

Hodeidah University
Faculty of engineering

Physical Chemistry

A course for second year engineers

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Introduction

Physical chemistry is the study of the underlying physical principles that govern the properties and behaviour of chemical systems. The knowledge of these principles is important and provides a framework for all branches of chemistry, whether we are synthesizing compounds in a research laboratory, manufacturing chemicals on an industrial scale or trying to understand the intricate biological processes in the cell. This module is intended to broaden your understanding of physical principles in chemistry. It deals with three main areas: **thermodynamics**, **quantum chemistry** and **chemical kinetics**. Studying thermodynamics enables the chemist to predict whether or not a reaction will occur when reactants are brought together under a specific set of conditions. Indeed industrial chemists often place more emphasis on speeding up the rate of a reaction than on its percentage yield. Organic chemists use kinetic studies to determine the mechanisms of reactions and to tell how fast products will be formed.

This course is about advanced concepts in physical chemistry that cover the topics of thermodynamics, chemical kinetics, and kinetic molecular theory. In our study of thermodynamics (thermodynamics comes from the Greek words for “heat” and “power”), we shall be looking at the first and second laws of thermodynamics as they apply to volume-pressure processes and energy changes associated with chemical reactions. The topics in chemical kinetics will look at rate laws and factors affecting the rates of chemical reactions. In molecular kinetic theory, we shall be looking at explaining the general behaviour of gases from a molecular point of view.

References

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- 4- R. G. Mortimer, *Physical Chemistry*, third edition, Elsevier Academic Press, 2008.
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Three basic states of matter

Gas: Fills a container, taking on the shape of the container. Similar to a liquid, except that particles are very widely spaced from one another, and inter-particle interactions are minimal.

Liquid: Does not fill a container, but takes the shape of the container. Similar to gases except particles are very closely spaced.

Solid: Does not fill a container, and does not conform to the shape of the container. Particles are very closely packed – still much dynamic motion in a solid which increases with heating.

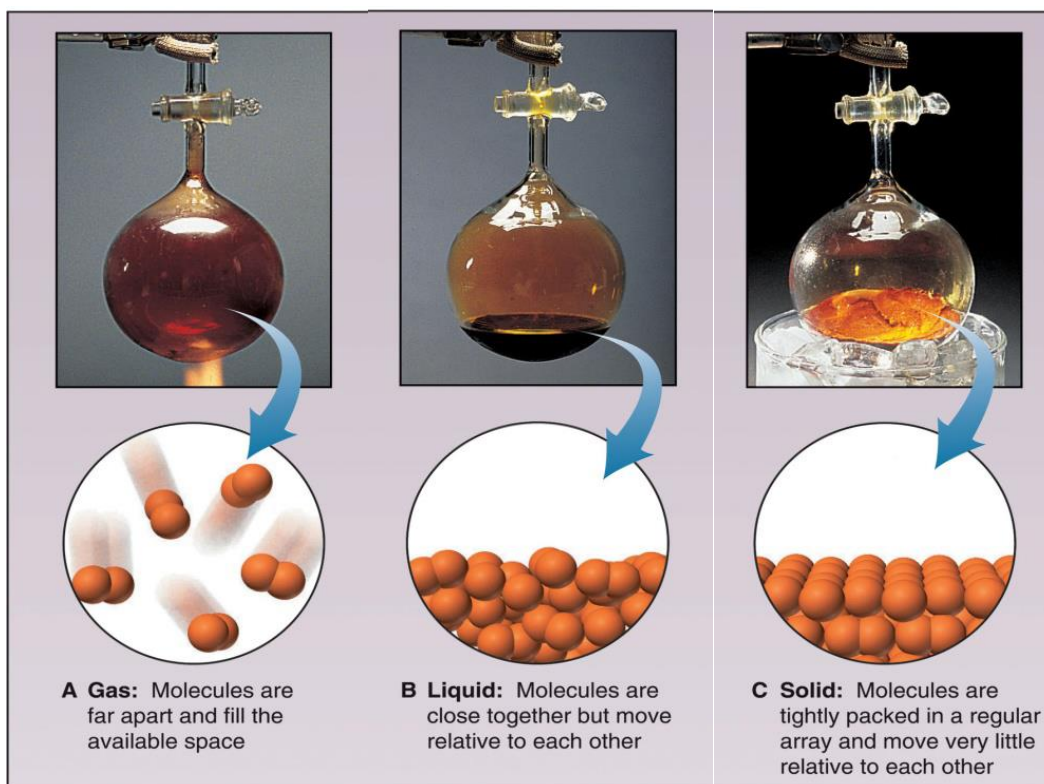


Figure 1.1 Three basic states of matter.

General properties of gases

- A gas is a state of matter which fills any container it occupies.
- Molecular picture of gas: Collection of widely separated molecules in random chaotic motion. Hence molecules move through space freely to fill any volume.
- Gases are highly compressible hence readily confined to smaller volume.
- Gases respond readily to changes in temperature and occupy a larger volume when heated and a smaller volume when cooled.
- Fundamental properties of gases described in terms of pressure P (units: Nm^{-2} , atm etc), Volume V (units: L (or dm^3), m^3 etc), temperature T (unit: K, $^{\circ}\text{C}$) and amount (unit: mol).
- General properties of gases are described in terms of three empirical laws developed by Boyle, Charles and Avogadro which may be used to predict the behaviour of gas under given conditions of temperature, pressure and volume.

Ideal Gas

- An Ideal gas is pictured as a collection of molecules or atoms which undergo continuous random motion (Brownian motion).
- The speeds of the gas particles increase as the temperature increases.
- The molecules are widely separated from one another, with the only interactions being with the side walls of the container and other molecules during infrequent collisions.
- The molecules are unaffected by intermolecular forces (e.g. dipole/dipole, van der Waals etc).
- The state of a gas is defined by its pressure P , volume V , temperature T and amount n .

Pressure (P) is the force exerted by gas against the walls of the container. The SI unit of P is pascal

$$1\text{Pa} = 1\text{Nm}^{-2} = 1\text{kg m}^{-1}\text{s}^{-2}.$$

There are several non-SI units of pressure; the *atmosphere* (atm), the *torr*, and the *bar*.

$$1\text{ atm} = 101325\text{ Pa} = 760\text{ torr} = 760\text{ mmHg}$$

$$1\text{ bar} = 100000\text{ Pa}$$

Volume (V) is the space occupied by the gas. The SI unit of volume is m^3 . Other unit is Liter (L) where

$$1\text{ L} = 1\text{ dm}^3 = 10^3\text{ cm}^3 = 10^{-3}\text{ m}^3$$

Temperature (T) determines the kinetic energy and rate of motion of the gas particles.

The SI unit of temperature is the *kelvin* (K). Other non-SI unit is Celsius ($^{\circ}\text{C}$)

$$\text{K} = ^{\circ}\text{C} + 273.15$$

Amount (n) is the quantity of gas present in a container. The SI unit of n is the *mole* (mol).

$$n = N/N_A$$

where $N_A = 6.023 \times 10^{23}$ (Avogadro's number). N is the number of molecules. Also,

$$n = M/M_w$$

where M is the mass of molecules and M_w is the molecular weight (molar mass) of one molecule.

The gas laws

Boyle's law (1661)

At constant temperature, the pressure of a fixed amount of gas is inversely proportional to its volume: $p \propto 1/V$

By treating n and T as constant, it becomes

$$PV = \text{constant} \quad (\text{at constant } n \text{ and } T) \quad (1.1)$$

If we compress a fixed amount of gas at constant temperature into half of its original volume, then its pressure will double. The graph is obtained by plotting experimental values of P against V for a fixed amount of gas at different temperatures and the curves predicted by Boyle's law. Each curve is called an isotherm because it depicts the variation of a property (in this case, the pressure) at a single constant temperature.

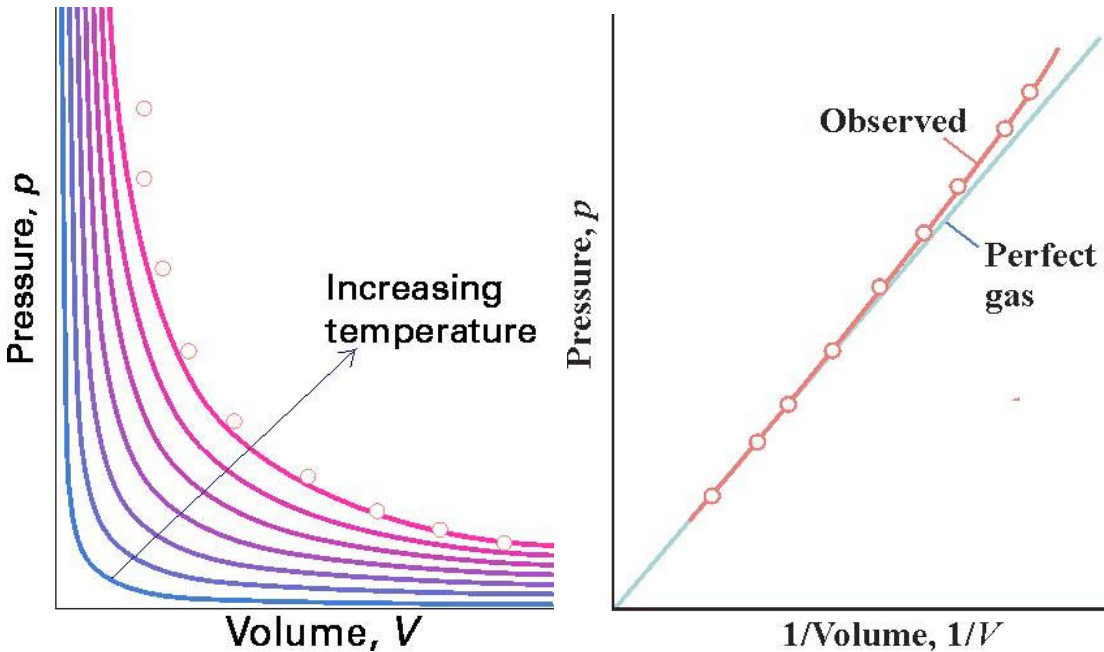


Figure 1.2 (a) Boyle's law (b) Experimental verification of Boyle's law

Example 1.1

Consider a gas of 100 mL confined to a cylinder under a pressure of 1 atm. What would be the volume of the same gas at a pressure of 1.3 atm?

Solution

Boyle's law states that the pressure of a gas (P) is inversely proportional to the volume (V) for a given amount of gas at constant temperature.

$$PV = k$$

where k is a constant, then, $P_1V_1 = P_2V_2$

$$V_2 = P_1V_1 / P_2$$

$$P_1 = 1 \text{ atm}, V_1 = 0.1 \text{ atm}, P_2 = 1.3 \text{ atm}, V_2 = ?$$

$$V_2 = 1 \text{ atm} \times 1.0 \text{ L} / 1.3 \text{ atm} = 0.0769 \text{ L}$$

Practice problem 1.1

A gas bubble has a volume of 0.500 cm^3 at the bottom of the lake where the pressure is 3.49 atm. What is the volume of the bubble at the surface of the lake where the pressure is 1 atm? Assume that the temperature is constant.

- (a) 10 dm^3 (b) $1.7 \times 10^3 \text{ dm}^3$ (c) 1.7 dm^3 (d) 1.7 cm^3

Charles's law (Gay-Lussac's law)

At constant pressure, the volume of a fixed amount of gas varies linearly with the temperature: $V = \text{constant} \times (\theta + 273.15)$

θ - the temperature on the Celsius scale. Typical plots of volume against temperature for a series of samples of gases at different pressures. At low pressures and for temperatures that are not too low the volume varies linearly with the Celsius temperature.

All the volumes extrapolate to zero as θ approaches the same very low temperature ($-273.15 \text{ }^\circ\text{C}$). A volume cannot be negative – this common temperature must represent the absolute zero of temperature, a temperature below which it is impossible to cool an object. The Kelvin scale ascribes the value $T = 0$ to this absolute zero of temperature. Charles's law takes the simpler form: At constant pressure, $V \propto T$.

$$V/T = \text{constant} \text{ (at constant } p \text{ and } n) \quad (1.2)$$

An alternative version of Charles's law, in which the pressure of a sample of gas is monitored under conditions of constant volume, is

$$p/T = \text{constant} \text{ (at constant } V \text{ and } n) \quad (1.3)$$

Example 1.2

A balloon is inflated to a volume of 2.5 L in a warm living room ($24 \text{ }^\circ\text{C}$). Then it is taken outside on a very cold winter's day ($-25 \text{ }^\circ\text{C}$). Assume that the quantity of air in the balloon and its pressure both remain constant. What will be the volume of the balloon when it is taken outdoors?

Solution

The volume of a fixed amount of gas at constant pressure is directly proportional to the absolute temperature.

$$V \propto T$$

$$V = kT$$

$$V/T = k$$

where k is a constant.

$$V_1/T_1 = V_2/T_2$$

Solving for V_2 with temperature in Kelvin scale gives us

$$V_2 = V_1 T_2 / T_1$$

$$V_1 = 2.5 \text{ L}, T_1 = 297 \text{ K}, T_2 = 248 \text{ k}, V_2 = (?)$$

$$V_2 = 2.5 \text{ L} \cdot 248 \text{ k} / 297 \text{ K} = 2 \text{ L}$$

Avogadro's principle

At a given temperature and pressure, equal volumes of gas contain the same numbers of molecules. If we double the number of molecules but keep the temperature and pressure constant, then the volume of the sample will double.

Avogadro's principle: at constant temperature and pressure, $V \propto n$.

This result follows from the perfect gas law by treating p and T as constants.

Avogadro's suggestion is a principle rather than a law (a direct summary of experience) because it is based on a model of a substance, in this case as a collection of molecules.

The molar volume, V_m , of any substance is the volume the substance occupies per mole of molecules.

Molar volume = (volume of sample) / (amount of substance)

$$V_m = V / n \quad (1.4)$$

Avogadro's principle implies – the molar volume of a gas should be the same for all gases at the same temperature and pressure.

Example 1.3

Cyclopropane (C_3H_6) is a gas used as an anesthetic. What would be the mass of 1.0 L of the gas measured at standard temperature and pressure?

The law states that at a fixed temperature and pressure, the volume of a gas is directly proportional to the amount of gas. At STP 1 mol of gas = 22.414 L.

Solution

$$\text{Mass gas} = 1.00 \text{ L} \times 1 \text{ mol} \times 42.8 \text{ gmol}^{-1} / 22.414 \text{ L} = 1.88 \text{ g}$$

Practice problem 1.2

A car travelling at 16 km/h produces 150 g CO per kilometer. How many moles of CO are produced per kilometer?

- (a) 5.4 (b) 3.4 (c) 5.0 (d) 53.6

The ideal gas law

In the previous sections we have looked at three historical laws that relate to two physical properties keeping all other properties constant. These laws and their mathematical expressions are shown below:

Boyle's law $P \propto 1/V$ where T and n are constant

Charles's law $V \propto T$ where P and n are constant

Avogadro's law $V \propto n$ where P and T are constant

The three gas laws can be combined to give a single general gas law $PV/T \propto n$

We can replace the proportionality symbol \propto with an equal sign by introducing proportionality constant. If the constant is given the symbol R , then

$$PV/T = nR$$

R is called the universal gas constant. The value and units of R depend on the units that are used for pressure, volume, temperature, and number of moles. The equation can be rearranged to the expression

$$PV = nRT \quad (1.5)$$

called the **ideal gas equation**. An ideal gas is one whose behavior can be accurately described by the ideal gas equation.

The constant of proportionality was found experimentally to be the same for all gases, is denoted R and called gas constant.

$$R = 8.31451 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= 8.31451 \text{ kPa L K}^{-1} \text{ mol}^{-1}$$

$$= 0.082058 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

$$= 62.364 \text{ L Torr K}^{-1} \text{ mol}^{-1}$$

$$= 1.98722 \text{ Cal K}^{-1} \text{ mol}^{-1}$$

Determination of Universal Gas Constant R

Assume 1 mole gas ($n = 1$). At STP, $P = 1 \text{ atm}$, $T = 273.15 \text{ K}$, $V_M = 22.414 \text{ dm}^3$. In SI units: $n = 1$, $P = 1 \text{ atm} = 1.013 \times 10^5 \text{ N m}^{-2}$, $V_M = 22.414 \times 10^{-3} \text{ m}^3$ since $1 \text{ dm}^3 = 1 \text{ L} = 10^{-3} \text{ m}^3$.

$$R = \frac{(1.013 \times 10^5 \text{ Nm}^{-2}) \times (22.414 \times 10^{-3} \text{ m}^3)}{(1 \text{ mol}) \times (273.15 \text{ K})} = 8.314 \text{ Nm mol}^{-1} \text{ K}^{-1} = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

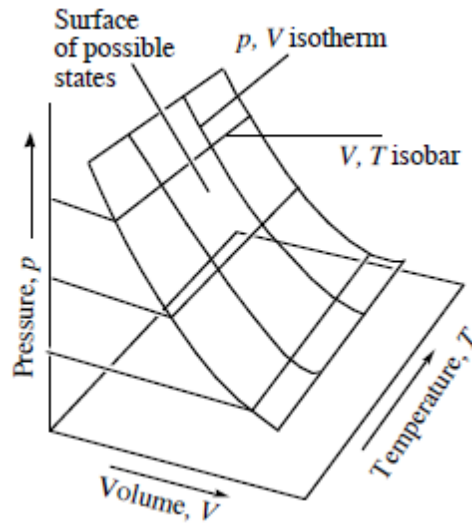


Figure 1.3 A plot of the pressure of a fixed amount of perfect gas against its volume and thermodynamic temperature. The surface depicts only possible states of a perfect gas: the gas cannot exist in states that do not correspond to points on the surface.

Example 1.4

How many moles of hydrogen are present in a 50 L vessel if the pressure is 10 atm and the temperature is 25 °C?

Solution

The volume, pressure and temperature are given. The ideal gas law relates all the quantities given.

$$PV = nRT$$

$$P = 10 \times 101325 \text{ Nm}^{-2} = 1.01 \times 10^6 \text{ Nm}^{-2}, V = 50 \times 10^{-3} \text{ m}^3, T = 298 \text{ K}, R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$n = 50 \times 10^{-3} \text{ m}^3 \times 1.01 \times 10^6 \text{ Nm}^{-2} / 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} = 20$$

Example 1.5

A chemist is investigating the conversion of atmospheric nitrogen to usable form by bacteria and needs to know the pressure in kilopascals exerted by 1.25 g of nitrogen gas in a flask of volume 250 mL at 20°C.

$$p = \frac{nRT}{V}$$

$$p = \frac{(1.25/28.02) \text{ mol} \times (8.31451 \text{ kPa L K}^{-1} \text{ mol}^{-1}) \times (20 + 273.15 \text{ K})}{0.250 \text{ L}}$$

$$= 435 \text{ kPa}$$

$$n_{N_2} = \frac{m}{M_{N_2}} = \frac{1.25 \text{ g}}{28.02 \text{ g mol}^{-1}} = \frac{1.25}{28.02} \text{ mol} \quad T/\text{K} = 20 + 273.15$$

For a given temperature and pressure all gases have the same molar volume. An earlier set of standard conditions – standard temperature and pressure (STP) - °C and 1 atm. The molar volume of a perfect gas at STP is 22.41 L mol^{-1} . It is convenient to report data in chemical research at a particular set of standard conditions. Standard ambient temperature and pressure (SATP) – a temperature of 25°C (more precisely, 298.15 K) and a pressure of 1 bar. The molar volume of a perfect gas at SATP is 24.79 L mol^{-1} .

Dalton's law of partial pressures

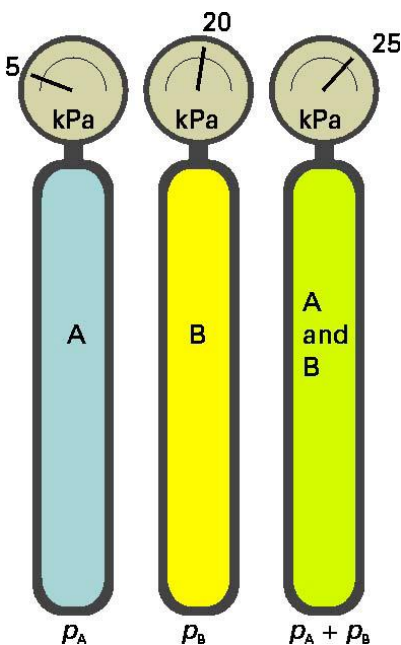


Figure 1.4 Mixture of perfect gases.

Dalton's law: The pressure exerted by a mixture of perfect gases is the sum of pressures that each gas would exert if it were alone in the container at the same temperature:

$$p = p_A + p_B + \dots = (n_A + n_B + \dots) RT/V = nRT/V \quad (1.6)$$

p_J – the pressure that a gas J would exert if it were alone in the container at the same temperature.

$$\text{For each gas: } p_J = n_J RT/V \quad (1.7)$$

Dalton's law is strictly valid only for mixtures of perfect gases but it can be treated as valid for most conditions we encounter.

For any type of gas in a mixture, the partial pressure, p_J , is defined as

$$p_J = x_J \times p \quad (1.8)$$

x_J – the mole fraction of J in the mixture. The mole fraction of J is the amount of J molecules expressed as a fraction of the total amount of molecules in the mixture.

In a mixture that consist of n_A A molecules, n_B B molecules, and so on, the mole fraction of J is

Mole fraction of J = (amount of J molecules)/(total amount of molecules)

$$x_J = n_J/n, \quad n = n_A + n_B + \dots, \quad \text{and} \quad x_A + x_B + \dots = 1 \quad (1.9)$$

and

$$p_A + p_B + \dots = (x_A + x_B + \dots)p = p$$

For a binary mixture consisting of two species:

$$x_A = n_A/(n_A + n_B), \quad x_B = n_B/(n_A + n_B), \quad x_A + x_B = 1 \quad (1.10)$$

For a mixture of perfect gases, we can identify the partial pressure of J with the contribution that J makes to the total pressure. Using $p = nRT/V$,

$$p_J = x_J p = x_J nRT/V = n_J RT/V \quad (1.11)$$

The value of $n_J RT/V$ is the pressure that an amount n_J of J would exert in the otherwise empty container.

Example 1.6

A container of volume 10.0 L holds 1.00 mol N_2 and 3.00 mol H_2 at 298 K. What is the total pressure in atmospheres if each component behaves as a perfect gas?

Solution

$$p = p_A + p_B = (n_A + n_B) RT/V$$

Use $R = 8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}$.

$$p = (1.00 \text{ mol} + 3.00 \text{ mol}) 8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1} \times (298 \text{ K}) / 10.0 \text{ L}$$

$$p = 9.78 \text{ atm}$$

Example 1.7

The mass percentage composition of dry air at sea level is approximately N_2 : 75.5; O_2 : 23.2; Ar: 1.3. What is the partial pressure of each component when the total pressure is 1 atm?

Solution

We expect species with a high mole fraction to have a proportionally high partial pressure, as partial pressures are defined by $p_J = x_J p$. To calculate mole fractions, we use the fact that the amount of molecules J of molar mass M_J in a sample of mass m_J is $n_J = m_J / M_J$.

The mole fractions are independent of the total mass of the sample, so we can choose the latter to be 100 g (for simplicity of calculations).

$$n(N_2) = 0.755 \times 100 \text{ g} / 28.02 \text{ g mol}^{-1} = 2.69 \text{ mol}$$

$$n(\text{O}_2) = 0.232 \times 100 \text{ g} / 32.00 \text{ g mol}^{-1} = 0.725 \text{ mol}$$

$$n(\text{Ar}) = 0.013 \times 100 \text{ g} / 39.95 \text{ g mol}^{-1} = 0.033 \text{ mol}$$

$$n = n(\text{N}_2) + n(\text{O}_2) + n(\text{Ar}) = 3.448 \text{ mol}$$

$$x(\text{N}_2) = n(\text{N}_2) / n = 2.69 \text{ mol} / 3.448 \text{ mol} = 0.780$$

$$x(\text{O}_2) = n(\text{O}_2) / n = 0.725 \text{ mol} / 3.448 \text{ mol} = 0.210$$

$$x(\text{Ar}) = n(\text{Ar}) / n = 0.033 \text{ mol} / 3.448 \text{ mol} = 0.0096$$

$$p(\text{N}_2) = x(\text{N}_2) p = 0.780 \times 1 \text{ atm} = 0.780 \text{ atm}$$

$$p(\text{O}_2) = x(\text{O}_2) p = 0.210 \times 1 \text{ atm} = 0.210 \text{ atm}$$

$$p(\text{Ar}) = x(\text{Ar}) p = 0.0096 \times 1 \text{ atm} = 0.0096 \text{ atm}$$

We have not had to assume that the gases are perfect: p_J are defined as $p_J = x_J p$ for any kind of gas.

Practice problem 1.3

In an experiment a mixture of oxygen and nitrogen gas is collected over water at 30 °C and 700 torr pressure. What is the partial pressure of oxygen, if the partial pressure of nitrogen is 550 torr? (Vapour pressure H₂O at 30 °C, 4.2455 kPa).

- (a) 118 torr (b) 120 (c) 115 (d) 119

Kinetic molecular theory of gases

Chiefly Rudolf Clausius (1822-1906), James Clerk Maxwell (1831-1879) and Ludwig Boltzmann (1844-1888) developed the kinetic molecular theory. Their theory is based on the following assumptions about the nature of gases at molecular level.

1. Molecules in a gas are in constant random motion and frequently collide with each other.
2. A gas consists of a large number of particles that are so small and separated by such large distances that their size is negligible. Attractive and repulsive forces between gas molecules are negligible.
3. Each molecule acts independent of the other molecules and is unaffected by their presence. At sufficiently low temperatures, all gases will condense into liquids suggesting the presence of intermolecular forces that become significant at low temperatures. Attractive forces are responsible for holding liquid and solid molecules together. The tendency for a gas to expand and fill the volume in which it occupies suggests the presence of negligible forces of attraction between molecules. Increasing pressure of a gas results in decrease of inter- particle distance and therefore more interaction between molecules.
4. Molecules collide with each other and the walls of the container. In these collisions, individual molecules may gain or lose energy. However, in a collection of molecules at constant temperature the total energy remains constant. The assumption is valid in the sense that if it were not true, then the pressure of a gas would decrease gradually as it is a consequence of collisions with the wall of the container.

5. The average kinetic energy of the molecules which is proportional to the temperature of the gas in Kelvin. Any two gases at the same temperature will have the same average kinetic energy.

Gas pressure derived from KMT analysis (Kinetic Equation of Gases)

The pressure of a gas can be explained by KMT as arising from the force exerted by gas molecules impacting on the walls of a container (assumed to be a cube of side length L and hence of Volume L^3 . In addition, area of each side is L^2 and the total area is $6L^2$).

We consider a gas of N molecules each of mass m contained in cube of volume $V = L^3$.

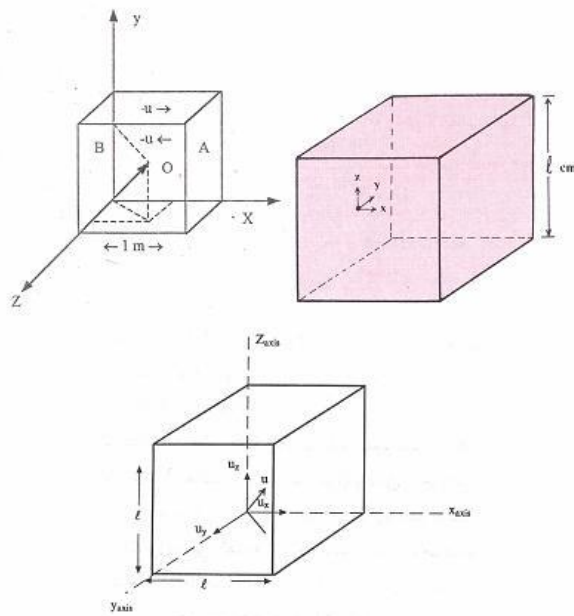


Figure 1.5 A gas container (assumed to be a cube of side length L and hence of Volume L^3).

When gas molecule collides (with speed v_x) with wall of the container perpendicular to x co-ordinate axis and bounces off in the opposite direction with the same speed (an elastic collision) then the momentum lost by the particle and gained by the wall is Δp_x

$$\Delta P_x = mv_x - (-mv_x) = 2mv_x$$

The particle impacts the wall once every $2L/v_x$ time units

$$\Delta t = \frac{2L}{v_x}$$

The number of collisions in 1 second is $v_x/2L$ collisions.

The force F due to the particle can then be computed as the rate of change of momentum with respect to time (Newton Second Law).

$$F = \frac{\Delta p}{\Delta t} = \frac{2mv_x}{2L/v_x} = \frac{mv_x^2}{L}$$

The force of the two sides along X-axis is

$$F = 2 \frac{m}{L} v_x^2$$

The magnitude of the velocity v of any particle j can also be calculated from the relevant velocity components v_x , v_y , and v_z .

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

Force acting on the six walls is

$$F = 2 \frac{m}{L} (v_x^2 + v_y^2 + v_z^2) = 2 \frac{m}{L} v^2$$

Force acting on the six walls from all N molecules can be computed by summing forces arising from each individual molecule j .

$$F = 2 \frac{m}{L} (v_x^2 + v_y^2 + v_z^2) = 2 \frac{m}{L} \sum_{i=1}^N v_i^2$$

Assuming that a large number of particles are moving randomly then the force on each of the walls will be approximately the same.

$$\langle v^2 \rangle = v_{rms}^2 = \frac{1}{N} \sum_{j=1}^N v_j^2$$

Then

$$F = 2 \frac{m}{L} N v_{rms}^2$$

The force can also be expressed in terms of the average velocity v_{rms}^2 where v_{rms} denotes the root mean square velocity of the collection of particles.

The pressure can be readily determined once the force is known using the definition $P = F/A$ where $A=6L^2$ denotes the area of the wall over which the force is exerted.

$$P = \frac{F}{A} = \frac{2 N m v_{rms}^2}{L \cdot 6L^2} = \frac{1 N m v_{rms}^2}{3 V}$$

$$PV = \frac{1}{3} N m v_{rms}^2 \quad (1.11)$$

Internal energy of an ideal gas

We have Average kinetic Energy of gas molecule is given by

$$\langle KE \rangle = \frac{1}{2} m v_{rms}^2 \quad (1.12)$$

Then

$$PV = \frac{1}{3} N m v_{rms}^2 = \frac{2}{3} \frac{1}{2} N m v_{rms}^2 = \frac{2}{3} N \left(\frac{1}{2} m v_{rms}^2 \right) = \frac{2}{3} N \langle KE \rangle$$

$$nRT = \frac{2}{3} N \langle KE \rangle$$

$$\langle KE \rangle = \frac{3 nRT}{2 N}$$

For N molecules

$$KE = N \langle KE \rangle = \frac{3}{2} nRT \quad (1.13)$$

Root-mean-square speed

We can derive a useful equation for u_{rms} . One of the results of the kinetic theory of gases is that the average kinetic energy of a gas is We have $n=N/N_A$ and $m=M/ N_A$ where M is the total mass of one mole of molecules and N_A is Avogadro's number. M_w is the molecular weight or mass of one mole.

$$KE = N \langle KE \rangle = \frac{1}{2} N m v_{rms}^2 = \frac{1}{2} n N_A m v_{rms}^2 = \frac{1}{2} n M_w v_{rms}^2 = \frac{3}{2} nRT$$

$$M_w v_{rms}^2 = 3RT$$

$$v_{rms} = \sqrt{\frac{3RT}{M_w}} \quad (1.14)$$

Example 1.8

Calculate the root-mean-square speed in meters per second for $Cl_2(g)$ molecules at $30^\circ C$.

Solution

The expression for u_{rms} is used

$$v_{rms} = \sqrt{\frac{3RT}{M_w}}$$

For chlorine $M_w = 70.91 \text{ g} = 7.09 \times 10^{-2} \text{ kg mol}^{-1}$, $T = 303 \text{ K}$, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
 Substituting in the equation

$$v_{rms} = \sqrt{\frac{3 \times 8.314 \times 303}{7.09 \times 10^{-2}}}$$

$$= 326 \text{ m s}^{-1}$$

Practice problem 1.4

At what temperature would the u_{rms} for Ne (g) be expected to be the same as that for He (g) at 300 K?

- (a) 1000 (b) 150 (c) 1500 (d) 1600

Distribution of molecular speeds

In a real gas sample at a given temperature T , all molecules do not travel at the same speed. Some move more rapidly than others.

- In a real gas the speeds of individual molecules span wide ranges with constant collisions continually changing the molecular speeds.
- Maxwell and independently Boltzmann analysed the molecular speed distribution in an ideal gas, and derived a mathematical expression for the speed distribution $f(v)$.
- This formula enables one to calculate various statistically relevant quantities such as the average velocity of a gas sample, the rms velocity, and the most probable velocity of a molecule in a gas sample at a given temperature T .

$$F(v) = 4\pi v^2 \left\{ \frac{m}{2\pi k_B T} \right\}^{3/2} \exp\left[-\frac{mv^2}{2k_B T} \right] \quad (1.15)$$

In Figure 1.6, the peak of the most probable speed increases as temperature increases. Also, it flattens out increasing with increasing temperature.

In Figure 1.7 light molecules have high average speed and a wide spread of speeds.

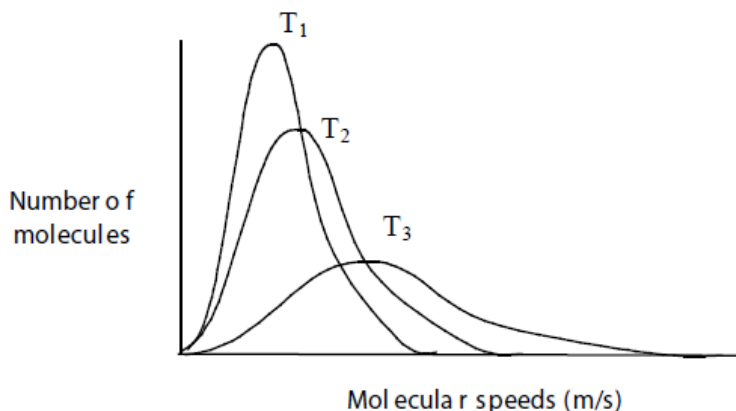


Figure 1.6 Maxwell-Boltzmann distributions of molecular speeds at three temperatures.

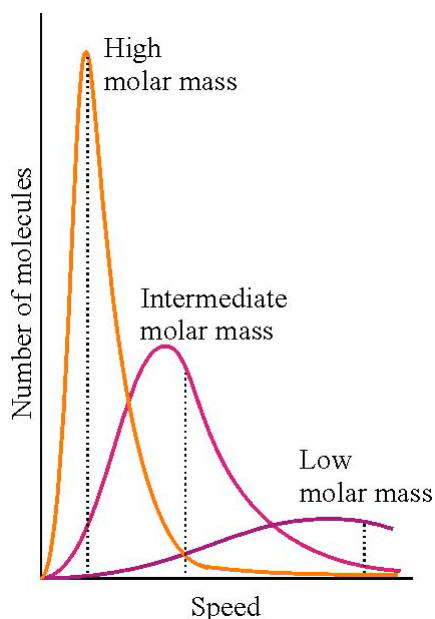


Figure 1.7 Maxwell-Boltzmann distribution of molecular speeds at three molar masses.

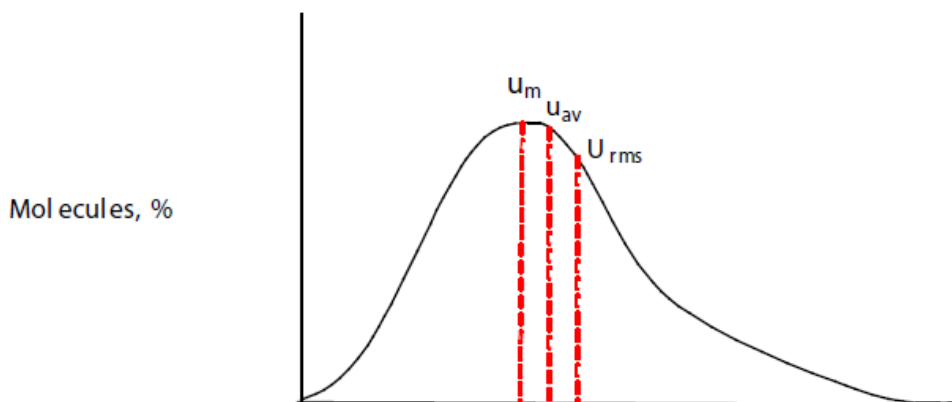


Figure 1.8 Diagram showing the different characteristics speeds for a sample of gas Molecules, %

Three characteristic speeds are shown in the diagram. More molecules have the speed u_m , known as the most probable or modal speed, than the other two. The simple average speed is u_{av} whilst u_{rms} is the square root of the average of the squares of speeds of all molecules in a sample.

Diffusion and effusion of gases

Diffusion is the migration of molecules of different substances as a result of the random motion of molecules. Although gas molecules are consistently having collisions resulting in frequent changes in direction, the net rate at which a gas moves in a particular direction depends on the average speed. Diffusion always proceeds from a region of higher

concentration to one of lower concentration.

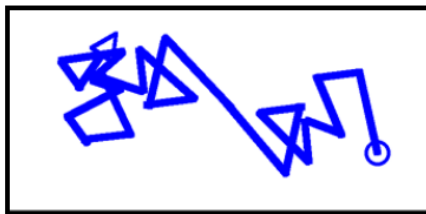


Figure 1.9 Path travelled by a single gas molecule in which each change in direction represents a collision.

Effusion is a process related to diffusion, it is the escape of gas molecules from their container through an orifice (pinhole). Consider the effusion of a mixture of gases through an orifice as shown in the figure below.

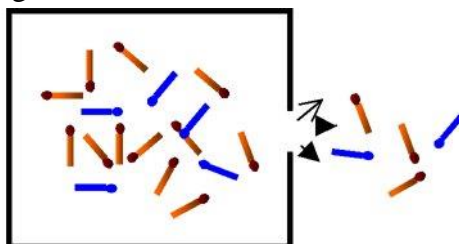


Figure 1.10 Path travelled by a single gas molecule in which each change in direction represents a collision.

The rates at which the two effusions can be compared are given below

$$\frac{\text{Rate effusion of A}}{\text{Rate effusion of B}} = \frac{u_{rms} (A)}{u_{rms} (B)} = \sqrt{\frac{3RT / M_A}{3RT / M_B}} \quad (1.16)$$

This result is a statement of Graham's law, which states that the rate of effusion (or diffusion) of two different gases are inversely proportional to the square roots of their molar masses.

In considering the equation above it is evident that lighter gases will effuse faster than the heavier gases. The consequences of the above theory maybe summarised that ratios of the root-mean-square speeds are equal to the ratios of

- rates of effusion
- effusion times
- amount of gas effused
- distance travelled by the molecules
- amount of gas effused
- molecular speeds

Example 1.9

Calculate the ratio of the diffusion rate for H_2O and D_2O (D is deuterium an isotope of hydrogen).

Molar mass $\text{H}_2\text{O} = 18.01 \text{ g mol}^{-1}$, $\text{D}_2\text{O} = 19.01 \text{ g mol}^{-1}$

$$\frac{\text{Rate diffusion } \text{H}_2\text{O}}{\text{Rate diffusion } \text{D}_2\text{O}} = \sqrt{\frac{M_{\text{D}_2\text{O}}}{M_{\text{H}_2\text{O}}}} = \sqrt{\frac{19.01 \text{ g mol}^{-1}}{18.01 \text{ g mol}^{-1}}} = 1.02$$

Practice problem 1.6

Two gases, HBr and CH_4 , effuse through a small opening. HBr effuses through the opening at a rate of $4 \text{ cm}^3 \text{ s}^{-1}$, at what rate will the CH_4 molecules effuse through the same opening.

(a) $9 \text{ cm}^3 \text{ s}^{-1}$ (b) $10 \text{ cm}^3 \text{ s}^{-1}$ (c) $8.5 \text{ cm}^3 \text{ s}^{-1}$ (d) $9 \text{ m}^3 \text{ s}^{-1}$

Real gases: deviation from ideal gas

Real gases do not conform to ideal gas behaviour. A plot of PV against pressure shows that whereas the PV is constant for an ideal gas, this is not true for real gases.

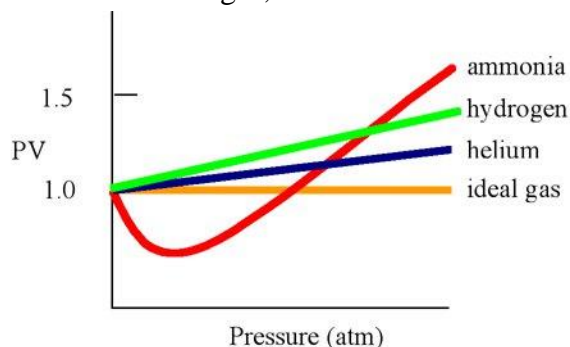


Figure 1.10 Plot of PV against pressure showing the behaviour for an ideal gas and real gases. Plot for NH_3 , H_2 , and He show deviation from the ideal gas curve.

Real gases do not follow the assumptions of the ideal gas behaviour. Deviations from ideal gas behaviour of varying degrees are seen when PV is plotted against P . Gases with only weak intermolecular forces give straight lines at low pressure and are close to the ideal gas behaviour. Significant deviation is observed for gases with strong intermolecular forces such as oxygen and nitrogen. Another assumption made when dealing with ideal gases is that molecules have no volume whereas real gases have a defined volume.

The compression factor

We can express the extent of deviation from ideal behaviour as a function of pressure (which is related to the density of the gas) by introducing a quantity called the Compressibility or Compression factor Z .

$$Z = \frac{PV}{nRT} = \frac{PV_m}{RT} \quad (1.17)$$

For an ideal gas $Z = 1$, and real gases exhibit Z values different from unity. Z values may be explained in terms of the operation of intermolecular forces.

At low pressures the molecules are far apart and the predominant intermolecular interaction is **attraction**. The molar volume V_m is less than that expected for an ideal gas: intermolecular forces tend to draw the molecules together and so reduce the space which they occupy. Under such conditions we expect that $Z < 1$.

As the pressure is increased the average distance of separation between molecules decreases and **repulsive** interactions between molecules become more important. Under such conditions we expect that $Z > 1$. When $Z > 1$, the molar volume is greater than that exhibited by an ideal gas: repulsive forces tend to drive the molecules apart.

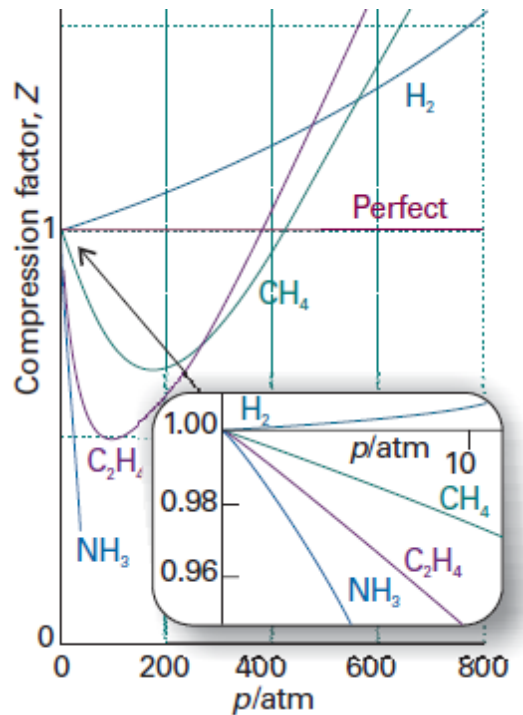


Figure 1.11 The variation of the compression factor, Z , with pressure for several gases at 0°C . A perfect gas has $Z = 1$ at all pressures. Notice that, although the curves approach 1 as $p \rightarrow 0$, they do so with different slopes.

The virial equation of state

The observation of a Z factor different from unity can be used to construct an empirical or observation based equation of state, by supposing that the ideal gas equation of state is only the first term of a more complex expression which can be expressed in terms of a mathematical power series. This is called the Virial equation of state.

$$Z = \frac{PV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots = 1 + B'P + C'P^2 \quad (1.18)$$

Note that the virial coefficients B , C , B' and C' are obtained by fitting the experimental Z vs P data to the virial equation of state. Their values depend on the identity of the gas and reflect the presence of intermolecular forces and interactions.

When the pressure P is small the molar volume V_m will be very large and so the second and third terms in the virial series will be very small and to a good approximation the virial equation of state reduces to the ideal gas equation of state.

The van der Waals equation of state

The ideal gas equation has been modified with corrections so that it fits with experimental data corresponding to real gases. One such effort was made by van der Waals. The van der Waals equation is the form

$$\left\{P + a \left(\frac{n}{V}\right)^2\right\}(V - nb) = nRT \quad (1.19)$$

where a and b are known as van der Waals constants. The constants are determined experimentally by measuring P , V and T under a set of different conditions.

The repulsive interactions between molecules are taken into account by supposing that they cause the molecules to behave as small but impenetrable spheres. The nonzero volume of the molecules implies that instead of moving in a volume V they are restricted to a smaller volume $V - nb$, where nb is approximately the total volume taken up by the molecules themselves.

The closest distance of two hard-sphere molecules of radius r , and volume $V_{\text{molecule}} = 4\pi r^3/4$, is $2r$, so the volume excluded is $= 4\pi(2r)^3/4$, or $8V_{\text{molecule}}$. The volume excluded per molecule is one-half this volume, or $4V_{\text{molecule}}$, so $b \approx 4V_{\text{molecule}} N_A$.

The pressure depends on both the frequency of collisions with the walls and the force of each collision. Both the frequency of the collisions and their force are reduced by the attractive forces, which act with a strength proportional to the molar concentration, n/V , of molecules in the sample. Therefore, because both the frequency and the force of the collisions are reduced by the attractive forces, the pressure is reduced in proportion to the square of this concentration. If the reduction of pressure is written as $-a(n/V)^2$, where a is a positive constant characteristic of each gas, the combined effect of the repulsive and attractive forces is the van der Waals equation of state.

Example 1.10

Use the van der Waals equation to calculate the pressure of nitrogen gas at 273.15 K and a molar volume of $22.414 \text{ L mol}^{-1}$. Compare with the pressure of an ideal gas at the same temperature and molar volume.

Solution

$$P = \frac{(8.134 \text{ J K}^{-1} \text{ mol}^{-1})(273.15 \text{ K})}{0.022414 \text{ m}^3 \text{ mol}^{-1} - 0.0000391 \text{ m}^3 \text{ mol}^{-1}} - \frac{0.1408 \text{ Pa m}^3 \text{ mol}^{-1}}{(0.022414 \text{ m}^3 \text{ mol}^{-1})^2}$$
$$= 1.0122 \times 10^5 \text{ Pa} = 0.9990 \text{ atm}$$

For the ideal gas

$$P = \frac{RT}{V_m} = \frac{(8.134 \text{ J K}^{-1} \text{ mol}^{-1})(273.15 \text{ K})}{0.022414 \text{ m}^3 \text{ mol}^{-1}} = 1.0132 \times 10^5 \text{ Pa} = 1.0000 \text{ atm}$$

Chapter 2

Thermodynamics

by Dr. Hasan Maridi

Thermodynamics, the concepts

Thermodynamics – concerned with the studies of transformation of energy from heat to work and vice versa.

Thermodynamics allows chemists to predict whether a chemical process will occur under a given set of conditions.

Thermodynamics – immense importance in chemistry – energy output of chemical reactions, why reactions reach equilibrium, what their composition is at equilibrium, how reactions in electrochemical (and biological) cells can generate electricity.

Branches of thermodynamics

Thermochemistry – deals with the heat output of chemical reactions.

Electrochemistry – the interaction between electricity and chemistry.

Bioenergetics – the deployment of energy in living organisms.

Equilibrium chemistry – the formulation of equilibrium constants, the equilibrium composition of solutions of acids and bases.

The energy

Energy is usually defined as the capacity to do work. Various processes in the body produce energy to operate the muscle and to maintain the body temperature. Energy is produced in some chemical processes while some chemical reactions require energy to take place.

The energy determines what molecules may form what reaction may occur, how fast they may occur, in which direction a reaction has a tendency to occur.

A gas at high temperature has more energy than at low temperature – it has a higher pressure and can do more work in driving out a piston.

Conservation of energy – the energy can be neither created nor destroyed but merely converted from one form to another or moved from place to place.

There are two forms of energy: kinetic energy and potential energy.

Kinetics energy – is the energy associated with motion of matter. A body of mass m moving with a velocity v will have a kinetic energy of $\frac{1}{2} m v^2$

Potential energy – is the energy a body has by virtue of its position in a force field.

Typical examples of force fields include gravitational, electrical and magnetic fields.

Consider a man drawing water from well through a height h . The process involves moving

object of mass m against the force of gravity, g , through a distance h . The potential energy change involved is given by mgh where g is the acceleration due to gravity.

Internal energy (U)

Internal energy represents the total energy of the system comprising two components: kinetic energy and potential energy. Kinetic energy is the energy associated with various types of molecular motion and movement of molecules. Potential energy arises from the attractive and repulsive forces within atoms or molecules. The internal energy from a chemistry point is the sum of the total kinetic and potential energy of the system.

Units of Energy

- From the expression of kinetic energy it can be seen that energy has units of $\text{kg m}^2 \text{s}^{-2}$
SI unit is Joule (J)
 $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$
- Another unit of energy commonly used in nutrition is the calorie (cal). It is defined as the energy required to raise the temperature of 1 g of water by 1°C .
 $1 \text{ cal} = 4.18 \text{ J}$

Example 2.1

What is the kinetic energy of a truck carrying yams with a mass of 2000 kg travelling at 50 km/h?

Solution

$$K.E. = \frac{1}{2}mv^2$$
$$K.E. = \frac{1}{2} \times 2000\text{kg} \times \left(\frac{50000\text{m}}{3600\text{s}}\right)^2 = 193 \text{ KJ}$$

Practice problem 2.1

How much potential energy does 1kg of water at the top of a waterfall that is 500 m deep possess? How much kinetic energy is converted in falling from the top to the base? Give the answer in joules and calories.

Thermodynamic systems and surroundings

The systems is that part of the universe that we choose to focus on or study (in an experiment – a reaction flask) whilst **the surroundings** is everything else outside the system (area of focus). Three types of system:

An open system – can exchange both energy and matter with its surroundings. (A flask that is not stoppered).

A closed system – can exchange energy but not matter with its surroundings. (A stoppered flask).

An isolated system – can exchange neither energy nor matter with its surroundings. (A sealed flask that is thermally, mechanically, and electrically insulated from its surroundings).

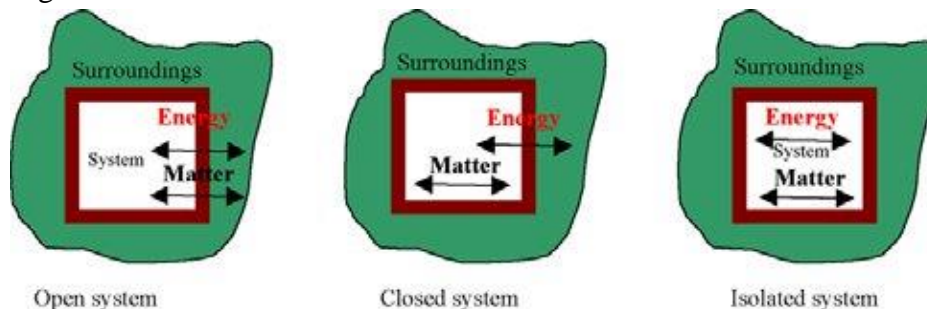


Figure 2.1 Different types of thermodynamic systems showing the types of energy and matter interactions with the surrounding.

Example 2.2

What type of system does a boiling kettle represent?

Solution

Both energy and matter can be transferred between a system and its surroundings. It is therefore an open system.

Practice problem 2.2

The vacuum flask is often used to illustrate one type of thermodynamics system. Which type is this?

- (a) Open system
- (b) Closed system
- (c) Isolated system
- (d) Closed-isolated system

State functions and non-state functions

Thermodynamics is concerned with changes in the state of the system as defined by macroscopic parameters such as composition, volume, pressure, temperature and energy. These properties are said to be state functions. Such properties depend only on the initial and final the states of the system and not on the path used to reach a certain condition. Work and heat on the other hand are examples of functions that depend on the route taken. Heat and work are therefore non-state functions.

Energy, work and heat

Energy can be exchanged between a closed system and its surroundings as work or as heat.

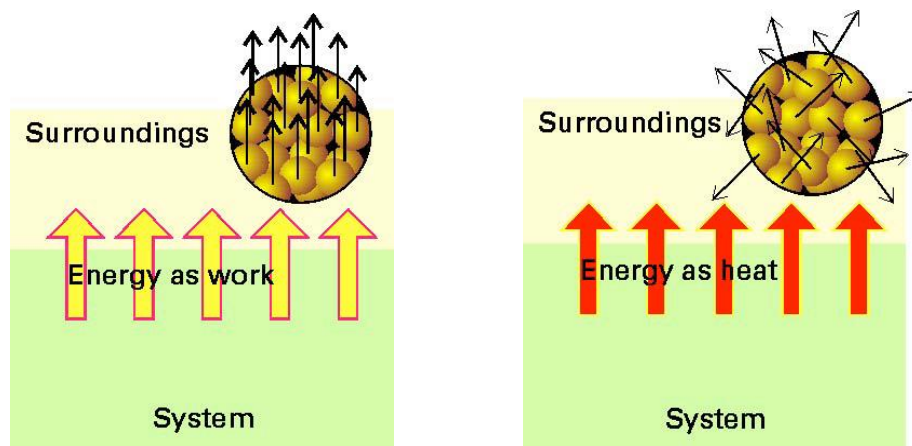


Figure 2.2 Molecular nature of work:

- (a) Work is the transfer of energy that achieves or utilizes uniform motion in the surroundings.
- (b) Heat is the transfer of energy that achieves or utilizes disorderly motion in the surroundings.

Work (w) is a transfer of energy that can cause motion against an opposing force. A process produces work if it can be used to change the height of a weight somewhere in the surroundings.

In simple language, work is said to have taken place when we do something. When an object is moved against an opposing force, work is done. Raising an object is an example of doing work. In chemistry, however, the most common work encountered is related to pressure-volume changes accompanying chemical reactions.

Heat (q) is a transfer of energy as a result of a temperature difference between the system and its surroundings.

When two bodies are in thermal contact, energy flows from the warmer body to the cooler one – thermal energy is transferred. The molecular explanation for this process is that the molecules are in constant random motion and have kinetic energy associated with them. When two objects are in contact, thermal energy is transferred until the average kinetic energy between the two bodies is the same (thermal equilibrium).

Directionality of energy transfers

Chemical changes involve release or gain of heat from the system to the surroundings. An **exothermic process** is one that releases heat to the surroundings. For example, combustion reactions are exothermic while a process such as vaporisation of water is endothermic. Energy is absorbed by the system in an **endothermic process** where thermal energy is transferred from the surroundings to the system.

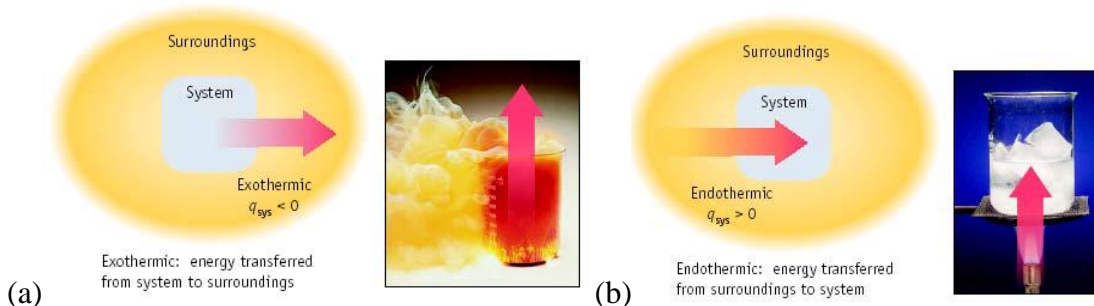


Figure 2.3 Directionality of Energy Transfers:

- (a) exothermic: heat transfers from the system to the surroundings.
- (b) endothermic: heat transfers from the surroundings to the system.

The conservation of energy

The total energy of a system – **internal energy**, U (or E): the total kinetic and potential energy of the molecules in the system. The change in internal energy:

$$\Delta U = U_f - U_i$$

U_f – internal energy at a final state

U_i – internal energy at an initial state

The internal energy is a state function: its value depends only on the current state of the system and is independent on how this state was prepared. It is a function of properties that determine the physical state of the system, i.e., pressure, volume, temperature, and amount of substance. Changing any of these variables changes U . The internal energy is an extensive property – it depends on the amount of substance. **The molar internal energy**, $U_m = U/n$ – intensive property, does not depend on the amount of substance, but depends on the temperature and pressure.

Internal energy, heat, and work are all measured in the same units, the joule (J):

$$1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$$

Changes in molar internal energy ΔU_m are typically expressed in kilojoules per mole (kJ mol^{-1}).

An energy of 1 cal is enough to raise the temperature of 1 g of water by 1°C :

$$1 \text{ cal} = 4.184 \text{ J}$$

Experimental finding: the internal energy of a system may be changed either by doing work on the system or by heating it. Heat and work are equivalent ways of changing a system's internal energy. It is also found experimentally that, if a system is isolated from the surroundings, then no change in internal energy takes place.

Suppose we consider an isolated system. It can neither do work nor supply heat – the internal energy cannot change.

First Law of thermodynamics

The first law of thermodynamics is essentially a statement of the law of the conservation of energy. It states that energy can neither be created nor destroyed. It also can be stated as: the internal energy of an isolated system is constant. It can only be redistributed or converted from one form to another. A useful way to express this in chemistry is through the equation

$$\Delta U = q + w \quad (2.5)$$

where q is the heat absorbed and w is the work done by the system. Although the internal energy cannot be directly measured, the two quantities heat and work are measurable quantities. If heat flows into the system (or the surroundings do work on the system), the internal energy of the system increases – the sign of w or q is positive. Conversely, if the heat flows out of the system or work is done by the system (at the expense of the system), the internal energy of the system will be negative.

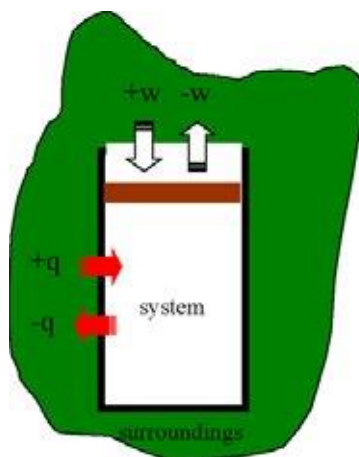


Figure 2.4 Summary of sign convention involving heat and work.

Volume- pressure work

The work often encountered with chemical processes is that associated with the formation or disappearance of gaseous substances. This type of work is called pressure-volume work, expansion work or PV-work.

Expansion work

To illustrate the relationship between volume-pressure changes and work, consider the

following system consisting of a piston. The system comprises a gas confined to a cylinder in which the external pressure is viewed as weights against the gas.

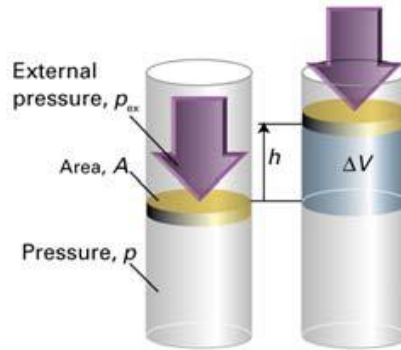


Figure 2.5 Pressure-volume work. Expanding gas against an object through a distance h .

Recall that pressure is the force per unit area. Force therefore is the product of pressure and area, $F = P_{ex}A$.

From classical physics, work= force x distance. Then, the work required moving an object through a distance h (or dz) against an opposing force F is

$$dw = -Fdz \quad (2.6)$$

where the negative sign is indicative that when the system does work against an opposing force, the internal energy of the system doing work will decrease.

The work done is then expressed as

$$dw = -P_{ex}dV \quad (2.7)$$

where $dV=Adz$.

Expansion against constant pressure

Consider the expansion of a gas confined in a cylinder as shown below.

The total work done in moving from an initial state 1 to 2 will involve a change in volume from V_i to V_f against a constant pressure P_{ex} . We can then write that

$$W = -\int_{V_i}^{V_f} P_{ex} dV = -P_{ex} \int_{V_i}^{V_f} dV = -P_{ex} (V_f - V_i) \quad (2.8)$$

or

$$W = -P_{ex} \Delta V \quad (2.9)$$

The area under the curve in Figure 6 represents the work done by the gas. A common example of this type of work is in an internal combustion engine of car where expanding gases are able to drive a piston. The lifting-off of rockets and space vehicles such as the space shuttle also involve expansion of gases

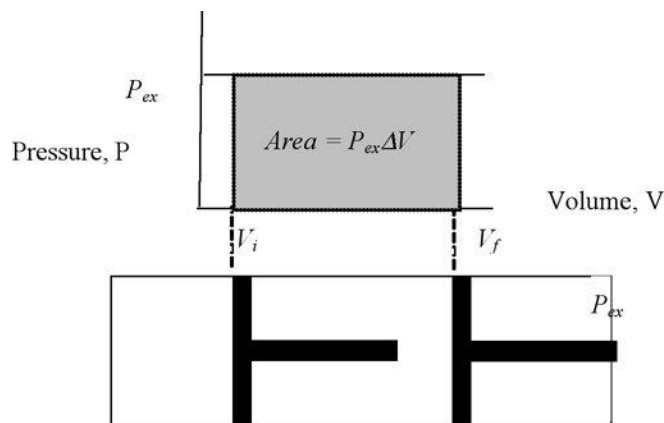


Figure 2.6 Work of expansion by a gas expanding against an external pressure.

Example 2.3

A gas expands by 0.5 L against a constant pressure of 1 atm at 25 °C. How much work is done in joules by the system against the surroundings?

Solution

The work done is given by

$$w = -P\Delta V,$$

$$P = 1 \text{ atm}, \quad \Delta V = 0.5 \text{ L}$$

$$w = -101325 \text{ Nm}^{-2} \times 5 \times 10^{-4} \text{ m}^3 = -50.6 \text{ Nm} = -50.6 \text{ J}$$

Example 2.4

A hydrocarbon is burned in a container with a movable piston with a cross-section area of 0.5 m². If the piston moved a distance of 30 cm against a pressure of 1 atm, how much work is done in the expansion?

Solution

In expanding, the piston sweeps through a volume = cross section area x distance covered.

$$\text{Change in volume } \Delta V = 0.5 \text{ m}^2 \times 0.3 \text{ m} = 0.15 \text{ m}^3, \quad P = 1 \text{ atm} = 101325 \text{ Nm}^{-2}$$

From equation (2.9),

$$w = -P_{\text{ex}}\Delta V = - (101325 \text{ Nm}^{-2} \times 0.15 \text{ m}^3) = - 15 199 \text{ J} = - 15.2 \text{ kJ}$$

Practice problem 2.4

A sample of gas is compressed from an initial volume of 4.0 L to a final volume of 1.0 L. What is the work done if the external pressure is 5 atm?

- (a) 5.0×10^3 (b) 1.8×10^3
- (c) 1.5×10^3 (d) 1.6×10^2

Reversible expansion of a gas

Suppose that the gas expands or contracts in such way that the external pressure equals the

pressure of the gas. Such expansion/compression is said to take place in a reversible manner. A *reversible* process is one in which the system and surroundings are continuously in equilibrium. This implies that the process takes place infinitesimally slowly so that there is plenty of time at each stage for equilibration with the surroundings.

Isothermal reversible expansion of a gas

The process described above could be done reversibly and under isothermal conditions (e.g. constant temperature water bath). Using the equation for an ideal case and equation (2.8), we can evaluate the work done during this process.

$$W = -nRT \int_{V_i}^{V_f} \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i} \quad (2.10)$$

The above expression will be positive if the initial volume, V_i , is greater than the final volume, V_f , indicating a compression process. The work done during the process may be drawn using an indicator diagram in Figure 2.7.

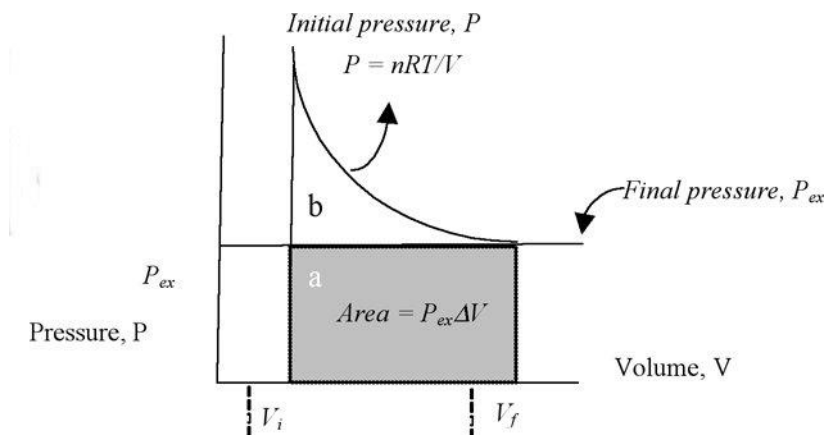


Figure 2.7 Indicator diagram for expansion at constant pressure and for the reversible process.

In comparing the two areas (a and b), it is clear that more work is done during a reversible expansion against a constant external pressure than during an irreversible expansion process. Maximum work is obtained during a reversible expansion because maximum work is ensured at every step – no wastage.

In Isothermal reversible expansion of a gas

$$\Delta U = 0! \quad \text{since } T_2 = T_1.$$

$$q_{rev} = -W_{rev}, \quad \text{from first law.}$$

Practice problem 2.5

Prove that equation (2.10) can be rewritten as

$$W = -nRT \ln \frac{P_i}{P_f}$$

Free expansion

Free expansion involves expansion with no opposing force. For example if the gas were to expand into a vacuum. In such a case $P_{ex} = 0$, so that the work done is equal to zero ($dw = 0$, $w = 0$) i.e. no work is done during free expansion of a gas.

Constant pressure and constant volume processes

These are the most common processes encountered in chemical reactions. It is thus instructive to consider the behaviour of the first law of thermodynamics in relation to such processes.

Constant volume processes

To carry out a reaction at constant volume we would need a sealed vessel to contain any gaseous products produced. Typical equipment used to perform such measurements is the bomb calorimeter, frequently used to carry out combustion reactions.

In the previous sections, we have seen that the change in internal energy U is given by

$$\Delta U = q + w \quad (2.11)$$

If work is done by the system then

$$w = -P_{ex}\Delta V \quad (2.12)$$

Thus,

$$\Delta U = q + (-P_{ex}\Delta V)$$

In the case of constant volume, ΔV is zero therefore

$$\Delta U = q_v \quad (2.13)$$

where q_v indicates that heat involved is at constant volume. The result is significant as it shows that the heat change at constant volume is equal to the change in internal energy of the system. Thus, we can experimentally determine the internal energy change for a reaction by measuring energy absorbed or released in the process.

Example 2.5

An ideal monoatomic gas is expanded at 298 K from an initial pressure of 1 atm to a final pressure of 5 atm isothermally and reversibly. Calculate the heat absorbed by the gas (q), work done on the gas (w) and the change in internal energy (ΔU).

Solution

Since the process is taking place isothermally and at constant pressure, $T_1 = T_2$, $\Delta T = 0$ and $\Delta U = 0$.

For a reversible process, the work done by the gas expanding isothermally and reversibly equation (12) can be used where the inverse relationship of pressure and volume is utilised i.e.

$$W = -RT \ln (V_f / V_i) = -RT \ln (P_i / P_f)$$

$$W = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \ln 5 = -3990 \text{ J mol}^{-1}$$

From the first law of thermodynamics, $\Delta U = q + w$

But $\Delta U = 0$, therefore $q = -w$

$$q = -w = 3990 \text{ J mol}^{-1}$$

Practice problem 2.6

Find the work done on the surroundings when 12 litres of an ideal gas, initially at a pressure of 10 atm is allowed to expand at constant pressure to 10 litres: (a) by reducing the external pressure to 1 atm; (b) by reducing pressure first to 5 atm, and then 1 atm; (c) allowing gas to expand into an evacuated space so that its total volume is 10 litres.

Constant pressure processes: enthalpy of reactions

Most chemical reactions take place at constant pressure, for example in the laboratory at atmospheric pressure. In such processes, volume changes do occur.

$$q_p = \Delta U + P_{ex}\Delta V \quad \text{at constant pressure} \quad (2.14)$$

Heat evolved or absorbed at constant pressure, q_p , is known as enthalpy (H), $q_p = \Delta H$.

Thermochemistry

Systems that are unstable (high potential energy) have a higher tendency to undergo chemical change than systems that are stable (lower potential energy). Chemical reactions whenever possible tend to spontaneously move from a state of higher potential energy to one of lower potential energy.

The study of the heat produced or required by chemical reactions is the thermochemistry. It is a branch of thermodynamics because a reaction vessel and its contents form a system, and chemical reactions result in the exchange of energy between the system and surroundings.

Enthalpy

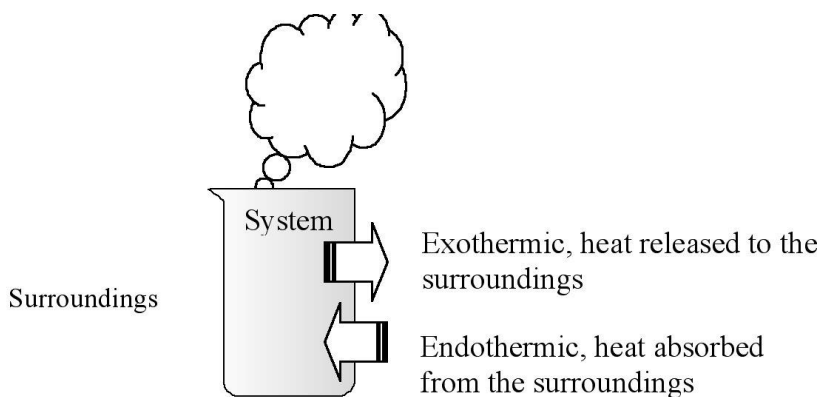


Figure 3.1 Diagram showing a reactions taking place in an open beaker. System in relations to its surroundings.

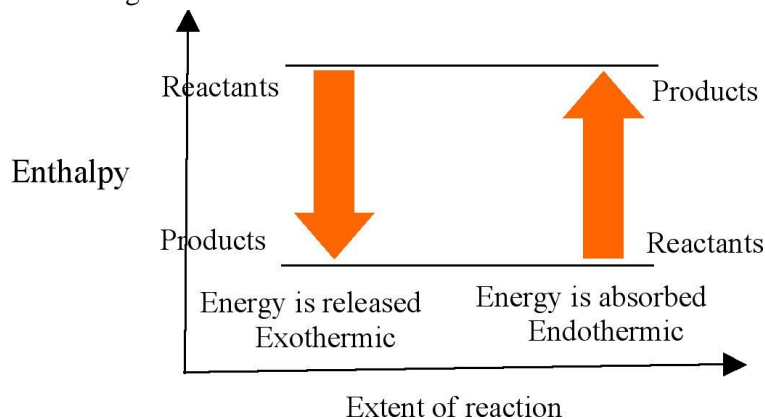


Figure 3.2 Diagram showing relative energy changes for an exothermic and endothermic reaction.

Chemical reactions involve either release or absorption of heat from the surroundings.

- When a chemical reaction occurs in which the system absorbs heat, the process is **endothermic** (it feels cold)
- When a chemical reaction occurs in which the system produces heat it is **exothermic** (it feels hot)

The heat of reaction is the quantity of heat exchanged between the system and its surroundings when chemical reactions occur. Heat will tend to flow until the system and surroundings are at the same temperature.

Many chemical and biological processes take place at constant pressure. The heat released under conditions of constant pressure is a thermodynamic function known as enthalpy (H), sometimes referred to as “heat content”.

The enthalpy (*heat inside*), H , of a system is defined as

$$H = U + pV \quad (3.1)$$

The enthalpy of a system is always greater than its internal energy.

Enthalpy is an extensive property.

Molar enthalpy, $H_m = H/n$

$$H_m = U_m + pV_m$$

For a perfect gas, $H_m = U_m + RT$

The difference between the molar enthalpy and molar internal energy of a perfect gas increases with temperature.

A property that depends only on its initial and final state is known as a state function.

Enthalpy is a state function. The enthalpy depends on the amount of substances reacting.

Its magnitude depends on the amounts of reactants that are consumed. Reversing thermochemical equations also results in reverse of enthalpy sign but with the same magnitude. Enthalpy change is also dependent on the state of the reactants and products i.e. must be specified.

The change in enthalpy, ΔH , is defined as the sum of the change in internal energy, ΔU , and the pressure-volume work done by the system.

The change in enthalpy ΔH , when a system changes from one state to another is independent of the path between two states.

The change in enthalpy (described or labeled as ΔH) is not measured directly but through the energy released as heat. The enthalpy change (ΔH) depends only on the initial and final states i.e.

$$\Delta H = H_f - H_i$$

Whether a reaction is exothermic or endothermic depends on the initial and final enthalpies of the reactants and products respectively.

- For **endothermic** reactions $H_{final} > H_{initial}$ **and ΔH is positive (+ ΔH)**
- For **exothermic** reactions $H_{final} < H_{initial}$ **and ΔH is negative (- ΔH)**

The diagram in figure 3.2 summaries exothermic and endothermic reactions. The diagram

shows that for exothermic reactions, the products are lower in energy than the reactants whilst in endothermic reaction the energy of the products is higher than that of the reactants. The increase in enthalpy and extent of reaction are depicted on the y and x axes respectively.

At constant pressure,

$$\Delta H = \Delta U + P\Delta V \quad (3.2)$$

If it is assumed that the gases produced in a reaction behave as ideal gases, we can solve for V using the perfect gas equation to give us

$$V = \frac{nRT}{P} \quad (3.3)$$

For a change in volume we can write

$$\Delta V = \Delta(nRT/P) \quad (3.4)$$

If the reaction is taking place at constant temperature and pressure

$$\Delta V = \Delta n(RT/P) \quad (3.5)$$

The change in volume for the reaction is essentially a change in number of moles of the species involved. Substituting equation (3.5) in equation (3.2), the enthalpy expression becomes

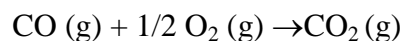
$$\Delta H = \Delta U + \Delta n_{gas}RT \quad (3.6)$$

where Δn_{gas} is given by $\Delta n_{gas} = \sum \Delta n_{gas, products} - \sum \Delta n_{gas, reactants}$ and represents the change in number of moles between the reactants and products.

Example 3.1

Carbon monoxide poisoning sometimes occurs during the cold season due to in-door use of charcoal braziers for heating. This occurs when the amount of oxygen is limited. With sufficient air (oxygen) the carbon monoxide reacts with oxygen to form carbon dioxide which is somewhat less harmful. Calculate ΔH for the reaction at 25 °C given that the change in internal energy for the reaction is - 281.7 kJ.

Solution



The enthalpy change enthalpy, ΔH , is defined as the sum of the change in internal energy, ΔU , and the pressure-volume work done by the system.

$$\Delta H = \Delta U + P\Delta V$$

Since there is no indication of pressure and volume an alternative method is used to work out the problem as shown in equation (2.20).

$$\Delta H = \Delta U + \Delta n_{gas}RT$$

$$\Delta n_{gas} = 1 \text{ mol CO}_2 - (1 \text{ mol CO} + 0.5 \text{ mol O}_2) = -0.5,$$

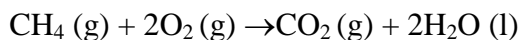
$$\Delta U = -281.7 \text{ kJ}, \quad R = 8.314 \text{ J K}^{-1}\text{mol}^{-1}, \quad T = 298 \text{ K}$$

Substituting the equation (23)

$$\begin{aligned} \Delta H &= -2.817 \times 10^5 \text{ J} + (-0.5 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}) \\ &= -2.817 \times 10^5 - 1.238 \times 10^3 \\ &= -282.9 \text{ kJ} \end{aligned}$$

Practice problem 3.1

One mole of methane reacted with oxygen at constant volume and at 298 K temperature according to the equation below.



What is the change in enthalpy, ΔH , for the reaction if 886 kJ of energy is liberated during the reaction?

- (a) - 881 kJ (b) - 891 kJ
(c) 891 kJ (d) - 886 kJ

Heat capacity

The heat capacity of an object is defined as the amount of heat energy required to raise its temperature by 1 K (or °C), mathematically expressed as

$$C = \frac{q}{\Delta T} \quad (3.7)$$

The heat capacity (C) measures the temperature change experienced by a substance as a result of heat flow. The heat capacity of 1 mole of a substance is called its **molar heat capacity** ($C_m = C/n$).

The heat capacity depends on whether a sample is maintained at constant volume ($C = C_V$) or constant pressure ($C = C_P$). The respective molar quantities are $C_{V,m}$ and $C_{P,m}$.

Specific heat (c) is the heat capacity of 1 gram of a substance or it is the quantity of the heat required to change the temp of 1g of a substance by 1 K (or °C).

$$c = \frac{q}{m\Delta T} \quad (3.8)$$

The specific heat of a substance can be determined experimentally by measuring the temperature change (ΔT) of a known mass (m) of the substance when it gains or loses a specific amount of heat (q).

The measurement of heat flow (q) is known as **calorimetry**.

Measurements of internal energy and enthalpy changes

We can use calorimetry to measure the heat produced or absorbed by a reaction, and can identify q with a change in internal energy (a constant-volume process) or a change of enthalpy (a constant-pressure process).

Experimental determination of heat evolved or released during chemical reactions is done using a calorimeter by measuring the temperature changes produced. If the calorimeter was isolated from the surroundings, the heat evolved in the reaction will be reflected in a rise in temperature of the system. The amount of heat evolved during the reaction can be determined from knowledge of how much energy is required to raise the temperature of a substance.

Constant volume calorimetry

To measure a change in internal energy we should use a fixed volume calorimeter (such as the bomb calorimeter) and monitor the energy released ($q < 0$) or supplied ($q > 0$) as heat by measuring the corresponding change in temperature.

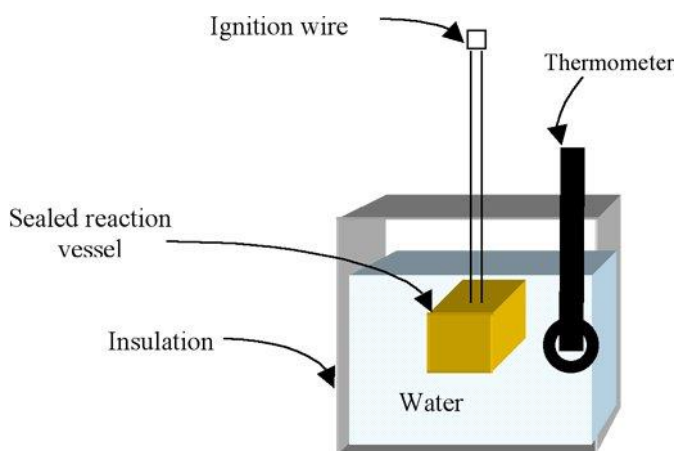


Figure 3.5 Constant volume calorimeter assembly with pressure regulatory valve. Reaction takes place in bomb immersed in water. Reaction is triggered using ignition wires.

In the calorimeter, the total heat capacity is $C_{\text{total}} = C_{\text{water}} + C_{\text{calorimeter}}$.

For a constant volume process, we can write the following expression for the heat capacity.

$$C_V = \frac{q_V}{\Delta T} = \frac{\Delta U}{\Delta T} \quad (3.9)$$

From the first law of thermodynamics we recall

$$\Delta U = q + w = q - P \Delta V$$

If the reaction is performed in a closed container called a bomb calorimeter then the volume remains constant and $\Delta V = 0$.

Hence the first law reduces to

$$\Delta U = q_v = C_v \Delta T$$

Electric heating for a measured time: $q = IVt$

$$\Delta H = \Delta U + \Delta (PV) = \Delta U + \Delta (nRT) = \Delta U + \Delta nRT, \quad (3.10)$$

where $\Delta n = \text{no. of moles of gaseous products} - \text{no. of moles of gaseous reactants}$ for the reaction of one mole of the substance of interest.

Example 3.2

Calculate the amount of heat required to raise the temperature of 9.25 L of water from 22.0 to 29.4 °C given that the specific heat of water is 4.18 J g⁻¹ °C⁻¹.

Solution

From equation (3.8)

$$c = \frac{q}{m\Delta T}$$

Solving for the quantity of heat transferred $q = \text{mass} \times \text{change in temperature} \times \text{specific heat of water}$.

$$\begin{aligned} q &= 9.25 \times 10^3 \text{ g} \times (29.4 - 22.0) \text{ }^\circ\text{C} \times 4.18 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1} \\ &= 286.3 \text{ kJ} \end{aligned}$$

Constant pressure calorimeter

An enthalpy change can be measured calorimetrically by monitoring the temperature change that accompanies a physical or chemical change at constant pressure: isobaric calorimeter.

A thermally insulated vessel open to the atmosphere: the heat released in the reaction is monitored by measuring the change in temperature. For a combustion reaction an adiabatic flame calorimeter may be used to measure ΔT when a given amount of substance burns in a supply of oxygen. Another route: to measure ΔU using a bomb calorimeter, and then convert ΔU to ΔH . Because solids and liquids have small molar volumes, for them pV_m is so small that the molar enthalpy and molar internal energy are almost identical: $H_m = U_m + pV_m \approx U_m$. If a process involves only solids or liquids, the values of ΔU and ΔH are almost identical. But this is not the case when gases are produced or consumed in the reaction.

For a constant pressure process, we can write the following expression for the heat capacity.

$$C_P = \frac{q_P}{\Delta T} = \frac{\Delta H}{\Delta T} \quad (3.11)$$

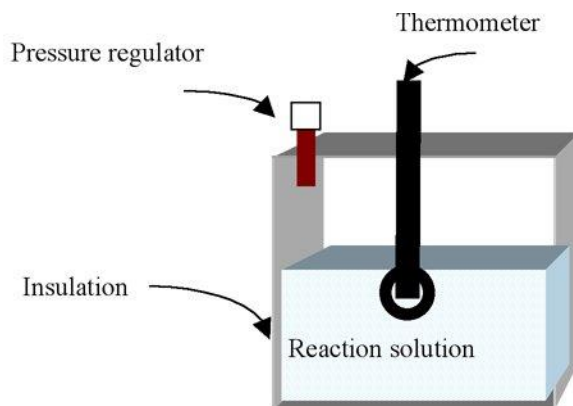


Figure 3.6 Diagrams showing energy changes during: (a) an exothermic reaction and (b) an endothermic reaction between the system and surroundings.

Example 3.3

Water is heated under $p = 1$ atm. When an electric current of 0.50 A from a 12 V supply is passed for 300 s, 0.798 g of water is vaporized. Calculate the molar internal energy and enthalpy changes at the boiling point (373.15 K).

Solution

$$\Delta H = q_p = IVt$$

$$\Delta H_m = 0.50 \text{ A} \times 12 \text{ V} \times 300 \text{ s} / (0.798/18.02) \text{ mol}$$

$$\Delta H_m = +41 \text{ kJ mol}^{-1} \quad \text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{O(g)} \quad \Delta n_g = +1 \text{ mol}$$

$$\Delta U_m = \Delta H_m - RT = +38 \text{ kJ mol}^{-1}$$

Practice problem 3.2

A sample of carbon, 3.0 g, was burned to carbon dioxide in a copper calorimeter. The mass of the calorimeter was 1.5 kg and the mass of water in the calorimeter was 2 kg. The initial temperature was 20 °C and the final temperature was 31 °C.

Calculate the heat liberated for the combustion of 1 g of carbon. The specific heat capacity of copper and water are 0.389 J g⁻¹ °C⁻¹ and 4.18 J g⁻¹ °C⁻¹.

(a) 3.2 x 10⁴ J (b) 9.3 x 10⁴ J

(c) 6.4 x 10⁴ J (d) 9.2 x 10⁴ J

Temperature dependence of reaction enthalpy

The heat capacity at constant pressure is expressed in the equation

$$C_p = \frac{dq_p}{dT} = \frac{dH}{dT} \quad (3.12)$$

Not all reactions take place at 298 K, so we must examine how the tabulated thermochemical data can be adapted for use under different conditions. We have seen before that the heat capacity at constant pressure is related to temperature by

$$\Delta H = C_p dT \quad (3.13)$$

If a substance is heated from an initial temperature T_1 to a temperature T_2 , the enthalpy change from $H(T_1)$ to $H(T_2)$ is according to the equation.

$$H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_p dT \quad (3.14)$$

It is assumed that no phase transition occurred between the two temperatures of interests T_1 and T_2 .

Practice problem 3.3

Prove that, $C_{p,m} - C_{v,m} = R$ for the ideal gas?

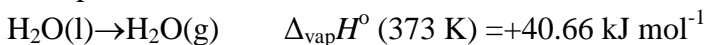
Hint: $\Delta H_m - \Delta U_m = R\Delta T$ divided by ΔT we get $C_{p,m} - C_{v,m} = R$

Standard enthalpy changes

Changes in enthalpy are normally reported for processes taking place under a set of standard conditions. In most of our discussions we shall consider the **standard enthalpy change**, ΔH° , the change in enthalpy for a process in which the initial and final substances are in their standard states. The **standard state** of a substance at a specified temperature is its pure form at 1 bar.

Enthalpies of physical change

The standard enthalpy change that accompanies a change of physical state is called the **standard enthalpy of transition**. The standard enthalpy of vaporization, $\Delta_{\text{vap}}H^\circ$, is one example.



Example 3.4

Find the energy needed to vaporate 1 L of water if you know that the standard enthalpy of vaporization of water is $40.66 \text{ kJ mol}^{-1}$ and the density of water is 1 g/mL .

Solution

$$d_{\text{H}_2\text{O}} = \frac{m_{\text{H}_2\text{O}}}{V_{\text{H}_2\text{O}}}$$

$$m_{\text{H}_2\text{O}} = d_{\text{H}_2\text{O}} \times V_{\text{H}_2\text{O}}$$

$$m_{\text{H}_2\text{O}} = (1 \text{ g/ml}) \times (1000 \text{ ml})$$

$$m_{\text{H}_2\text{O}} = 1000 \text{ g}$$

$$n_{\text{H}_2\text{O}} = \frac{m_{\text{H}_2\text{O}}}{\text{Mw}_{\text{H}_2\text{O}}}$$

$$n_{\text{H}_2\text{O}} = \frac{1000\text{g}}{(2 \times 1 + 16)}$$

$$n_{\text{H}_2\text{O}} = 55.56 \text{ mol}$$

$$1 \text{ mol (H}_2\text{O)} \longrightarrow 40.6 \text{ kJ}$$

$$55.56 \text{ mol} \longrightarrow \Delta H_v$$

$$\Delta H_v = \frac{40.6 \text{ kJ} \times 55.56 \text{ mol}}{1 \text{ mol}}$$

$$\Delta H_v = 2255.74 \text{ kJ}$$

Enthalpies of chemical change

Enthalpy changes accompanying chemical reactions:

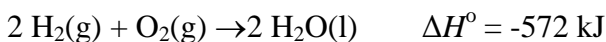


This equation is called **thermochemical equation**.

During hydrogenation of ethane, the enthalpy of the system decreases by 137 kJ – if the reaction takes place at constant pressure, 137 kJ of heat is released into the surroundings when 1 mol CH₂=CH₂ combines with 1 mol H₂ at 25°C.

If we write ΔH° , we mean the change of enthalpy that occurs when the reactants in their standard states change into products in their standard states:

Pure, unmixed reactants → pure, separated products (in their standard states)



When 2 mole H₂ as pure hydrogen gas at 1 bar combines with 1 mole O₂ as pure oxygen gas at 1 bar to form 2 mole H₂O as pure liquid water at 1 bar, the initial and final temperature being 25°C, the enthalpy of the system decreases by 572 kJ and (at constant *p*), 572 kJ of heat is released into the surroundings.

A thermochemical equation is a balanced reaction equation accompanied with the enthalpy change associated with it.

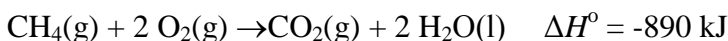
The heat evolved or absorbed during a chemical reaction is the enthalpy change. In

chemistry we normally do our experiments at standard conditions of temperature and pressure (STP). So, the results from the measurements are usually at STP.

The standard reaction enthalpy,

$$\Delta_r H^\circ = \sum_{\text{Products}} \nu H_m^\circ - \sum_{\text{Reactants}} \nu H_m^\circ \quad (3.15)$$

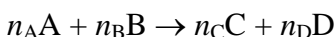
Combustion – the complete reaction of a compound with oxygen (complete oxidation):



The standard enthalpy of combustion, $\Delta_c H^\circ$ – the standard reaction enthalpy for the complete oxidation of an organic compound to CO_2 gas and liquid H_2O if the compound contains C, H, and O, and to N_2 gas if N is present. $\Delta_c H^\circ$ – a molar quantity.

Standard enthalpies of formation

The **standard enthalpy of formation**, $\Delta_f H^\circ$, of a substance is the standard reaction enthalpy for the formation of the compound from its elements in their reference states. The **reference state** of an element is its most stable state at the specified temperature and 1 bar. The value of $\Delta_f H^\circ$ for the overall reaction is the sum of these ‘unforming’ and forming enthalpies. The enthalpy of an unforming step is the negative of the enthalpy of formation. Consider the reaction



The standard enthalpy of reaction is calculated as:

$$\Delta H = \text{Sum of enthalpies of products} - \text{Sum of enthalpies of reactants}$$

Mathematically written as

$$\Delta_r H^\circ = (n_C \Delta_f H^\circ_c + n_D \Delta_f H^\circ_D) - (n_A \Delta_f H^\circ_A + n_B \Delta_f H^\circ_B)$$

$$\Delta_r H^\circ = \sum_{\text{Products}} \nu \Delta_f H^\circ - \sum_{\text{Reactants}} \nu \Delta_f H^\circ \quad (3.16)$$

The standard enthalpy of formation, $\Delta_f H^\circ$, for the pure elements ($\text{Cu}(\text{s})$, $\text{N}_2(\text{g})$, $\text{Fe}(\text{s})$, $\text{Na}(\text{s})$, $\text{Cl}_2(\text{g})$, $\text{Hg}(\text{L})$) is equal to zero at any temperature.

Example 3.5

Find $\Delta(PV)$ and ΔU for the reaction of



Solution

Since the single product, H₂O, is liquid, $\Delta n(g) = -3.000 \text{ mol}$

$$\Delta(PV) = \Delta n(g)RT = (-3)(8.3145 \text{ JK}^{-1} \text{ mol}^{-1})(298.15 \text{ K})$$

$$= -7437 \text{ J mol}^{-1} = -7.437 \text{ kJ mol}^{-1}$$

$$\Delta H = 2\Delta_f H^\circ (\text{H}_2\text{O}) - 0 - 0 = -571.660 \text{ kJ mol}^{-1}$$

$$\Delta U = -571.660 \text{ kJ mol}^{-1} - (-7.437 \text{ kJ mol}^{-1}) = -564.223 \text{ kJ mol}^{-1}$$

Example 3.6

The standard reaction enthalpy of $2\text{HN}_3(\text{l}) + 2\text{NO}(\text{g}) \rightarrow \text{H}_2\text{O}_2(\text{l}) + 4\text{N}_2(\text{g})$ is calculated as follows:

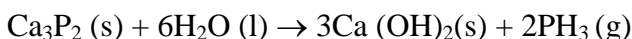
$$\Delta_r H^\circ = \{ \Delta_f H^\circ (\text{H}_2\text{O}_2, \text{l}) + 4 \Delta_f H^\circ (\text{N}_2, \text{g}) \} - \{ 2 \Delta_f H^\circ (\text{HN}_3, \text{l}) + 2 \Delta_f H^\circ (\text{NO}, \text{g}) \}$$

$$= \{ -187.78 + 4(0) \} \text{ kJ mol}^{-1} - \{ 2(264.0) + 2(90.25) \} \text{ kJ mol}^{-1}$$

$$= -896.3 \text{ kJ mol}^{-1}$$

Example 3.7

Phosphine gas may be prepared using by the following reaction.



Use the standard enthalpies of formation given below to calculate the standard enthalpy change for the above reaction.

Substance	ΔH_f° (kJ mol ⁻¹)
Ca ₃ P ₂ (s)	-504
Ca(OH) ₂ (s)	-986
PH ₃ (g)	+ 90
H ₂ O (l)	-286

Solution

The enthalpy change for the reaction is given by the following relationship.

$$\Delta_r H^\circ = \text{Sum of enthalpies of products} - \text{Sum of enthalpies of reactants}$$

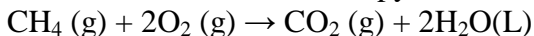
$$\Delta_r H^\circ = [3 \times (-986) + (3 \times 90)] - [(-504) + 6 \times (-286)]$$

$$= (-3048 + 270 + 504 + 1716) \text{ kJ}$$

$$= 558 \text{ kJ}$$

Example 3.8

Calculate the standard enthalpy of the reaction



If you know that

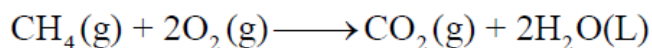
$$\Delta H_f^\circ(\text{CH}_4(\text{g})) = -74.9 \text{ kJ}$$

$$\Delta H_f^\circ(\text{O}_2(\text{g})) = 0$$

$$\Delta H_f^\circ(\text{CO}_2(\text{g})) = -393.5 \text{ kJ}$$

$$\Delta H_f^\circ(\text{H}_2\text{O}(\text{L})) = -285.8 \text{ kJ}$$

Solution



$$\Delta H^\circ = \underbrace{\sum n_{\text{P}}(\Delta H_f^\circ)_{\text{P}}}_{\text{products}} - \underbrace{\sum n_{\text{R}}(\Delta H_f^\circ)_{\text{R}}}_{\text{Reactants}}$$

$$\Delta H^\circ = [\Delta H_f^\circ(\text{CO}_2) + 2\Delta H_f^\circ(\text{H}_2\text{O})] - [\Delta H_f^\circ \text{CH}_4 + 2\Delta H_f^\circ(\text{O}_2)]$$

$$\Delta H^\circ = [(-393.5) + 2(-285.8)] - [(-74.9) + 2(0)]$$

$$\Delta H^\circ = -890.2 \text{ kJ}$$

Practice problem 3.4

The enthalpy change for the combustion of 1 mole of pentane to carbon dioxide and water is -3526 kJ. Calculate the standard enthalpy of formation of pentane given the following standard enthalpies of formation:

$$\text{CO}_2(\text{g}) \quad \Delta_f H^\circ = -393 \text{ kJ mol}^{-1}$$

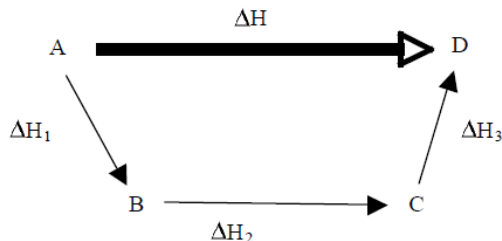
$$\text{H}_2\text{O}(\text{l}) \quad \Delta_f H^\circ = -286 \text{ kJ mol}^{-1}$$

- (a) -160 kJ
- (b) 155.2 kJ
- (c) -155.2 kJ
- (d) -77.6 kJ

Hess's law

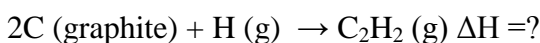
Hess's law states that when a reaction takes place to form products, the change in enthalpy is the same regardless of whether it is in a single step or involves several stages. For example, in the hypothetical reaction below, the overall enthalpy change is given by $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$ (3.18)

The significance of the law is that it enables calculation of enthalpies for reactions that maybe difficult or two dangerous for us to perform in the laboratory. Many thermochemical data can be found in Tables for use in calculations for various chemical reactions.



One restriction of Hess's law is that all the enthalpies must be measured at the same temperature and pressure. All enthalpy changes measured under these conditions are referred to as standard enthalpy changes denoted by ΔH^0 . The reactant and products must be in their standard states. The standard state of a pure substance being the form (gas, liquid or solid) in which a substance is most stable at 1 atm pressure and a specified temperature.

Example 3.9

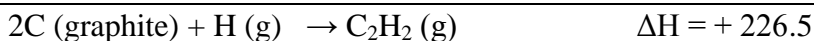


If you know that

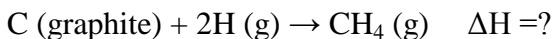
- a- $\text{C (graphite)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \quad \Delta H = - 393.5 \text{ kJ}$
- b- $\text{H}_2(\text{g}) + 1/2\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O(L)} \quad \Delta H = - 285.9 \text{ kJ}$
- c- $2\text{C}_2\text{H}_2(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 4\text{CO}_2(\text{g}) + 2\text{H}_2\text{O(L)} \quad \Delta H = - 2598.8 \text{ kJ}$

Solution

- a- $2\text{C (graphite)} + 2\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) \quad \Delta H = - 787\text{kJ}$
- b- $\text{H}_2(\text{g}) + 1/2\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O(L)} \quad \Delta H = - 285.9 \text{ kJ}$
- c- $2\text{CO}_2(\text{g}) + \text{H}_2\text{O(L)} \rightarrow \text{C}_2\text{H}_2(\text{g}) + 5/2\text{O}_2(\text{g}) \quad \Delta H = + 1299.4\text{kJ}$



Practice problem 3.5



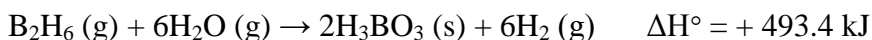
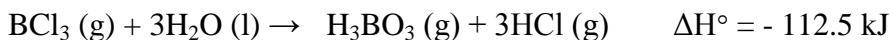
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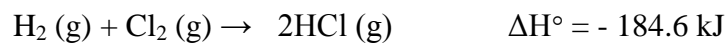
- a- $\text{C (graphite)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \quad \Delta H = - 393.5 \text{ kJ}$
- b- $\text{H}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O(L)} \quad \Delta H = - 285.9 \text{ kJ}$
- c- $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O(L)} \quad \Delta H = - 890 \text{ kJ}$

- (a) - 75.3 kJ
- (b) + 75.3 kJ
- (c) -150.6 kJ
- (d) +150.6 kJ

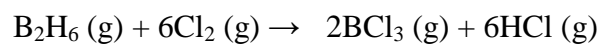
Practice problem 3.6

Given the following thermochemical equations





Calculate the value of ΔH° for the reaction



- (a) 492.2 kJ
- (b) 389.2 kJ
- (c) 3892 kJ
- (d) -389.2 kJ

Chapter 4

Spontaneity in Chemical Change

by Dr. Hasan Maridi

Spontaneous processes

Some things happen and some things don't.

- A ball rolls down a hill but never spontaneously rolls back up a hill.
- Steel rusts spontaneously if exposed to air and moisture. The iron oxide in rust never spontaneously changes back to iron metal and oxygen gas.
- A gas fills its container uniformly. It never spontaneously collects at one end of the container.
- Heat flow always occurs from a hot object to a cooler one. The reverse process never occurs spontaneously.
- Wood burns spontaneously in an exothermic reaction to form CO₂ and H₂O, but wood is never formed when CO₂ and H₂O are heated together.
- At temperatures below 0°C water spontaneously freezes and at temperatures above 0°C ice spontaneously melts.

For chemical systems, when heat is released from the system to the surroundings during a chemical reaction, the energy of the system decreases. The system energy changes from a higher state to a lower one. The analogue of the previous examples leads to the proposition that exothermic processes have a tendency to proceed spontaneously. Exothermic processes are generally spontaneous. Several endothermic processes are spontaneous.

Typical examples include:

- the melting of ice in which heat is absorbed and the energy of the system increases
- evaporation of water from a surface is also endothermic
- and so is the expansion of carbon dioxide into a vacuum

Conclusion – the enthalpy change alone is not sufficient to determine whether a change is spontaneous or not.

A **spontaneous process** is a process that occurs without external intervention. A

non-spontaneous process is a process that requires external action to start. A reaction that does occur under the given set of conditions is called a spontaneous reaction. If a reaction does not occur under specified conditions, it is said to be non-spontaneous.

Spontaneity and disorder

All the examples that we have considered for spontaneous processes are characterised by a change to a more disordered state. In other words, there is an increase in the degree of randomness. In addition, there is no change in energy involved in the process.

Mixing of two gases

Two ideal gases are confined to two chambers separated by a valve as shown in the diagram below.

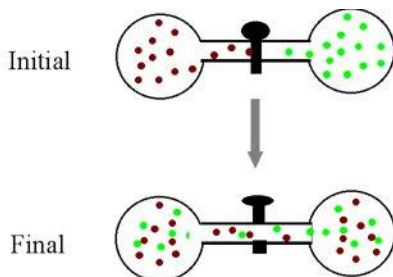


Figure 4.1 Illustration of the mixing of two gases. Gases spontaneously migrate to opposite chambers once the valve is opened.

When the tap is opened, the gases migrate into opposite chambers and mix. Mixing continues until the partial pressures in each chamber are uniform. One characteristic of an ideal gas is that the internal energy depends only on temperature. When the two gases mix at constant temperature, the change in internal energy (ΔU) is equal the change in enthalpy (ΔH), which is equal to zero (i.e. $\Delta U = \Delta H = 0$). Thus, it can be concluded that enthalpy change is not the driving force for the spontaneous mixing of the gases.

Consider a similar experiment to the one above in which the gas is confined one chamber (A) separated from a chamber (B) that has been evacuated.

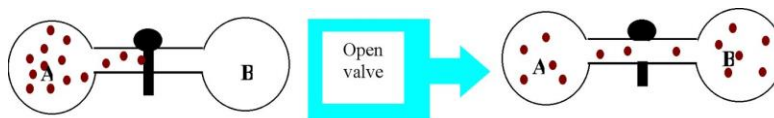


Figure 4.2 Illustration of free expansion of a gas into a vacuum. Molecules spontaneously migrate to the chamber with a vacuum.

Upon opening the tap, gas molecules move from the left chamber (A) to the right chamber (B) resulting in an increase in disorder as each molecule has a larger volume to travel around

- no work is performed on the system or the surroundings
- heat is neither evolved nor absorbed in the process
- the process is spontaneous and irreversible.

There is evidently no change in energy. The process therefore is not spontaneous to minimize energy but is driven by the tendency to increase disorder. In both cases, the degree of randomness increases and the manner in which energy is distributed among the

gas molecules changes. The driving force is the tendency of the molecules to achieve a maximum state of disorder.

The thermodynamic function that measures the degree of disorder of the system is called **entropy**, S . In mixing of the two gases in the example above, entropy of the system increases so that ΔS is greater than zero. The more disordered the state, the larger its entropy.

Entropy is a function that depends only on the initial and final state of the system. The change in entropy accompanying a process can be written as

$$\Delta S = S_{final} - S_{initial} \quad (4.1)$$

The value of S is positive if the degree of disorder increases, and is negative if disorder decreases. The reactions in the following example help illustrate this point.

Example 4.1

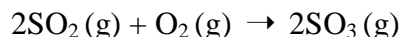
$\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$ entropy decreases since the liquid state is more ordered than the gaseous state.

$2\text{NH}_4\text{NO}_3(\text{s}) \rightarrow 2\text{N}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g}) + \text{O}_2(\text{g})$ entropy increases since the reaction yields a large amount of gas.

Example 4.2

Make qualitative predictions of entropy changes in the following processes.

(a) Reaction of sulphur dioxide with oxygen to form sulphur trioxide.



(b) Vaporisation of one mole of water $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$

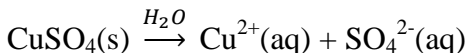
Solution

(a) The number of moles of gaseous products is smaller than that of the reactants. Three moles of reactants giving 2 moles of products. Entropy decreases.

(b) Molecules in the vapour phase have greater freedom of movement. Entropy increases.

Practice problem 4.1

Suggest if there is an increase or decrease in entropy for the reaction shown below.



Entropy measures the spontaneous dispersal of energy :How much energy is spread out in a process, or how widely spread out it becomes – at a specific temperature.

Mathematically we can define entropy change as energy dispersed/temperature.

$$\Delta S = q_{\text{rev}} / T \quad (4.2)$$

Since ΔS is independent of the path taken. We assume that the process proceeds via a reversible process so that the changes in heat are independent of the path taken, $q = q_{rev}$.

The use of entropy as the sole criteria for predicting spontaneous processes is somewhat problematic. One classical example is the freezing of water spontaneously at -10°C . Ice is a more ordered state and yet the process occurs spontaneously. This apparent difficulty is overcome by considering the change in entropy for both the system and the surroundings. The combined change of the system and surroundings entropy is called the entropy change of the universe expressed mathematically by

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} \quad (4.3)$$

For a spontaneous (irreversible process), that produces an increase in entropy, in both the system and surroundings, the universe gains in entropy. We can therefore write that

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} > 0 \quad (4.4)$$

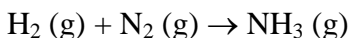
This is the mathematical representation of the ***second law of thermodynamics***, which states that all spontaneous processes produce an increase in entropy of the universe.

This helps us explain the spontaneous freezing of water despite a having a negative entropy. In freezing heat is absorbed from the surroundings, the entropy change in the surroundings is therefore positive. In this case, the entropy increase in the surroundings is higher than the decrease in entropy of the system. Thus, the total entropy of the universe is positive when water freezes.

The First Law uses the internal energy to identify permissible changes; the Second Law uses the entropy to identify the spontaneous changes among those permissible changes.

Entropy and reversible processes

In chemistry you have met a number of reactions that are reversible reactions. A common example is the reaction of hydrogen and nitrogen to give ammonia.



The reaction can go in both directions to give either ammonia (forward) or hydrogen and nitrogen in the reverse direction. Another example of a reversible process is the phase transition of ice to liquid water. However, for ice to melt in a thermodynamic sense we would need to apply a minute amount of heat so that only a small amount of ice melts. If a small amount of heat was then withdrawn, the water would change back into ice. In a perfect reversible phase change of ice to water, the surroundings return to their initial state

without affecting the rest of the universe. The entropy change in the system is given by

$$\Delta S = \Delta H_{\text{rev}}/T \quad (4.5)$$

where $\Delta H_{\text{rev}} = q_{\text{rev}}$

Example 4.3

Calculate the entropy change when one mole of water is converted into water vapour at 100 °C. The heat of vaporisation is 40.6 kJ mol⁻¹.

Solution

For a process occurring at constant temperature, the change in entropy, ΔS , is equal to the heat absorbed divided by temperature. At constant pressure $q = \Delta H$. Thus

$$\Delta S = \Delta H_{\text{vap}}/T = 40.6 \times 10^3 \text{ J} / 373 \text{ K} = 108.8 \text{ J K}^{-1}$$

Practice problem 4.2

The entropy change for the vaporisation of mercury is 86.5 J K⁻¹mol⁻¹ at standard pressure. Calculate the boiling point if the enthalpy of vaporisation is 54.5 kJ mol⁻¹.

- (a) 6250 K (b) 650 K
(c) 0.630 K (d) 630 K

Effect of temperature and volume

The entropy of a system increases with increasing temperature. The number of ways in which energy is able to distribute also increases as temperature increases. When the temperature is low, approaching absolute zero, the kinetic energy of the random motion of the molecules is small. The number of ways to distribute energy is fewer and hence low entropy. Consider for example molecules in a solid. Molecules are at fixed locations within the lattice structure. These molecules have vibrational motion about their location. When the solid absorbs energy in form of heat, the vibrations of the molecules increases and the molecules are no longer found at a fixed point. The number of ways to spreading energy has increased.

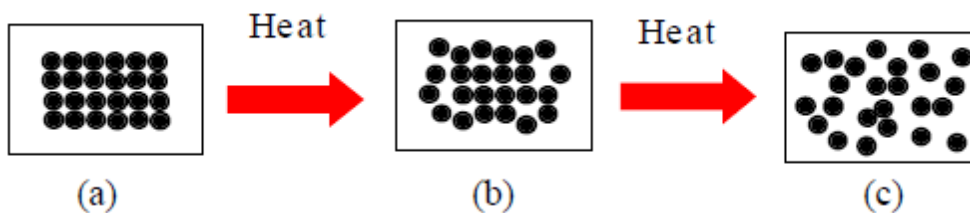


Figure 4.3 Illustration of the molecules locations in the three states.

In figure 4.3: (a) Many substances at a very low temperature form highly ordered structures (crystals). There are fewer ways to distribute energy. (b) As temperature increases, molecules have greater motion and are no longer found in fixed locations. Molecules move more freely with greater ways to distribute energy. (c) With still more heat added, molecules acquire more mobility, molecules are randomly distributed and have many ways to distribute energy.

Variation of entropy with temperature

The fact that entropy is influenced by temperature was highlighted qualitatively in the sections above. A quantitative analysis can be done by evaluating equation (2). For a system changing from an initial state with temperature (T_i) to a final temperature (T_f), the total entropy change for the process is found by integrating equation (2).

$$S(T_2) = S(T_1) + \int_{T_1}^{T_2} \frac{dq_{\text{rev}}}{T}$$

$$\Delta S = \int_{T_1}^{T_2} \frac{dq_{\text{rev}}}{T}$$

For a constant pressure process, the heat change dq can be related to the heat capacity C_P , $dq = C_P dT$

So that

$$S(T_2) = S(T_1) + \int_{T_1}^{T_2} \frac{C_P dT}{T}$$

Similarly, for a process taking place at constant volume the heat capacity (C_V) can be used in the expression

$$S(T_2) = S(T_1) + \int_{T_1}^{T_2} \frac{C_V dT}{T}$$

The overall entropy change between a temperature T_1 and T_2 is found by integrating and finding the solutions for the constant pressure and volume processes as shown below.

Expression for constant pressure process

$$S(T_2) = S(T_1) + C_P \ln (T_2 / T_1)$$

Expression for constant volume process

$$S(T_2) = S(T_1) + C_V \ln (T_2 / T_1)$$

These equations enable us to calculate the entropy change by measuring the heat capacity at different temperatures and evaluating the integrals. The change in entropy is calculated as a difference in entropy between the temperatures of interest and absolute zero temperature, $T = 0$.

Example 4.4

What is the change in entropy if a sample of solid magnesium is heated from 27 °C to 227 °C at 1 atm pressure? The specific heat capacity in region 0 – 600 °C varies according to the expression

$$C_p = 26.0 + 5.46 \times 10^{-2} T - 28.6 \times 10^{-4} T^2$$

Solution

The change in entropy in the temperature range 300 - 500 K can be calculated by applying equation (6).

$$S(T_2) = S(T_1) + \int_{T_1}^{T_2} \frac{C_p dT}{T}$$

Making necessary substitutions,

$$\begin{aligned} \Delta S &= \int_{300_1}^{500_2} \frac{26.0}{T} dT + \int_{300}^{500} 5.46 \times 10^{-3} dT - \int_{300}^{500} 28.6 \times 10^{-4} \frac{dT}{T^3} \text{ J K}^{-1} \\ &= 26.0 \ln [T]_{300}^{500} - 5.46 \times 10^{-3} \times [T]_{300}^{500} + \frac{28.6 \times 10^{-4}}{2} \left[\frac{1}{T^2} \right]_{300}^{500} \text{ J K}^{-1} \\ &= 26.0 \ln \frac{500}{300} + 5.46 \times 10^{-3} \times 200 + 14.3 \times 10^{-4} \left[\frac{1}{500^2} - \frac{1}{300^2} \right] \text{ J K}^{-1} \end{aligned}$$

Practice problem 4.3

What is the change in entropy when 1 mole of water at 0 °C is heated to form steam at 110 °C at atmospheric pressure. The specific heat capacity is 4.18 J K⁻¹ g⁻¹ and the enthalpy of vaporisation is 2257 J g⁻¹.

- (a) 5.8 (b) 140
(c) 132.1 (d) 8.3

Standard Entropies

Standard entropies are measured at 298 K and 1 atm with units of J K⁻¹. Using tabulated standard enthalpy values entropy changes for chemical reaction may be calculated as the difference between the sum of entropies of the products and the reactants.

$$\Delta S^\circ = \sum S^\circ (\text{products}) - \sum S^\circ (\text{reactants}) \quad (4.12)$$

Effect of volume

An increase in the volume of a gas results in increased entropy. There are a greater number of possible states to gas molecules due to the larger space. Let us examine the expansion of an ideal gas confined in a piston.

For an ideal gas that expands at constant temperature the expression for the change in entropy is

$$\Delta S = \frac{1}{T} \int dq$$

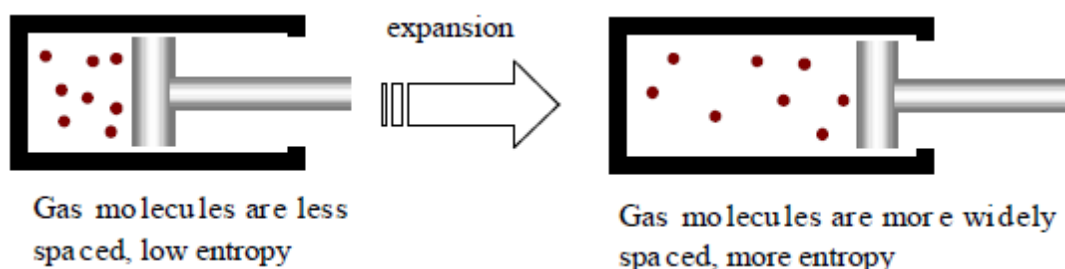


Figure 4.5 Gas molecules have greater space when the piston moves outwards.

We know from chapter 2 that for an isothermal reversible process

$$q_{\text{rev}} = -w = nRT \int_{V_i}^{V_f} \frac{dV}{V} = nRT \ln \frac{V_2}{V_1}$$

therefore the change in entropy can be expressed as

$$\Delta S = nR \ln(V_2 / V_1) \quad (4.15)$$

The equation can be transformed to relate to pressure using the volume-pressure inverse relationship.

$$\Delta S = nR \ln(P_1 / P_2) \quad (4.16)$$

Absolute entropies and the third law of thermodynamics

At $T = 0$, all energy of thermal motion has been quenched, and in a perfect crystal all the atoms or ions are in a regular, uniform array. The localization of matter and the absence of thermal motion suggest that such materials also have zero entropy. This conclusion is consistent with the molecular interpretation of entropy, because $S = 0$ if there is only one way of arranging the molecules and only one microstate is accessible (the ground state).

As temperature is reduced, entropy is also reduced and reaches a minimum at absolute zero. This leads us to the statement of **the third law of thermodynamics**, which states that *at absolute zero the entropy of a perfect crystalline substance is zero*.

Third-law entropies

Entropies reported on the basis that $S(0) = 0$ are called **Third-law entropies** (and often just ‘entropies’). When the substance is in its standard state at the temperature T , the **standard (Third-Law) entropy** is denoted $S^\ominus(T)$.

The **standard reaction entropy**, $\Delta_r S^\ominus$, is defined, like the standard reaction enthalpy, as the difference between the molar entropies of the pure, separated products and the pure, separated reactants, all substances being in their standard states at the specified temperature:

$$\Delta_r S^\ominus = \sum_{\text{Products}} \nu S_m^\ominus - \sum_{\text{Reactants}} \nu S_m^\ominus \quad (4.17)$$

In this expression, each term is weighted by the appropriate stoichiometric coefficient ν . Standard reaction entropies are likely to be positive if there is a net formation of gas in a reaction, and are likely to be negative if there is a net consumption of gas.

Illustration 3.6 Calculating a standard reaction entropy

To calculate the standard reaction entropy of $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$ at 25°C , we use the data in Table 2.7 of the *Data Section* to write

$$\begin{aligned} \Delta_r S^\ominus &= S_m^\ominus(\text{H}_2\text{O}, \text{l}) - \{S_m^\ominus(\text{H}_2, \text{g}) + \frac{1}{2}S_m^\ominus(\text{O}_2, \text{g})\} \\ &= 69.9 \text{ J K}^{-1} \text{ mol}^{-1} - \{130.7 + \frac{1}{2}(205.0)\} \text{ J K}^{-1} \text{ mol}^{-1} \\ &= -163.4 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

The negative value is consistent with the conversion of two gases to a compact liquid.

Gibbs free energy

What factors ultimately determine that a reaction proceeds spontaneously? Spontaneous reactions are often exothermic (negative enthalpy, $\Delta H < 0$) and are accompanied by an increase in entropy (increase in disorder, $\Delta S > 0$). Both enthalpy and entropy appear to influence whether a reaction occurs spontaneously or not. Furthermore, spontaneous reactions are those where the final state (products) tend to be of lower energy than the initial state (reactants). Another factor for consideration in predicting if a chemical reaction or process is spontaneous is temperature. Some reactions are spontaneous only at high temperature and not at low temperature. Why?

We define a new function that reflects the balance between enthalpy, entropy and

temperature, known as Gibbs free energy (G or simply Gibbs function).

$$G = H - TS \quad (4.18)$$

The expression reflects the stored energy (H), inherent disorder (S) at a given temperature (T in Kelvin). Since all the parameters in the equation are state functions so is G . The change in Gibbs energy is

$$\Delta G = \Delta H - T\Delta S \quad (4.19)$$

at constant temperature. The change of free energy (energy available to do work) depends primarily on the magnitudes of ΔH and $T\Delta S$ (enthalpy and entropy terms).

Consider the reaction below.



The reaction will behave in three ways depending on the value of ΔG .

$\Delta G < 0$ Reaction proceeds to give products C, D

$\Delta G = 0$ This represents an equilibrium condition in which the rates for the forward reactions is equal to that of the reverse reaction

$\Delta G > 0$ The reverse process is favoured to produce A, B

In general we can conclude that the direction of spontaneous change in either the forward or reverse is that which leads to a decrease in free energy. In summary if:

$\Delta G < 0$ Reaction is spontaneous in the forward direction.

$\Delta G = 0$ Reaction is at equilibrium.

$\Delta G > 0$ Reaction is spontaneous in reverse direction.

Example 4.5

In the sublimation of iodine crystals at 25 °C and atmospheric pressure, the process is accompanied by an enthalpy change of 39.3 kJ mol⁻¹ and an entropy change of 86.1 J K⁻¹. At what temperature will iodine crystals (solid) be in equilibrium with its vapour (gaseous iodine)?

The change in Gibbs free energy (ΔG) is related to the change in enthalpy (ΔH) and entropy (ΔS) by $\Delta G = \Delta H - T\Delta S$

At equilibrium $\Delta G = 0$ and T in the equation therefore the equilibrium temperature T_{eq} .

Thus,

$$0 = \Delta H - T_{eq} \Delta S$$

Solving for T_{eq}

$$T_{eq} = \Delta H / \Delta S = 39.3 \times 10^3 / 86.1 = 454 \text{ K}$$

Practice problem 4.4

Determine the melting point of sodium chloride (table salt) if 30.3 kJ is required to melt the crystals and that the process involves an increase in entropy of $28.2 \text{ J K}^{-1} \text{ mol}^{-1}$.

- (a) 1.071 (b) 1070
(c) 1000 (d) 1075

Standard free energy, ΔG°

Gibbs function consists of two thermodynamic state functions, which can be used to calculate standard free energies. For a chemical reaction, the standard free energy of change (ΔG°) is related to the formation of the products from the reactants. The standard being defined as before for ΔH° and ΔS° .

Properties of Gibbs function are very much similar to those of ΔH° that is

- ΔG° is zero for free energies of formation of elements in their standard state.
- ΔG° changes sign when the process is reversed but with the same magnitude.
- For a process comprising several steps, the total free energy change is the sum of the ΔG° s associated with each individual steps.

The free energy change for a chemical reaction can be calculated if the standard free energies of formation of the reactants and products are known.

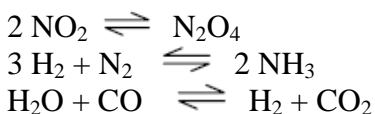
$$\Delta G^\circ = \sum a \Delta G^\circ_f (\text{products}) - \sum b \Delta G^\circ_f (\text{reactants}) \quad (4.20)$$

Chemical Equilibrium

Heat is energy flowing from a high temperature object to a low temperature object. When the two objects are at the same temperature, there is no net flow of energy or heat. That is why a covered cup of coffee will not be colder than or warmer than the room temperature after it has been in there for a few hours. This phenomenon is known as **equilibrium**. In this example, we deal with the flow of energy.

Equilibria happen in phase transitions. For example, if the temperature in a system containing a mixture of ice and water is uniformly 273.15 K, the net amount of ice formed and the melt will be zero. The amount of liquid water will also remain constant, if no vapour escape from the system. In this case, three phases, ice (solid) water (liquid), and vapour (gas) are in equilibrium with one another. Similarly, equilibrium can also be established between the vapour phase and the liquid at a particular temperature. Equilibrium conditions also exist between solid phases and vapour phases. These are **phase equilibria**.

In Stoichiometry calculations, chemical reactions may not be as complete as we have assumed. For example, the following reactions are far short of completion.



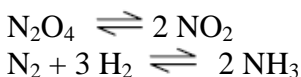
Let us consider only the first reaction in this case. At room temperature, it is impossible to have pure NO_2 or N_2O_4 . However, in a sealed tube (closed_system), the ratio

$$\frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2}$$

is a constant. This phenomenon is known as **chemical equilibrium**.

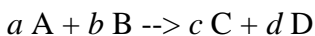
Reversible chemical reactions

Heat transfer, vapourization, melting, and other phase changes are physical changes. These changes are reversible and you have already experienced them. Many chemical reactions are also reversible. For example



The Law of Mass Action

Such a law of nature is called the law of mass action or mass action law. The law of mass action is universal, applicable under any circumstance. However, for reactions that are complete, the result may not be very useful. We introduce the mass action law by using a general chemical reaction equation in which reactants A and B react to give product C and D.



where a, b, c, d are the coefficients for a balanced chemical equation.

When equilibrium is established,

rate forward = rate reverse

$$K_f [A]^a [B]^b = K_b [C]^c [D]^d$$

Then

$$K_f / K_b = [C]^c [D]^d / [A]^a [B]^b$$

The **mass action law** states that if the system is at equilibrium at a given temperature, then the following ratio is a constant.

$$\frac{[C]^c [D]^d}{[A]^a [B]^b} = K_{eq} \equiv K_c$$

(5.1)

The **equilibrium constant, K_c or K_{eq}** , is the ratio of the equilibrium concentrations of products over the equilibrium concentrations of reactants each raised to the power of their stoichiometric coefficients.

The square brackets "[]" around the chemical species represent their **concentrations**. This is the **ideal law of chemical equilibrium** or **law of mass action**.

The equilibrium concentrations of reactants and products may vary, but the value for K_c remains the same. Equilibrium can be approached from either direction.

The units for K depend upon the units used for concentrations. If M is used for all concentrations, K has units of $M^{c+d-(a+b)}$

Equilibrium systems are dynamic (in constant chemical change) and reversible (chemical change can be approached from either direction).

Meaning of K_c , Which is favored, Reactant or Product?

If the K_c value is large ($K_c \gg 1$), the equilibrium lies to the right and the reaction mixture contains mostly products.

If the K_c value is small ($K_c \ll 1$), the equilibrium lies to the left and the reaction mixture contains mostly reactants.

If the K_c value is close to 1 ($0.10 < K_c < 10$), the mixture contains appreciable amounts of both reactants and products.

The reaction quotient Q

If the system is not at equilibrium, the ratio is different from the equilibrium constant. In such cases, the ratio is called a **reaction quotient** which is designated as Q .

$$\frac{[C]^c [D]^d}{[A]^a [B]^b} = Q \quad (5.2)$$

A system not at equilibrium tend to become equilibrium, and the changes will cause changes in Q that its value approaches the equilibrium constant, K

Predicting the direction of reaction

If $Q > K$, the reaction will go to the left. The ratio of products over reactants is too large & the reaction will move toward equilibrium by forming more reactants.

If $Q < K$, the reaction will go to the right. The ratio of products over reactants is too small & the reaction will move toward equilibrium by forming more products.

If $Q = K$, the reaction mixture is already at equilibrium, so no shift occurs.

The reaction: $N_2O_4 \rightleftharpoons 2 NO_2$

The reaction coordinate diagram shows how the concentration of N_2O_4 and NO_2 changes as the reaction approaches equilibrium. This is also reflected in Q . As the reaction proceeds to the right, N_2O_4 to NO_2 , the Q value increases, N_2O_4 becomes smaller and NO_2 becomes larger. The reaction finally reaches equilibrium at t_{eq} , at which time the concentration of N_2O_4 and NO_2 remains constant. Equilibrium is reached and the reaction quotient becomes equal to the equilibrium constant. $Q = K_c$.

Initial and Equilibrium Concentration Ratios for the N_2O_4 - NO_2 System at 100°C						
Exp't	Initial		Ratio (Q)	Equilibrium		Ratio (K)
	$[N_2O_4]$	$[NO_2]$	$[NO_2]^2/[N_2O_4]$	$[N_2O_4]_{eq}$	$[NO_2]_{eq}$	$[NO_2]_{eq}^2/[N_2O_4]_{eq}$
1	0.1000	0.0000	0.0000	0.0491	0.1018	0.211
2	0.0000	0.1000	∞	0.0185	0.0627	0.212
3	0.0500	0.0500	0.0500	0.0332	0.0837	0.211
4	0.0750	0.0250	0.00833	0.0411	0.0930	0.210

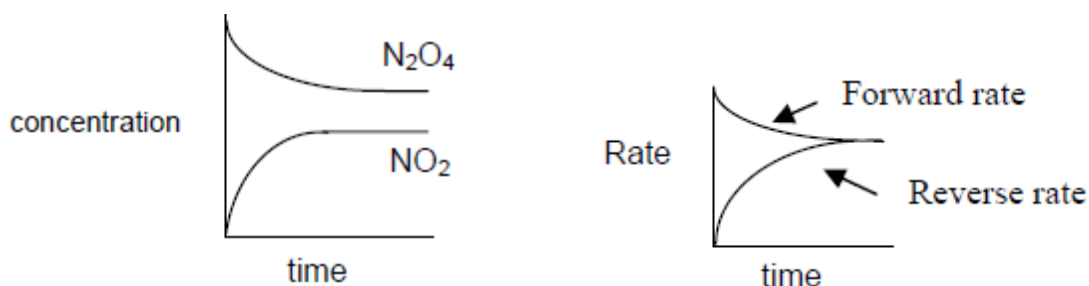
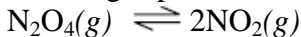


Figure 5.1 Concentration changes of N_2O_4 and NO_2 and rate change of the reaction.

Homogeneous equilibria: reactants and products exist in a single phase.

For the gas phase reaction:



The equilibrium constant with the concentrations of reactants and products expressed in terms of molarity, K_c , is:

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

Gas Phase Expressions can also be expressed by K_p

The K_p expression is written using equilibrium partial pressures of reactants and products.

$$\frac{[P_C]^c [P_D]^d}{[P_A]^a [P_B]^b} = K_p \quad (5.3)$$

For the reaction given above, the K_p expression is:

$$K_p = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}}$$

Since pressure and molarity are related by the Ideal Gas Law, the following equation relates K_p and K_c :

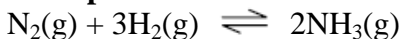
$$K_p = K_c(RT)^{\Delta n} \quad (5.4)$$

where $R = 0.0821 \text{ L atm / K mol}$; $T = \text{temperature in Kelvin}$

$\Delta n = \text{moles of gaseous products} - \text{moles of gaseous reactants}$.

Note that $K_c = K_p$ when the number of gas molecules are the same on both sides.

Example 5.1



Where the concentrations at equilibrium are:

$$[\text{NH}_3] = 3.1 \times 10^{-2} \text{ M}$$

$$[\text{N}_2] = 8.5 \times 10^{-2} \text{ M}$$

$$[\text{H}_2] = 3.1 \times 10^{-3} \text{ M}$$

What is the value of equilibrium constant K ?

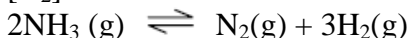
$$K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(3.1 \times 10^{-2})^2}{(8.5 \times 10^{-2})(3.1 \times 10^{-3})^3} = 3.8 \times 10^4$$

Example 5.2

$$[\text{NH}_3] = 3.1 \times 10^{-2} \text{ M}$$

$$[\text{N}_2] = 8.5 \times 10^{-2} \text{ M}$$

$$[\text{H}_2] = 3.1 \times 10^{-3} \text{ M}$$



Just the reverse of the previous example, What is the value of K ?

$$K' = \frac{[\text{N}_2][\text{H}_2]^3}{[\text{NH}_3]^2} = \frac{1}{K} = 2.6 \times 10^{-5}$$

Practice problem 5.1

Consider the following equilibrium, at 480 °C:



- What is the value of K_p for: $4\text{HCl}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{Cl}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$
- What is the value of K_p : $\text{Cl}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons 2\text{HCl}(\text{g}) + 1/2\text{O}_2(\text{g})$
- What is the value of K_c : $2\text{Cl}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g}) \rightleftharpoons 4\text{HCl}(\text{g}) + \text{O}_2(\text{g})$

Heterogeneous equilibria

In Heterogeneous equilibria, reactants and products are present in more than one phase.

Example 5.3



You would think that the equilibrium constant would be

$$K' = \frac{[\text{CO}_2][\text{CaO}]}{[\text{CaCO}_3]}$$

But heterogeneous equilibrium does not depend on the amounts of pure solid or liquids present. Therefore

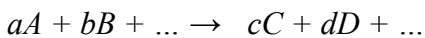
$$K = [\text{CO}_2]$$

Free energy and equilibrium constant

The free energy of the reaction is zero at equilibrium, $\Delta G = 0$ and $\Delta G^\circ = 0$ for the standard state. The condition of equilibrium is attained when two opposing processes are occurring at equal rates. It is often desirable to describe equilibrium under non-standard conditions. The change in free energy under a variety of conditions is calculated in relation to its standard value.

$$\Delta G = \Delta G^\circ + RT \ln Q \quad (5.5)$$

For a reaction of the general type



$$Q = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} \quad (5.6)$$

Where Q is the reactions quotient calculated for a reaction under non-standard conditions. At equilibrium $Q_C = K_C$, $Q_P = K_P$ and $Q = K_{eq}$. For the condition where $\Delta G = 0$, equation (5.5) becomes

$$0 = \Delta G^\circ + RT \ln Q \quad (5.7)$$

so that

$$\Delta G^\circ = -RT \ln(K_{eq}) \quad (5.8)$$

Equation (5.3) relates the standard free energies and to measurable quantities T and the equilibrium composition.

All chemical reactions comprise a forward and a reverse reaction to varying extents. The system is always seeking a minimum in energy. Therefore, the direction of spontaneous change is one that decreases Gibbs function from either direction as shown in Figure 5.2. The graph depicts the change in free energy for a hypothetical reaction. The free energy is observed to be decreasing both from the left and right. A minimum is reached at some point which corresponds to the equilibrium point. The plot shows that the standard free energy is the difference between the standard molar free energies of formation of the reactants and products.

The equilibrium constant for a reaction can be calculated by solving equation (5.8).

$$K = e^{\frac{-\Delta G^\circ}{RT}} \quad (5.9)$$

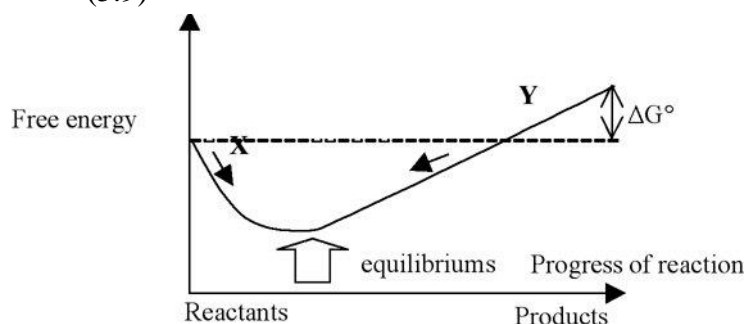


Figure 5.2 Plot showing free energy against extent of reaction. Shows free energy, equilibrium position and direction of spontaneous change.

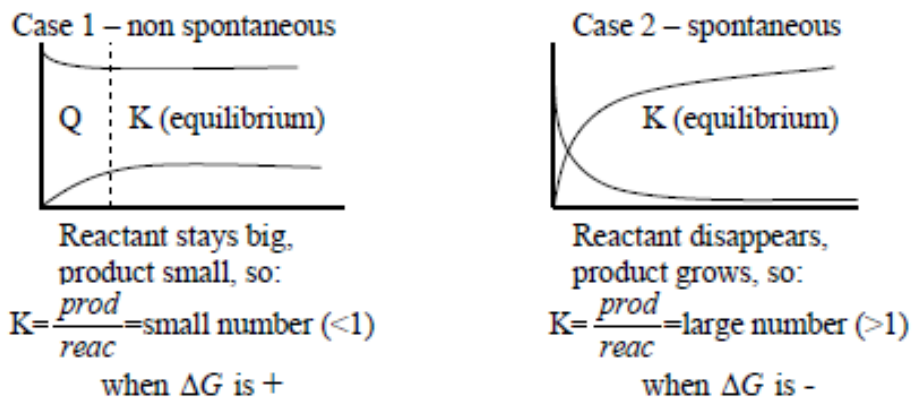
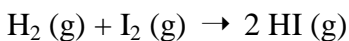


Figure 5.3 Plot showing the spontaneous and non-spontaneous process conditions.

Example 5.4

The reaction of hydrogen and iodine to form hydrogen iodide at 763 K has a standard free energy of formation $-12.1 \text{ kJ mol}^{-1}$.



What is the equilibrium constant for the reaction?

Solution

At equilibrium the standard free energy of formation is given by

$$\Delta G^\circ = -RT \ln K_{\text{eq}} \text{ equation}$$

In this example $\Delta G^\circ = -12.1 \text{ kJ mol}^{-1}$, $T = 763 \text{ K}$ and $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$. Hence

$$\ln K = - \frac{2 \times (-12.1 \times 10^3 \text{ J mol}^{-1})}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 763 \text{ K}}$$

$$\ln K = 3.81$$

Taking the antilog $K = 45$

Practice problem 5.2

Dinitrogen tetroxide is a common rocket fuel, which at 25°C dissociates into nitrogen dioxide forming an equilibrium between the two gases. The equilibrium mixture depends on the temperature of the mixture. What is the change in Gibbs free energy if the quantities of the two gases present in a 1 L container are 11.5 g N_2O_4 and 2.54 g NO_2 . The standard Gibbs free energy for the reaction is $+4853 \text{ J}$.

Equilibrium electrochemistry

The principles of thermodynamics can be applied to solutions of electrolytes. For that we need to take into account activity coefficients: they differ significantly from 1 on account of the strong ionic interactions in electrolyte solutions. These coefficients are best treated as empirical quantities, but it is possible to estimate them in very dilute solutions. This chapter describes thermodynamic properties of reactions in electrochemical cells, in which, as the reaction proceeds, it drives electrons through an external circuit.

Thermodynamic arguments can be used to derive an expression for the electric potential of such cells and the potential can be related to their composition. Two major topics: (1) the definition and tabulation of standard potentials; (2) the use of these standard potentials to predict the equilibrium constants and other thermodynamic properties of chemical reactions.

Electrochemical cells

An electrochemical cell consists of two electronic conductors (metal or graphite) dipping into an electrolyte (an ionic conductor), which may be a solution, a liquid, or a solid. The electronic conductor and its surrounding electrolyte – **electrode**. The physical structure containing them – **an electrode compartment**. The two electrodes may share the same compartment (left). If the electrolytes are different, then the two compartments may be joined by a **salt bridge** – and electrolyte solution that completes the electrical circuit by permitting ions to move between the compartments (right). Alternatively, the two solutions may be in direct physical contact (through a porous membrane) and form a **liquid junction**.

There are two types of electrochemical cells: **galvanic** (ones that spontaneously produce electrical energy) and **electrolytic** (ones that consume electrical energy).

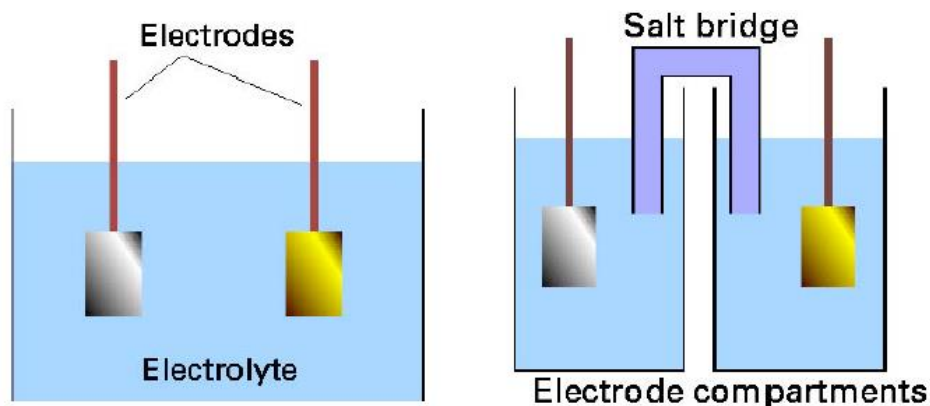


Figure 6.1 An electrochemical cells.

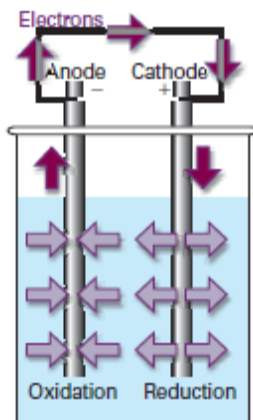
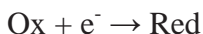


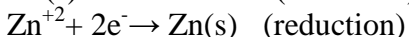
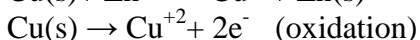
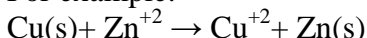
Figure 6.2 When a spontaneous reaction takes place in a galvanic cell, electrons are deposited in the anode and collected from the cathode, and so there is a net flow of current. Note that the + sign of the cathode can be interpreted as indicating the electrode at which electrons enter the cell, and the sign of the anode is where the electrons leave the cell.

Half-reactions and electrodes

Oxidation is the removal of electrons from a species, a **reduction** is the addition of electrons to a species, and a **redox reaction** is a reaction in which there is a transfer of electrons from one species to another. In general we write a couple as Ox/Red and the corresponding reduction half-reaction as



For example:



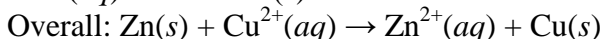
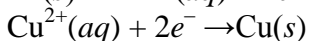
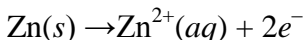
Electrochemical cells consist of two electrodes: an **anode** (the electrode at which the oxidation reaction occurs) and a **cathode** (the electrode at which the reduction reaction occurs).

A Zn electrode dipping in $\text{Zn}^{2+}(\text{aq})$ solution, connected to a Cu electrode dipping in $\text{Cu}^{2+}(\text{aq})$ solution.

The two electrodes are connected by an electrical conductor, which permits the flow of electrons from one electrode to the other.

The two solutions are connected by a porous partition or a “salt bridge,” which permits the flow of ions.

The electrode processes consist of **oxidation** (loss of electrons) at one electrode and **reduction** (gain of electrons) at the other:



The electrode at which oxidation takes place is called the **anode**. The electrode at which reduction takes place is called the **cathode**.

In electrochemical cells, the anode is negatively charged because electrons are given to the electrode by the species undergoing oxidation. The cathode is positively charged because electrons are removed from it by the species undergoing reduction.

So, when an electrochemical cell is written as indicated above, the electron-flow in the external circuit is from the electrode on the left to the electrode on the right.

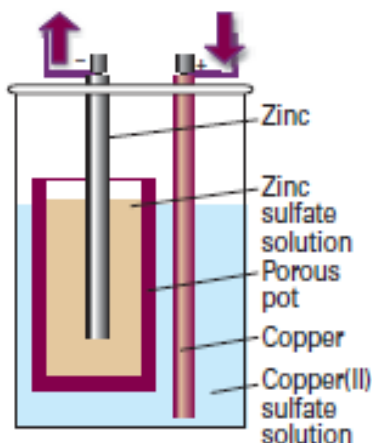


Figure 6.3 In the Daniell cell. The copper electrode is the cathode and the zinc electrode is the anode. Electrons leave the cell from the zinc electrode and enter it again through the copper electrode.

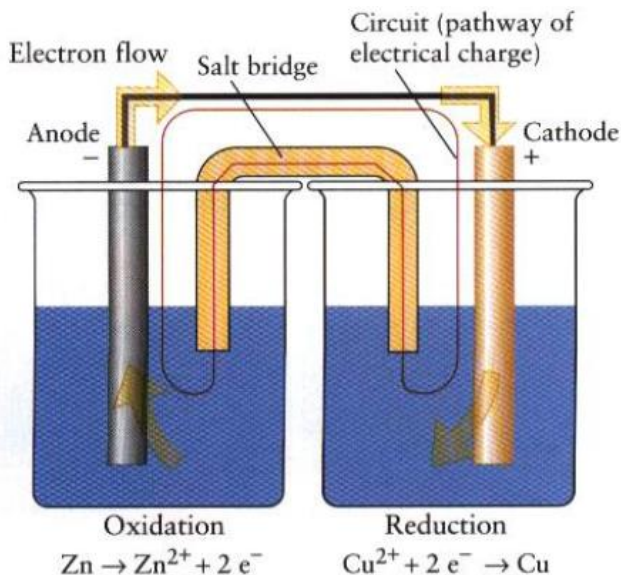


Figure 6.4 The salt bridge, essentially an inverted U-tube full of concentrated salt solution in a jelly, has two opposing liquid junction potentials that almost cancel.

Varieties of cells

The simplest type of cell has a single electrolyte common to both electrodes (as in Fig. 6.1). In some cases it is necessary to immerse the electrodes in different electrolytes, as in the

‘Daniell cell’ in which the redox couple at one electrode is Cu^{2+}/Cu and at the other is Zn^{2+}/Zn (Fig. 6.3).

In a cell with two different electrolyte solutions in contact, as in the Daniell cell, there is an additional source of potential difference across the interface of the two electrolytes. The contribution of the liquid junction to the potential can be reduced by joining the electrolyte compartments through a salt bridge (Fig. 6.4).

The cell reaction

The current produced by a galvanic cell arises from the spontaneous reaction taking place inside it. **The cell reaction** – the reaction in the cell written on the assumption that the right-hand electrode is the cathode and the reduction is taking place in the right-hand compartment. We’ll see later how to predict if the right-hand electrode is in fact the cathode; if it is, then the cell reaction is spontaneous as written. If the left-hand electrode turns out to be the cathode, then the reverse of the cell reaction is spontaneous.

Conventions and notations

There are a few conventions and notations used for short-hand representation of electrochemical cells.

An electrochemical cell is viewed as the combination of two “half-cells.” Each half-cell consists of an electrode, which may participate in the cell reaction, and chemicals in contact with that electrode.

Vertical lines are used to indicate important phase boundaries across which half-cell reactions take place. Often, the electrolyte concentration is also shown.

When two half-cells are combined to make an electrochemical cell, the half-cell in which oxidation takes place is written on the left-hand side and the half-cell in which reduction takes place is written on the right.

The electrodes are written on the “outside” with the electrolytes in-between.

A double vertical line is drawn between the two electrolytes to indicate a physical separation, either by a porous membrane or a salt-bridge.

Example

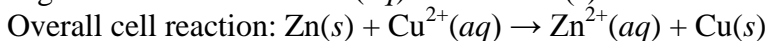
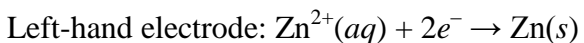
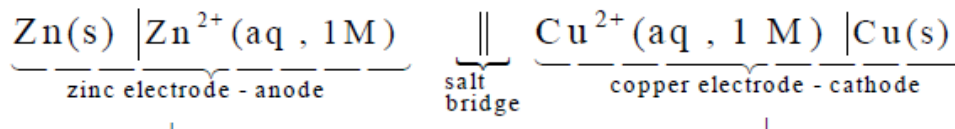
In the standard Daniel cell:



Or:



Or:



The cell potential

A galvanic cell does electrical work as the reaction drives electrons through an external circuit. The work done by a given transfer of electrons depends on **the cell potential** – the potential difference between the two electrodes (measured in volts, $1 \text{ V} = 1 \text{ J C}^{-1}$). Large cell potential – large amount of electrical work can be done by given number of electrons traveling between the electrodes.

The maximum electrical work that a system (the cell) can do is given by ΔG . For a spontaneous process at constant temperature and pressure $w_{e,\max} = \Delta G$

The force that drives this reaction is, of course, the decrease in free energy, ΔG .

The force that drives the reaction is manifested in the form of the **electromotive force (emf)** or cell voltage, denoted as E , which can be measured using a Wheatstone bridge, under conditions in which no current is drawn from the cell.

If the concentrations of the ions are maintained at 1 mol kg^{-1} (or 1 m), the cell is called the **standard Daniel cell** and the cell emf is called the **standard cell emf**, denoted as E° .

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \quad (6.1)$$

where E°_{cathode} and E°_{anode} are the standard reduction potential.

To identify which the electrode is cathode and which is anode, we can use this rule:

$$E^\circ_{\text{cathode}} > E^\circ_{\text{anode}} \quad (6.2)$$

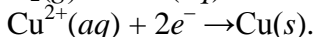
The fact that the spontaneous cell reaction leads to the oxidation of $\text{Zn}(s)$ to $\text{Zn}^{2+}(aq)$ and the reduction of $\text{Cu}^{2+}(aq)$ to $\text{Cu}(s)$ indicates that the tendency for $\text{Cu}^{2+}(aq)$ ions to accept electrons (to get reduced) is greater than that for $\text{Zn}^{2+}(aq)$ ions. In the terminology of electrochemistry, we say that $\text{Cu}^{2+}(aq)$ has a greater **reduction potential** than $\text{Zn}^{2+}(aq)$.

Standard Electrode Potentials

The difference in the reduction potentials of the two electrodes chosen to make up the cell determines the total cell emf.

A scale of reduction potentials is needed to quantitatively assign the reduction potentials of various electrodes used to make up electrochemical cells.

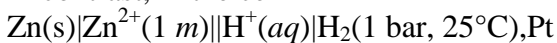
Since there is no way to measure the reduction potential of a single electrode, the hydrogen electrode is chosen as the ultimate standard. The Hydrogen electrode operating at 25°C and 1 bar pressure is assigned a reduction potential of 0.0 V . If we were to construct a cell using a $\text{Cu}(s)|\text{Cu}^{2+}(1 \text{ m})$ electrode and the standard hydrogen electrode $[\text{Pt}, \text{H}_2(1 \text{ bar}, 25^\circ\text{C})|\text{H}^+(1 \text{ m})]$, the electrode reactions would be



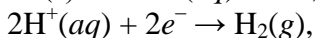
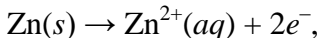
The measured emf of such a cell would be 0.3419 V . Therefore, we say that the standard reduction potential of the $\text{Cu}(s)|\text{Cu}^{2+}(1 \text{ m})$ electrode is $+0.3419 \text{ V}$.

The fact that Cu^{2+} ions undergo spontaneous reduction indicates that the tendency for $\text{Cu}^{2+}(aq)$ ions to accept electrons (to get reduced) is greater than that for H^+ ions.

In contrast, in the cell



the cell reactions will be

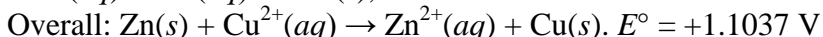
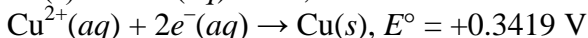
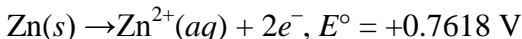


and the measured cell emf will be -0.7618 V . In this case, it is clear that the tendency for H^{+} ions to accept electrons is greater than for the $\text{Zn}^{2+}(aq)$ ions.

Therefore, the reactions and electrode potentials in the cell



will be



Other Standard Electrodes

A hydrogen electrode is difficult to set up and is not portable. Therefore, other standard electrodes have been adopted.

The $\text{Ag}|\text{AgCl}(s)|\text{Cl}^{-}(1\text{ m})$ electrode:

This electrode consists of a silver wire in contact with solid AgCl which, in turn, is in contact with 1 m KCl solution. The reduction potential of this electrode is measured by constructing the cell

$\text{Pt}, \text{H}_2(1\text{ bar}, 25^\circ\text{C})|\text{H}^{+}(1\text{ m})||\text{Cl}^{-}(1\text{ m})|\text{AgCl}(s)|\text{Ag}(s)$ in which the following reactions take place:

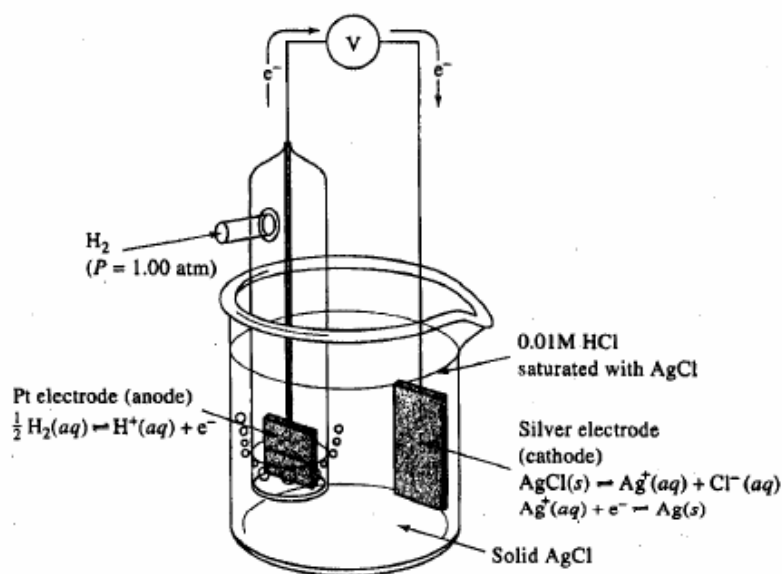
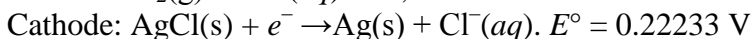
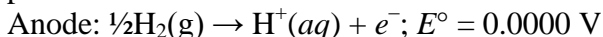


Figure 6.4 A galvanic cell without a liquid junction.

The Standard Calomel electrode

The half-cell is $\text{Hg}(l)|\text{Hg}_2\text{Cl}_2(s)|\text{Cl}^-(1\text{ }m)$. Calomel is the common name for the mercury (II) chloride used in this electrode. The electrode develops a half-cell reduction potential of 0.3337 V.

If saturated potassium chloride solution used (rather than 1 *m*), the half-cell potential is 0.2412 V, and the electrode is called the saturated calomel electrode.

Another very common reference electrode is the glass electrode, which is essentially a thin-walled glass bulb filled with 0.1 *m* HCl, in contact with a $\text{AgCl}(s)|\text{Ag}$ electrode. The glass membrane is permeable to H^+ ions and, therefore, the glass electrode is commonly used for pH determinations

The Thermodynamics of Electrochemical Cells

The relationship between the standard cell emf E° and the standard Gibbs free energy ΔG° is

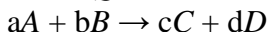
$$\Delta G^\circ = -nFE^\circ \quad (6.3)$$

where the superscript on G and E denotes the standard concentrations (strictly speaking, activities) of the electrolytes in the cell. F is Faraday constant = $eN_A = 96,500\text{ C mol}^{-1}$ and n is the number of electrons transferred in cell reaction.

Under non-standard concentrations, we use the relationship

$$\Delta G = \Delta G^\circ + RT \ln Q \quad (6.4)$$

where Q is the reaction quotient for the cell reaction. So, for a cell reaction



in which n electrons are involved, we write

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (6.5)$$

and

$$\Delta G = \Delta G^\circ + RT \ln Q$$

or, in terms of cell emf's,

$$-nFE = -nFE^\circ + RT \ln Q$$

This is easily simplified to give

$$E = E^\circ - \frac{RT}{nF} \ln Q \quad (6.6)$$

This is called **the Nernst equation**, and is one of the most important equations in electrochemistry. The Nernst equation is the basis for many practical applications of electrochemical principles.

At equilibrium,

$$K=Q$$

$$W=0$$

$$\Delta G=0$$

$$E_{\text{cell}}=0$$

Then,

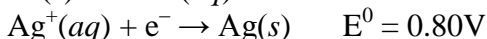
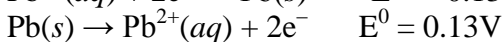
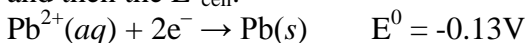
$$K = e^{\frac{-\Delta G^0}{RT}} = e^{\frac{nFE^0}{RT}} \quad (6.7)$$

Example: Calculating K and ΔG^0 from E^0_{cell}

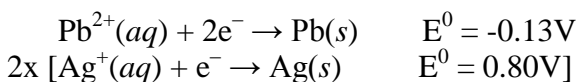
Lead can displace silver from solution. As a consequence, silver is a valuable by product in the industrial extraction of lead from its ore. Calculate K and ΔG^0 at 25^0C for this reaction.

Solution

Break the reaction into half-reactions, find the E^0 for each half-reaction and then the E^0_{cell} .



$$E^0_{\text{cell}} = 0.80 - (-0.13) = 0.93 \text{ V}$$



$$\Delta G^0 = -nFE^0_{\text{cell}} = -(2)(96.5 \text{ kJ/mol V})(0.93\text{V}) = -1.8 \times 10^2 \text{ kJ}$$

$$K = e^{\frac{-\Delta G^0}{RT}} = e^{\frac{nFE^0}{RT}}$$

$$K = 2.6 \times 10^{31}$$

Example: Using the Nernst equation to calculate E_{cell}

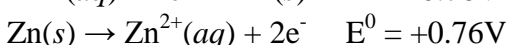
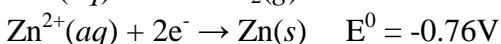
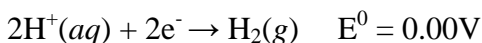
In a test of a new reference electrode, a chemist constructs a voltaic cell consisting of a Zn/Zn^{2+} half-cell and an H_2/H^+ half-cell under the following conditions:

$$[\text{Zn}^{2+}] = 0.010\text{M} \quad [\text{H}^+] = 2.5\text{M} \quad P_{\text{H}_2} = 0.30\text{atm}$$

Calculate E_{cell} at 25^0C .

Solution

Find E^0_{cell} and Q in order to use the Nernst equation



$$\text{We have } E^0_{\text{H}} > E^0_{\text{Zn}}$$

We Know that $E^0_{\text{cathode}} > E^0_{\text{anode}}$, then, H is cathode where the reduction is occur and Zn is anode where the oxidation.

$$E^0_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}} = E^0_{\text{H}} - E^0_{\text{Zn}} = 0.0 \text{ V} - (-0.76 \text{ V}) = 0.76 \text{ V}$$

In the reaction contains gases, we can be write the partial pressures of gases instead of their concentrations

$$Q = P_{\text{H}_2} \times [\text{Zn}^{2+}] / [\text{H}^+]^2 = (0.30)(0.010) / (2.5)^2 = 4.8 \times 10^{-4}$$

$$E = E^o - \frac{RT}{nF} \ln Q$$

$$E_{\text{cell}} = E^o_{\text{cell}} - 0.0592 \text{V} \log Q / n = 0.86 \text{V}$$

Example

A voltaic cell consisting of a Cu/Cu²⁺ half-cell and an Ag/Ag⁺ half-cell under the following conditions:

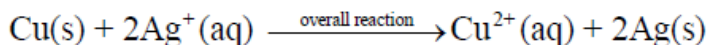
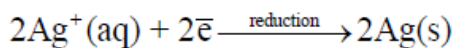
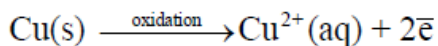
$$[\text{Cu}^{2+}] = 0.01 \text{M} \quad [\text{Ag}^+] = 0.005 \text{M} \quad E^0_{\text{Cu}} = 0.34 \text{ V}, \quad E^0_{\text{Ag}} = 0.8 \text{ V}$$

- Which is the cathode and which is anode
- Write the two half-reactions and the overall reaction,
- Determine the standard cell potential E^0 for the reaction
- Find the reaction quotient Q
- Calculate the total cell potential E_{cell} at 25°C.

Solution

- We use the rule $E^0_{\text{cathode}} > E^0_{\text{anode}}$
where E^0_{cathode} and E^0_{anode} are the standard reduction potential.
 $E^0_{\text{Ag}} > E^0_{\text{Cu}}$
then Ag is cathode and Cu is anode.

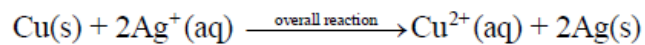
- Break the reaction into half-reactions,



- the E^0 for the reaction

$$E^0_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}} = E^0_{\text{Ag}} - E^0_{\text{Cu}} = 0.8 \text{ V} - 0.34 \text{ V} = 0.46 \text{ V}$$

- To find Q



$$Q = \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2}$$

$$Q = \frac{(0.01)}{(0.005)^2}$$

(e) The cell potential is

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{RT}{nF} \ln Q$$

$$E_{\text{cell}} = 0.46 - \frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{2 \times 96500} \ln \left(\frac{0.01}{(0.005)^2} \right)$$

$$E_{\text{cell}} = 0.38 \text{ V}$$

Appendix A. Key Concepts (Glossary)

Absolute temperature scale. This refers to a temperature scale that uses the absolute zero of temperature as the lowest temperature.

Absolute zero. The lowest temperature theoretically attainable. It is the temperature at which the kinetic energy of atoms and molecules is minimal.

Adiabatic boundary. A boundary that does not permit energy transfer as heat.

Avogadro's law. At constant pressure and temperature, the volume of a gas is directly proportional to the number of moles of the gas present.

Bomb calorimeter. A calorimeter in which there is no net loss of heat from the calorimeter to the surroundings. It is used to measure the heat of a combustion reaction. The measured heat of reaction at constant volume, $q_v = \Delta U$.

Boyle's law. The volume of a fixed mass of a gas maintained at constant temperature is inversely proportional to the gas pressure.

Calorimeter. A device for measuring the heat transfer.

Charles's law. The volume of a fixed amount of gas maintained at constant pressure is directly proportional to the absolute temperature.

Closed system. A system with a boundary through which matter cannot be transferred.

Dalton's law. The total pressure of a mixture of gases is just a sum of the pressures that each gas would exert if it were present alone.

Diffusion. The spreading of a substance (usually a gas) into a region where it is not originally present due to the random motion of the molecules.

Dipoles. A pair of separated opposite charges. The dipole moment (μ) is the product of the positive charge and the distance separating the charges.

Endothermic process. A process that absorbs energy as heat from its surroundings.

Energy. The capacity to do work.

Enthalpy (H). A thermodynamic quantity used to describe heat changes taking place at constant pressure, $H = U + PV$.

Enthalpy change. The heat (under certain familiar conditions) involved in a process; symbolized ΔH . At constant pressure, $\Delta H = \Delta U + P\Delta V$.

Entropy (S). A direct measure of the degree of disorder or randomness of a system.

Equilibrium. A condition in which an infinitesimal change in a variable in the opposite direction results in opposite change in the state. In chemical reactions, it represents the situation in which the reactants and products are producing each other at the same rate.

Exothermic process. A process that releases energy as heat.

Free energy (G). The energy available to do useful work. Defined by $G = H - T\Delta S$. Changes in free energy are useful in indicating the conditions under which a reaction will occur.

First law of thermodynamics. Energy can be converted from one form to another but can not be created or destroyed.

Gibbs Free Energy. See free energy.

Heat capacity. The quantity of heat required to change the temperature of a substance by one degree usually expressed as $\text{J } ^\circ\text{C}^{-1}$ or $\text{cal } ^\circ\text{C}^{-1}$.

Heat of reaction. The energy change accompanying a chemical reaction.

Heat. The transfer of energy as a result of a temperature difference.

Hess's law. The law that states that the enthalpy change for an overall or net process is the sum of enthalpy changes for the individual steps in the process.

Ideal gas. A hypothetical gas whose pressure-volume-temperature behaviour can be accounted for by the ideal gas equation.

Ideal gas constant (R). The numerical constant appearing in the ideal gas equation. The constant has a value of $0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$ or $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$. An ideal gas (perfect gas) is a hypothetical gas that obeys the ideal gas equation.

Ideal gas equation. An equation expressing the relationship between pressure, volume, temperature, and amount of gas. Mathematically stated as $PV = nRT$, where n is the number of moles, P is the pressure of gas and V the volume of gas.

Internal energy. Total energy of the system; symbolized by E . The sum of all the kinetic energies and potential energies of the particles within the system.

Isobaric calorimeter. A calorimeter for the studying processes at constant pressure.

Isolated system. A system with a boundary through which neither matter nor energy can be transferred.

Kelvin (temperature). The SI base unit of temperature. The Kelvin temperature is an absolute temperature. The lowest attainable temperature is $0 \text{ K} = -273.15 \text{ } ^\circ\text{C}$. It is related to the Celsius temperature through the expression $T (\text{K}) = T(^{\circ}\text{C}) + 273.15$.

Kinetic-molecular theory of gases. The treatment of gas behaviour in terms of random motion of molecules. It is a model used for describing gas behaviour based on a set of assumptions.

Open system. A system with a boundary through which both matter and energy can be exchanged with the surroundings.

Potential energy. The energy due to the position or arrangement. Associated with forces of attraction and repulsion.

Pressure-volume work. The work associated with the expansion or compression of gases.

Root-mean-square-velocity. The square root of the average of the squares of speeds of all molecules in a sample.

Specific heat. The quantity of heat required to change the temperature of one gram of substance by one degree Celsius.

Standard conditions of temperature and pressure. Refers to conditions at a temperature of exactly 273.15 K ($^{\circ}\text{C}$) and a pressure of 101325 Pa (1 atm or 760 mmHg).

Standard enthalpy of formation. The heat change involved when 1 mol of the substance is made from its elements in their standard state; symbolized

Standard enthalpy of reaction. The enthalpy change when a reaction is carried out under

standard states conditions.

Standard enthalpy. The change in enthalpy for a process in which the initial and final substances are in their standard state, symbolized ΔH .

Standard temperature and pressure (STP). At 273 K ($^{\circ}\text{C}$) and 101325 Pa (1 atm).

State function. Property that depends only on the current state of the system and is independent of how that state has been prepared. A function that depends only on the initial and final states of the system.

Surroundings. The part of the world outside the system where we make our measurements.

System. Part of the world in which we have specific interest.

van der Waals equation. An equation used to describe the P , V , and T of a non-ideal gas.

van der Waals forces. A term used to describe the dipole-dipole, dipole-induced dipole and dispersion forces

Work. The transfer of energy by motion against an opposing force.