\Delta t} = -\frac{\Delta[H_2]}{\Delta t} = -\frac{\Delta[I_2]}{\Delta t} = \frac{1}{2} \times \frac{\Delta[HI]}{\Delta t}$$

Although it is more common to talk about the rate of formation of a product or the rate of disappearance of a reactant, the rate of reaction is also used and care must be given to the differences caused by the coefficients in the balanced equation. In general, the rate of reaction is related to the rates of formation or disappearance as follows.

$$\text{rate of reaction} = \frac{\Delta x}{\Delta t} = \frac{\text{rate of formation of product}}{\text{coefficient of product}} = \frac{\text{rate of disappearance of reactant}}{\text{coefficient of reactant}}$$

The Rate of Reaction (10.1)

10.1-7. Exercise

EXERCISE 10.1:

At some time during the reaction $N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$, the rate of formation of ammonia is 0.024 $M{\cdot}s^{-1}$. What is the rate of the reaction and what are the rates of disappearance of each of the reactants at this time?

rate of reaction = ______________ $M{\cdot}s^{-1}$

rate of disappearance of N_2 = ______________ $M{\cdot}s^{-1}$

rate of disappearance of H_2 = ______________ $M{\cdot}s^{-1}$

10.1-8. Exercise

EXERCISE 10.2:

The rate of formation of N_2 was found to be 0.32 M/s.

$$4\ NH_3(g) + 3\ O_2(g) \rightarrow 2\ N_2(g) + 6\ H_2O(g)$$

The rate of reaction at this time was: ______________ M/s

The rate of disappearance of NH_3 at that time was: ______________ M/s

The rate of disappearance of O_2 was: ______________ M/s

The rate of formation of water was: ______________ M/s

10.2. Rate Laws

Introduction

Rates are used to determine the **rate law** of a reaction, which shows how the rate varies with the concentrations of reactants.

Objectives

- Determine the rate of a reaction given the rate law, the rate constant, and concentrations of reactants.
- Determine the rate constant given the rate law and a rate at a given set of concentrations.

10.2-1. Definitions

The manner in which the rate varies at a given temperature is expressed by the rate law for the reaction. Rate laws can be very complicated, but they often take the form of a constant times the concentrations of the reactants each raised to some exponent. The exponent of a reactant's concentration is called the ***reactant order*** of that reactant, while the sum of the exponents of all reactants is referred to as the ***reaction order***.

Reaction	Rate Law	Reaction and Reactant Orders
a $H_2 + I_2 \rightarrow 2\ HI$	rate = $k_a[H_2][I_2]$	A second order reaction that is first order in H_2 and first order in I_2.
b $2\ HI \rightarrow H_2 + I_2$	rate = $k_b[HI]^2$	A second order reaction that is second order in HI.
c $2\ N_2O_5 \rightarrow 4\ NO_2 + O_2$	rate = $k_c[N_2O_5]$	A first order reaction that is first order in N_2O_5.

Table 10.2

It is important to recognize the following.

The exponents in a rate law are not necessarily the stoichiometric coefficients in the balanced equation. The exponents must be determined experimentally.

Thus, **Reaction c** is first order in N_2O_5 even though the stoichiometric coefficient of N_2O_5 is two. The rate constants k_a and k_b are called second-order rate constants, while k_c is a first-order rate constant. The reaction rate has units of concentration per unit time, but the units of the rate constant depend on the reaction order.

First Order	Second Order
$k_c = \frac{\text{rate}}{[N_2O_5]} = \frac{M\cdot s^{-1}}{M} = s^{-1}$	$k_b = \frac{\text{rate}}{[HI]^2} = \frac{M\cdot s^{-1}}{M^2} = M^{-1}\cdot s^{-1}$

Table 10.3

Thus, the units of a first order rate constant are s^{-1} and the units of a second order rate constant are $M^{-1}\cdot s^{-1}$.

10.2-2. Exercise

EXERCISE 10.3:

The rate of decomposition of 0.10 M N_2O_5 at 298 K is 0.022 $M\cdot\text{min}^{-1}$.

$$2\ N_2O_5 \rightarrow 4\ NO_2 + O_2$$

rate of reaction = ______________ $M\cdot\text{min}^{-1}$

k_{298} = ______________ min^{-1}

The reaction continues until the concentration of N_2O_5 has dropped to 0.042 M. At that point,

rate of reaction = ______________ $M\cdot\text{min}^{-1}$

rate of formation of NO_2 = ______________ $M\cdot\text{min}^{-1}$

10.3. Determining Rate Laws

Introduction

The exponents of each of the concentrations in a rate law must be determined experimentally. In this section, we apply the method of initial rates and concentration versus time data to obtain rate laws.

Objectives

- Use the method of initial rates to determine the rate law of a reaction.

10.3-1. Introduction

In the method of initial rates, average rates of reaction are determined at the beginning of the reaction. The time interval of the experiment must be small enough that only a small fraction of the reactants is consumed. This assures that the average rate is close to the instantaneous rate ($\Delta t \rightarrow 0$). The method has the advantage that the concentrations are initial (makeup) concentrations, which means that they are predetermined. In addition, the initial concentrations of the products are zero, so the reverse reaction can be ignored. This is a real advantage when studying reactions where the forward and reverse reactions compete with one another at appreciable product concentrations.

10.3-2. Method

At least one experiment must be performed for each unknown in the rate law: one for the rate constant and one for each reactant order. For example, the rate law for the generic reaction, A + B → products has the form $R =$

$k[\mathrm{A}]^a[\mathrm{B}]^b$, so a minimum of three rates must be measured using different initial concentrations of A and B in order to determine the values of k, a, and b. The three rates can be expressed as

$$R_1 = k[\mathrm{A}]_1^a[\mathrm{B}]_1^b \quad R_2 = k[\mathrm{A}]_2^a[\mathrm{B}]_2^b \quad R_3 = k[\mathrm{A}]_3^a[\mathrm{B}]_3^b$$

If all three experiments are carried out at the same temperature, all three rate constants are the same. Thus, the rate constant can be eliminated by dividing the rates by one another to produce the following two equations.

$$\frac{R_1}{R_2} = \frac{\cancel{k}[\mathrm{A}]_1^a[\mathrm{B}]_1^b}{\cancel{k}[\mathrm{A}]_2^a[\mathrm{B}]_2^b} = \left(\frac{[\mathrm{A}]_1}{[\mathrm{A}]_2}\right)^a \left(\frac{[\mathrm{B}]_1}{[\mathrm{B}]_2}\right)^b \text{ and } \frac{R_2}{R_3} = \frac{\cancel{k}[\mathrm{A}]_2^a[\mathrm{B}]_2^b}{\cancel{k}[\mathrm{A}]_3^a[\mathrm{B}]_3^b} = \left(\frac{[\mathrm{A}]_2}{[\mathrm{A}]_3}\right)^a \left(\frac{[\mathrm{B}]_2}{[\mathrm{B}]_3}\right)^b$$

We now have two equations in two unknowns that can be solved for a and b by taking the logarithms of both sides. However, the algebra can be simplified by experimental design. If the concentration of B is kept constant in Experiments 1 and 2 ($[\mathrm{B}]_1 = [\mathrm{B}]_2$), and the concentration of A is kept constant in Experiments 2 and 3 ($[\mathrm{A}]_2 = [\mathrm{A}]_3$) then the ratio of rates simplifies to the following.

$$\frac{R_1}{R_2} = \frac{[\mathrm{A}]_1^a\cancel{[\mathrm{B}]_1^b}}{[\mathrm{A}]_2^a\cancel{[\mathrm{B}]_2^b}} = \left(\frac{[\mathrm{A}]_1}{[\mathrm{A}]_2}\right)^a \text{ and } \frac{R_2}{R_3} = \frac{\cancel{[\mathrm{A}]_2^a}[\mathrm{B}]_2^b}{\cancel{[\mathrm{A}]_3^a}[\mathrm{B}]_3^b} = \left(\frac{[\mathrm{B}]_2}{[\mathrm{B}]_3}\right)^b \qquad \text{Ratios of Rates} \qquad (10.2)$$

The ratios are all known, so the exponents can be determined with the use of logs as shown in Equation 10.3.

$$a = \frac{\log\left(\dfrac{R_1}{R_2}\right)}{\log\left(\dfrac{[\mathrm{A}]_1}{[\mathrm{A}]_2}\right)} \text{ and } b = \frac{\log\left(\dfrac{R_2}{R_3}\right)}{\log\left(\dfrac{[\mathrm{B}]_2}{[\mathrm{B}]_3}\right)} \qquad \text{The Orders of the Reactants} \qquad (10.3)$$

The orders can often be determined by inspection in cases where the ratios are simple fractions. Most of the examples that we will deal with can be done by inspection (no logs required).

10.3-3. Decomposition of HI Exercise

EXERCISE 10.4:

The kinetics of the decomposition of HI at 700 °C were followed by monitoring the appearance of iodine. Fresh HI was added to the reaction flask, and the times required for the concentration of the iodine to reach 1.00×10^{-4} M were determined at different initial concentrations of HI.

Exp	**Initial [HI] (*M*)**	**Time (s)**
1	0.0200	140.3
2	0.0400	35.1

Determine the order of HI and the specific rate constant for the decomposition at 700 °C.

1) Convert the times into rates of formation of I_2.

$R_1 =$ ______________ M/s

$R_2 =$ ______________ M/s

2) Determine the ratio of the rates. (Divide the larger by the smaller to avoid fractions.)

$R_2/R_1 =$ ______________

3) Determine the corresponding ratio of concentrations.

$[\mathrm{HI}]_2/[\mathrm{HI}]_1 =$ ______________

4) Use Equation 10.3 and the results of steps 2 and 3 to determine the order of HI. The order is an integer.

order = ______________

5) Use the rate law you have now determined and one of the concentration–rate pairs to determine the second order rate constant for the reaction.

$k =$ ______________ $M^{-1}\cdot\mathrm{s}^{-1}$

10.3-4. Formation of HI Exercise

EXERCISE 10.5:

The kinetics of the formation of HI at 700 °C were followed by measuring the time required for the concentration of the iodine to drop by 1.00×10^{-4} M.

Exp	$[\mathbf{H_2}](M)$	$[\mathbf{I_2}](M)$	Time (s)
1	0.0100	0.0100	16.0
2	0.0200	0.0100	8.00
3	0.0200	0.0200	4.00

Determine the order of H_2 and I_2 and the specific rate constant for the formation of HI at 700 °C.

1) The rate of reaction equals the rate at which I_2 disappears, so we must first convert the times into rates of disappearance of I_2.

$R_1 =$ ______________ M/s

$R_2 =$ ______________ M/s

$R_3 =$ ______________ M/s

2) Pick the best ratio of rates to use to determine the order of H_2.
R_2/R_1
R_3/R_2
R_3/R_1

3) Determine the ratio of the rates to use to determine the order of H_2.

ratio = ______________

4) Determine the corresponding ratio of concentrations.

ratio = ______________

5) Use Equation 10.3 and the results of steps 3 and 4 to determine the order of H_2.

order of H_2 = ______________

6) Pick the best ratio of rates to use to determine the order of I_2.
R_2/R_1
R_3/R_2
R_3/R_1

7) Determine the ratio of the rates to use to determine the order of I_2.

ratio = ______________

8) Determine the corresponding ratio of concentrations.

ratio = ______________

9) Use Equation 10.3 and the results of Steps 7 and 8 to determine the order of I_2.

order of I_2 = ______________

10) Use the rate law you have now determined and the data from one experiment to determine the rate constant for the reaction.

$k =$ ______________ M/s

10.3-5. Exercise

EXERCISE 10.6:

The initial rates data at some temperature for the reaction $NO(g) + H_2(g) \longrightarrow N_2O(g) + H_2O(g)$ are given in the following table.

Exp	**[NO] (M)**	**[H2](M)**	**Rate (M/min)**
1	0.10	0.80	0.26
2	0.30	0.80	2.34
3	0.30	0.40	1.17

The order of NO is ______________

The order of H_2 is ______________

The specific rate constant at this temperature is $k =$ ______________ $M^{-2} \cdot s^{-1}$

First-order Kinetics

10.3-6. Integrated Rate Law

Consider the generic first order reaction A → products, which has the following rate law.

$$-\frac{\Delta[A]}{\Delta t} = k[A]$$

The above can be rearranged as follows to get the [A] terms on the same side of the equation

$$-\frac{\Delta[A]}{[A]} = k\Delta t$$

which can be solved by the following integration

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -k \int_0^t dt$$

to produce the following two expressions that relate concentration and time.

$$\begin{aligned} \ln [A] &= \ln [A]_0 - kt \\ \ln\left(\frac{[A]}{[A]_0}\right) &= -kt \end{aligned} \qquad \text{The Integrated Rate Equation for a First Order Reaction} \qquad (10.4)$$

where $[A]_0$ is the concentration of A at $t = 0$, i.e., the initial concentration. Equation 10.4 shows that a plot of ln [A] versus time for a first order reaction is a straight line with a slope of $-k$ and an intercept of ln $[A]_o$.

This behavior can also be expressed as an exponential.

$$[A] = [A]_0 e^{-kt} \qquad \text{Exponential Form of the Integrated Rate Equation} \qquad (10.5)$$

Equation 10.5 shows that the concentration of a reactant drops exponentially with time. This behavior is called ***exponential decay***. We conclude the following.

A reactant in a first order reaction undergoes exponential decay, and a plot of ln [A] vs. t for its decay is linear with a slope of $-k$.

10.3-7. Determining a Concentration Exercise

EXERCISE 10.7:

The decomposition of dimethyl ether, $H_3C{-}O{-}CH_3(g) \longrightarrow CH_4(g) + H_2(g) + CO(g)$ is first order with a rate constant of 4.00×10^{-4} s^{-1} at 500 °C. If the initial concentration of dimethyl ether is 0.050 *M*, what is its concentration after 1.00 hour?

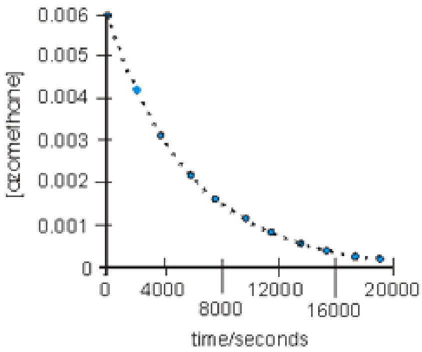
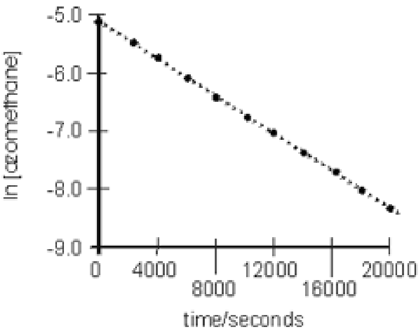
$[\mathrm{HC_3{-}O{-}CH_3}[=$ ______________ *M*

10.3-8. First Order Behavior Exercise

EXERCISE 10.8:

The concentrations of azomethane at various times during its decomposition at 300 °C are shown in the table below. Verify that the decomposition is first order and determine the first-order rate constant at 300 °C.

The decomposition reaction is $H_3C{-}N{=}N{-}CH_3(g) \longrightarrow C_2H_6(g) + N_2(g)\cdot$

***t* (s)**	**[A]**	**ln [A]**	**[A] vs *t***	**ln [A] vs *t***
0	0.00600	−5.116		
2000	0.00436	−5.436		
4000	0.00316	−5.756		
6000	0.00230	−6.076		
8000	0.00167	−6.396		
10000	0.00121	−6.716		
12000	0.00088	−7.036		
14000	0.00064	−7.356		
16000	0.00046	−7.676		
18000	0.00034	−7.996		
20000	0.00024	−8.316		

The reaction is first order because a plot of ln [A] versus *t* is linear.

What is the first order rate constant?

$k =$ ______________ s^{-1}

10.3-9. Half-life Definition

The ***half-life***, $t_{1/2}$, of a reaction is the time required for half of the existing reactant to disappear. Consider the graph shown in Figure 10.5. The initial concentration of A (azomethane) is 0.006 *M*, so the half-life is the time required for the concentration to drop to 0.003 *M*. As shown in the figure, this occurs after 4330 s, the half-life of the reaction. After another half-life (another 4330 s) the concentration has dropped to 0.0015 *M*, which is half of 0.003 *M*. After a third half-life the concentration is again halved. **Thus the half-life of a first order reaction is constant.**

The concentration of a reactant after *n* half-lives is given by the following.

$$[\mathrm{A}] = \frac{[\mathrm{A}]_0}{2^n}$$

Thus, after five half-lives ($5 \times 4330 = 21{,}650$ s) the concentration of azomethane is $(1/2)^5(0.006\ M) = 1.9 \times 10^{-4}\ M$.

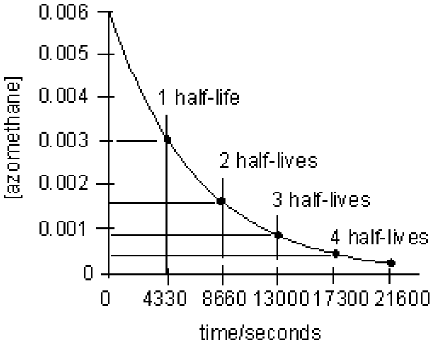


Figure 10.5: The Half-life of Azomethane The half-life of the decomposition of azomethane at 300 °C is 4330 seconds. Thus, the concentration is halved every 4330 seconds.

10.3-10. Half-life Equation

At the half-life, $t = t_{1/2}$ and $[\mathrm{A}] = [\mathrm{A}]_0/2$. Substitution of these half-life quantities into Equation 10.4 yields

$$\ln\left(\frac{[\mathrm{A}]_0/2}{[\mathrm{A}]_0}\right) = \ln\left(\frac{1}{2}\right) = -\ln 2 = -kt_{1/2}$$

Note that the identity $\ln(1/x) = -\ln(x)$ was used. Solving for the half-life,

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k} \qquad \text{The Half-life of a First Order Reaction} \tag{10.6}$$

The half-life of the azomethane decomposition can be determined from its first order rate constant determined in Exercise 10.8 ($k = 1.60 \times 10^{-4}\ \mathrm{s}^{-1}$) with Equation 10.6 as follows

$$t_{1/2} = \frac{0.693}{1.60 \times 10^{-4}} = 4330\ \mathrm{s}$$

which is the same value observed in the previous section. As shown in the following exercise, Equation 10.6 can also be used to determine the value of the first-order rate constant from a half-life.

10.3-11. Half-life Exercise

EXERCISE 10.9:

If a first-order reaction has a 23.5 minute half-life, how long would it take for it to reach 90.0% completion?

$k =$ ______________ min^{-1}
$[\mathrm{A}]/[\mathrm{A}]_0 =$ ______________
$t =$ ______________ min

Second-order Kinetics

10.3-12. Integrated Rate Law

Consider the generic second order reaction 2 A → products, which has the following rate law.

$$-\frac{\Delta[\mathrm{A}]}{\Delta t} = k\Delta[\mathrm{A}]^2$$

The above can be rearranged as follows to get the [A] terms on the same side of the equation,

$$-\frac{\Delta[\mathrm{A}]}{[\mathrm{A}]^2} = k\Delta t$$

which can be solved by the following integration

$$-\int_{[\mathrm{A}]_0}^{[\mathrm{A}]} \frac{d[\mathrm{A}]}{[\mathrm{A}]^2} = k\int_0^t dt$$

to produce the following expression that relates concentration and time.

$$\frac{1}{[\mathrm{A}]} = \frac{1}{[\mathrm{A}]_0} + kt \qquad \text{The Integrated Rate Equation for a Second Order Reaction} \qquad (10.7)$$

Thus a plot of $1/[\mathrm{A}]$ vs. t for a second order reaction is a straight line with an intercept of $1/[\mathrm{A}]_0$ and a slope equal to the rate constant.

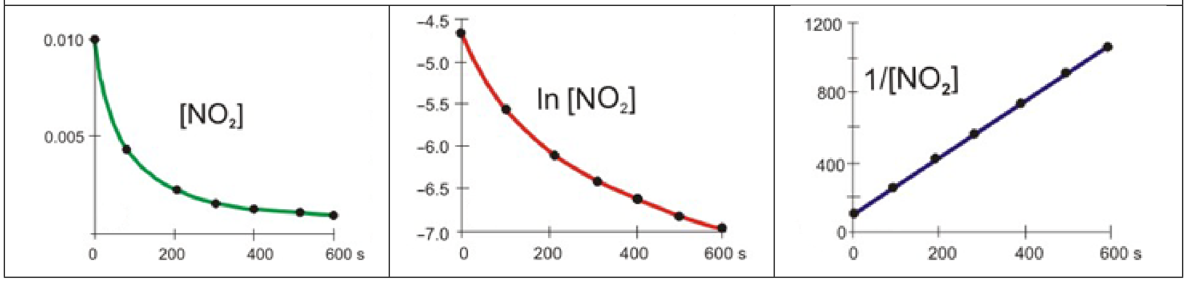
10.3-13. Reaction Order Exercise

EXERCISE 10.10:

The concentration of NO_2 versus time during its decomposition at 350 °C is shown in the table below. The natural logarithms and reciprocals of the concentrations are also included in the table. Determine if the decomposition is first or second order and the rate constant for the decomposition at 350 °C.
The decomposition reaction is $2\ NO_2(g) \rightarrow 2\ NO(g) + O_2(g)$.

t (s)	$[NO_2]$	ln $[NO_2]$	$1/[NO_2]$
0.0	0.0100	−4.605	100
100.0	0.0038	−5.565	261
200.0	0.0024	−6.045	422
300.0	0.0017	−6.368	583
400.0	0.0013	−6.612	744
500.0	0.0011	−6.808	905
600.0	0.0009	−6.972	1066

Plots



Refer to the plots above to view the kinetics of the decomposition of NO_2 graphically. Then determine the NO_2 order in the decomposition.

Is this a first or second order reaction?
- first order reaction
- second order reaction

The rate constant for the rate of disappearance of NO_2 is: $k =$ ____________ $M^{-1}{\cdot}s^{-1}$

The rate constant for the rate of reaction is: $k =$ ____________ $M^{-1}{\cdot}s^{-1}$

Another Look at the Relationship Between Equilibrium and Kinetics

10.3-14. Decomposition of HI Review

At equilibrium, the rates of the forward and reverse reactions are equal.

Recall that HI decomposes into H_2 and I_2, but it can also be formed from H_2 and I_2. If we represent these competing processes as $2\ \mathrm{HI} \rightleftharpoons \mathrm{H_2} + \mathrm{I_2}$ then the decomposition of HI is the forward reaction with a rate constant k_f, and the formation of HI is the reverse reaction with a rate constant k_r. We studied the competing reactions using the method of initial rates. The resulting rate laws were the following.

$$\begin{array}{ll} 2\ \mathrm{HI} \rightarrow \mathrm{H_2} + \mathrm{I_2} & -\dfrac{\Delta[\mathrm{HI}]}{\Delta t} = 2k_\mathrm{f}[\mathrm{HI}]^2 \\ \mathrm{H_2} + \mathrm{I_2} \rightarrow 2\ \mathrm{HI} & \dfrac{\Delta[\mathrm{HI}]}{\Delta t} = 2k_\mathrm{r}[\mathrm{H_2}][\mathrm{I_2}] \end{array}$$

The specific rate constants at 700 °C were found to be $k_\mathrm{f} = 1.8 \times 10^{-3}\ M^{-1}\cdot\mathrm{s}^{-1}$ and $k_\mathrm{r} = 6.3 \times 10^{-2}\ M^{-1}\cdot\mathrm{s}^{-1}$. The '2' in the rate laws is due to the coefficient of HI in the balanced equation.

10.3-15. Deviation from Second Order Kinetics

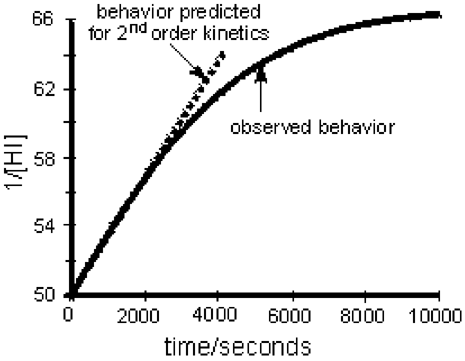


Figure 10.6: A plot of 1/[HI] versus time for the decomposition of HI at 700 °C The reaction is second order in HI, but the plot is not linear at later times because of competition from the reverse reaction.

The decomposition of HI is second order in HI, so a plot of 1/[HI] versus time for the decomposition should be linear. As shown in Figure 10.6, the plot is linear at the beginning of the experiment, but it deviates from linearity after about 2000 s. The curvature of the line indicates that [HI] is greater than predicted by simple second order kinetics. The higher than expected concentration of HI results because it is being formed by the formation reaction. As the reaction proceeds, the decomposition slows because the concentration of HI drops, but the rate of formation increases because the concentrations of H_2 and I_2 are increasing. The net rate of disappearance of HI is equal to the rate at which it disappears in the decomposition minus the rate at which it forms in the formation. At equilibrium, the concentration of HI no longer changes because it is formed at the same rate that it disappears. Thus, at equilibrium,

$$\begin{array}{rcl} \text{rate of appearance of HI} & = & \text{rate of disappearance of HI} \\ k_\mathrm{f}[\mathrm{HI}]^2 & = & k_\mathrm{r}[\mathrm{H_2}][\mathrm{I_2}] \end{array}$$

Gathering concentrations on one side and rate constants on the other, and substituting the known rate constants, we obtain the following:

$$\frac{k_\mathrm{f}}{k_\mathrm{r}} = \frac{1.8\mathrm{e}{-3}\ \mathrm{s}^{-1}}{6.3\mathrm{e}{-2}\ \mathrm{s}^{-1}} = 0.029 = \frac{[\mathrm{H_2}][\mathrm{I_2}]}{[\mathrm{HI}]^2} = K_\mathrm{c}$$

which is the equilibrium constant for the reaction $2\ \mathrm{HI}(g) \rightleftharpoons \mathrm{H_2}(g) + \mathrm{I_2}(g)$. We conclude that the equilibrium constant is equal to the ratio of the forward and reverse rate constants. The equilibrium concentrations in the decomposition of 0.020 M HI at 700 °C are $[\mathrm{HI}] = 0.015\ M$, and $[\mathrm{H_2}] = [\mathrm{I_2}] = 0.0025\ M$. Using the known equilibrium concentrations and rate constants, we can determine the rates of formation and disappearance of HI as follows.

- rate of formation $= 2k_\text{f}[\text{HI}]^2 = 2(1.8 \times 10^3\ M^{-1}{\cdot}\text{s}^{-1})(0.015\ M)^2 = 8.0 \times 10^{-7}\ M/\text{s}$
- rate of disappearance $= 2k_\text{r}[\text{I}_2][\text{H}_2] = 2(6.3 \times 10^{-2}\ M^{-1}{\cdot}\text{s}^{-1})(0.0025\ M)(0.0025\ M) = 8.0 \times 10^{-7}\ M/\text{s}$

The reaction reaches equilibrium because HI is formed at the same rate that it is consumed. Thus, while the net concentrations are no longer changing at equilibrium, the reaction has not stopped.

10.4. Reaction Mechanisms and Rate Laws

Introduction

The rate law of a reaction gives us some clues about the steps involved in the reaction. In this section, we examine some simple examples.

Objectives

- Identify the intermediates in a reaction mechanism and use an experimental rate law to identify the rate-determining step.
- Determine the molecularity of an elementary step.
- Determine if a mechanism is consistent with the rate law.

10.4-1. Elementary Reactions

Most reactions do not occur in a single step, but by a series of elementary steps called the ***reaction mechanism***. Consider the decomposition of azomethane,

$$\text{H}_3\text{C}{-}\text{N}{=}\text{N}{-}\text{CH}_3 \longrightarrow \text{C}_2\text{H}_6 + \text{N}_2$$

which proceeds by a two-step mechanism.

1 $\text{H}_3\text{C–N=N–CH}_3 \rightarrow 2\ \text{CH}_3 + \text{N}_2$

2 $2\ \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$

In the first step, the two N–C bonds break and the N≡N bond forms, and in the second, the highly reactive CH_3 groups quickly combine to form ethane. The individual steps of the mechanism are called ***elementary reactions*** because they each represent a single molecular event that results in a reaction. The two elementary reactions above combine to give the reaction mechanism for the decomposition of azomethane. The sum of the elementary processes must yield the net reaction. The two CH_3 (methyl) groups that are formed in the first step are consumed in the second. Since they appear in the mechanism, but not in the net reaction, the methyl groups are called ***intermediates***. Intermediates typically are short-lived, but they can frequently be observed during reaction and sometimes even isolated. Indeed, evidence for a proposed intermediate is excellent support for a mechanism.

10.4-2. Molecularity

The number of molecules reacting in an elementary reaction is called the ***molecularity*** of the elementary reaction. There are only three molecularities.

Number of Particles	Molecularity
1	***unimolecular***
2	***bimolecular***
3	***termolecular***

Termolecular processes are very rare because the simultaneous collision of three reactant molecules is very rare. Processes with molecularities greater than three do not occur at all. Thus, the first step in the decomposition of azomethane is unimolecular while the second step is bimolecular.

10.4-3. The Rate Law of an Elementary Process

In order for two or three molecules to react, they must collide with one another. As a result, the rate of an elementary reaction is proportional to the collision frequency of the reactants. The ***collision frequency***, which is the number of collisions between the reacting particles in a specified volume per unit time, can be shown to be directly proportional to the product of the molar concentrations of the colliding particles. Thus, we conclude the following.

The rate law of an elementary reaction is equal to a proportionality constant (the rate constant) times the product of the molar concentrations of the reactants.

This means we can write the rate law expression for elementary processes from their chemical equation. For example,

$$\mathrm{A + B \rightarrow C} \qquad \text{rate} = k[\mathrm{A}][\mathrm{B}]$$

$$\mathrm{2\ A \rightarrow D} \qquad \text{rate} = k[\mathrm{A}][\mathrm{A}] = k[\mathrm{A}]^2$$

Most reactions do not occur in a single step, so their rate laws cannot be determined from the overall balanced equation. They can be determined only by experiment.

10.4-4. Rate-Determining Step

The rate law of a reaction is a combination of the rate laws of the elementary reactions of which it is composed. Thus, mechanisms are proposed based on the observed rate law. A mechanism is acceptable only if the rate law derived from it agrees with the experimentally determined rate law. It is often the case that more than one mechanism yields the experimental rate law, so mechanisms are usually proposed, not proven. However, finding evidence for a proposed intermediate strongly supports a proposed mechanism and can sometimes prove that it is correct.

Combining the rate laws of the elementary processes into a reaction rate law can be a formidable task for complicated reactions, so we restrict our discussion to a special case: reactions in which one step of the multi-step mechanism is much slower than any of the others. In this case,

- the rate of reaction is determined by the rate of the slow step, which is called the ***rate-determining step*** (RDS), and the rate law of the reaction is the rate law of the RDS.

10.4-5. Rate-Determining Step Example

EXAMPLE:

As a simple example of a process with a rate-determining step, consider one in which three workers are constructing chairs in an assembly line. The process involves combining four legs (L), two arms (A), one back (B), and a seat (S) to make a chair (L_4A_2SB): $4\ L + 2\ A + B + S \rightarrow L_4A_2SB$. The chairs are assembled in a three-step process:

1 $S + B \rightarrow SB$

2 $SB + 4\ L \rightarrow L_4SB$

3 $L_4SB + 2\ A \rightarrow L_4A_2SB$

The SB units, which are intermediates, are made at a rate of 60 an hour and placed in a box for the next worker. The second worker attaches the four legs, which takes longer to do, and he can only produce 20 of the L_4SB units per hour.The final worker can make 40 chairs an hour if all of the components are available, but the L_4SB units arrive at a rate of only 20 an hour. Consequently, the final worker makes a chair and then waits for the second worker to put another unit in the box. The third step cannot proceed any faster than the second step for lack of supplies. The first worker starts making units at a rate of 60 an hour and puts them in the box, but they are removed from the box at a rate of only 20 an hour. Consequently, the box gets full and the first worker must wait for the second worker to remove a unit before a new SB unit can be made. The **first step has reached equilibrium**, and the rate at which SB units are produced is limited by the rate at which the second worker removes units from the box. The rates of the two rapid steps are limited by the slow (rate-determining) step, so only 20 chairs an hour can be produced in this assembly line.

10.4-6. Intermediates and the Rate Law

The rate law of a reaction is based on the rate law of the rate-determining step, but the rate laws of reactions considered in this chapter involve the concentrations of only reactants—no products and no intermediates. Consequently, the concentrations of any intermediates that appear in the rate law of the RDS must be eliminated to obtain the experimental rate law. This is done by assuming that the rapid steps that precede the rate-determining step all reach equilibrium. Thus, the concentrations of any intermediate can be obtained in terms of the concentrations of the reactants and the equilibrium constants of the preceding reactions. This results in the following two properties of the rate law.

- The rate constant of a reaction is composed of the rate constant of the RDS and equilibrium constants of previous steps.
- The rate law of a reaction contains only those reacting molecules that appear in the RDS and steps prior to the RDS.

10.4-7. Determining a Rate Law from a Mechanism

Let us determine the rate law for the reaction with the following mechanism.

1 $NO + O_2 \rightarrow NO_3$

2 $NO + NO_3 \rightarrow 2\ NO_2$

The rate law can contain only the concentrations of reactants in the net equation, so we begin by writing the net equation. NO_3 is an intermediate that is formed in Step 1 and consumed in Step 2, so the net equation is:

$$2\ NO + O_2 \rightarrow 2\ NO_2$$

Only NO and O_2 appear as reactants in the net equation, so only they can appear in the rate law. The rate law of the reaction is the rate law of the RDS. We will do this problem twice, assuming each step to be rate-determining. Remember that the rate law of an elementary process equals the rate constant times the concentrations of the reactants each raised to an exponent equal to their coefficients in the balanced equation.

If Step 1 is RDS: $NO + O_2 \rightarrow NO_3$ is the RDS, so the rate law of the RDS is rate $= k[NO][O_2]$. The rate law of the RDS contains the concentrations of reactants in the net equation only, so this result would be acceptable for the rate law of the reaction.

If Step 2 is RDS: $NO + NO_3 \rightarrow 2\ NO_2$ is the RDS, so the rate law of the RDS is rate $= k'\,[NO][NO_3]$. NO_3 is an intermediate, so it cannot appear in the rate law. To eliminate NO_3, we assume that the first (rapid) step reaches equilibrium to get an expression for $[NO_3]$ in terms of reactant concentrations. The equilibrium constant expression for the first reaction is

$$K = \frac{[NO_3]}{[NO][O_2]}$$

solving for the NO_3 concentration, we obtain

$$[NO_3] = K[NO][O_2]$$

Substitution of this expression into the rate law for the RDS, yields the following.

$$\text{rate} = k'\,[NO]K[NO][O_2] = k'K[NO]^2[O_2]$$

Substituting k for $k'K$, we obtain the rate law expression.

$$\text{rate} = k[\text{NO}]^2[\text{O}_2]$$

The result contains the concentrations of only reactants in the net equation, so it would be acceptable for the rate law of the reaction. Note that the rate law of the reaction is equal to the product of the rate constant of the RDS and the equilibrium constant of the previous step.

We could arrive at the same rate laws by using the rule that the concentrations of only those molecules involved in the RDS and prior steps appear in the rate law. Thus, only one NO appears in the rate law if the first step is rate-determining because the second NO does not appear until the second step.

10.4-8. Rate Law from Mechanism Exercise

EXERCISE 10.11:

The reaction, $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$ is believed to occur by the following two-step mechanism.

1 $2\ NO_2(g) \rightarrow NO_3(g) + NO(g)$

2 $NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$

What is the molecularity of Step 1?
- unimolecular
- bimolecular
- termolecular

What is the molecularity of Step 2?
- unimolecular
- bimolecular
- termolecular

Which of the following is an intermediate?
- NO_2
- CO
- NO_3
- CO_2

Assume that Step 1 is the RDS to determine the reactant orders.

order of NO_2: ______________ order of CO: ______________

Assume that Step 2 is the RDS to determine the reactant orders.

order of NO_2: ______________ order of CO: ______________

10.4-9. A Three-step Mechanism Exercise

EXERCISE 10.12:

The reaction of nitric oxide with hydrogen, $2\ NO(g) + 2\ H_2(g) \rightarrow N_2(g) + 2\ H_2O(g)$ is believed to proceed by the following three-step mechanism, which is consistent with the experimental rate law.

1 $2\ NO \rightleftharpoons N_2O_2$ rapid equilibrium with equilibrium constant K_1

2 $N_2O_2 + H_2 \rightarrow N_2O + H_2O$ slow step with rate constant k_2

3 $N_2O + H_2 \rightarrow N_2 + H_2O$ fast step

Use the above mechanism to determine the order of each reactant.

order of NO: ______________ order of H_2: ______________

10.5. The Effect of Temperature on Reaction Rates

Introduction

The rate of reaction depends upon both the reactant concentrations and the temperature. We have discussed the concentration dependence in the rate law, and we now treat the temperature dependence.

Prerequisites

- CAMS 9.9 Activation Energy

Objectives

- Use the Arrhenius equation to solve for a variable.
- Sketch a potential energy profile for a reaction and interpret it in either the forward or reverse direction.
- Define reaction coordinate, transition state, and activation energy.

10.5-1. Activation Energy

The rate of reaction depends upon both the reactant concentrations and the temperature. We have discussed the concentration dependence and now treat the temperature dependence. Consider the reaction between methyl iodide and hydroxide ion.

$$\mathrm{ICH_3 + OH^{1-} \longrightarrow I^{1-} + H_3COH}$$

The reaction is an elementary process, so it is first order in each reactant. In order for the reaction to occur, a hydroxide ion must collide with a CH_3I molecule, and it must collide between the three hydrogen atoms. As the distance between the hydroxide ion and the carbon atom decreases, the carbon-iodine bond stretches, and the three hydrogen atoms are pushed back, which forces the H–C–H angles to increase from 109°. As shown in Figure 10.7, these changes result in an energy increase, which reaches a maximum when the bond angle is 120° and the carbon is five-coordinate.

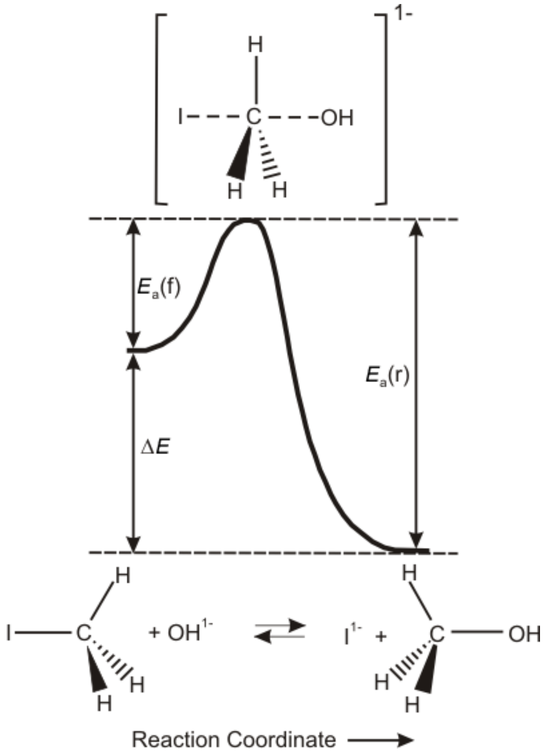


Figure 10.7: Energy diagram for $CH_3I + OH^{1-} \rightarrow CH_3OH + I^{1-}$

The five-coordinate species (at the top of Figure 10.7) is called the **transition state** of the reaction because the reaction must proceed through this state to make the transition from reactants to products. The transition state can lead to or be formed from either side of the reaction (iodide ion can collide with CH_3OH to lead to the same transition state). The transition state cannot be isolated or directly observed. It is not an intermediate but rather a highly energetic species through which the reaction proceeds. The energy required to reach the transition state is called the activation energy. Figure 10.7 shows that the variation of energy along a complicated combination of C–I and C–O bond lengths and H–C–H bond angles is called the **reaction coordinate**. The activation energy of the forward reaction, $E_\mathrm{a}(\mathrm{f})$, is much less than that of the reverse reaction, $E_\mathrm{a}(\mathrm{r})$, because the energy of the reactants is greater than the energy of the products; i.e., the reaction is exothermic.

10.5-2. Activation Energy Factors

There are two factors that dictate whether a collision achieves the transition state: the **steric factor** and the energy factor. The steric factor indicates the fraction of collisions in which the reactants have the correct orientation to react. As shown in Figure 10.8, there are a number of ways in which CH_3I and OH^{1-} can collide, but only a fraction have the correct orientation to reach the transition state.

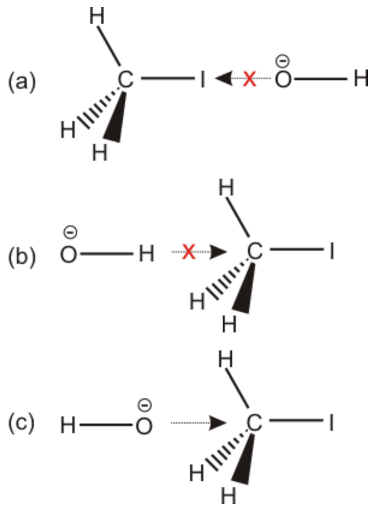


Figure 10.8: Steric Factor Collisions like (a) and (b) cannot lead to the transition state because the reactants are not aligned properly. Collision (c) can lead to the transition state but only if the colliding particles have sufficient energy to overcome the activation energy.

The energy factor arises because even if the reactants have the correct orientation to react, they cannot do so unless there is sufficient energy in the collision to overcome the activation energy and achieve the transition state. The average energy available in a collision depends on the thermal energy ($\sim RT$), and the fraction of collisions with sufficient energy to overcome the activation energy is given by $\boldsymbol{e^{-E_\mathrm{a}/RT}}$.

The rate constant represents the fraction of collisions that lead to the transition state, and it is the product of the steric and energy factors as shown in Equation 10.8.

$$k = A\exp\left(-\frac{E_\mathrm{a}}{RT}\right) = Ae^{-E_\mathrm{a}/RT} \qquad \text{Arrhenius Equation} \qquad (10.8)$$

A, which is referred to as the ***pre-exponential***, includes the steric factor. Equation 10.8, known as the ***Arrhenius equation***, shows the temperature dependence of the rate constant. Thus, as the temperature increases, the thermal energy increases, and the fraction of collisions with sufficient energy to achieve the transition state increases. Increasing the temperature, however, increases the rate of both the forward and reverse reactions.

10.5-3. Arrhenius Plot

If a plot of ln k versus $1/T$ is linear for a reaction, then the reaction displays Arrhenius behavior.

If we take the natural logarithm of both sides of Equation 10.8, we can rewrite the Arrhenius equation as shown in Equation 10.9.

$$\ln k = \ln A - \frac{E_\mathrm{a}}{R} \cdot \frac{1}{T} \qquad \text{Logarithmic Form of the Arrhenius Equation} \tag{10.9}$$

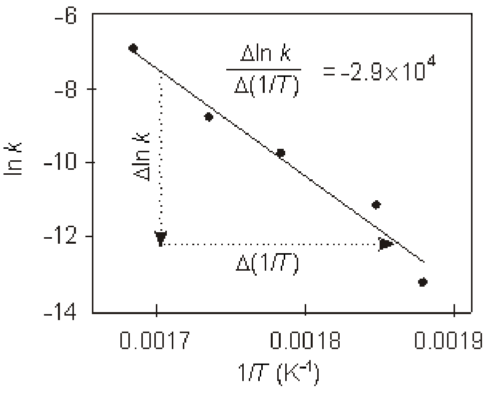
A plot of ln k vs. $1/T$ is called an ***Arrhenius plot***. If a reaction follows Arrhenius behavior, then the plot is linear with **slope** $= -E_\mathrm{a}/R$ and **intercept** $=$ ln A.

An Arrhenius plot is an excellent way to obtain the activation energy of a reaction.

10.5-4. Arrhenius Exercise

EXERCISE 10.11:

The following rate constants have been measured for the decomposition of azomethane.

	T (K)	k (s^{-1})	$1/T$ (K^{-1})	ln k	ln k vs. $1/T$
1	532	1.8e−6	0.00188	−13.23	
2	541	1.5e−5	0.00185	−11.11	
3	560	6.0e−5	0.00179	−9.72	
4	576	1.6e−4	0.00174	−8.74	
5	593	9.5e−4	0.00169	−6.96	

What is the activation energy for the reaction?

$E =$ ________________ kJ/mol

10.5-5. Using Only Two Temperatures

Determining the activation energy graphically is the best procedure, but it is often the case that only two data points are known. In these cases, we need consider only two temperatures: T_1 and T_2 and the two rate constants, k_1 and k_2, at those temperatures. In addition, only two temperatures are needed to determine a rate constant at one temperature given the activation energy and rate constant at another temperature.

To get the expression for only two temperatures, apply Equation 10.9 to each point and then take the difference to eliminate the ln A term and obtain the following.

$$\ln k_2 - \ln k_1 = \ln\left(\frac{k_2}{k_1}\right) = \frac{E_\mathrm{a}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Determining One Rate Constant from Another (10.10)

Equation 10.10 is an excellent way to determine a rate constant at one temperature given the rate constant at another temperature and the activation energy. However, we can also solve the expression for the activation energy, which allows us to determine the activation energy given the rate constants at two temperatures.

$$E_a = \frac{R \ln\left(\dfrac{k_2}{k_1}\right)}{\dfrac{1}{T_1} - \dfrac{1}{T_2}} \qquad \text{Activation Energy from the Rate Constants at Two Temperatures} \tag{10.11}$$

However, care must always be taken when assuming a linear relationship with only two points. The activation energies derived from the above expression can deviate substantially from that determined from the best fit when the two points do not lie on the best line.

10.5-6. Activation Energy Exercise

EXERCISE 10.14:

The rate constants for the decomposition of azomethane at 532 and 593K are 1.8e−06 s^{-1} and 9.5e−04 s^{-1}, respectively. Estimate the activation energy of the decomposition from this data.

$E_a =$ ______________ kJ/mol

What would the rate constant be at 550 K?

$k =$ ______________ s^{-1}

10.5-7. Activation Energy from Ratio Exercise

EXERCISE 10.15:

What is the activation energy of a reaction, if its rate at 75 °C is four times what it is at 25 °C?

$E =$ ______________ kJ/mol

10.6. Catalysis

Introduction

Catalysts increase the rate of reaction but are unchanged by it. They function by altering the path (mechanism) of the reaction so as to reduce the activation energy.

Prerequisites

- CAMS 14.5 Metals as Catalysts

Objectives

- Explain how the addition of a catalyst affects the reaction rate.

10.6-1. Review

Heterogeneous catalysts are in a different phase (usually solid) than the reactants. Look at the material listed as a prerequisite for this section for a discussion of the catalytic converter and the surface catalyzed hydrogenation of ethene to ethane. Homogeneous catalysts are in the same phase as the reaction. (See the discussion of the titanocene catalyzed polymerization of ethene discussed in the prerequisite.) Catalysts increase the rates of both the forward and reverse reactions, but they do not affect the equilibrium constant. Thus, they increase the rate at which equilibrium is established but not the amount of product that is formed. Catalysts not only increase the rate of reaction, they also lower the temperature required for reaction. Catalysts can also be very specific, increasing the rate of desired reactions without affecting the rates of undesired reactions. Enzymes are very specialized catalysts used by biological organisms.

10.6-2. Ozone's Role in the Stratosphere

High-energy ultraviolet (UV) light ($E = h\nu$) from the sun can damage living tissue because its energy is sufficient to break bonds in DNA, thus damaging genes. Fortunately, UV radiation is absorbed by ozone (O_3) in the stratosphere:

$$O_3 + h\nu \rightarrow O_2 + O$$

O can go on to react with another O_2 to regenerate the ozone, which helps maintain the ozone level in the stratosphere. However, the oxygen atom can also react with an ozone molecule as shown below.

$$O_3 + O \rightarrow 2\ O_2 \qquad \text{(Reaction 1)}$$

This reaction would deplete the ozone level, but it has a fairly high activation energy (17 kJ/mol) and few collisions in the stratosphere result in reaction.

CFC's (chlorofluorocarbons), which are used as air conditioner refrigerants and in the production of plastics, are very stable and relatively unreactive. However, they absorb high-energy photons in the stratosphere to produce chlorine atoms. Consider the photochemical (caused by light) decomposition of CF_2Cl_2 (Freon-12):

$$CF_2Cl_2 + h\nu \rightarrow CF_2Cl + Cl$$

The Cl atoms produced in reactions of this type can go on to catalyze the reaction between O and O_3. The behavior is discussed in the following section.

10.6-3. Ozone Depletion

The Cl atoms formed in the photochemical decomposition of CFC's can go on to catalyze the reaction between O and O_3 by the following two-step mechanism.

1 $O_3 + Cl \rightarrow OCl + O_2$

2 $OCl + O \rightarrow Cl + O_2$

The activation energy for Step 1 is only 2.1 kJ/mol, so it proceeds quite rapidly. The energy diagram for the reaction is given in the figure below. Summing Steps 1 and 2 yields *Reaction 1* given in the previous section, with Cl forming OCl as an intermediate.

Catalytic Cl lowers the activation energy for the reaction from 17 kJ/mol down to 2 kJ/mol and dramatically speeds the reaction, but it does not affect the initial or final states, so it does not affect the thermodynamics and equilibrium constant of the reaction.

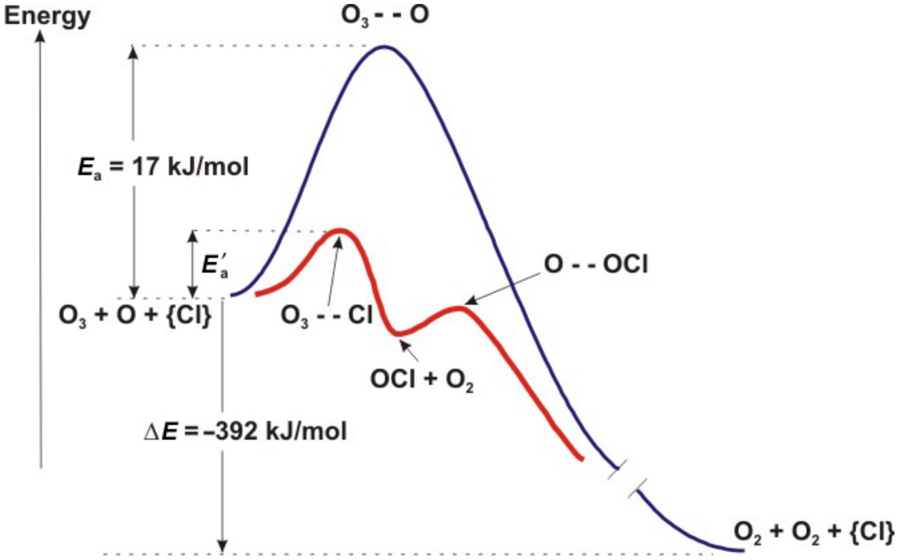


Figure 10.9: Catalytic Cl Lowers the Activation Energy from 17 to 2 kJ/mol Energy diagram for the reaction $O_3(g) + O(g) \rightarrow 2\ O_2(g)$ (a) in the absence and (b) in the presence of catalytic chlorine atoms (blue curve). The activation energy E'_a is 2.1 kJ/mol. Note that OCl lies in a shallow well between the reactants and the products, which is typical of intermediates, while the transition states O_3–O, O_3–Cl, and O–Cl all lie at peak maxima.

10.7. Exercises and Solutions

Select the links to view either the end-of-chapter exercises or the solutions to the odd exercises.

CHAPTER 11 – NUCLEAR CHEMISTRY

Introduction

Most of chemistry focuses on the changes in the electronic structure of the atoms and molecules because it is those changes that result in bond breaking and bond formation (i.e., in chemical reactivity). In this, our final chapter, we examine reactions that involve changes in the nucleus. This branch of chemistry is called ***nuclear chemistry*** or radiochemistry.

11.1 The Nucleus

Introduction

All of the positive charge (protons) of an atom is concentrated in a very small volume called the nucleus. The repulsive force between the protons is very large, so the force responsible for holding the nucleus together is also very large. In this section, we discuss the origin of that force and the characteristics of a nucleus that dictate whether or not it is stable.

Objectives

- Determine the number of protons and neutrons in a nucleus given its symbol or atomic number and its mass number.
- Determine the atomic weight of an element from the masses and natural abundance of its isotopes.
- Calculate the mass defect of a nucleus from the number of protons and neutrons it contains and the mass of the nucleus.
- Convert between mass and energy.
- Determine the binding energy per nucleon of a nucleus and predict which of several nuclei is most stable.

11.1-1. Terms

There are three major subatomic particles: electrons, protons, and neutrons. Their masses and charges are summarized in Table 11.1. Notice that electrons and protons carry a net charge but neutrons are neutral. Also, the mass of the neutron and the proton are each very close to 1 amu ($M_m \sim 1$ g/mol) while the mass of an electron is much smaller. Because neutrons and protons reside within the nucleus, they are referred to as ***nucleons***. The number of protons in the nucleus is given by the ***atomic number***, Z, while the number of nucleons (protons plus neutrons) in the nucleus is given by the ***mass number***, A. The symbol N will be used to denote the number of neutrons in the nucleus. Thus, we can write

$$A = Z + N \qquad \text{The Mass Number} \tag{11.1}$$

The mass of a neutron and a proton are each 1.0 amu, so the mass number is the integer that is closest to the mass of the nucleus. For example, a carbon atom that contains 6 protons and 6 neutrons has a mass number of 12, and its mass is 12.0 amu.

Particle	**Mass (amu)**	**Charge**
electron	0.000549	−1
proton	1.00728	+1
neutron	1.00867	0

Table 11.1: Major Subatomic Particles

- An amu is an atomic mass unit. The mass of an atom expressed in amu is numerically equal to its molar mass.
- The charge is given in terms of the fundamental unit of charge, which is 1.6e−19 C.

11.1-2. Isotopes

The atomic number is the number that characterizes the atom. Two atoms with different atomic numbers are atoms of different elements, but atoms of the same atomic number are atoms of the same element, even if they have different masses. Atoms with the same atomic number but different mass numbers are called ***isotopes***. Thus, isotopes of the same element have the same number of protons but have a different number of neutrons (N). Isotopes are distinguished by indicating their mass number as superscripts in front of the symbol of the element. For example, ^{13}C (read "carbon-13"), is an isotope of carbon that has seven neutrons ($N = A - Z = 13 - 6 = 7$). The atomic mass of ^{13}C is 13.003 amu.

The atomic mass scale is based on the assignment of the mass of a carbon-12 atom (^{12}C), which is defined as exactly 12 amu. The reason that the molar mass of naturally occurring carbon is 12.011 g/mol and not 12.000 g/mol is that the molar mass of an element is the mass-weighted average of the masses of all of its naturally occurring isotopes. Naturally occurring carbon is a mixture that is 98.9% ^{12}C and 1.1% ^{13}C, so a mole of carbon contains 0.989 mol ^{12}C and 0.011 mol ^{13}C and has a mass of

$$(0.989 \text{ mol } ^{12}\text{C})(12.000 \text{ g/mol}) + (0.011 \text{ mol } ^{13}\text{C})(13.003 \text{ g/mol}) = 12.011 \text{ g}$$

Thus, any element whose atomic mass is not nearly an integer must have more than one naturally occurring isotope.

11.1-3. Isotope Exercise

EXERCISE 11.1:

Determine the molar mass of magnesium given the masses and abundances of the three isotopes. Express all masses to 0.01 g.

Isotope	Mass	Abundance
^{24}Mg	23.9850	78.70%
^{25}Mg	24.9858	10.13%
^{26}Mg	25.9826	11.17%

Mass of ^{24}Mg in one mole of magnesium = ____________ g

Mass of ^{25}Mg in one mole of magnesium = ____________ g

Mass of ^{26}Mg in one mole of magnesium = ____________ g

Molar mass of magnesium = ____________ g/mol

Nuclear Stability

11.1-4. Binding Energy

The ***binding energy*** of a nucleus is the energy required to separate the nucleus into its nucleons. The binding energy of a ^{12}C nucleus is the energy change for the following process:

$$^{12}\text{C} \rightarrow 6 \text{ p} + 6 \text{ n} \qquad \Delta E = 8.90 \times 10^{09} \text{ kJ}$$

Just as it is the energy per bond rather than the atomization energy dictates molecular stability, it is the energy per nucleon not the total binding energy that dictates the nuclear stability. The binding energy per nucleon of a ^{12}C nucleus is

$$\frac{8.90 \times 10^{09}\ \text{kJ}}{12\ \text{nucleons}} = 7.42 \times 10^{08}\ \text{kJ/nucleon}$$

As shown in Figure 11.1, nuclei with mass numbers close to that of iron ($A = 56$) are the most stable.

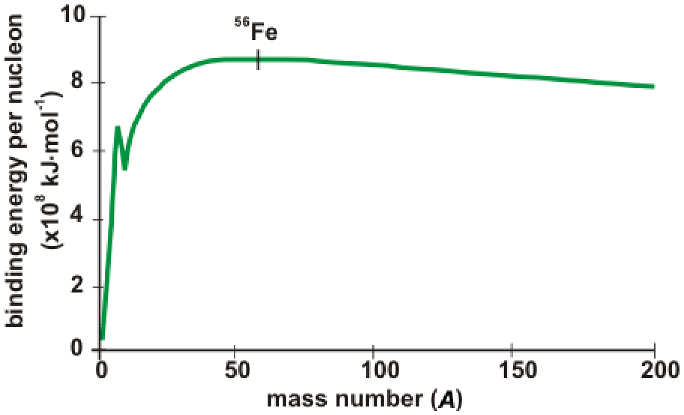


Figure 11.1: Binding Energy per Nucleon Versus Mass Number The binding energy per nucleon (nuclear stability) reaches a maximum for nuclei with mass numbers in the range of 50–60.

11.1-5. Mass Defect

Consider the process where a ^{12}C nucleus disintegrates into its nucleons: $^{12}\text{C} \rightarrow 6\ \text{p} + 6\ \text{n}$. The mass of a ^{12}C nucleus is the mass of the atom (exactly 12 amu) less the mass of the six electrons, so

$$\begin{aligned}\text{mass of } ^{12}\text{C nucleus} &= \text{mass of atom} - \text{mass of electrons}\\ &= 12.0000\ \text{amu} - (6\ \text{e})(0.000549\ \text{amu/e})\\ &= 11.9967\ \text{amu}\end{aligned}$$

$$\begin{aligned}\text{mass of } ^{12}\text{C nucleons} &= (6\ \text{p})(1.00728\ \text{amu/p}) + (6\ \text{n})(1.00867\ \text{amu/n})\\ &= 12.0957\ \text{amu}\end{aligned}$$

- The initial and final masses of the process are not equal, and the mass difference is called the ***mass defect***, Δm.

For the process $^{12}\text{C} \rightarrow 6\ \text{p} + 6\ \text{n}$, $\Delta m = 12.0957 - 11.9967 = 0.0990$ amu, which is 0.0990 g/mol or 9.90×10^{-5} kg/mol.

$$\begin{aligned}\Delta m &= \text{final mass} - \text{initial mass}\\ &= \text{mass of product} - \text{mass of reactant}\end{aligned} \qquad \text{Mass Defect} \qquad (11.2)$$

11.1-6. Mass-Energy

The origin of mass defect can be understood in terms of Einstein's famous equation that relates mass and energy.

$$E = mc^2 \qquad \text{Equivalence of Mass and Energy} \qquad (11.3)$$

Or, in terms of changes in energy due to changes in mass:

$$\Delta E = \Delta mc^2 \qquad \text{Equivalence of Mass and Energy Change} \qquad (11.4)$$

Equation 11.3 and Equation 11.4 show the equivalence of mass and energy, and the term ***mass-energy*** is sometimes used to express the equivalence. Indeed, the law of conservation of mass and the law of conservation of energy are combined into the law of conservation of mass-energy:

- The total mass-energy of the universe is constant.

The binding energy of a nucleus is determined from its mass defect and the application of Equation 11.4. However, a joule is a kg·m^2·s^{-2}, so, in order to obtain ΔE in joules,

- Δm must be expressed in kg
- $c = 2.998 \times 10^8$ m·s^{-1}

11.1-7. Binding Energy Exercise

EXERCISE 11.2:

The mass defect of a ^{12}C nucleus is 0.0990 amu. What is its binding energy?

Binding energy = ______________ J/mol

11.1-8. Binding Energy per Nucleon Exercise

EXERCISE 11.3:

Determine the binding energy per nucleon for a ^{64}Zn nucleus (atomic mass = 63.9291 amu).

Particle Masses (amu)	
electron	0.000549
proton	1.00728
neutron	1.00867

Number of nucleons

protons = ______________

neutrons = ______________

Mass of nucleons

protons = ______________ amu

neutrons = ______________ amu

Mass of nucleus = ______________ amu

Mass defect = ______________ amu

Binding energy = ______________ J/mol

Binding energy per nucleon = ______________ J/mol-nucleon

11.1-9. Nuclear Stability Exercise

EXERCISE 11.4:

Determine the binding energy per nucleon for ^{56}Fe ($Z = 26$) and ^{209}Bi ($Z = 83$) nuclei. The atomic masses are ^{56}Fe = 55.9349 amu and ^{209}Bi = 208.9804 amu.

Particle Masses (amu)	
electron	0.000549
proton	1.00728
neutron	1.00867

	Fe	Bi	
Mass of nucleons			amu
Mass of nucleus			amu
Mass defect			amu
Binding energy			J/mol
Binding energy/nucleon			J/mol-nucleon

Which nucleus is more stable?

^{56}Fe
^{209}Bi

11.2 Nuclear Reactions and Radioactivity

Introduction

Most nuclei found in nature are stable, and those that are not are said to be ***radioactive***. ***Radioactive nuclei*** spontaneously emit particles and electromagnetic radiation to change into other, more stable, nuclei. Radioactive nuclei are also called ***radioisotopes***. All of the first 83 elements except technetium ($Z = 43$) have at least one stable nucleus. However, the ^{209}Bi nucleus is the heaviest stable nucleus. Furthermore, many of the elements that have stable nuclei also have radioisotopes. In this section, we examine the different types of radioactive decay and present some observations that help us predict the mode of decay that a particular radioisotope is likely to undergo. We begin with a discussion about how nuclear reactions are written.

Objectives

- Define the terms "radioactive" and "radioisotopes."
- Identify a missing particle in a nuclear reaction.
- Identify the decay particles by name and symbol.
- Predict the probable mode of decay of an unstable nucleus.

Writing Nuclear Reactions

11.2-1. Particles

As in chemical reactions, nuclear reactions involve balancing both mass and charge. In a chemical reaction, the charge is given explicitly on each ion, but in a nuclear reaction, the charge is the charge on the nucleus, and that is given by the atomic number. Thus, the atomic number is included with the symbol in nuclear reactions to aid in charge balance. For example, element X with a mass number A and an atomic number Z is represented as

$$^{A}_{Z}X$$

and chlorine-37 is

$$^{37}_{17}\text{Cl}$$

The following table lists the names and symbols of several small particles that are encountered in many nuclear reactions.

Particle	**Second Name**	**Symbol**	**Comment**
proton		$^{1}_{1}\text{p}$	mass = 1, charge = 1
neutron		$^{1}_{0}\text{n}$	mass = 1, charge = 0
electron	beta particle	$^{\ 0}_{-1}\text{e} = ^{\ 0}_{-1}\beta = \beta^-$	mass = 0, charge = −1
positron		$^{\ 0}_{+1}\text{e} = ^{\ 0}_{+1}\beta = \beta^+$	mass = 0, charge = +1, a positively charged electron
helium nucleus	***alpha particle***	$^{4}_{2}\text{He} = ^{4}_{2}\alpha = \alpha$	mass = 4, charge = +2, the heaviest common particle

Table 11.2: Common Particles in Nuclear Reactions

11.2-2. Balancing a Nuclear Equation

In a nuclear equation, the masses are represented by the mass numbers and the charges by the atomic numbers:

- **charge balance**: The sum of the atomic numbers (Z) must be the same on both sides of the equation.
- **mass balance**: The sum of the atomic masses (A) must be the same on both sides of the equation.

11.2-3. Identifying a Product Exercise

EXERCISE 11.5:

Determine the atomic mass, number, and symbol of the unknown particle, X, in each reaction.

Do not include A or Z in the symbol, and use the following symbols for common particles:

- beta = e-
- positron = e+
- alpha = He

Reaction	A	Z	Symbol
$^{69}_{30}\text{Zn} \rightarrow\ ^{69}_{31}\text{Ga} + X$			
$^{27}_{13}\text{Al} + \alpha \rightarrow n + X$			
$^{65}_{30}\text{Zn} \rightarrow\ ^{65}_{29}\text{Cu} + X$			
$^{59}_{26}\text{Fe} \rightarrow \beta + X$			
$^{213}_{83}\text{Bi} \rightarrow\ \alpha + X$			

11.2-4. Trends in Nuclear Stability

Nuclear forces are not understood well enough to allow us to predict whether a nucleus is stable or not. Neutrons play an important role in holding the nucleus together, and every stable nucleus (except ^{1}H and ^{3}He) contains at least one neutron per proton. Figure 11.2 shows the number of protons and neutrons in the stable nuclei, which lie in a narrow band, referred to as the ***band of stability*** (shown as the blue line in Figure 11.2). Only one neutron per proton is sufficient for the lighter elements. However, the number of neutrons exceeds the number of protons in the stable nuclei of the larger elements. The following two rules summarize two empirical observations about nuclear stability that indicate the importance of the neutron to proton ratio and the size of the nucleus

- **Neutron/proton ratios**: The neutron/proton ratio remains near one through the third period ($Z = 18$), then it begins to rise reaching a maximum of 1.52 for ^{209}Bi $\left(N/Z = \dfrac{(209-83)}{83} = 1.52\right)$, the heaviest stable nucleus. The N/Z ratio is high to the left of the band of stability, so elements in that region tend to be β emitters as a β emmission converts a neutron into a proton ($\mathrm{n} \rightarrow \mathrm{p} + \mathrm{e}$), which lowers N/Z. The N/Z ratio is low to the right of the band of stability, so elements in this region tend to emit positrons or capture electrons, both of which convert protons to neutrons, which increases N/Z.
- **Total number of protons**: There are no stable nuclei with atomic numbers greater than 83. All elements with $Z > 83$ are radioactive. Heavy elements tend to emit α particles because they are the most massive particles.

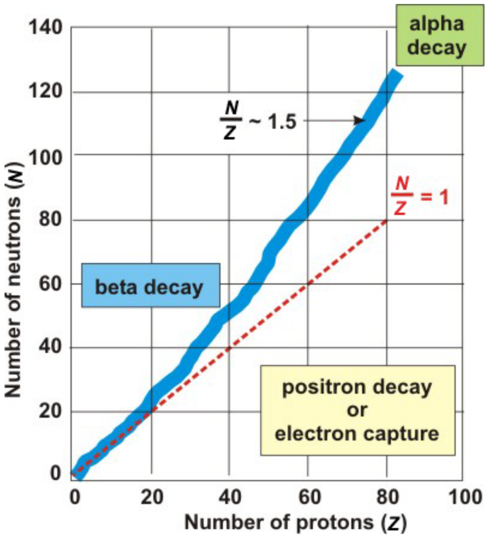


Figure 11.2: *N/Z* for Stable Isotopes The number of protons and neutrons in the stable nuclei is shown as the blue line, which represents the band of stability.

11.2-5. Alpha Decay

Alpha decay is the loss of an alpha particle. The loss reduces the mass number by four and the atomic number by two.

- **The alpha particle is the most massive particle of the common decay particles, so alpha decay is the most common mode of decay for the heavy nuclei.**

For example, ^{238}U undergoes α-decay to ^{234}Th:

$$^{238}_{92}\mathrm{U} \rightarrow {}^{238}_{90}\mathrm{Th} + {}^{4}_{2}\mathrm{He}$$

α-decay is not limited to the heavier nuclei, but it is found in only a few of the lighter elements. ^{8}Be is the lightest element to undergo alpha decay:

$$^{8}_{4}\mathrm{Be} \rightarrow 2\,{}^{4}_{2}\mathrm{He}$$

11.2-6. Beta Decay

Beta decay is the ejection of an electron by the nucleus. It results in an increase of one in the atomic number. The ejected electron is produced by the disintegration of a neutron, n → p + e. Because beta decay results from the conversion of a neutron into a proton, it decreases the neutron/proton ratio. As such,

- **β-decay reduces the proton/neutron ratio, so it is the common mode of decay for those nuclei lying above the belt of stability.**

For example, the neutron/proton ratio of ^{14}C is $8/6 = 1.3$, which is well above the value of 1.0 found for stable nuclei of the first three periods. Consequently, ^{14}C undergoes β-decay to a stable ^{14}N nucleus with $N/Z = 7/7 = 1.0$:

$$^{14}_{6}\mathrm{C} \rightarrow\ ^{14}_{7}\mathrm{N} +\ ^{0}_{-1}\mathrm{e}$$

α-decay, the most common decay among the heavy elements, is the loss of two protons and two neutrons, which increases N/Z slightly. Thus, successive α-decays produce isotopes with unfavorable N/Z ratios. Consequently, some heavy nuclei formed by α-decay undergo β-decay in order to maintain N/Z 1.5.^{234}Th, formed from the α-decay of ^{238}U, is a heavy nucleus and might be expected to undergo α-decay, but it also has a very high neutron/proton ratio of $\frac{(234-90)}{90} = 1.60$.

- **Reducing a high neutron/proton ratio is usually favored over reducing the mass in heavy nuclei.**

Consequently, ^{234}Th undergoes β-decay to ^{234}Pa, which has a N/Z ratio of 1.57:

$$^{234}_{90}\mathrm{Th} \rightarrow\ ^{234}_{91}\mathrm{Pa} +\ ^{0}_{-1}\mathrm{e}$$

11.2-7. Positron Decay

Positron decay is the emission of a positron and has the opposite effect of β-decay. It reduces the atomic number as it converts a proton into a neutron.

$$^{1}_{1}\mathrm{p} \rightarrow\ ^{1}_{0}\mathrm{n} +\ ^{0}_{+1}\mathrm{e}$$

- **Positron decay reduces the atomic number by one, so it is a common mode of decay for nuclei below the belt of stability.**

Positron emission of ^{13}N produces ^{13}C, which results in an increase of N/Z from 0.86 to 1.2:

$$^{13}_{7}\mathrm{N} \rightarrow\ ^{13}_{6}\mathrm{C} +^{0}_{+1} \mathrm{e}$$

A positron is the antimatter analog of the electron because it is identical to the electron in every respect except charge. Occasionally, the emitted positron collides with an orbital electron. The collision results in the annihilation of the two particles, so all of their mass is converted into a large amount of energy, which is released in the form of gamma radiation:

$$\beta^- + \beta^+ \rightarrow \gamma$$

Gamma radiation is high energy electromagnetic radiation and has no mass or charge.

11.2-8. Electron Capture

Electron capture (EC) is the capture by the nucleus of an electron from an inner-shell orbital. EC, like positron emission, increases the neutron/proton ratio by converting a proton into a neutron,

$$^{1}_{1}\mathrm{p} +^{0}_{-1} \mathrm{e} \rightarrow\ ^{1}_{0}\mathrm{n}$$

- **EC reduces the neutron/proton ratio so it is a common decay used by nuclei below the belt of stability.**

For example, ^{7}Be ($N/Z = 0.75$) undergoes electron capture to become ^{7}Li ($N/Z = 1.3$) :

$$^{7}_{4}\text{Be} + ^{0}_{-1}\text{e} \rightarrow ^{7}_{3}\text{Li}$$

11.2-9. Summary

Use the following rules to predict the mode of decay of a nucleus:

- Heavy nuclei ($Z > 83$) undergo alpha decay if their N/Z ratios are not too high.
- Nuclei with N/Z ratios above the band of stability undergo beta decay.
- Nuclei with N/Z ratios below the band of stability undergo either positron decay or electron capture.
- Reducing a high N/Z ratio (beta decay) is usually favored over reducing nuclear mass (alpha decay).

The above rules are summarized in Figure 11.2, which shows the common modes of decay in the regions where they are common.

11.2-10. Predicting the Mode of Decay Exercise

EXERCISE 11.6:

(a) The most abundant isotope of krypton is ^{84}Kr. Predict the mode of decay of the radioactive nucleus ^{76}Kr and determine the identity of the heavy product.

The mode of decay:
alpha
beta
positron or EC

Heavy Product:

$A =$ ____________

symbol: ____________

(b) Cobalt occurs naturally as ^{59}Co. Predict the mode of decay of the radioactive nucleus ^{62}Co and determine the identity of the heavy product.

The mode of decay:
alpha
beta
positron or EC

Heavy Product:

$A =$ ____________

symbol: ____________

(c) Predict the mode of decay of the radioactive nucleus ^{33}Cl and determine the identity of the heavy product.

The mode of decay:
alpha
beta
positron or EC

Heavy Product:

$A =$ ____________

symbol: ____________

(d) Predict the mode of decay of the radioactive nucleus ^{220}Fr and determine the identity of the heavy product.

The mode of decay:
alpha
beta
positron or EC

Heavy Product:

$A =$ ____________

symbol: ____________

11.3 Kinetics of Radioactivity

Introduction

Radioactive decay is an elementary process involving only one particle, so it follows first order kinetics. In this section, we examine the rate equation and the half-life of radioactive nuclei and then show how nuclear decay can be used to determine the age of materials.

Objectives

- Determine the time required for a given fraction of a radioactive material to disappear given the half-life or rate constant for the decay.
- Determine the age of an organic material given its ^{13}C rate of decay, the rate of ^{13}C decay in living organisms, and the half-life of ^{13}C.

11.3-1. The Rate Law

The first order decay of a nucleus is explained by the integrated rate law for first order kinetics (Equation 10.4), which is reproduced below:

$$\ln\left(\frac{[\mathrm{A}]}{[\mathrm{A}]_0}\right) = -kt$$

[A] and $[\mathrm{A}]_0$ are the concentrations of A at time t and the beginning of the measurement, respectively. Molar concentration is moles per liter, so $[\mathrm{A}] = \frac{n}{V}$ and $[\mathrm{A}]_0 = \frac{n_0}{V}$. The volumes cancel in the ratio, so $\frac{[\mathrm{A}]}{[\mathrm{A}]_0} = \frac{n}{n_0}$, where $n = \frac{m}{\mathrm{M_m}}$ and $n_0 = \frac{m_0}{\mathrm{M_m}}$. The molar masses cancel in the ratio of moles, so the ratio can be expressed as a ratio of moles or masses.

$$\ln\left(\frac{n}{n_0}\right) = \ln\left(\frac{m}{m_0}\right) = -kt \qquad \text{Logarithmic Form of the Integrated Rate Law for Nuclear Decay} \tag{11.5}$$

Equation 11.5 can be expressed as an exponential instead of a logarithm as follows:

$$n = n_0 e^{-kt} \qquad \text{Exponential Form of the Integrated Rate Law for Nuclear Decay} \tag{11.6}$$

Radioactive decay is exponential. Radioactive decays are usually characterized by their half-lives rather than their rate constants. Equation 10.6, which relates the half-life to the first order rate constant, is reproduced below:

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

11.3-2. Nuclear Decay Rate Exercise

EXERCISE 11.7:

Magnesium-23 undergoes positron decay. What is the product of the decay?

symbol: ______________

17.9% of a ^{23}Mg remained after 30.0 seconds. What is its half-life?

$t_{1/2} =$ ______________ s

How long would it take for 99.90% of a sample to disintegrate?

$t =$ ______________ s

Radioactive Dating

11.3-3. Introduction

Radioactive dating is the process of determining the age of an object from its radioactive components. It is based on Equation 11.5, which indicates that the time required for some known initial amount of radioisotope to decay to another known amount can be determined if the rate constant (half-life) for the decay is known. Determining the amount of radioisotope present in the object today is straightforward, and we outline the approximations used in two techniques to obtain the initial amounts. One technique is used for historical time scales and the other for geological time scales.

11.3-4. Carbon-14 Dating

Historical ages are frequently determined with carbon-14 dating, which is based on the fact that there is a constant exchange of carbon containing compounds between living organisms and the atmosphere. Atmospheric CO_2 is used in photosynthesis to produce organic compounds that are ingested by animals, and the carbon that was in the CO_2 becomes incorporated into the compounds in the organism. The organism returns some of the carbon back to the atmosphere in the form of CO_2 to continue the cycle. A small fraction of the carbon is in the form of radioactive ^{14}C, which is formed in the upper atmosphere by the following reaction:

$$^{14}_{7}\mathrm{N} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{14}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{p}$$

^{14}C then undergoes beta decay with a half-life of 5730 years ($k = 1.21 \times 10^{-4}\ \mathrm{yr}^{-1}$).

$$^{14}_{6}\mathrm{C} \rightarrow {}^{14}_{7}\mathrm{N} + {}^{0}_{-1}\mathrm{e}$$

The two competing processes have resulted in an equilibrium ^{14}C:^{12}C ratio in the atmosphere of about 1:10^{12}, which is also maintained in all living organisms. Consequently, all living organisms show ^{14}C radioactivity of 15.3 disintegrations per minute per gram of carbon ($\mathrm{d{\cdot}min^{-1}{\cdot}g^{-1}}$). However, when the organism dies, it no longer replaces the decaying ^{14}C, and the disintegration rate drops. The age of a material can be estimated by measuring the rate of ^{14}C disintegration by the following method:

1 Determine the ratio $\frac{n}{n_0}$ as the ratio of the ^{14}C disintegration rates.

$$\frac{n}{n_0} = \frac{\text{observed rate of disintegration}}{\text{initial rate of disintegration}} = \frac{\text{observed rate of disintegration}}{15.3\ \mathrm{d{\cdot}min^{-1}{\cdot}g^{-1}}}$$

2 Use Equation 11.5 with the above ratio and the known rate constant for the decay to determine its age (t).

$$t = -\frac{\ln(n/n_0)}{1.21\mathrm{e}{-04}\ \mathrm{yr}^{-1}}$$

11.3-5. Carbon Dating Exercise

EXERCISE 11.8:

A piece of charred bone found in the ruins of an American Indian village has a ^{14}C disintegration rate of 9.2 d·min^{-1}·g^{-1}. Determine the approximate age of the bone. The rate of decay in living species is 15.3 d·min^{-1}·g^{-1}.

age = ______________ years

11.3-6. Dating Geological Times

Carbon dating can be used to estimate the age of materials that are up to 50,000 years old. The rate of ^{13}C decay for older objects is too slow to be measured. Thus, when a geological age is required, a radioisotope with a much longer half-life must be used. One method used to determine the age of rocks is based on the decay of ^{238}U to ^{206}Pb, a process with a half-life of 4.5×10^9 yr. In this method, it is assumed that all of the ^{206}Pb found in the rock originated from ^{238}U, which is represented by the following:

$$\frac{n}{n_0} = \frac{\text{mol } ^{206}\text{Pb in sample}}{(\text{mol } ^{206}\text{Pb} + \text{mol } ^{238}\text{U}) \text{ in sample}}$$

This presumes that none of the lead was in the rock when it was formed, which is an acceptable assumption if there is not much of the more abundant ^{208}Pb present in the sample.

11.4 Nuclear Radiation and Living Tissue

Introduction

When visible light is absorbed by a molecule, the electrons can be excited into excited states, but they soon find their way back to the ground state. Thus, the visible light excited the molecule; but, because the electron was not lost, the radiation is said to be ***nonionizing radiation***. Radio and TV waves, microwaves, and visible light are some examples of nonionizing radiation. However, when radiation of greater energy interacts with the molecule, the electron can be lost to produce an ion. This kind of radiation is said to be ***ionizing radiation***. Ionizing radiation includes alpha and beta particles, gamma rays, and x-rays. Unlike nonionizing radiation, ionizing radiation can be very harmful to living tissue.

Objectives

- Distinguish between ionizing and nonionizing radiation.
- Compare the penetrating power of α-particles, β-particles and γ-rays.

11.4-1. Some Examples

In order for ionizing radiation to be harmful, it must encounter the tissue. Thus, ionizing radiation produced in an experiment conducted in a laboratory next door would have to pass through at least one wall and your clothing before it could harm you. The ability of radiation to pass through material is called its penetrating power. The penetrating power decreases as the mass and charge of the particle increases. Alpha particles are both highly charged and massive, which results in very poor penetrating power. Alpha particles are stopped by a piece of paper or by the layer of dead skin cells covering the body. They can be very damaging to internal organs, but they must be ingested or inhaled to do so.

Approximately 40% of the background radiation to which humans are exposed is produced by radon, which is formed during the decay of ^{238}U to ^{206}Pb. The other members of this decay pathway are also radioactive, but they are solids and remain in the rock. Radon, on the other hand, is a noble gas and can escape from the rock and into our homes. It is a source of alpha particles that has been attributed to up to 10% of lung cancer deaths. As a gas, radon is readily inhaled and, after inhalation, the resulting alpha particles bombard the lung tissue. ^{218}Po is also an alpha emitter ($t_{1/2} = 3$ minutes), but it is a solid and is not exhaled. Thus, exposure to radon can produce a constant bombardment of lung tissue by alpha particles, which damages the growth-regulation mechanism of the cells, causing the uncontrolled cell reproduction we call cancer.

Beta particles are not as highly charged and not nearly as massive as alpha particles. Consequently, they have greater penetrating power. However, even beta particles are stopped by a sheet of metal or wood. Beta particles can cause damage to the skin and the surface of organs, but they also do their worst damage if ingested or inhaled. Gamma rays are photons and have excellent penetrating power because they have neither charge nor mass. Dense materials like lead or concrete are required to stop gamma rays. Recall that gamma rays are used to carry excess energy away from a nuclear reaction. Consequently, many radioisotopes emit gamma rays. ^{60}Co is a gamma emitter that is used in cancer treatment by bombarding the tumor with gamma rays to destroy the cancerous cells.

11.5 Nuclear Fission

Introduction

Fission reactions are extremely exothermic and are the basis for nuclear power plants (controlled fission) and weaponry (uncontrolled fission). In this section, we examine both the process and its uses.

Objectives

- Describe nuclear fission and chain reactions.
- Define critical mass and explain its origin.
- Explain how fission is controlled in a nuclear reactor.
- Describe what is meant by "meltdown."

11.5-1. Chain Reactions

Nuclear fission is the process of splitting a large nucleus into smaller nuclei. The most common example is the fission of ^{235}U, which uses a neutron to start the reaction, but the reaction then produces three more neutrons.

$$^{235}_{92}\mathrm{U} + \ ^{1}_{0}\mathrm{n} \rightarrow \ ^{92}_{36}\mathrm{Kr} + \ ^{141}_{56}\mathrm{Ba} + 3\ ^{1}_{0}\mathrm{n}$$

Reactions like the fission of ^{235}U, in which one of the products of the reaction initiates further reaction, are called ***chain reactions***. Table 11.3 shows the number of product particles produced in the fission of ^{235}U and Figure 11.3 is a schematic of the reaction. In general, 3^n neutrons are produced in the n^{th} step. Thus, in the 10th step, 3^{10} or 59,049 neutrons are produced.

Step	^{141}Ba	^{92}Kr	Neutrons
1	1	1	3
2	3	3	9
3	9	9	27
4	27	27	81

Table 11.3

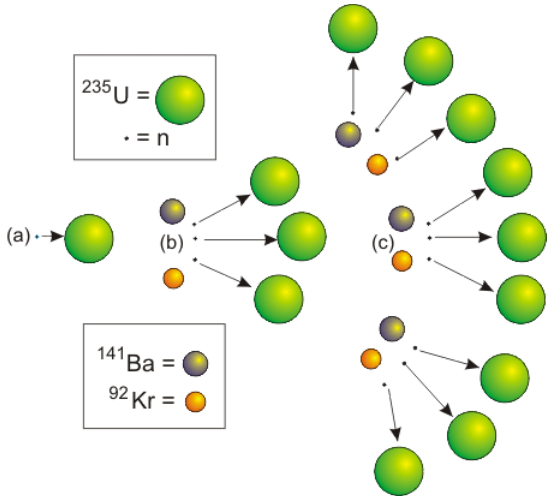


Figure 11.3: Chain Reaction

11.5-2. Rate of Fission Reaction

The ^{235}U fission reaction involves a bimolecular collision between a neutron and a ^{235}U nucleus, so the rate of this elementary reaction is proportional to the product of the two concentrations:

$$\text{rate} = k[\text{n}][^{235}\text{U}] \qquad \text{Rate of Fission} \tag{11.7}$$

where [n] is the concentration of neutrons. As the reaction proceeds, the concentration of neutrons increases faster than the concentration of ^{235}U decreases, which causes the rate of the reaction to increase. Furthermore, each step of the reaction produces three times the energy of the previous step. If it is not controlled, the chain reaction results in an explosion as a vast amount of energy is released in a very short period of time.

Equation 11.7 indicates that the rate of fission can be reduced by reducing either [n] or [^{235}U]. ^{235}U does not undergo a chain reaction in nature because both concentrations are low. The natural abundance of ^{235}U in uranium ore is only 0.7%, which means that [^{235}U] is low. Indeed, the uranium must be enriched to levels of around 4% if it is to serve as a nuclear fuel.

11.5-3. Energy Released by Fission Exercise

EXERCISE 11.9:

Fission reactions have large mass defects, and the large amounts of energy they give off makes them useful in energy production and weaponry. Determine how much energy is released by the fission of 1.00 g of ^{235}U in the following fission reaction:

$$^{235}_{92}\text{U} + {}^{1}_{0}\text{n} \rightarrow {}^{92}_{36}\text{Kr} + {}^{141}_{56}\text{Ba} + 3\,{}^{1}_{0}\text{n}$$

The masses are:

U = 235.0439
Kr = 91.9263
Ba = 140.9144
n = 1.0087

Determine the mass defect for the fission of one mole of ^{235}U.

mass of products = ______________ g
mass of reactants = ______________ g
Δm = ______________ g

Determine ΔE for the fission of one mole of ^{235}U.

$\Delta E =$ _______________ J

How much heat is released in the fission of one gram of ^{235}U?

$\Delta E =$ _______________ J

11.5-4. Critical Mass

Even enriched uranium does not get out of control if the sample size is kept small because many of the neutrons produced in the fission process are near the surface and escape the sample without colliding with other ^{235}U nuclei. However, as the sample size increases, the fraction of neutrons initiating fission increases. The minimum mass of uranium required to maintain a chain reaction is called the ***critical mass***. At the critical mass, one neutron from each fission encounters a uranium nucleus. Masses that are less than the critical mass are said to be subcritical. Subcritical masses cannot sustain a chain reaction because less than one neutron per fission initiates a subsequent fission. Masses in excess of the critical mass are called supercritical. In a supercritical mass, most of the neutrons initiate further reaction. The critical mass of ^{235}U, which depends upon its purity, the shape of the sample, and the energy of the neutrons, ranges from about 15 kg to over 50 kg.

11.5-5. Atomic Bomb

The atomic bomb is an example of uncontrolled fission. The design of the first bomb, shown schematically in Figure 11.4, is quite simple. It is transported with the fissionable uranium divided into two sections, each with a subcritical mass and located at the opposite ends of a large gun barrel. A chemical explosive, TNT, is used to send one subcritical mass into the other. The combined mass of the two samples exceeds the critical mass, and an uncontrolled chain reaction is initiated. The first bomb dropped on Japan at the end of World War II produced an explosion equivalent to 19,000 tons of TNT.

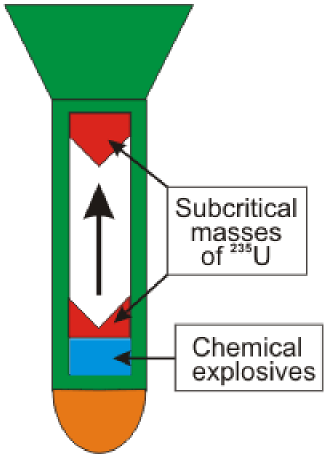


Figure 11.4: Schematic of an Atomic Bomb Chemical explosive (TNT) is used to drive one subcritical mass into another. If the sum of the two subcritical masses exceeds the critical mass, an uncontrolled chain reaction is initiated.

11.5-6. Nuclear Reactor

A nuclear reactor is a controlled chain reaction. A schematic representation of a nuclear reactor is shown in Figure 11.5. Enriched ^{235}U in the form UO_2 is contained in fuel rods that are tubes made of a zirconium alloy. A constant rate of reaction is maintained by varying the height of the control rods, which function by absorbing neutrons. When there is new fuel present, the rods are lowered to capture a greater number of neutrons, but as the fuel is consumed, the rods are raised to increase the number of neutrons available to initiate fission. Heat generated by the nuclear reaction is carried out of the reactor core by high-pressure water (300 °C, 2250 psi) in the primary water loop. Over $30,000$ gal/min can flow through this loop in a large reactor. The heat is used to boil water in a steam generator. The escaping steam in a secondary water loop drives a turbine connected to a generator. The steam leaving the turbine is condensed and cooled in the condenser with cooling water from a lake or river.

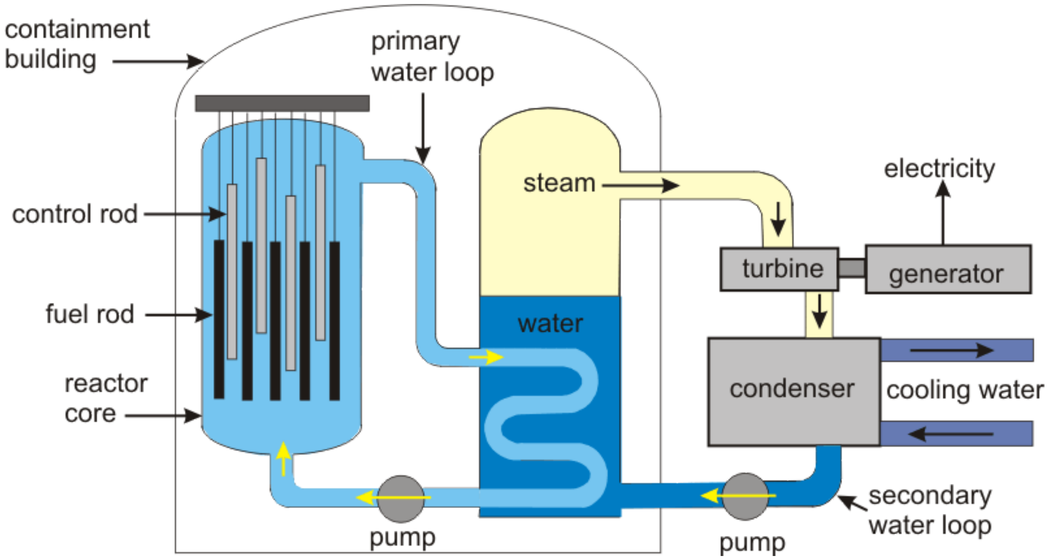


Figure 11.5: Schematic of a Nuclear Power Plant

11.5-7. Concerns

The fuel in a nuclear plant cannot explode like an atomic bomb, but if the reaction gets out of control, the reactor can experience a meltdown. The worst nuclear disaster occurred at Chernobyl in the Ukraine in 1986. Operators disabled the safety system to carry out some tests. During the tests, the reactor cooled and nearly shut down, so, to avoid a costly shutdown, they removed most of the control rods. In the absence of the control rods and with the safety system disabled, the reactor heated beyond safe limits. The excess heat boiled the superheated water and melted the fuel rods, which then mixed with the superheated water. High-pressure steam generated by boiling the superheated water blew off the top of the reactor, and spread the radioactive fuel into the atmosphere. A malfunction of the cooling system was also responsible for the Three Mile Island accident in 1979, but no explosion accompanied that partial meltdown and only a very small amount of radiation was released.

Nuclear reactors are built with many levels of safeguards that have proved effective in preventing accidents except in the case of gross operator error. However, there is one other problem presented by the use of nuclear power. The major concern surrounding nuclear power today is nuclear waste disposal. Not all of the radioactive fuel in the fuel rod can be consumed, and many of the products of the fission reactions are radioactive with long half-lives. Two problems arise: where do you store this radioactive waste, and how do you get it there? Nobody wants to live near a nuclear waste site, and there is major opposition to the transport of radioactive material along our highways and railways. However, a national repository for radioactive waste has been developed at Yucca Mountain, Nevada.

11.6 Nuclear Fusion

Introduction

In ***nuclear fusion***, two lighter atoms combine, or fuse, to form a heavier atom. It is the process that powers the sun and other stars.

Objectives

- Describe nuclear fusion and the problems associated with controlling it.

11.6-1. Deuterium Plus Tritium

As in fission, some of the mass of the fusing nuclei is converted into energy. The most studied fusion reaction is the fusion of deuterium (^{2}H) with tritium (^{3}H) to form helium and a neutron:

$$ {}^{2}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{1}_{0}\mathrm{n} \qquad \Delta E = -1.7\mathrm{e}09\ \mathrm{kJ} $$

Even with a natural abundance of only 0.015%, deuterium is a readily available isotope because it is present in all water. Tritium atoms can be prepared by bombarding lithium atoms with the neutrons released in the above reaction:

$$ {}^{6}_{3}\mathrm{Li} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{3}_{1}\mathrm{H} + {}^{4}_{2}\mathrm{He} \qquad \Delta E = -4.6\mathrm{e}08\ \mathrm{kJ} $$

The fusion of deuterium and tritium offers almost limitless energy.

11.6-2. Problems

The reason we do not have fusion power plants is that the activation energy for a fusion reaction is enormous. The potential energy of two nuclei as a function of the distance between them rises very sharply at distances less than the bond length. The rise in energy is due to the repulsion between the two positively charged nuclei; but, in order for fusion to occur, this high repulsion energy must be overcome. Consequently, extremely high temperatures are required to bring about fusion. For this reason, fusion reactions are also called ***thermonuclear***. Instead of a critical mass that must be exceeded, fusion reactions have temperatures that must be exceeded. The fusion of deuterium and tritium has the lowest threshold temperature for any fusion reaction, a mere 40,000,000 K! The uncontrolled fusion of deuterium and tritium is called a hydrogen bomb. The threshold temperatures required for the fusion in a hydrogen bomb are achieved by first detonating a fission bomb!

In order to achieve controlled fusion, the nuclei not only have to have sufficient energy to fuse, they must also be held together long enough for fusion to occur. As we shall see in the next section, stars use enormous gravitational fields to both heat the nuclei and to confine them. Scientists on Earth are trying two techniques to produce fusion in the laboratory. In magnetic confinement, the nuclei are confined by a strong magnetic field and heated by powerful microwaves. In inertial confinement, a pellet of frozen hydrogen is compressed and heated by an intense energy beam so quickly that fusion occurs before the atoms can fly apart. Fusion has been achieved in the laboratory, but the nuclei fly apart before a self-sustained reaction can be initiated. Consequently, more energy is pumped into the system than is extracted from it. However, it is expected that fusion reactions that produce more energy than they consume will soon be achieved.

11.7 Origin of the Heavy Elements

Introduction

Nature has mastered fusion in nuclear reactors called stars, and the by-products of these thermonuclear reactions are the elements that populate the periodic table. The universe is comprised mostly of hydrogen, and the story of how the heavier elements came into being is illuminating.

Objectives

- Explain where and how elements are formed.

11.7-1. Birth of a Star

Hydrogen atoms in space are attracted to one another by gravitational forces. As the number of atoms that are attracted to one another increases, the gravitational forces between the atoms also increase, causing the system to begin to collapse. As the body of hydrogen atoms collapses, the pressure at the center begins to build, and the increase in pressure results in an increase in temperature. If there is sufficient mass, the system continues to collapse until the temperature reaches about 4×10^7 K, at which point the density is about 100 g/cm^3. At this temperature, the protons begin to fuse, and a star is born. Further collapse of the star is offset by the enormous energy released by the fusion process, and the star stabilizes as long as the fuel lasts. The overall reaction is:

$$4\,{}^{1}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + 2\,{}^{0}_{1}\mathrm{e} + 2\,\gamma$$

11.7-2. Red Giant

After about 10% of the hydrogen has been consumed, the core again begins to collapse. When the temperature reaches about 2 × 10^8 K and the density is around 10,000 g/cm^3, ^{4}He begins to burn:

$$3\,{}^{4}_{2}\mathrm{He} \rightarrow {}^{12}_{6}\mathrm{C}$$

The energy released by burning helium expands the hydrogen into a sphere over a hundred times larger than the original star. At this point, the star is called a red giant. When the concentration of ^{12}C gets sufficiently high, it begins to burn and produce other elements.

$$\begin{aligned}
&{}^{12}\mathrm{C} + {}^{4}\mathrm{He} \rightarrow {}^{14}\mathrm{N} + {}^{2}\mathrm{H}\\
&{}^{12}\mathrm{C} + {}^{4}\mathrm{He} \rightarrow {}^{16}\mathrm{O}\\
&{}^{12}\mathrm{C} + {}^{12}\mathrm{C} \rightarrow {}^{24}\mathrm{Mg}\\
&{}^{12}\mathrm{C} + {}^{16}\mathrm{O} \rightarrow {}^{28}\mathrm{Si}\\
&{}^{12}\mathrm{C} + {}^{12}\mathrm{C} \rightarrow {}^{23}\mathrm{Na} + {}^{1}\mathrm{H}
\end{aligned}$$

11.7-3. White Dwarf

Further collapse and heating produces elements up to ^{56}Fe. Reactions of this type are highly exothermic, but reactions to form elements heavier than ^{56}Fe are endothermic and are produced by neutron capture, which is a very slow process. Thus, once a star contains mostly ^{56}Fe, there is no further nuclear fuel and the star collapses to a **white dwarf** with a radius similar to Earth's and a density of 10^4 to 10^8 g/cm^3. This is the fate that awaits our sun.

11.7-4. Neutron Star

However, if the star is large enough, the collapse continues to even greater densities and temperatures of 4×10^9 K, where many neutron releasing reactions are initiated:

$${}^{56}\mathrm{Fe} + \text{ energy } \rightarrow 13\,{}^{4}\mathrm{He} + 4\,{}^{1}\mathrm{n}$$

This final collapse occurs in minutes or less with the release of immense amounts of energy and neutrons. The elements in the outer shell of the star absorb many neutrons almost simultaneously and very large masses ($A = 238$) are achieved. The shell is then blown off at near the speed of light in a supernova, leaving a core of many solar masses, a diameter ~10 km, and a density of 10^{14} g/cm^3. At such pressures, electrons are captured by the protons to form neutrons. Eventually, the core consists of nothing but neutrons and is called a **neutron star**. It is interesting to realize that all of the atoms that are heavier than iron were formed in supernovas, which makes a gold necklace all the more interesting.

11.8 Exercises and Solutions

Links to view either the end-of-chapter exercises or the solutions to the odd exercises are available in the HTML version of the chapter.

PERIODIC TABLE

1 **1A**	**2** **2A**	**3** **3B**	**4** **4B**	**5** **5B**	**6** **6B**	**7** **7B**	**8** **8B**	**9** **8B**	**10** **8B**	**11** **1B**	**12** **2B**	**13** **3A**	**14** **4A**	**15** **5A**	**16** **6A**	**17** **7A**	**18** **8A**
1 **H** 1.01																	2 **He** 4.00
3 **Li** 6.94	4 **Be** 9.01											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.88	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.39	31 **Ga** 69.72	32 **Ge** 72.61	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 **Kr** 83.80
37 **Rb** 85.48	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.07	45 **Rh** 102.91	46 **Pd** 106.42	47 **Ag** 107.87	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.71	51 **Sb** 121.75	52 **Te** 127.60	53 **I** 126.90	54 **Xe** 131.29
55 **Cs** 132.91	56 **Ba** 137.33	57 **La** 138.91	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.84	75 **Re** 186.21	76 **Os** 190.23	77 **Ir** 192.22	78 **Pt** 195.08	79 **Au** 196.97	80 **Hg** 200.59	81 **Tl** 204.38	82 **Pb** 207.2	83 **Bi** 208.98	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** 226.03	89 **Ac** 227.03	104 **Rf** (261)	105 **Db** (262)	106 **Sg** (263)	107 **Bh** (264)	108 **Hs** (265)	109 **Mt** (268)									

58 **Ce** 140.11	59 **Pr** 140.91	60 **Nd** 144.24	61 **Pm** (145)	62 **Sm** 150.36	63 **Eu** 151.97	64 **Gd** 157.25	65 **Tb** 158.93	66 **Dy** 162.5	67 **Ho** 164.93	68 **Er** 167.26	69 **Tm** 168.93	70 **Yb** 173.04	71 **Lu** 174.97
90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np** 237.05	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (262)

Legend:

1	Atomic number
H	**Symbol**
1.01	Atomic mass

Metals **Metalloids** **Nonmetals**

ACID-BASE TABLE

Acid Name	**ConjugateAcid**	$\mathbf{K_a}$	$\mathbf{pK_a}$	**Conjugate Base**	**Base Name**
perchloric acid	$HClO_4$	$>> 1$	< 0	ClO_4^{1-}	perchlorate ion
hydrohalic acid	HX ($X = I, Br, Cl$)	$>> 1$	< 0	X^{1-}	halide ion
sulfuric acid	H_2SO_4	$>> 1$	< 0	HSO_4^{1-}	hydrogen sulfate ion
nitric acid	HNO_3	$>> 1$	< 0	NO_3^{1-}	nitrate ion
hydronium ion	H_3O^{1+}	1.0	0.00	H_2O	water
iodic acid	HIO_3	0.17	0.77	IO_3^{1-}	iodate ion
oxalic acid	$H_2C_2O_4$	5.9×10^{-2}	1.23	$HC_2O_4^{1-}$	hydrogen oxalate ion
sulfurous acid	H_2SO_3	1.5×10^{-2}	1.82	HSO_3^{1-}	hydrogen sulfite ion
hydrogen sulfate ion	HSO_4^{1-}	1.2×10^{-2}	1.92	SO_4^{2-}	sulfate ion
phosphoric acid	H_3PO_4	7.5×10^{-3}	2.12	$H_2PO_4^{1-}$	dihydrogen phosphate ion
hydrofluoric acid	HF	7.2×10^{-4}	3.14	F^{1-}	fluoride ion
nitrous acid	HNO_2	4.0×10^{-4}	3.40	NO_2^{1-}	nitrite ion
lactic acid	$HC_3H_5O_3$	6.4×10^{-5}	3.85	$C_3H_5O_3^{1-}$	lactate ion
formic acid	$HCHO_2$	1.8×10^{-4}	3.74	CHO_2^{1-}	formate ion
hydrogen oxalate ion	$HC_2O_4^{1-}$	6.4×10^{-5}	4.19	$C_2O_4^{2-}$	oxalate ion
hydrazoic acid	HN_3	1.9×10^{-5}	4.72	N_3^{1-}	azide ion
acetic acid	$HC_2H_3O_2$	1.8×10^{-5}	4.74	$C_2H_3O_2^{1-}$	acetate ion
carbonic acid	H_2CO_3	4.3×10^{-7}	6.37	HCO_3^{1-}	hydrogen carbonate ion
hydrogen sulfite ion	HSO_3^{1-}	1.0×10^{-7}	7.00	SO_3^{2-}	sulfite ion
hydrosulfuric acid	H_2S	1.0×10^{-7}	7.00	HS^{1-}	hydrogen sulfide ion
dihydrogen phosphate ion	$H_2PO_4^{1-}$	6.2×10^{-8}	7.21	HPO_4^{2-}	hydrogen phosphate ion
hypochlorous acid	$HClO$	3.5×10^{-8}	7.46	ClO^{1-}	hypochlorite ion
ammonium ion	NH_4^{1+}	5.6×10^{-10}	9.25	NH_3	ammonia
hydrocyanic acid	HCN	4.0×10^{-10}	9.40	CN^{1-}	cyanide ion
hydrogen carbonate ion	HCO_3^{1-}	4.7×10^{-11}	10.33	CO_3^{2-}	carbonate ion
hydrogen phosphate ion	HPO_4^{2-}	4.8×10^{-13}	12.32	PO_4^{3-}	phosphate ion
hydrogen sulfide ion	HS^{1-}	1.3×10^{-13}	12.89	S^{2-}	sulfide ion
water	H_2O	1.0×10^{-14}	14.00	OH^{1-}	hydroxide ion
ammonia	NH_3	$<< 10^{-14}$		NH_2^{1-}	amide ion
hydroxide ion	OH^{1-}	$<< 10^{-14}$		O^{2-}	oxide ion

BOND ENERGIES

C–H	413
C–F	485
C–Cl	328
C–Br	276
C–I	234

N–H	391
N–F	272
N–Cl	200
N–Br	243

O–H	463
O–F	190
O–Cl	203
O–Br	235
O–I	234

H–H	436
H–F	565
H–Cl	431
H–Br	366
H–I	299

F–F	159
Cl–Cl	243
Br–Br	193
I–I	151

C–C	347
C=C	612
C≡C	820

N–N	163
N=N	418
N≡N	941

N–O	201
N=O	607

C–N	293
C=N	615
C≡N	891

C–O	358
C=O	799
C≡O	1072

O–O	146
O=O	495

Common Bond Energies (kJ/mol)

List of Element Names, Symbols, Atomic Numbers and Masses

Elements	Symbol	Atomic Number	Atomic Mass
Actinium	Ac	89	227.03
Aluminum	Al	13	26.98
Americium	Am	95	(243)
Antimony	Sb	51	121.8
Argon	Ar	18	39.95
Arsenic	As	33	74.92
Astatine	At	85	(210)
Barium	Ba	56	137.3
Berkelium	Bk	97	(247)
Beryllium	Be	4	9.012
Bismuth	Bi	83	208.98
Bohrium	Bh	107	(264)
Boron	B	5	10.81
Bromine	Br	35	79.90
Cadmium	Cd	48	112.4
Calcium	Ca	20	40.08
Californium	Cf	98	(251)
Carbon	C	6	12.01
Cerium	Ce	58	140.1
Cesium	Cs	55	132.9
Chlorine	Cl	17	35.45
Chromium	Cr	24	52.00
Cobalt	Co	27	58.93
Copernicum	Cn	112	(277)
Copper	Cu	29	63.55
Curium	Cm	96	(247)
Dubnium	Db	105	(262)
Dysprosium	Dy	66	162.5
Einsteinium	Es	99	(252)
Erbium	Er	68	167.3
Europium	Eu	63	151.96
Fermium	Fm	100	(257)
Fluorine	F	9	18.99
Francium	Fr	87	(223)
Gadolinium	Gd	64	157.3
Gallium	Ga	31	69.72
Germanium	Ge	32	72.61
Gold	Au	79	196.97

Hafnium	Hf	72	178.5
Helium	He	2	4.003
Hessium	Hs	108	(265)
Holmium	Ho	67	164.9
Hydrogen	H	1	1.008
Indium	In	49	114.8
Iodine	I	53	126.9
Iridium	Ir	77	192.2
Iron	Fe	26	55.85
Krypton	Kr	36	83.8
Lanthanum	La	57	138.9
Lawrencium	Lr	103	(262)
Lead	Pb	82	207.2
Lithium	Li	3	6.941
Lutetium	Lu	71	174.97
Magnesium	Mg	12	24.31
Manganese	Mn	25	54.94
Meitnerium	Mt	109	(268)
Mendelevium	Md	101	(258)
Mercury	Hg	80	200.6
Molybdenum	Mo	42	95.94
Neodymium	Nd	60	144.2
Neon	Ne	10	20.18
Neptunium	Np	93	(237.05)
Nickel	Ni	28	58.69
Niobium	Nb	41	92.91
Nitrogen	N	7	14.01
Nobelium	No	102	(259)
Osmium	Os	76	190.2
Oxygen	O	8	15.99
Palladium	Pd	46	106.4
Phosphorus	P	15	30.97
Platinum	Pt	78	195.1
Plutonium	Pu	94	(244)
Polonium	Po	84	(209)
Potassium	K	19	39.09
Praseodymium	Pr	59	140.9

Promethium	Pm	61	(145)
Protactinium	Pa	91	(231.04)
Radium	Ra	88	(226.03)
Radon	Rn	86	(222)
Rhenium	Re	75	186.2
Rhodium	Rh	45	102.9
Rubidium	Rb	37	85.47
Ruthenium	Ru	44	101.1
Rutherfordium	Rf	104	(261)
Samarium	Sm	62	150.4
Scandium	Sc	21	44.96
Seaborgium	Sg	106	(263)
Selenium	Se	34	78.96
Silicon	Si	14	28.09
Silver	Ag	47	107.9
Sodium	Na	11	22.99
Strontium	Sr	38	87.62
Sulfur	S	16	32.07
Tantalum	Ta	73	180.9
Technetium	Tc	43	(98)
Tellurium	Te	52	127.6
Terbium	Tb	65	158.9
Thallium	Tl	81	204.4
Thorium	Th	90	232.04
Thulium	Tm	69	168.9
Tin	Sn	50	118.7
Titanium	Ti	22	47.88
Tungsten	W	74	183.9
Uranium	U	92	238.0
Ununnilium	Uun	110	(269)
Unununium	Uuu	111	(272)
Vanadium	V	23	50.94
Xenon	Xe	54	131.3
Ytterbium	Yb	70	173.0
Yttrium	Y	39	88.91
Zinc	Zn	30	65.39
Zirconium	Zr	40	91.22

FUNDAMENTAL CONSTANTS

Energy

- 1 joule (J) = 1 kg $\cdot$ m^2 $\cdot$ s^{-2}
- 1 calorie (cal) = 4.184 J
- 1 V = 96.485 kJ/mol

Force

- 1 newton (N) = 1 kg $\cdot$ m/s^2

Length

- 1 meter (m) = 39.37 inches (in)
- 1 inch = 2.54 centimeters (cm)—exact
- 1 Å = 10^{-10} m

Mass

- 1 kilogram (kg) = 2.205 pounds (lb)
- 1 lb = 453.6 grams (g)
- 1 amu = 1.661 × 10^{-24} g

Pressure

- 1 atm = 760 mm Hg (torr) = 1.01325 × 10^5 Pa

Volume

- 1 liter (L) = 1000 mL = 1000 cm^3

Physical Constants

Avogadro's number	$N_\mathrm{A} = 6.0221 \times 10^{23}$ mol^{-1}
Electronic charge	$e = 1.6022 \times 10^{-19}$ coulomb (C)
Electron rest mass	$m_\mathrm{e} = 9.1094 \times 10^{-31}$ kg
Faraday constant	$\mathcal{F} = 9.6485 \times 10^{4}$ C $\cdot$ mol^{-1}
Gas constant	R = 0.08206 L $\cdot$ atm $\cdot$ mol^{-1} $\cdot$ K^{-1} = 8.3145 J $\cdot$ mol^{-1} $\cdot$ K^{-1} = 1.9872 cal $\cdot$ mol^{-1} $\cdot$ K^{-1}
Neutron rest mass	$m_\mathrm{n} = 1.675 \times 10^{-27}$ kg
Planck's constant	$h = 6.6261 \times 10^{-34}$ J $\cdot$ s
Proton rest mass	$m_p = 1.6726 \times 10^{-27}$ kg
Speed of light (in vacuum)	$c = 2.9979 \times 10^{8}$ m $\cdot$ s^{-1}

Physical Constants

Temperature

$$
\begin{aligned}
0\text{ K} &= -273.15^\circ \text{ Celsius (C)} \\
&= -459.67^\circ \text{ Fahrenheit (F)} \\
^\circ\text{F} &= (9/5)^\circ\text{C} + 32^\circ \\
^\circ\text{C} &= (5/9)(^\circ\text{F} - 32^\circ) \\
\text{K} &= ^\circ\text{C} + 273.15
\end{aligned}
$$

SI Prefixes

- 10^{9} giga (G)
- 10^{6} mega (M)
- 10^{3} kilo (k)
- 10^{-1} deci (d)
- 10^{-2} centi (c)
- 10^{-3} milli (m)
- 10^{-6} micro (μ)
- 10^{-9} nano (n)
- 10^{-12} pico (p)

SELECTED STANDARD REDUCTION POTENTIALS AT 298 K

Reduction half-reactions			**E°(V)**
$Li^{1+}(aq) + e^{1-}$	$\rightleftharpoons$	$Li(s)$	−3.04
$K^{1+}(aq) + e^{1-}$	$\rightleftharpoons$	$K(s)$	−2.92
$Ba^{2+}(aq) + 2\ e^{1-}$	$\rightleftharpoons$	$Ba(s)$	−2.92
$Ca^{2+}(aq) + 2\ e^{1-}$	$\rightleftharpoons$	$Ca(s)$	−2.84
$Na^{1+}(aq) + e^{1-}$	$\rightleftharpoons$	$Na(s)$	−2.71
$Mg^{2+}(aq) + 2\ e^{1-}$	$\rightleftharpoons$	$Mg(s)$	−2.36
$Al^{3+}(aq) + 3\ e^{1-}$	$\rightleftharpoons$	$Al(s)$	−1.66
$U^{3+}(aq) + 3\ e^{1-}$	$\rightleftharpoons$	$U(s)$	−1.66
$Ti^{2+}(aq) + 2\ e^{1-}$	$\rightleftharpoons$	$Ti(s)$	−1.63
$Mn^{2+}(aq) + 2\ e^{1-}$	$\rightleftharpoons$	$Mn(s)$	−1.18
$2\ H_2O + 2\ e^{1-}$	$\rightleftharpoons$	$H_2(g) + 2\ OH^{1-}(aq)$	−0.83
$Zn^{2+}(aq) + 2\ e^{1-}$	$\rightleftharpoons$	$Zn(s)$	−0.76
$Cr^{3+}(aq) + 3\ e^{1-}$	$\rightleftharpoons$	$Cr(s)$	−0.74
$HCHO(aq) + 2\ H_2O + 2\ e^{1-}$	$\rightleftharpoons$	$CH_3OH(aq) + 2\ OH^{1-}(aq)$	−0.59
$Fe^{2+}(aq) + 2\ e^{1-}$	$\rightleftharpoons$	$Fe(s)$	−0.44
$2\ H_2O + 2\ e^{1-}$	$\rightleftharpoons$	$H_2(g) + 2\ OH^{1-}(aq)$	−0.41*
$Cd^{2+}(aq) + 2\ e^{1-}$	$\rightleftharpoons$	$Cd(s)$	−0.40
$PbSO_4(s) + 2\ e^{1-}$	$\rightleftharpoons$	$Pb(s) + SO_4^{2-}(aq)$	−0.36
$In^{3+}(aq) + 3\ e^{1-}$	$\rightleftharpoons$	$In(s)$	−0.34
$Co^{2+}(aq) + 2\ e^{1-}$	$\rightleftharpoons$	$Co(s)$	−0.28
$Ni^{2+}(aq) + 2\ e^{1-}$	$\rightleftharpoons$	$Ni(s)$	−0.23
$Sn^{2+}(aq) + 2\ e^{1-}$	$\rightleftharpoons$	$Sn(s)$	−0.14
$Pb^{2+}(aq) + 2\ e^{1-}$	$\rightleftharpoons$	$Pb(s)$	−0.13
$2\ H^{1+}(aq) + 2\ e^{1-}$	$\rightleftharpoons$	$H_2(g)$	0.00
$Sn^{4+}(aq) + 2\ e^{1-}$	$\rightleftharpoons$	$Sn^{2+}(aq)$	+0.15
$Cu^{2+}(aq) + e^{1-}$	$\rightleftharpoons$	$Cu^{1+}(aq)$	+0.16
$ClO_4^{1-}(aq) + H_2O(l) + 2\ e^{1-}$	$\rightleftharpoons$	$ClO_3^{1-}(aq) + 2\ OH^{1-}(aq)$	+0.17
$AgCl(s) + e^{1-}$	$\rightleftharpoons$	$Ag(s) + Cl^{1-}(aq)$	+0.22
$PbO_2(s) + 2\ H^{1+}(aq) + 2\ e^{1-}$	$\rightleftharpoons$	$PbO(s) + H_2O$	+0.28
$Cu^{2+}(aq) + 2\ e^{1-}$	$\rightleftharpoons$	$Cu(s)$	+0.34
$Ag_2O(s) + H_2O + 2\ e^{1-}$	$\rightleftharpoons$	$2\ Ag(s) + 2\ OH^{1-}(aq)$	+0.34
$ClO_3^{1-}(aq) + H_2O(l) + 2\ e^{1-}$	$\rightleftharpoons$	$ClO_2^{1-}(aq) + 2\ OH^{1-}(aq)$	+0.35
$O_2(g) + 2\ H_2O + 4\ e^{1-}$	$\rightleftharpoons$	$4\ OH^{1-}(aq)$	+0.40
$I_2(s) + 2\ e^{1-}$	$\rightleftharpoons$	$2\ I^{1-}(aq)$	+0.54
$ClO_2^{1-}(aq) + H_2O(l) + 2\ e^{1-}$	$\rightleftharpoons$	$ClO^{1-}(aq) + 2\ OH^{1-}(aq)$	+0.59
$2\ AgO(s) + H_2O + 2\ e^{1-}$	$\rightleftharpoons$	$Ag_2O(s) + 2\ OH^{1-}(aq)$	+0.60
$O_2(g) + 2\ H^{1+}(aq) + 2\ e^{1-}$	$\rightleftharpoons$	$H_2O_2(aq)$	+0.70
$Fe^{3+}(aq) + e^{1-}$	$\rightleftharpoons$	$Fe^{2+}(aq)$	+0.77
$BrO^{1-}(aq) + H_2O + 2\ e^{1-}$	$\rightleftharpoons$	$Br^{1-}(aq) + 2\ OH^{1-}(aq)$	+0.77

Reduction half-reactions			**E°(V)**
$Ag^{1+}(aq) + e^{1-}$	$\rightleftharpoons$	$Ag(s)$	+0.80
$O_2(g) + 4\ H^{1+}(aq) + 4\ e^{1-}$	$\rightleftharpoons$	$2\ H_2O$	+0.82*
$H_2O_2(aq) + 2\ e^{1-}$	$\rightleftharpoons$	$2\ OH^{1-}(aq)$	+0.88
$ClO^{1-}(aq) + H_2O + 2\ e^{1-}$	$\rightleftharpoons$	$Cl^{1-}(aq) + 2\ OH^{1-}(aq)$	+0.89
$Hg^{2+}(aq) + 2\ e^{1-}$	$\rightleftharpoons$	$Hg(l)$	+0.85
$NO_3^{1-}(aq) + 4\ H^{1+}(aq) + 3\ e^{1-}$	$\rightleftharpoons$	$NO(g) + 2\ H_2O$	+0.96
$VO_2^{1+}(aq) + 2\ H^{1+}(aq) + e^{1-}$	$\rightleftharpoons$	$VO^{2+}(aq) + H_2O$	+1.00
$Br_2(l) + 2\ e^{1-}$	$\rightleftharpoons$	$2\ Br^{1-}(aq)$	+1.09
$ClO_4^{1-}(aq) + 2\ H^{1+}(aq) + 2\ e^{1-}$	$\rightleftharpoons$	$ClO_3^{1-}(aq) + H_2O(l)$	+1.19
$O_2(g) + 4\ H^{1+}(aq) + 4\ e^{1-}$	$\rightleftharpoons$	$2\ H_2O$	+1.23
$Cr_2O_7^{2-}(aq) + 14\ H^{1+}(aq) + 6\ e^{1-}$	$\rightleftharpoons$	$2\ Cr^{3+}(aq) + 7\ H_2O$	+1.33
$Cl_2(g) + 2\ e^{1-}$	$\rightleftharpoons$	$2\ Cl^{1-}(aq)$	+1.36
$Au^{3+}(aq) + 3\ e^{1-}$	$\rightleftharpoons$	$Au(s)$	+1.50
$MnO_4^{1-}(aq) + 8\ H^{1+}(aq) + 5\ e^{1-}$	$\rightleftharpoons$	$Mn^{2+}(aq) + 4\ H_2O$	+1.51
$PbO_2(s) + 4\ H^{1+}(aq) + SO_4^{2-}(aq) + 2\ e^{1-}$	$\rightleftharpoons$	$PbSO_4(s) + 2\ H_2O$	+1.69
$H_2O_2(aq) + 2\ H^{1+}(aq) + 2\ e^{1-}$	$\rightleftharpoons$	$2\ H_2O(l)$	+1.76
$S_2O_8^{2-}(aq) + 2\ e^{1-}$	$\rightleftharpoons$	$2\ SO_4^{2-}(aq)$	+2.01
$O_3(g) + 2\ H^{1+}(aq) + 2\ e^{1-}$	$\rightleftharpoons$	$O_2(g) + H_2O$	+2.07
$F_2(g) + 2\ e^{1-}$	$\rightleftharpoons$	$2\ F^{1-}(aq)$	+2.87

* The half-cell potentials for the O_2/H_2O and the H_2O/H_2 systems are for neutral (pH = 7) water and are not standard reduction potentials where $[OH^{1-}]$ or $[H^{1+}] = 1.0$ M.

THERMODYNAMIC PROPERTIES

Selected Values of Standard Thermodynamic Properties at 298.15 K

Substance	$\Delta H^\circ_\mathrm{f}$ kJ/mol	$\Delta G^\circ_\mathrm{f}$ kJ/mol	S° J/mol·K
Aluminum:			
$\mathrm{Al}(s)$	0	0	28.3
$\mathrm{AlCl_3}(s)$	−704.2	−628.8	110.7
$\mathrm{Al_2O_3}(s)$	−1676	−1582	50.92
Barium:			
$\mathrm{Ba}(s)$	0	0	28.3
$\mathrm{Ba^{2+}}(aq)$	−538.36	−560.7	13
$\mathrm{BaCO_3}(s)$	−1219	−1139	112
Boron:			
$\mathrm{B}(s)$	0	0	5.86
$\mathrm{BF_3}(g)$	−1137.0	−1120.3	254.12
Bromine:			
$\mathrm{Br_2}(l)$	0	0	152.23
$\mathrm{Br_2}(g)$	30.91	3.13	245.38
$\mathrm{Br}(g)$	111.9	82.40	174.90
$\mathrm{Br^{1-}}(aq)$	−120.9	−102.8	80.71
$\mathrm{HBr}(g)$	−36	−53.5	198.59
Calcium:			
$\mathrm{CaO}(s)$	−635.1	−603.5	38.2
$\mathrm{Ca(OH)_2}(s)$	−986.09		
$\mathrm{CaCO_3}(s)$	−1206.9	−1128.8	92.9
Carbon:			
$\mathrm{C}(s$, graphite$)$	0	0	5.740
$\mathrm{C}(s$, diamond$)$	1.987	2.900	2.38
$\mathrm{C}(g)$	716.681	671.289	157.987
$\mathrm{CO}(g)$	−110.52	−137.15	197.56
$\mathrm{CO_2}(g)$	−393.51	−394.36	213.6
$\mathrm{CO_2}(aq)$	−412.9	−386.2	121
$\mathrm{CCl_4}(g)$	−103	−53.7	309.7
$\mathrm{CCl_4}(l)$	−135.4	−68.6	216.4
$\mathrm{HCN}(g)$	135	125	201.7
$\mathrm{CH_4}(g)$	−74.9	−50.6	186.15
$\mathrm{CS_2}(g)$	117.4	67.15	237.7
$\mathrm{CS_2}(l)$	89.70	65.27	151.3
$\mathrm{C_2H_2}(g)$	226.7	209.2	200.8
$\mathrm{C_2H_4}(g)$	52.28	68.12	219.5
$\mathrm{C_2H_6}(g)$	−84.67	−32.89	229.5

Substance	ΔH°_f kJ/mol	ΔG°_f kJ/mol	S° J/mol·K
$CH_3OH(g)$	−201.2	−161.9	237.6
$CH_3OH(l)$	−237.6	−166.23	126.8
$C_2H_5OH(g)$	−235.1	−168.6	282.6
$C_2H_5OH(l)$	−277.7	−174.76	160.7
$CH_3COOH(l)$	−484.5	−390	160
$CH_3CHO(g)$	−166	−133.7	266
$C_4H_{10}(g)$	−124.73	−15.71	310.0
$C_4H_{10}(l)$	−147.6	−15.0	231.0
$C_6H_6(g)$	82.927	129.66	269.2
$C_6H_6(l)$	49.028	124.50	172.8
$C_8H_{18}(l)$	−226		
Chlorine:			
$Cl_2(g)$	0	0	223.0
$Cl(g)$	121.7	105.7	165.2
$Cl^{1-}(aq)$	−167.2	−131.2	56.5
$HCl(g)$	−92.30	−95.31	186.80
$HCl(aq)$	−167.2	−131.2	56.5
Chromium:			
$Cr_2O_3(s)$	−1138	−1059	81.2
$(NH_4)_2Cr_2O_7(s)$	−1807		
Copper:			
$Cu(s)$	0	0	33.15
$CuO(s)$	−157	−128	42.63
$CuSO_4(s)$	−771.36	−661.9	110
$Cu_2S(s)$	−79.5	−86.2	120.5
Fluorine:			
$F_2(g)$	0	0	202.7
$F(g)$	78.99	61.92	158.64
$F^{1-}(aq)$	−332.6	−278.8	−13.8
$HF(g)$	−271	−273	173.67
Hydrogen:			
$H_2(g)$	0	0	130.57
$H(g)$	217.97	203.26	114.60
$H^{1+}(aq)$	0	0	0
$H_2O(l)$	−285.83	−237.2	69.91
$H_2O(g)$	−241.82	−228.59	188.7
Iodine:			
$I_2(s)$	0	0	116.14
$I_2(g)$	62.438	19.36	260.6
$I(g)$	106.84	70.283	180.68
$HI(g)$	26.5	1.71	206.48

Substance	ΔH_f° kJ/mol	ΔG_f° kJ/mol	S° J/mol·K
Iron:			
$Fe(s)$	0	0	27.3
$FeO(s)$	−271.9	−255.2	60.75
$Fe_2O_3(s)$	−824.2	−742.2	87.40
$Fe_3O_4(s)$	−1117.1	−1014.2	146.4
Lead:			
$Pb(s)$	0	0	68.85
$Pb^{2+}(aq)$	1.6	−24.3	21
$PbBr_2(s)$	−277.4	−260.7	161
$PbCl_2(s)$	−359	−314	136
$PbO(s)$	−219.0	−189.2	66.5
Magnesium			
$Mg(s)$	0	0	32.69
$MgO(s)$	−601.7	−569.4	26.94
$MgCl_2(s)$	−641.6	−592.1	89.6
Nitrogen:			
$N_2(g)$	0	0	191.5
$N(g)$	472.704	455.5	153.19
$NH_3(g)$	−46.11	−16.5	192.3
$NH_3(aq)$	−80.29	−26.57	111.3
$NH_4Cl(s)$	−314.4	−203.0	94.6
$NH_4NO_3(s)$	−365.5	−184.0	151.1
$NO(g)$	90.29	86.60	210.65
$NO_2(g)$	33.84	51.84	240.45
$N_2O_4(g)$	9.66	98.28	304.3
Oxygen:			
$O_2(g)$	0	0	205.03
$O(g)$	249.17	231.75	160.95
$O_3(g)$	143	163	238.82
Phosphorus:			
$P_4(s)$	0	0	41.08
$P(g)$	316.4	280.0	163.2
$PCl_3(g)$	−288.07	−269.6	311.7
$PCl_3(l)$	−319.6	−272.4	217
$PH_3(g)$	5.4	13.4	210.2
$P_4O_{10}(s)$	−1640.1		
$POCl_3(g)$	−542.2	−502.5	325
$POCl_3(l)$	−597.0	−520.9	222
$H_3PO_4(aq)$	−1288.3	−1142.6	158.2
Potassium			
$K(s)$	0	0	64.67
$KCl(s)$	−436.7	−409.2	82.59
$KClO_3(s)$	−397.7	−296.3	143.1

Substance	ΔH°_f kJ/mol	ΔG°_f kJ/mol	S° J/mol·K
Silicon:			
Si(s)	0	0	18.7
Si(g)	368.2	323.9	167.8
SiO_2(s)	−910.94	−856.67	41.84
SiH_4(g)	34	56.9	204.5
Silver:			
Ag(s)	0	0	42.55
Ag^{1+}(aq)	105.90	77.11	73.93
AgCl(s)	−127.0	−109.70	96.11
Ag_2O(s)	−31.05	−11.20	121.3
Ag_2S(s)	−32.6	−40.7	144.0
Sodium:			
Na(s)	0	0	51.45
Na^{1+}(aq)	−240.1	−261.9	59.0
NaCl(s)	−411.1	−384.0	72.12
Sulfur:			
S(s, rhombic)	0	0	31.8
SO_2(g)	−296.83	−300.19	248.1
SO_3(g)	−395.72	−371.1	256.6
S_2(g)	129	79.30	228.2
H_2S(g)	−20.6	−33.6	205.7
H_2SO_4(l)	−813.989	−690.101	156.90
H_2SO_4(aq)	−909.3	−744.6	20.08
Tin:			
Sn(s)	0	0	51.2
SnO(s)	−286	−257	56.5
SnO_2(s)	−580.7	−519.7	52.3
$SnCl_4$(l)	−545.2	−474.0	259
$SnCl_4$(g)	−471.5	−432.2	366
Titanium:			
Ti(s)	0	0	30.6
Ti(g)	468	422	180.3
TiO_2(s)	−944.7	−889.5	50.3
$TiCl_4$(l)	−804.2	−737.2	252.3
$TiCl_4$(g)	−763.2	−726.8	354
Zinc:			
Zn(s)	0	0	41.6
ZnO(s)	−348.0	−318.2	43.6
$ZnCl_2$(s)	−415.1	−369.4	111.5

Selected Values of Standard Thermodynamic Properties at 298.15 K

SELECTED SOLUBILITY PRODUCT CONSTANTS

Substance	$K_{\mathbf{sp}}$ at **25 °C**
Aluminum	
$Al(OH)_3$	1.9×10^{-33}
Barium	
$Ba(OH)_2$	5.0×10^{-3}
$BaCO_3$	8.1×10^{-9}
$BaSO_4$	1.1×10^{-10}
$Ba_3(PO_4)_2$	3.4×10^{-23}
Cadmium	
$Cd(OH)_2$	2.5×10^{-14}
$CdCO_3$	5.2×10^{-12}
CdS	8.0×10^{-27}
Calcium	
$Ca(OH)_2$	5.5×10^{-6}
$CaCO_3$	4.8×10^{-9}
$Ca_3(PO_4)_2$	1.0×10^{-26}
CaF_2	3.9×10^{-11}
Chromium	
$Cr(OH)_3$	6.3×10^{-31}
Cobalt	
$Co(OH)_2$	1.6×10^{-15}
CoS	4.0×10^{-21}
Copper	
$Cu(OH)_2$	2.2×10^{-20}
Cu_2S	1.6×10^{-48}
$CuCO_3$	1.4×10^{-10}
CuS	6.3×10^{-36}
Iron	
$Fe(OH)_2$	8.0×10^{-16}
FeS	6.3×10^{-18}
$Fe(OH)_3$	2.5×10^{-39}
$FePO_4$	9.9×10^{-29}

Substance	$K_{\mathbf{sp}}$ **at 25 °C**
Lead	
$Pb(OH)_2$	2.8×10^{-16}
PbF_2	3.7×10^{-8}
$PbCl_2$	1.7×10^{-5}
$PbBr_2$	6.3×10^{-6}
PbI_2	6.5×10^{-9}
$PbCrO_4$	1.8×10^{-14}
$PbSO_4$	1.7×10^{-8}
PbS	8.4×10^{-28}
Magnesium	
$Mg(OH)_2$	1.8×10^{-11}
Manganese	
$Mn(OH)_2$	1.9×10^{-13}
$MnCO_3$	8.8×10^{-11}
MnS	5.6×10^{-16}
Nickel	
$Ni(OH)_2$	1.6×10^{-14}
Silver	
$AgCl$	1.8×10^{-10}
$AgBr$	5.0×10^{-13}
AgI	8.3×10^{-17}
$AgCN$	1.2×10^{-16}
Ag_2S	6.3×10^{-50}
Ag_2CrO_4	1.1×10^{-12}
Ag_3PO_4	2.6×10^{-18}
Tin	
$Sn(OH)_2$	1.4×10^{-28}
SnS	1.3×10^{-23}
Zinc	
$ZnCO_3$	1.0×10^{-10}
$Zn(OH)_2$	4.5×10^{-17}
ZnS	1.1×10^{-21}

VAPOR PRESSURE OF WATER AT VARIOUS TEMPERATURES

T (°C)	**P°(torr)**	**T (°C)**	**P°(torr)**
0	4.6	50	92.5
5	6.5	55	118.0
10	9.2	60	149.9
15	12.8	65	187.5
20	17.5	70	233.7
25	23.8	75	289.1
30	31.8	80	355.1
35	41.2	85	433.6
40	55.3	90	525.8
45	71.9	95	633.9

1 torr = 1 mm Hg

FREEZING POINT DEPRESSION AND BOILING POINT ELEVATION DATA FOR SOME SOLVENTS

Solvent	FreezingPoint (°C)	k_f ($^\circ\mathrm{C} \cdot m^{-1}$)	BoilingPoint (°C)	k_b ($^\circ\mathrm{C} \cdot m^{-1}$)
Acetic Acid	16.6	3.90	117.9	3.07
Benzene	5.5	4.90	80.1	2.53
Chloroform	−63.5	4.70	61.7	3.63
Cyclohexane	6.6	20.0	80.7	2.79
Ethanol	−117.3	1.99	78.5	1.22
para-Xylene	11.3	4.30		
Water	0.0	1.86	100.0	0.512