Benha University, Faculty of Science, Chemistry Department

General Chemistry (Chm 100)

Part 2

For 1st year students

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Chapter 1

Gases

Gases are believed to consist of widely separated molecules in rapid motion. Any two (or mere) gases can be mixed in any proportion to prepare a perfectly uniform mixture; no such generalization can be made for liquids. Since the molecules of a gas are separated by comparatively large distances, the molecules of one gas can easily fit between the molecules of another gas. This molecular model can also be used to explain the fact that gases are readily compressed. Compression consists of forcing gas molecules closer together.

A gas expands to fill any container into which it is introduced. When a gas that has an odor is released into a room, it can soon be detected in all parts of the room. Gases diffuse because the gas molecules are in constant, rapid motion. Furthermore, in the course of their random motion gas molecules strike the walls of the container. These impacts explain the fact that gases exert pressure.

1. Pressure

Pressure is defined as force per unit area. The pressure of a gas is equal to the force that the gas exerts on the walls of the container divided by the surface area of the container:

$$\text{pressure} = \frac{force}{area}$$

The SI unit of pressure is the pascal (abbreviated Pa), which is defined as the pressure equivalent to a force of one newtoa (1 N = 1 kg. m/s^2) acting *on* one square meter;

$$1 \text{ pa} = \frac{1N}{1\,m^2}$$

$$= \frac{1\,kg.m/s^2}{1\,m^2} = 1\,kg/\text{m.s}^2$$

The chemist, however, usually measures gas pressures by relating them to the pressure of the atmosphere.

A barometer is used to measure the pressure that the atmosphere exerts on the surface of the earth. This instrument was devised in the seventeenth century by Evangelista Torricelli, a pupil of Galileo. A tube, approximately 850 mm in

Figure (1) Barometer

length and sealed at one end, is filled with mercury and inverted in an open container of mercury (Figure 1) The mercury falls in the tube but does not completely run out. The pressure of the atmosphere on the surface of the mercury in the dish supports the column of mercury in the tube.

The space above the mercury inside the tube is a nearly perfect vacuum. Since mercury is not very volatile at room temperature, only a negligible amount of mercury vapor occupies this space. Therefore, practically no pressure is exerted on the upper surface of the mercury in the column. The pressure inside the tube and above the reference level shown in Figure (1) results from the weight of the mercury column alone. This pressure is equal to the atmospheric pressure outside the tube and above the reference level.

The height of mercury in the tube serves as a measure of the atmospheric pressure. When the atmospheric pressure rises, it pushes the mercury higher in the tube. Remember that pressure is force per unit area. Whether the tube has a relatively large or small cross-sectional area, a given atmospheric pressure will support the mercury in the tube to the same height.

The pressure of the atmosphere changes from day to day and from place to place. The average pressure at sea level supports a column of mercury to a height of 760 mm; this value is called 1 atmosphere (abbreviated atm). The definition of the standard atmosphere, however, is given in terms of the pascal:

$$1 \text{ atm} = 101325 \text{ Pa} - 101.325 \text{ kPa}$$

The pressure equivalent to a height of 1 mm of mercury is called 1 lorr (named for Torricelli); therefore,

$$1 \text{ atm} = 760 \text{ torr}$$

The International Committee of Weights and Measures recommends that pressures not be recorded in torrs. The preceding relationship can be used to convert readings made in terms of the height of a mercury column (in torrs) into atmospheres.

A manometer, a device that is used to measure the pressure of a sample of a gas, is patterned after the barometer. The type of manometer shown in Figure 8.2 consists of a U tube containing mercury. One arm of the U tube is open to the atmosphere; atmospheric pressure is exerted on the mercury in this arm. The other arm is connected to a container of a gas in such a way that the gas exerts pressure on the mercury in this arm.

If the gas sample were under a pressure equal to atmospheric pressure, the mercury would stand at the same level in both arms of the U tube. In the experiment illustrated in Figure 8.2, the gas pressure is greater than atmospheric pressure. The difference in height between the

Figure (2) A type of manometer

two mercury levels (in mm of mercury) must be added to the barometric pressure (in mm of mercury or in torr) to obtain the pressure of the gas (in mm of mercury or in torr). If the pressure of the gas were less than atmospheric, the mercury in the left arm of the manometer shown in Figure 8.2 would stand at a higher level than the mercury in the right arm, and the difference in height would have to be subtracted from atmospheric pressure.

2. Boyle's Law

The relationship between the volume and the pressure of a sample of a gas was studied by Robert Boyle in 1662. Boyle found that increasing the pressure on a sample of a gas couses the volume of the gas to decrease proportionately. If the pressure is doubled, the volume is cut in half. If the pressure is increased threefold, the volume is decreased to one-third its original value. Boyle's law states that at constant temperature the volume of a sample of gas varies inversely with the pressure.

$$V \propto \frac{1}{P}$$

The proportionality can be changed into an equality by the introduction of a constant, k:

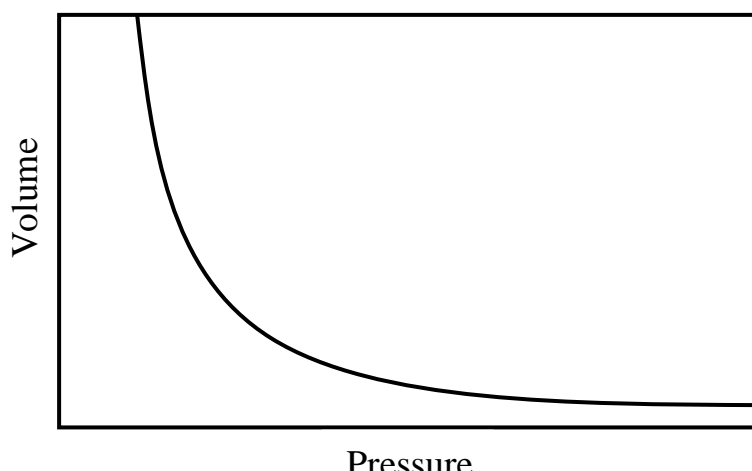$$V = \frac{1}{P} \quad \text{or} \quad PV = k$$

Figure 3:Pressure-volume curve for an ideal gas(Boyle`s law)

The value of the constant depends upon the size of the sample and the temperature. Pressure volume data for an ideal gas are plotted in Figure (3). The volume of a gas is customarily measured in liters. The liter is defined as 1 cubic decimeter ($1 dm^3 = 1000 cm^3$). Since there are 1000 ml in 1 liter, I ml is $1 cm^3$.

Example 1.

A sample of a gas occupies 360 ml under a pressure of 0.750 atm. If the temperature is held constant, what volume will the sample occupy under a pressure of 1.000 atm?

Solution

First, we tabulate the data given in the problem:

Initial conditions: $V = 360$ ml $P = 0.750$ atm

Final conditions: $V = ?$ ml $P = 1.000$ atm

The final volume can be obtained by correcting 'the initial volume for the change in pressure. The units sought are the same as the units of the quantity given:

? ml — 360 ml (pressure correction)

Correction factors are *not* the same as *conversion* factors. A correction factor is not equal to 1. We can derive two pressure-correction factors from the data given:

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(1.000 atm/0.750 atm)   (0.750 atm/1.000 atm)

Which one should be used?

Since the pressure *increases* from 0.750 atm to 1.000 atm, the volume must *decrease*. The correction factor must be a fraction less than 1, Hence,

? ml = 360 ml $\left(\frac{0.750\ atm}{1.000\ atm}\right)$ 270 ml

Example (2)

At 0°C and 5.00 atm, a given sample of a gas occupies 75.0 liter. The gas is compressed to a final volume of 30.0 liter at 0°C. What is the final pressure?

Initial conditions: V = 75.0 liter   P = 5.00 atm   t = 0°C

Final conditions: V = 30.0 liter   P = ? atm   t = 0°c

The initial pressure must be corrected for the volume change. The temperature is constant, so no temperature correction is necessary:

? atm = 5.00 atm (volume correction)

Volume and pressure are inversely related. Since the volume decreases, the pressure must increase. The volume-correction factor must be a fraction greater than I. We put the larger volume measurement in the numerator of the factor:

?atm = 5.00atm $\left(\frac{75.0\ liter}{30.0\ liter}\right)$ 12.5 atm .

 3 Charles' Law

The relationship between the volume and the temperature of a gas sample was studied by Jacques Charles in 1787. His work was considerably extended by Joseph Gay-Lussac in 1802.

A gas expands when it is heated at constant pressure. Experimental data show that for each Celsius degree rise in temperature, the volume of a gas increases 1/273 of its value at 0°C if the pressure is held constant. A

sample of a gas that has a volume of 273 ml at 0°C would expand 1/273 of 273 ml, or 1 ml, for each degree rise in temperature. At 1°C, the volume of the sample would be 274 ml. At 10^0C, the volume would have increased by 10 ml to a value of 283 ml. At 273°C, the sample would have expanded 273 ml to a volume of 546 ml, which is double the original volume. These data are recorded in Table (1).

Although the volume increases in a regular manner with increase in temperature, the volume is *not* directly proportional to the Celsius temperature. An increase in temperature from 1°C to 10°C, for example, does not increase the volume tenfold but only from 274 ml to 283 ml. An absolute temperature scale, with temperatures measured in kelvins, is defined in such a way that volume *is* directly proportional to kelvin temperature.

Table 1: The variations of volume with the

Volume	Temperature	
(ml)	ºC	K
273	0	273
274	1	274
283	10	283
546	273	546

A kelvin reading (denoted by *T)* is obtained by adding 273 to the Celsius temperature (denoted by t)

T = t + 273

Note that absolute temperatures are given in kelvins (abbreviated K), not degrees kelvin, and that the degree sign is not used in the abbreviation. Absolute *it* peratures are listed in the last column in Table (1).

The fact that volume is directly proportional to absolute temperature readily recognized from the data in Table 8.1 since the volume was selectee point up this relationship. For example, when the absolute temperature is doubles (273 K to 546 K), the volume doubles (273 ml to 546 ml). The volume of any sample of a gas varies directly with *absolute* temperature if the pressure is he constant. This generalization is known as Charles' law:

$$V \propto T$$

$$V = kT$$

The numerical value of the proportionality constant k depends upon the pressure and the size of the gas sample.

The absolute temperature scale was first proposed by William Thorns; Lord Kelvin, in 1848; the unit is named in his honor. Any absolute measures scale must be based on a zero point that represents the complete absence of property being measured. On scales of this type, negative values are impossible A length given in centimeters is an absolute measurement since 0cm represent the complete absence of length. One can say that 10cm is twice 5 cm because these are absolute measurements.

The Celsius temperature scale is not an absolute scale. The zero point, 0°C is the freezing point of water, not the lowest possible temperature, Negative Celsius temperatures are possible, and doubling the Celsius temperature of sample of a gas does not double the volume of the gas. On the other hand, the kelvin scale is absolute: 0 K is the lowest possible temperature, and negative kelvin temperatures are as impossible as negative lengths or negative volumes. Doubling the kelvin temperature of a sample of gas doubles the volume.

If volume versus temperature is plotted for a sample of a gas, a straight line results Figure (4). Since volume is directly proportional to

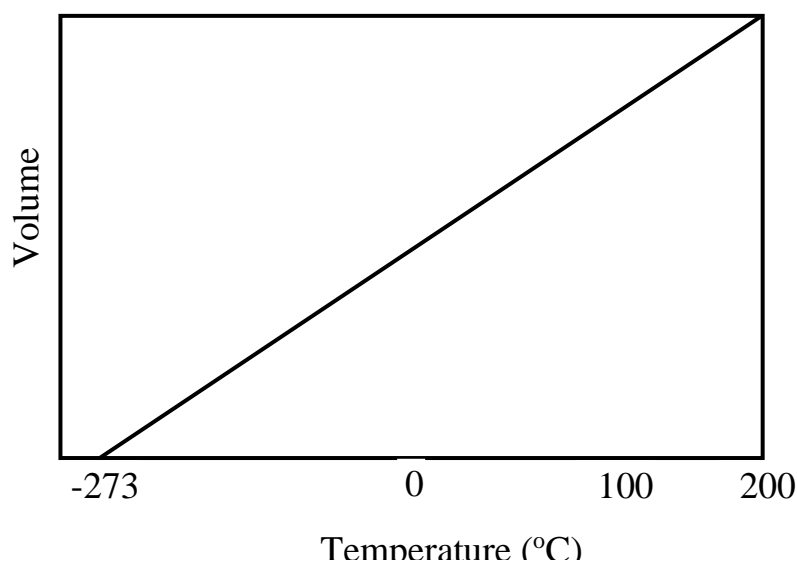absolute temperature the volume of the gas *theoretically* should be zero at absolute zero.

Figure 4:Temperature-volume curve for an ideal gas(Charles`s law)

Upon cooling, gases liquefy and then solidify before temperatures this low are reached. No substance exists as a gas at a temperature near absolute zero. The straight line temperature-volume curve, however, can be extended to a volume of zero.

The temperature that corresponds to zero volume is 273.15^0C. The kelvin is the same size as the: Celsius degree, but the zero point of the keivin scale is moved to 273.15°C. Exact conversion of a Celsius temperature into kelvins can be accomplished, therefore, by adding 273.15 to the Celsius reading:

$$T = t + 273.15 \tag{3}$$

For most problem work, this value can be rounded off to 273 without introducing significant error.

Example 3.

A sample of a gas has a volume of 79.5 ml at 45°C What volume will the sample occupy at 0°C when the pressure is held constant?

Solution

We tabulate the data given in the problem. The Celsius temperatures *(t)* are converted into absolute temperatures *(T): T=* t + 273,

Initial conditions: $V = 79.5$ ml $t = 45°C$ T = 318 K

Final conditions; $V = ?$ ml $t = 0°C$ *T* = 273 K

Therefore,

? ml = 79.5 ml (temperature correction)

Since the temperature decreases from 318 K to 273 K, the volume must decrease. A correction factor with a value less than 1 must be used:

? ml = 79.5 ml $\left(\frac{273\ k}{318\ k}\right) = 68.2$ml

(4) Amontons' Law

The pressure of a gas confined in a container increases when the gas is heated. The mathematical relationship between pressure and temperature is similar to that between volume and temperature. The pressure of a gas varies directly with *absolute* temperature when the volume is constant:

$P \propto T$

$P = kT$ (4)

In this instance the value of *k* depends upon the amount of gas considered and its volume.

This generalization is sometimes called **Amontons' law.** In 1703, Guillaume Amontons constructed an air thermometer based on the principle that the pressure of a gas is a measure of the temperature of the gas.

Example 4.

A 10.0 liter container is filled with a gas 10 a pressure of 2.00 atm at 0°C. At what temperature will the pressure inside the container be 2.50 atm?

Solution

Initial conditions V = 10.0 liter P = 2,00 atm   T = 273 K

Final conditions: V = 10.0 liter P = 2.50 atm T = ? K

No volume correction is needed since the volume is constant. All temperatures] must be expressed in kelvins in any gas problem. Therefore, ? K — 273 K (pressure correction)

Pressure varies directly with absolute temperature. The temperature must increase] to produce the increase in pressure observed. A factor greater than 1 must be used :

$$? K = 273 \text{ k } \left(\frac{2.50 \text{ } atm}{2.00 \text{ } atm} \right) = 341 \text{ K}$$

The answer can then be converted to the Celsius scale:

$t = T - 273$

  = 341 K - 273 K - 68°C

5. Ideal Gas Law

The volume of a gas, at fixed temperature and pressure, Varies directly with the number of moles of gas considered. Obviously, 1 mol of gas (a gram molecular weight) occupies half the volume that 2 mo! occupy when the temperature and pressure of both samples are the same. Furthermore, the volume of I mol of a given gas is the game as the volume of 1 mol of any other gas if the volumes are measured at the same temperature and pressure (Avogadro's principle, described in Section 8.8), If M is the number of moles of gas,

$V \propto n$ or $V = kn$

The Correction Factor Method for Solving Gas Law Problems

1. Tabulate the data given in the problem. List the *initial conditions (V, P,* and t) and the *final conditions (V, P,* and *t).*

2. Convert temperature readings that are given in degrees Celsius *(t)* into kelvins *(T). T = t + 273.15.* For most problem work 273 is acceptable.

3. The solution consists of finding the *final* value of one of the three variables (V, P or T) by correcting the *initial* value of this variable. Multiply the initial value by correction factors to correct for changes in the other two variables.

4. Consider each correction separately. A correction factor consists of a fraction derived from the initial and final values of the same variable *(V, P,* or T). One of these values is placed in the numerator of the factor, the other in the denominator. Two fractions, therefore, can be derived—one numerically greater than 1, the other, less than 1. Decide whether the change being considered should result in an increase or a decrease in the value being corrected. On this basis, select the fraction to be employed as the correction factor.

5. Since the units in the numerator and denominator of a correction factor are the same, they cancel. The answer has the same units as the value being corrected.

6. If a temperature is sought, it will be obtained in kelvins. The Celsius equivalent may be found at the end of the process: *t = T — 273.15.*

The numerical value of the proportionality constant, *k,* depends upon the temperature and pressure of the gas.

The relationship can be combined with expressions for Boyle's law and Charles' law to give a general equation relating volume, temperature, pressure, and number of moles. Volume is inversely proportional to pressure and directly proportional to absolute temperature and to number of moles:

$$V \propto \frac{1}{P} \quad V \propto T \quad V \propto n$$

Therefore,

$$V \propto \left(\frac{1}{P}\right)(T)(n)$$

The proportionality can be changed into an equality by the use of a constant. In this case, the constant is given the designation *R:*

$$V = R \left(\frac{1}{P}\right) (T) (n)$$

Rearrangement gives

Table 2: The different values of gas constant (R)

R	Units
8.2056×10^{-2}	liter-atm/(K-mol)
8.3143×10^3	liter-Pa/(K-mol)
8.3143	J/(K.mol)

$$PV = nRT$$

Under ordinary conditions of temperature and pressure, most gases conform well to the behavior described by this equation. Deviations occur, however, under extreme conditions (low temperature and high pressure). A hypothetical gas that follows the behavior described by the equation exactly, under all conditions,, is called an ideal gas. The equation is known, therefore, as the equation of state for an ideal gas.

By convention, standard temperature and pressure (STP) are defined as 0°C (which is 273,15 K) and exactly 1 atm pressure. The volume of 1 mol of an ideal gas at STP, derived from experimental measurements, is 22.4136 liter. These data can be used to evaluate the ideal gas constant, R. Solution of the equation of state for R yields

$$R = \frac{PV}{nT}$$

Substitution of the data for the STP molar volume of an ideal gas gives

$$R = \frac{(\text{latm})(22.4136 \text{ liter})}{(\text{lmol})(273.15K)} = 0.082056 \text{ liter.atm/(K.mol)}$$

When this value of R is employed, volume must be expressed in liters, pressure in atmospheres, and temperature in kelvins. Values of R in other units appear in Table 2.

The number of moles of gas in a sample, n, is equal to the mass of the sample g, divided by the molecular weight of the gas, M:

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

Substitution of (g/M) for n in PV = nRT gives

$$PV = \left(\frac{g}{M}\right) RT$$

Many problems can be solved by use of this form of the equation of st

Example 5 .

The volume of a sample of a gas is 462 ml at 35°C and 1.15 atm. Calculate the volume of the sample at STP.

Solution

Initial conditions: V = 462 ml   T = 308 K   P = 1.15 atm

Final conditions: V = ?ml   T = 273 K   P = 1.00 atm

The correction factor approach can be used to solve the problem:

? ml = 462 ml (temperature correction)(pressure correction)

Each of these corrections is considered separately. First, the decrease in temperature, from 308 K to 273 K, causes the volume to decrease by a factor of (273 K/ 308 K). Second, the decrease in pressure, from 1.15 atm to 1.00 atm, causes the volume to increase by a factor of (1.15 atm/1.00 atm) since pressure and volume are inversely related:

$$?ml = 462 \text{ ml} \left(\frac{273\ k}{308\ k}\right) \left(\frac{1.15\ atm}{1.00\ atm}\right) = 471 \text{ ml}$$

Example 6

At what pressure will 0.250 mol of N_2(g) occupy 10.0 liter at 100°C?

Solution

P = ? atm   V = 10.0 liter   n = 0.250 mol   T = 373 K

Problems in which only one set of conditions are stated are readily solved by substitution in the equation of state:

PV = nRT

P(10.0 liter) = (0.250 mol)[0.0821 liter. atm/(K.mol)](373 K)

P = 0.766 atm

Example 8.7

How many moles of CO are present in a 500 ml sample of CO(g) collected at 50°C and 1.50 atm?

Solution

The units of the values substituted into PV = nRT must correspond to the units in which R is expressed. Therefore, we express the volume in liters and the temperature m kelvins:

$PV = nRT$

(1.50 atm)(0.500 liter) = n[0.0821] liter atm/(K.mol)](323 K)

$n = 0.0283$ mol

Example 8.

What volume will 10.0 g of CO_2(g) occupy at 27°C and 2.00 atm?

Solution

The problem can be solved in one step if *(g/M) is* substituted for *n* in the equation of state. The molecular weight of CO_2 is 44.0:

$PV = \left(\dfrac{g}{M}\right) RT$

$(2.00\text{atm})V = \left(\dfrac{10.0\ g}{44.0\ g/mol}\right) [0.0821 \text{ liter.atm/(K.mol)}](300 \text{ K})$

V = 2.80 liter

Example 9

What is the density of $NH_3(g)$ at 100°C and 1.15 atm ?

Solution

The density of a gas is the number of grams of gas in 1 liter. We can find the density, therefore, by setting V equal to 1.00 liter and solving for g. The molecular weight of NH_3 is 17.0:

$$PV= \left(\frac{g}{M}\right) RT$$

(1.15 atm)(I.00 liter) $= \left(\frac{g}{17.0g/mol}\right)$ [0.0823 liter.atm/(K.mol)l(373 K)

$g = 0.638$ g

The density is 0.638 g/liter.

Example 10.

(a) Cyclopropane is a gas that is used as a general anesthetic. The gas has a density of 1.50 g/liter at 50°C and 0.948 atm. What is the molecular weight of cyclopropane?

(b) The empirical formula of cyclopropane is CH_2. What is the molecular formula of the compound?

Solution

(a) Since the; density is 1.50 g/liter, 1.50 g of the gas will occupy 1.00 liter under the conditions specified:

$$PV= \left(\frac{g}{M}\right) RT$$

(0.948 atm)(l.00 liter) $= \left(\frac{1.50g}{M}\right)$ [0.082I liter-atm/(K-mol)](323 K)

$M = 42.0$g/mol

(b) The formula weight of the empirical formula, CH_2, is 14.0. If we divide this formula weight into the molecular weight, we get (42.0/14.0) = 3. There are, therefore, three times as many atoms in the molecule as are indicated by the empirical formula. The molecular formula of cyclopropane is C_3H_6.

6. Kinetic Theory of Gases

The kinetic theory of gases provides a model to explain the regularity that is observed in the behavior of all gases. In 1738, Daniel Bernoulli explained Boyle's law by assuming that the pressure of a gas results from the collisions of gas molecules with the walls of the container. Bernoulli's explanation constitutes an early, and simple, expression of key aspects of the kinetic theory. The theory was enlarged and developed in the middle of the nineteenth century by many scientists, notably Kronig, Clausius, Maxwell, and Boltzmann.

The kinetic theory of gases includes the following postulates:

1. Gases consist of molecules widely separated in space. The actual volume of the individual molecules is negligible in comparison to the total volume of the gas as a whole. The word molecule is used here to designate the smallest panicle of any gas; some gases (for example, the noble gases) consist of uncombined atoms.

2. Gas molecules are in constant, rapid, straight-line motion; they collide with each other and with the walls of the container. Although energy may be transferred from one molecule to another in these collisions, no kinetic energy (which is energy of motion) is lost.

3. The average kinetic energy of the molecules of a gas depends upon the temperature, and it increases as the temperature increases. At a given temperature, the molecules of all gases have the same average kinetic energy.

4. The attractive forces between gas molecules are negligible.

The gas laws can be explained by the kinetic theory. Consider Boyle's law. According to the theory, gas pressure is caused by molecular collisions with the walls of the container. If the number of molecules per

unit volume (the molecular concentration) is increased, a higher pressure will result because of the larger-number of collisions per unit time. Reducing the volume of a gas crowds the molecules into a smaller space, which produces a higher molecular concentration and a proportionally higher pressure.

Charles' law and Amontons' law relate the properties of gases to changes in temperature. The average kinetic energy of the molecules of a gas is proportional to the absolute temperature. At absolute zero, the kinetic energy of the molecules is theoretically zero; the molecules are at rest. Since the volume of the molecules of an ideal gas is negligible, the volume of an ideal gas at absolute zero is theoretically zero.

As the temperature is increased, the molecules move at increasing speeds. The collisions of the gas molecules with the walls of the container become increasingly more vigorous and more frequent. As a result, the pressure increases in the manner described by Amontons' law.

The pressure of a gas that is being heated can be held constant if the gas is allowed to expand. The increasing volume keeps the pressure constant by reducing the number of collisions that the molecules make with the container walls in a given time. In this way, the decreasing frequency of the collisions compensates for the increasing intensity of the collisions. Charles1 law describes this situation.

Derivation of the Ideal Gas Law from the Kinetic Theory

The equation of state for an ideal gas may be derived as follows. Consider a sample of gas that contains N molecules that have a mass of m each. If this sample is enclosed in a cube /cm on a side, the total volume of the gas is l^3 cm^3. Although the molecules are moving in every possible direction, the derivation is simplified if we assume that one-third of the molecules ($\frac{1}{3}$N) are moving in the direction of the x axis, one-third in the

y direction, and one-third in the 2 direction. For a very large number of molecules, this is a valid simplification since the velocity of each molecule may be divided into an x component, a y component and a z component.

The pressure of the gas on any wall (surface area l^2 cm^2) is due to the impacts of the molecules on that wall. The force of each impact can be calculated from the change in momentum per unit time. Consider the shaded wall in Figure (5) and take into account only those molecules moving in the direction of the x axis. A molecule moving in this direction will strike this wall every 2 x /cm of its path, since after an impact it must go to the opposite wall (a distance of /cm) and return (a distance of /cm) before the next impact. If the molecule is moving with a velocity of μ cm/s, in one second it will have gone μ cm and have made μ/2/ collisions with the wall under consideration.

Momentum is mass times velocity. Before an impact, the momentum of the molecule is mu; after an impact, the momentum is -mu (the sign is changed because the direction is changed—velocity takes into account speed and direction). Therefore, the change in momentum equals 2 mu.

In one second a molecule makes μ/2/ collisions, and the change in momentum per collision is 2mu, Therefore, in one second the total change in momentum per molecule is

$$\frac{\mu}{2l} \ 2mn \ = \frac{m\mu^2}{l}$$

The total change in momentum (force) for all of the molecules striking the wail in one second is:

Figure 5: Derivations of the ideal gas law

$$\frac{N}{3} \; X \; \frac{m\mu^2}{l}$$

In this expression, μ^2 is the average of the squares of all the molecular velocities. Pressure is force per unit area, and the area of the wall is l^2 cm^2. Therefore, the pressure on the wall under consideration is

Nmu2 1 Nmu1

$$p = \frac{Nm\mu^2}{3l} \; X \; \frac{1}{l^2} \; = \frac{Nm\mu^2}{3l^3}$$

Since the volume of the cube is l^3 cm^3, $V = l^3$, and

$$P = \frac{Nm\mu^2}{3V} \quad \text{or} \quad PV \; = \; \tfrac{1}{3} \, Nm\mu^2$$

This equation can be written

$$PV = (\tfrac{2}{3}N) \, (\tfrac{1}{2} \, m\mu^2)$$

The kinetic energy of any body is one-half the product of its mass times the square of its speed. The average molecular kinetic energy, therefore, is ($\tfrac{1}{2} \, m\mu^2$). By substitution:

$$PV = (\tfrac{2}{3}N(KE)$$

The average molecular kinetic energy. KE, is directly proportional to the absolute temperature, T; the number of molecules, N, is proportional to the number of moles, n. Substitution of these terms requires the inclusion of a constant since these are proportionalities, not equalities. The required constant can be combined with the $\tfrac{2}{3}$ (also a constant); thus,

$$PV = nRT \hspace{5cm} (6)$$

8.3 Gay-Lussac's Law of Combining Volumes and Avogadro's Principle

In 1808, Joseph Gay-Lussac reported the results of his experiments with reacting gases. When measured at constant temperature and pressure, the volumes of gases that are used or produced in a chemical reaction can be expressed in ratios of small whole numbers. This statement is called Gay-Lussac's law of combining volumes.

One of the reactions that Gay-Lussac studied is the reaction in which hydrogen chloride gas is produced from hydrogen gas and chlorine gas. If the volumes of all the gases are measured at the same temperature and pressure,

1 volume hydrogen + 1 volume chlorine → 2 volumes hydrogen chloride

For example,

10 liter hydrogen + 10 liter chlorine → 20 liter hydrogen chloride

Gay-Lussac did not know the formulas for these substances and did not chemical equations. The volume ratio, however, is given by the coefficient. the gases in the chemical equation

$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$
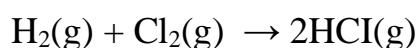
The law is applicable only to gases. The volumes of solids and liquids cannot be treated in this way.

The explanation for the law of combining volumes was proposed in 1811 by Amedeo Avogadro. Avogadro's principle states: equal volumes of all gases at the same temperature and pressure contain the same number of molecules.

Gay-Lussac's data show that equal volumes of $H_2(g)$ and $Cl_2(g)$ react. Since the reaction requires equal numbers of H_2 and Cl_2 molecules, a given volume of either gas must contain the same number of molecules. According to Gay-Lussac, the volume of $HCl(g)$ produced is twice the

volume of $H_2(g)$ used. The equation shows that the number of HCI molecules produced is twice the number of H_2 molecules used. We conclude that the number of HCI molecules in a "volume" is the same as the number of H_2 molecules in a "volume." The same comparison can be made between HCI and Cl_2.

The total volume of the reacting gases need not equal the volume of the gases produced. This fact is illustrated by another of Gay-Lussac's examples:

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$
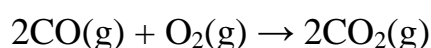
The volume ratio for this reaction is

2 volumes $CO(g)$ + 1 volume $O_2(g) \rightarrow$ 2 volumes $CO_2\{g)$
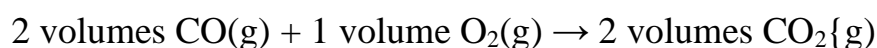
The relative numbers of molecules involved in the reaction are given by the chemical equation. If we take *2x CO* molecules, then

2x molecules $CO(g)$ + *x* molecules $O_2(g) \rightarrow$ 2v molecules $CO_2(g)$

By comparing these two statements, we see that one "volume" of any of the gases contains the same number of molecules, *x.*

Example 11

(a) What volume of oxygen is required for the complete combustion of 15.0 liter of ethane, $C_2H_6(g)$, if all gases are measured at the same temperature and pressure according to the following equation:

$$2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(g)$$
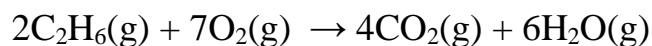
(b) What volume of carbon dioxide gas is produced?

Solution

(a) The relationship between the volume of $C_2H_6(g)$ and the volume of $O_2(g)$ is given by the coefficients of the chemical equation

2 liter C_2H_6 = 7 liter O_2

This relationship is used to derive a conversion factor:

? liter O_2 = 15.0 liter C_2H_6 $\left(\dfrac{7\ liter\ O_2}{2\ liter\ C_2\ H_6}\right)$ = 52.5 liter O_2

(b) In this case, the relationship is

2 liter C_2H_6 = 4 liter CO_2

Therefore,

?literCO_2 = 15.0 liter C_2H_6 $\left(\dfrac{4\ liter\ CO_2}{2\ liter\ C_2\ H_6}\right)$ = 30.0 liter CO_2

According to Avogadro's principle, equal volumes of any two gases at the same temperature and pressure contain the same number of molecules. Conversely, equal numbers of molecules of any two gases under the same conditions of temperature and pressure will occupy equal volumes. A mole of a substance contains 6.022 x 10^{23} molecules (Avogadro's number). A mole of a gas, therefore, should occupy the same volume as a mole of any other gas if they are both measured under the same conditions of temperature and pressure. At STP this volume, called the STP molar volume of a gas, is 22.414 liters. The molecular weight of a gas, therefore, is the mass, in grams, of 22.4 liter of the gas at STP. For most gases, the deviation from this ideal is; less than 1%.

The STP molar volume of a. gas can be used to solve some probkms. All such calculations, however, can also be made by using the equation of state, $P\ V = nR\ T$.

Example (12)

What is the density of fluorine gas, $F_2(g)$, at STP?

Solution

The molecular weight of F_2 is 38.0:

1 mol F_2 = 38.0 g F_2

At STP the volume of a mole of any gas is 22.4 liter:

1 molF_2 = 22.4 liter F_2

Therefore,

? g F_2 = 1 liter F_2 $\left(\frac{1\ mol\ F_2}{22.4\ liter\ F_2}\right)\left(\frac{38.0\ g\ F_2}{1\ mol\ F_2}\right)$ 1.70 g F_2.

The density is 1.70 g/liter.

Example 13

What is the molecular weight of a gas that has a density of 1.34 g/liter at STP?

Solution

? g = 1 mol $\left(\frac{22.4\ liter}{1\ mol}\right)\left(\frac{1.34\ g}{1\ liter}\right)$ 30.0g

The molecular weight of the gas is 30.0 g/mol.

9 Stoichiometry and Gas Volumes

Stoichiometric problems may be based on the volumes of gases that are involved in a chemical reaction. Gay-Lussac's law of combining volumes is used to solve problems that deal with the volumes of two gases (see Section 8.8). Some problems concern the relationship between the volume of a gas and the mass of another substance. Examples of this type of problem follow. The clue to their solution is as usual, the mole.

Example 14

A 0.400 g sample of sodium azide, NaN_3(s), is heated and decomposes:

$2NaN_3(s) \rightarrow 2Na(s) + 3N_2(g)$

What volume of N_2(g), measured at 25°C and 0.980 atm, is obtained?

Solution

We find the number of moles of NaN_3 in the sample. Since

1 molNaN_3 = 65.0gNaN_3

? mol NaN_3 = 0.400 g NaN; $\left(\frac{1\ mol\ NaN_3}{65.0\ g\ NaN_3}\right)$ 0.00615 mol NaN_3

From the chemical equation, we derive
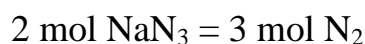
2 mol NaN_3 = 3 mol N_2

Therefore,

? mol N_2 = 0.00615 mol NaN_3 $\left(\frac{3 \ molN_2}{2 \ mol \ NaN_3}\right)$ = 0.00923 mol N_2

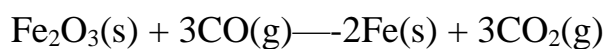We find the volume of $N_2(g)$ by using the equation of state:

$PV = nRT$

(0,980 atm) V = (0.00923 mol)[0.0821 liter atm/(K.mol)](298 K)

V = 0.230 liter

Example 15

How many liters of CO(g), measured at STP, are needed to reduce 1.00 kg of $Fe_2O_3(s)$? The chemical equation is

$Fe_2O_3(s) + 3CO(g)$——$2Fe(s) + 3CO_2(g)$

Solution

We first find the number of moles of Fe_2O_3 in 1000 g of Fe_2O_3. Since

1 mol Fe_2O_3 = 159.6 g Fe_2O_3

? mol Fe_2O_3 = 1000 g Fe_2O_3 $\left(\frac{1 \ mol \ Fe_2O_3}{159.6 \ g \ Fe_2O_3}\right)$ = 6.27 mol Fe_2O_3

From the equation, we see that

1 mol Fe_2O_3 = 3 mol CO

Therefore,

? mol CO - 6.27 mol Fe_2O_3 $\left(\frac{3 \ mol \ CO}{1 \ mol \ Fe_2O_3}\right)$ = 18.8 mol CO

At STP,

1 mol CO - 22.4 liter CO

Therefore,

? liter CO - 18.8 mol Co $\left(\frac{22.4 \ liter \ CO}{1 \ mol \ CO}\right)$ = 42l liter CO

The last step could have been solved by using the equation of state:

$PV = nRT$

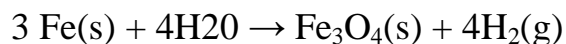(1 atm) V = (18.8 mol)[0.0821 liter.atm/(K-mole)](273 K)

V = 421 liter

Example 16

How many grams of Fe are needed to produce 100 liter of $H_2(g)$, measured at STP? The equation is

$3\ Fe(s) + 4H20 \rightarrow Fe_3O_4(s) + 4H_2(g)$

Solution

First, the number of moles of H_2 is found. At STP,

1 mol H_2 = 22.4 liter H_2

?mol H_2 = 100 liter H_2 $\left(\dfrac{1\ mol\ H_2}{22.4\ liter\ H_2}\right)$ = 4.46 mol

(The last step could also be accomplished by substituting in PV = nRT.)

From the equation,

3 mol Fe = 4 mol H_2

 we find,

? mol Fe = 4.46 mol H_2 $\left(\dfrac{3\ mol\ Fe}{4\ mol\ H_2}\right)$ = 3.35 mol Fe

The atomic weight of Fe is 55.8, therefore

? g Fe = 3.35 mol Fe $\left(\dfrac{55.8\ g\ Fe}{4\ mol\ Fe}\right)$ = 187 g Fe

Calculations That Are Based on Chemical Equations and That Involve Gas Volumes

The following types of problems may be encountered :

1. A volume of gas A is given and the volume of gas B is sought,

a. The volumes of both gases are measured under the same conditions of temperature and pressure. Use Gay-Lussac's law of combining volumes. (See Example .11.)

b. The volumes of the two gases are measured under different conditions. Use Gay-Lussac's law of combining volumes to find the volume of gas B under the conditions given for gas A. Use correction factors to correct this volume of gas B so that it: conforms to this final conditions given in the problem.

2. A mass of substance A is given and the volume of gas B is sought. a. Find the number of moles of A.

b. Use this number of moles of A to find the number of moles of B. The mole relationship of B to A is .given by the chemical equation,

c. Find the volume of gas B by substituting in PV = nRT; n is the number, of moles found in step (b); P and Tare the conditions under which the vohune of 5 is measured, (See Examples 8.14 and 8.15.)

3. A volume of gas A is given and the mass of substance B is sought.

a. Determine the number of moles of gas A by using PV = nRT

b. Use this number of moles of A to find the number of moles of B. The mole relationship of B to A is given by the chemical equation.

c. find the mass of B from the number of moles of B determined in step (b). One mole of B is the molecular weight of B in grams. (See example 16)

Solutions to problems of types 2 and 3 may be simplified if the gas volumes are measured at STP. The volume of 1 mol of any gas at STP is 22,4 liters. This relationship can be used in steps 2(c) and 3(a) in place of PV = nRT. See examples 15 and 16).

10. Dalton's Law of Partial Pressures

The behavior of a mixture of gases that do not react with one another is frequently of interest. The pressure that a component of such a mixture would exert if it were the only gas present in the volume under consideration is the partial pressure of the component. Dalton's law of partial pressures (1801) states that the total pressure of a mixture of gases that do not react is equal to the sum of the partial pressures of all the gases present. If the total pressure is P_{total}, and the partial pressures are P_A, P_B, P_C,....,

$$P_{total,} = P_A + P_B + P_C + ...$$

Suppose that 1 liter of gas A at 0.2 atm pressure and 1 liter of gas B at 0.4 atm pressure are mixed. If *the final volume is 1 liter* and the temperature is constant, the pressure of the mixture will be 0.6 atm.

According to the kinetic theory, the molecules of gas A have the same average kinetic energy as the molecules of gas B since the two gases are at the same temperature. Furthermore, the kinetic theory assumes that the gas molecules do not attract one another if the gases do not react chemically. Consequently, the act of mixing two or more gases does not change the average kinetic energy of any of the gases. Each gas exerts the same pressure that it would exert if it were the only gas present in the container.

If n_A mol of gas A and n_B mol of gas B are mixed, the total number of moles of gas in the mixture is $(n_A + n_B)$. The ratio of the number of moles of A to the total number of moles present is called the mole fraction of A, X_A:

$$X_A = \frac{n_A}{n_A + n_B} = \frac{n_A}{n_{total}}$$

The fraction of the total pressure that is due to gas A is given by the mole fraction of A. The partial pressure of A, therefore, is

$$P_A \left(\frac{n_A}{n_A+n_B}\right) P_{total} = X_A P_{total}$$

The partial pressure of B is equal to the mole fraction of B times the total pressure :

$$P_B \left(\frac{n_B}{n_A+n_B}\right) P_{total} = X_B P_{total}$$

Notice that the sum of the mole fraction is one:

$X_A + X_B = 1$

$$\frac{n_A}{n_A + n_B} + \frac{n_B}{n_A + n_B} = \frac{n_A + n_B}{n_A + n_B} = 1$$

Suppose that a mixture contains 1 mol of A and 4 mol of B. Then, the total number of moles is five, the mole fraction of A is one-fifth, and the mole fraction of B is four-fifths. The partial pressure of A, therefore, is one-fifth of the total pressure, and the partial pressure of B is four-fifths of the total pressure.

A gas evolved in-the course of a laboratory experiment is frequently collected over water if it is not very soluble in water. The gas is conducted into an inverted bottle that has been filled with water. The gas displaces the water, and the collected gas is mixed with water vapor. The total pressure of the mixture is the sum of the partial pressure of the gas and the partial pressure of the water vapor. In Figure 8.6, the total pressure is equal to the barometric pressure since the water stands at the same level inside the bottle as outside it. The pressure of the dry gas is found by subtracting the vapor pressure of water at the temperature of the experiment (Table 3) from the barometric pressure.

Figure 6: Schematic diagram of the collection of gas over water

Table 3: The vapour pressure of water at different temperatures

Temperature (°C)	Pressure (atm)	(torr)	Temperature (°C)	Pressure (atm)	(torr)
0	0.0060	4.6	25	0.0313	*23.8*
1	0.0065	4.9	26	0.332	25.2
2	0.0070	5.3	27	0.0352	26.7
3	0.0075	5.7	28	0.0373	28.3
4	O0080	6.1	29	0.0395	30.0
5	0.0086	6.5	30	0.0419	31.8
6	0.0092	7.0	31	0.0443	33.7
7	0.0099	7.5	32	0.0470	35.7
8	0.0106	8.0	33	0.0496	37.7
9	0.0113	8.6	34	0.0525	39.9
10	0.0121	9.2	35	0.0555	42.2
11	0.0130	9.8	40	0.0728	55.3
12	0.0138	10.5	45	0.0946	71.9
13	0.0148	11.2	50	0.122	92.5
14	0.0158	12.0	55	0.155	118.0
15	0.0168	12.8	60	0.197	149.4
16	0.0179	13.6	65	0.247	187.5
17	0.0191	14.5	70	0.308	233.7
18	0.0204	15.5	75	0.380	289.1
19	0.0217	16.5	80	0.467	355.1
20	0.0231	17.5	85	0.571	433.6
21	0.245	18.7	90	0.692	525.8
22	0.0261	19.8	95	0.834	633.9
23	0.0277	21.1	100	1.000	760.0
24	0.0294	22.4	105	1.192	906.1

Example 17

A 370 ml sample of oxygen is collected over water at $23°C$ and a barometric pressure of 0.992 atm. What volume would this sample occupy dry and at STP?

Solution

The vapor pressure of water at $23°C$ is 0.0277 atm. Consequently, the initial pressure of the oxygen is

0.992 atm - 0.028 atm = 0.964 atm Therefore,

Initial conditions: $V = 370$ ml $p = 0.964$atm $T = 296$ K

Final conditions: $V = ?$ ml $P = 1.000$ atm $T = 273$ K

$? \text{ ml} = 370 \text{ ml } \left(\frac{0.964 \, atm}{1.000 \, atm}\right) \left(\frac{273 \, K}{296 \, K}\right) = 329 \text{ ml}$

Example 18

A mixture of 40.0 g of oxygen and 40.0 g of helium has a total pressure of 0.900 atm. What is the partial pressure of oxygen?

Solution

The molecular weight of O_2 is 32.0. Forty grams of O_2 is 40.0/32.0, or 1.25, mol of O_2. Helium is a monatomic gas. Its atomic weight is 4.00. Therefore, 40.0/4.0, or 10.0, mol of He is present in the mixture. Therefore,

$X_{O2} = \dfrac{n_{o2}}{n_{o2} + n_{He}}$

$X_{O2} = \dfrac{1.25 \, mol}{(1.25 + 10.0) \, mol} = \dfrac{1.25 \, mol}{11.2 \, mol} = 0.112$

The partial pressure of O_2 is

$P_{o2} = X_{o2}P_{total}$

$= (0.112)(0.900 \text{atm})$

$= 0.101$ atm

11 Molecular Speeds

In Section 7 we derived the expression

$$PV = \tfrac{1}{3}Nmu^2$$

For one mole of a gas, the number of molecules, *N,* is Avogadro's number, and N times the mass of a single molecule, *m,* is the molecular weight, *M:*

$$PV = \tfrac{1}{3}Mu^2$$

Also for one mole, *PV = RT.* thus,

$$RT = \tfrac{1}{3}Mu^2.$$

Rearranging and solving for the molecular speed, we obtain

$$u = \sqrt{3RT}$$

The speed, *u,* In this equation, as in previous equations, is the root-mean-square speed. The value of the root-mean-square speed is obtained by taking the square root of the average of the squares of all of the molecular speeds; it is the speed of a molecule that possesses average kinetic energy at the temperature under consideration.

In order to solve the equation for the root-mean-square speed, *R* must be expressed in appropriate units. If *u* is to be obtained in m/s and *M* is expressed in g/mol, the appropriate value of *R* is 8,3143 x 10^3 g.m^2/(s^2.K-mol). If *M* is expressed in kg/mol, *R* is 8.3143 J/(K-mol).

The speed of a hydrogen molecule that has the average kinetic energy at 0°C is 1.84 x 10^3 m/s. The diffusion of one gas through another gas, however, does not occur this rapidly. Although a given molecule travels at a high speed, its direction is continually being changed through collisions with other molecules. At 1 atm pressure and 0°C a hydrogen molecule, on the average, undergoes about 1.4 x 10^{10} collisions in one second. The average distance traveled between collisions is only 1.3 x 10^{-5} cm; this value is called the mean free path of hydrogen.

Not all of the molecules of a gas have the same kinetic energy and travel at the same speed. Since energy can be exchanged in these collisions, the speed as well as the direction of a molecule changes continually. In any sample of a gas, however, there is a large number of molecules, so that the molecular speeds are distributed over a range in a definite manner.

Distributions of the molecular speeds of a gas, called Maxwell-Boltzmann at two temperatures are shown in Figure 8.7. The fraction of
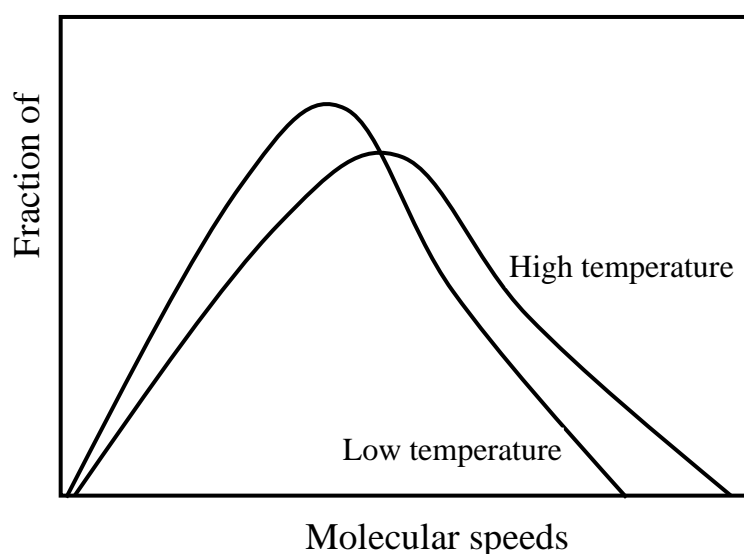

Figure 7:Distribution of molecular speeds

the total number of molecules that has a particular speed is plotted against molecular speed. Each curve has a maximum, and the speed corresponding to the maximum is the most probable speed for that distribution. In other words, more molecules move at this speed than at any other. Comparatively few molecules possess very high or very low speeds.

When the temperature of a gas is increased, the curve broadens and shifts toward higher speeds. Fewer molecules than previously move at the lower speeds and more molecules move at the higher speeds. The addition of heat has caused the molecules, on the average, to move faster.

The speed of a hydrogen molecule that has the average kinetic energy at 0°C is 1.84×10^3 m/s; at 100°C, it is 2.15×10^3 m/s.

A typical curve for the distribution of molecular energies is shown in Figure 8. Distribution curves of this type can be drawn for liquids and solids as well as gases.
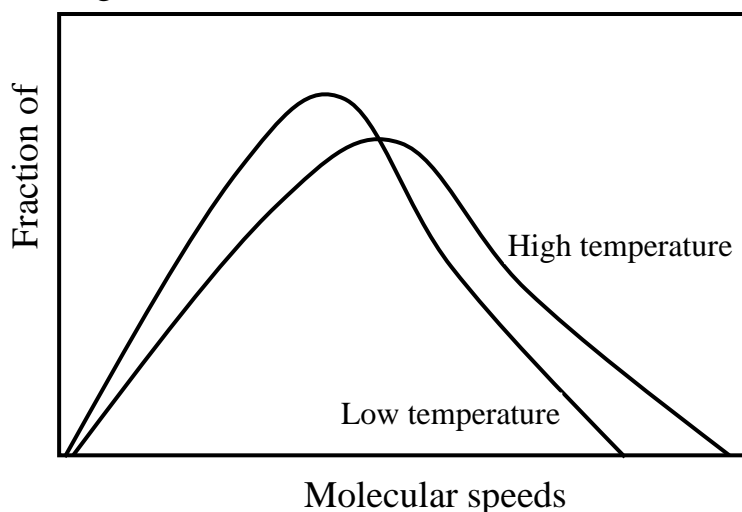

Figure 8:Distribution of molecular speeds

12. Graham's Law of Effusion

Suppose that samples of two gases, A and B, are confined separately in identical containers under the same conditions of temperature and pressure. The kinetic theory of gases states that gases at the same temperature have the same average kinetic energy. The average kinetic energy of the molecules of gas A (KE_A), therefore, is the same as the average kinetic energy of the molecules of gas B (KE_B)

$$KE_A = KE_B$$

The kinetic energy of a body with a mass m moving in a straight line at a constant speed μ is

$KE = \frac{1}{2}mu^2$.

Therefore,

$KE_A = \frac{1}{2}m_A u^2_A$ and $KE_B = \frac{1}{2}m_B u^2_B$

The molecules of gas A (or gas B) do not all move at the same speed. The symbol u_A (as well as u_B) stands for the speed of a molecule that has the average kinetic energy. Since

$$KE_A = KE_B$$

or

$$m_A u^2_A = m_B u^2_B$$

By rearranging the equation, we get

$$\frac{u^2_A}{u^2_B} = \frac{m_B}{m_A}$$

Extracting the square root of both sides of the equation gives us

$$\frac{u_A}{u_B} = \sqrt{\frac{m_B}{m_A}}$$

The ratio of the molecular masses, m_B/m_A, is the same as the ratio of the molecular weights, M_B/M_A. Therefore,

$$\frac{u_A}{u_B} = \sqrt{\frac{M_B}{M_A}}$$

Now let us suppose that each container has an identical, extremely small opening (called an orifice) in it. Gas molecules will escape through these orifices; the process is called molecular effusion. The rate of effusion, r, is equal to the rate at which molecules strike the orifice, which in turn is proportional to molecular speed, u. Molecules that move rapidly will effuse at a faster rate than slower moving molecules. The ratio u_A/u_B, therefore, is the same as the ratio of the effusion rates, r_A/r_B:

$$\frac{r_A}{r_B} \sqrt{\frac{M_B}{M_A}}$$

This equation is an expression of Graham's law of effusion, which Thomas Graham experimentally derived during the period 1828 to 1833.

The relationship may also be expressed in terms of *gas densities.* Since the density of a gas, d, is proportional to the molecular weight of the gas, *M* (see Example 13), Graham's law may also be written

$$\frac{r_A}{r_B} \quad \sqrt{\frac{d_B}{d_A}}$$

It is not surprising that the lighter of two molecules with the same kinetic energy will effuse more rapidly than the heavier one. (Notice the *inverse* relationship.) The molecular weight of O_2 is 32, and the molecular weight of H_2 is 2.

Since

$$\frac{r_{H2}}{r_{O2}} = \sqrt{\frac{M_{O2}}{M_{H2}}}$$

$$\frac{r_{H2}}{r_{O2}} = \sqrt{\frac{32}{2}} = \sqrt{16} = 4$$

Hydrogen will effuse four times more rapidly than oxygen.

Example 19

What is the molecular weight of gas X if it effuses 0.876 times as rapidly as $N_2(g)$?

Solution

The ratio of the rate of effusion of gas X to the rate of effusion of $N_2(g)$ is

$$\frac{r_x}{r_{N2}} = 0.876$$

The molecular weight of N_2 is 28.0. Therefore,

$$\sqrt{\frac{M_{N2}}{M_x}} = \frac{r_x}{r_{N2}}$$

$$\sqrt{\frac{28.0}{M_x}} = 0.876$$

We square both sides of the equation and solve for M_x:

$$\frac{28.0}{M_x} = 0.767$$

$$M_x = \frac{28.0}{0.767} = 36.5$$

13. Real Gases

The gas laws describe the behavior of an ideal or perfect gas a gas defined by the kinetic theory. Under ordinary conditions of temperature and pressure, real gases follow the ideal gas laws fairly closely. At low temperatures and/or high pressures, however, they do not.

For an ideal gas, $PV = nRT$, and hence

$$\frac{PV}{RT} = n$$

If we consider one mole of an ideal gas, $n = 1$, and $PV/RT = 1$. In Figure 9, PV/RT the so called compressibility factor) is plotted against pressure for several gases. The curves for the real gases deviate significantly from that for an ideal gas (a straight line at $PV/RT = 1$). There are two reasons for the deviations.
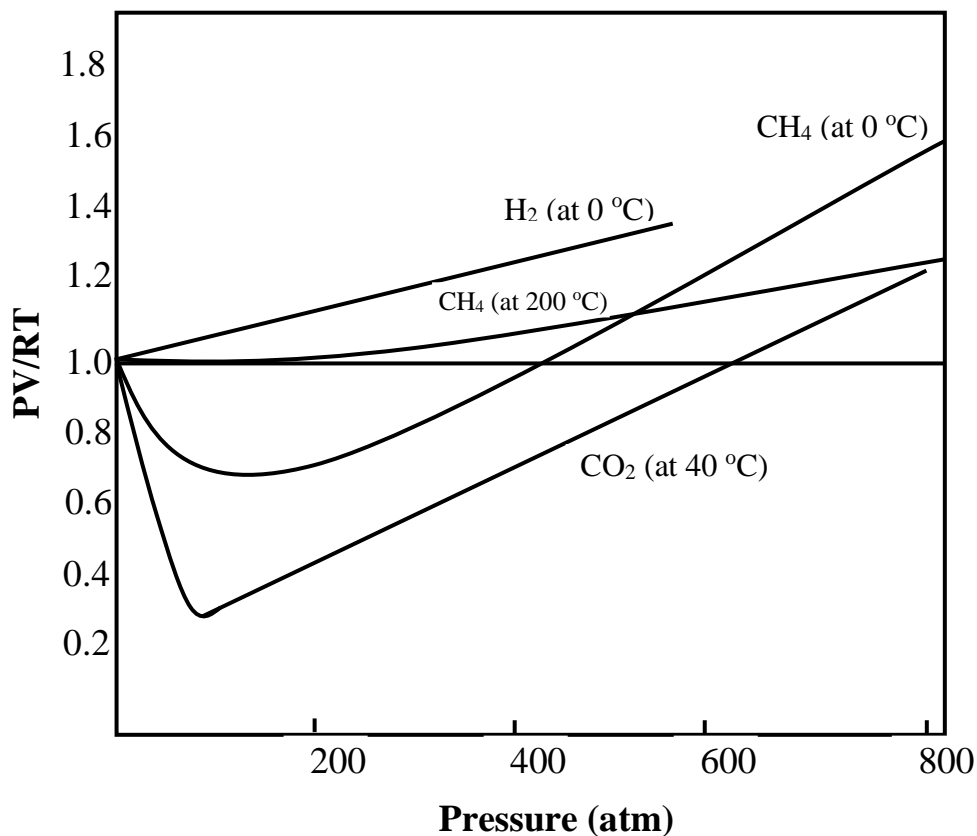

Figure 9:PV/RT versus pressure for several gases at temperatures indicated

1. Intermolecular forces of attraction. The kinetic theory assumes that there are no attractive forces between gas molecules. Such attractions must exist, however, because all gases can be liquefied. Intermolecular attractions hold the molecules together in the liquid state.

If we assume that *P* in the expression *PV/RT is* the applied pressure, a deviation from ideality would be apparent in the measured volume, *V.* Intermolecular forces of attraction *reduce* the volume by pulling the gas molecules together. In this respect, they augment the applied pressure. Furthermore, the higher the applied pressure, the more the effect of intermolecular attractions will be felt since gas molecules are closer together at higher pressures. This factor tends to cause the value *PV/RT* to be *less* than 1.

2. Molecular volume. The kinetic theory assumes that gas molecules are points in space and that the actual volume of the molecules is not significant. At absolute zero, the temperature at which molecular motion stops, therefore, the volume of an ideal gas is zero. Real gases, of course, do not have zero molecular volumes. When the applied pressure is increased, the space between the molecules is reduced, but the molecules themselves cannot be compressed. The result is that the measured volume is *larger* than the volume calculated for an ideal gas, where the molecular volume is neglected. Again, the deviation is more pronounced at higher pressures. The molecules are closer together at higher pressures and the molecular volume is a larger fraction of the total volume. This factor tends to cause the value *PV\RT* to be *greater* than 1.

These two factors operate at the same time and against one another. Which factor predominates depends upon the experimental conditions. In Figure 8.9, those portions of the curves that are *below* the *PVJRT = 1* line correspond to conditions under which the effect of intermolecular

attractive forces is predominant. For those portions that are *above* this line, molecular volume is the predominant effect.

Examine the curves for H_2 (at 0°C), CH_4 (at 0°C), and CO_2 (at 40°C). The curve for CO_2 falls farther below the *PV/RT = 1* line than the curve for any other gas. We conclude that the attractions between CO_2 molecules are greater than those between the molecules of the other gases. Indeed, since the curve for H_2 lies entirely above this line, the forces of attraction between H_2 molecules must be so weak that at 0°C they cause little deviation from ideality.

Compare the curve for CH_4 at 0°C to that for the same gas at 200°C. As a result of intermolecular attractions, part of the curve for CH_4 at 0°C lies below the *PV/RT — * line. The curve for the gas at the higher temperature lies entirely above this line. At high temperatures, gas molecules move so rapidly that the attractive forces between the molecules have little effect. At low temperatures, however, the molecules move more slowly. The attractive forces pull the molecules together so that the observed volume is less than that predicted by the gas law. The curves of Figure 8.9 show, therefore, that real gases follow the ideal gas laws most closely at low pressures and high temperatures.

Johannes van der Waals in 1873 modified the equation of state for an ideal gas to take into account these two effects. The van der Waals equation is

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

The numerical values of the constants *a* and *b* for each gas are determined by experiment. Typical values are listed in Table 8.4.

The term $n^2 a/V^2$ is added to the measured pressure, *P,* to correct for the intermolecular attractive forces. Pressure is caused by the collisions of the gas molecules with the walls of the container. The effect of a given

collision would be greater if the molecule were not held back by the attraction of other molecules. Consequently, the pressure that is measured is *less* than it would be if these attractive forces did not exist. The term n^2a/V^2 is added to P so that $(P + n^2a/V^2)$ represents the pressure of an ideal gas, one in which there are no molecular forces.

The term (n/V) represents a concentration (mol/liter). If x molecules are confined in a liter, there are $(x - 1)$ ways for a given molecule to collide or interact with another molecule since it cannot collide with itself. This factor applies to all the molecules; therefore, a total of $\frac{1}{2} x(x - 1)$ possible interactions exists for the entire collection of molecules. The fraction $\frac{1}{2}$ is added so that a given interaction is not counted twice—once for each of the molecules entering into it. If a large

Table 4: The values of a, b constants for some gases

	a	b
	$(\text{liter}^2 \text{ atm} / \text{mol}^2)$	$(\text{liter} / \text{mol})$
H_2	0.244	0.0266
He	0.0341	0.0237
N_2	1.39	0.0391
O_2	1.36	0.0318
Cl_2	6.49	0.0562
NH_3	4.17	0.0371
CO	1.49	0.0399
CO_2	3.59	0.0427

number of molecules are present, $(x - 1)$ is approximately equal to x, and the proportionality is $\frac{1}{2}x^2$ to a good approximation. Hence the number of interactions between gas molecules is proportional to the *square* of the concentration. The van der Waals constant a may be regarded as a

proportionality constant (incorporating the 1/2), and the correction term is n^2a/V^2.

The constant *b.* multiplied by n, is subtracted from the total volume of the gas to correct for that portion of the volume that is not compressible because of the intrinsic volume of the gas molecules. A given gas molecule cannot move through the entire volume of the container since other molecules are present. The volume through which they can move can be obtained by subtracting an amount called the excluded volume from the total volume.

If the molecules are assumed to be spherical and have a radius *r,* the excluded volume per molecule is not merely the volume of the molecule, $\frac{4}{3}\pi r^3$. Since the closest approach of *two* molecules is *1r* (Figure 8.10), the excluded volume for *two* molecules is $\frac{4}{3}\pi(2r)^3$ which is $8(\frac{4}{3}\pi r^3)$. For one molecule this volume is $4(\frac{4}{3}\pi r^3)$, which is four times the molecular volume. Hence, for a mole of molecules, *N* molecules.

Figure 10: van der Waals correction, *b.* for excluded volume

14. Liquefaction of Gases

Liquefaction of a gas occurs under conditions that permit the intermolecular attractive forces to bind the gas molecules together in the liquid form. If the pressure is high, the molecules are close together, and

the effect of the attractive forces is appreciable. The attractive forces are opposed by the motion of the gas molecules; thus, liquefaction is favored by low temperatures where the average kinetic energy of the molecules is low. The behavior of a gas deviates more and more from ideality as the temperature is lowered and the pressure is raised. At extremes of these conditions, gases liquefy.

The higher the temperature of a gas, the more difficult it is to liquefy and the higher the pressure that must be employed (Table 8.5). For each gas ther is a temperature above which it is impossible to liquefy the gas no matter how high the applied pressure. This temperature is called the critical temperature of the gas under consideration. The critical pressure is the minimum pressure needed to liquefy a gas at its critical temperature. The critical constants of some common gases are listed in Table 6.

Table 5: Critical temerature at different pressures

Critical temperature (K)	Critical pressure (atm)
5.3	2.26
33.3	12.8
126.1	33.5
134.0	35.0
154.4	49.7
190.2	45.6
304.2	72.8

The critical temperature of a gas gives an indication of the strength of the intermolecular attractive forces of that gas. A substance with weak attractive forces would have a low critical temperature; above this temperature, the molecular motion is too violent to permit the relatively weak forces to hold the molecules in the liquid state. The substances of Table 8.6 are listed in order of increasing critical temperature; the

magnitude of the intermolecular attractive forces (related to the *a* of Table 8.4) increases in this same order. Helium, which has weak attractive forces, can exist as a liquid below 5.3 K only; the strong attractive forces of water permit it to be liquefied up to a temperature of 647.2 K. The critical constants have been used to evaluate the constant of the van der Waals equation.

The data of Table 6 show that it is necessary to cool many gases below room temperature (ca. 295 K) before these substances can be liquefied. Commercial

Table 6: Critical temerature and critical pressures for some gases

Gas	Critical temperature (K)	Critical pressure (atm)
He	5.3	2.26
H_2	33.3	12.8
N_2	126.1	33.5
CO	134.0	35.0
O_2	154.4	49.7
CH_4	190.2	45.6
CO_2	304.2	72.8
NH_3	405.6	111.5
H_2	647.2	217.7

liquefaction procedures make use of the Joule-Thomson effect to cool-gases. When a compressed gas is allowed to expand to a lower pressure, the gas cools. In the expansion, work is done against the intermolecular attractive forces. The energy used in performing this work must be taken from the kinetic energy of the gas molecules themselves; hence, the temperature of the gas decreases. This effect was studied by

James Joule and William Thomson (Lord Kelvin) during the years 1852-1862. The liquefaction of air is accomplished by first allowing cooled, compressed air to expand. The temperature of the air falls to a lower level. This cooled air is used to precool entering compressed air, and the expansion of this compressed air results in the attainment of even lower temperatures. The cooled, expanded air is recycled through the compression chamber. Eventually the cooling and compression produce liquid air.

Chapter 2
Liquids and Solids

The kinetic energies of gas molecules decrease when the temperature is lowered. Consequently, the intermolecular attractive forces cause the gas molecules to condense into a liquid when the gas has been cooled sufficiently. The molecules are closer together and the attractive forces exert a greater influence in a liquid than in a gas. Molecular motion, therefore, is more restricted in the liquid state than in the gaseous state.

Additional cooling causes the kinetic energies of the molecules to decrease further and ultimately produces a solid. In a crystalline solid the molecules assume positions in a crystal lattice, and the motion of the molecules is restricted to vibration about these fixed points.

The comparatively high kinetic energies of gas molecules cause the inter-motecular attractive forces to assume a role that can be minimized in the development of a satisfactory theory of gases. The comparatively low kinetic energies of molecules (or ions) in crystals are easily overcome by the attractive forces to produce highly ordered, crystalline structures that have been well characterized by diffraction techniques. Our understanding of the intermediate state, the liquid state, however, is not so complete as that of the other two states.

1. Intermolecular Forces of Attraction

Atoms are held together in molecules by covalent bonds, but what forces attract molecules to each other in the liquid and solid states? There are several types of attractive forces that hold molecules together which, taken as a group, are called intermolecular attractive forces. Two types are discussed in this section, and a third is presented in the next section.

Dipole-dipole forces occur between polar molecules. Molecules of this type have dipoles and line up in an electric field (see Section 6.5). Dipole-dipole forces are caused by the attractions of the positive and negative poles of the molecules for one another. In a crystal of a polar molecular substance, the molecules are lined up in a way that reflects the dipole-dipole forces (Figure .1).

Electronegativity differences between atoms can be used to predict the degree of polarity of a diatomic molecule as well as the positions of the positive and negative poles. A prediction concerning the polarity of a molecule that contains more than two atoms, however, must be based upon a knowledge of the geometry molecule, the polarities of the bonds, *and the arrangement ofnonbonding electron pairs.*
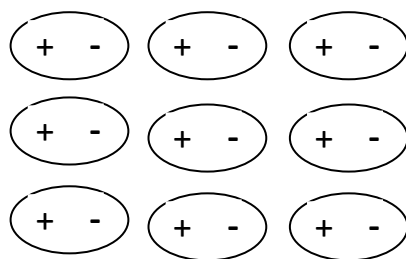

Figure 1: Orientation of polar molecules in a crystal

Consider the three molecules (CH_4, NH_3, and H_2O) represented in Figure 2. The dipole moment of a molecule is the result of the individual bond dipoles and the nonbonding electron pairs of the molecule. In each of the molecules under consideration, the central atom is more electronegative than the H atoms bonded to it. The negative end of each *bond* dipole, therefore, points toward the central atom. In CH_4, the tetrahedral arrangement of the four polar C—H bonds produces a molecule that is not polar; CH_4 has no dipole moment. The center of positive charge of the *molecule* (derived by considering all four bonds) falls in the center of the C atom and coincides with the center of negative charge for the molecule.

On the other hand, the trigonal pyramidal NH_3 molecule is polar (its dipole moment is 1.49 D). The three polar bonds and nonbonding electron pair are arranged so that the'molecule has a dipole with the negative end directed toward the top of the trigonal pyramid and the positive end toward the bottom. Similarly, the angular H_2O molecule is polar (its dipole moment is 1.85 D). The polar bonds and the nonbonding electron pairs contribute to a dipole with the negative end directed toward the O atom and the positive end directed toward a point halfway between the two H atoms.

The influence that a nonbonding pair of electrons has on the dipole moment of a molecule is seen in the case of NF_3. The NF_3 molecule has a structure similar to that of NH_3 (Figure 2), but the direction of the polarity of the bonds is the reverse of that in NH_3 since F is more electronegative than N. Nitrogen trifiuoride has a dipole moment of 0.24 D, a surprisingly low value in view of the highly polar nature of the N—F bonds. The N—F bond dipoles combine to give the molecule a dipole with the negative end in the direction of the base of the pyramid, but the contribution of the nonbonding electron pair works in the opposite direction and reduces the total polarity of the molecule.

What intennolecular forces attract *nonpolar* molecules to each other in the liquid and solid state? Such molecules do not have permanent dipoles, but nevertheless, they can be liquefied. Some type of intennolecular force, therefore, must exist in addition to the dipole-dipole force.

The existence of London forces (dispersion forces) is postulated. These forces are thought to arise from the motion of electrons. At one instant of time, the electron cloud of a molecule may be distorted so that a dipole is produced in which one part of the molecule is slightly more negative than the rest. At the next instant, the positions of the negative

and positive poles of the dipole will be different because the electrons have moved. Over a period of time (a very short period of time electrons move rapidly), the effects of these instantaneous dipoles cancel so that a nonpolar molecule has no permanent dipole moment.

The instantaneous, fluctuating dipole of a molecule, however, induces matching dipoles in neighboring molecules (lined up in the same way that permanent dipoles are aligned). The motion of the electrons of neighboring molecules is synchronized (see Figure 9.3). The force of attraction between these instantaneous dipoles constitutes the London force. *The strongest London forces occur between large, complex molecules, which have large electron clouds that are easily distorted, or polarized.*

Figure 2: Analysis of the polarities of the methane (CH_4), ammonia (NH_3), and water (H_2O) molecules. (Arrows point toward the negative end of the individual dipoles that compose the dipole moment of the molecule.)
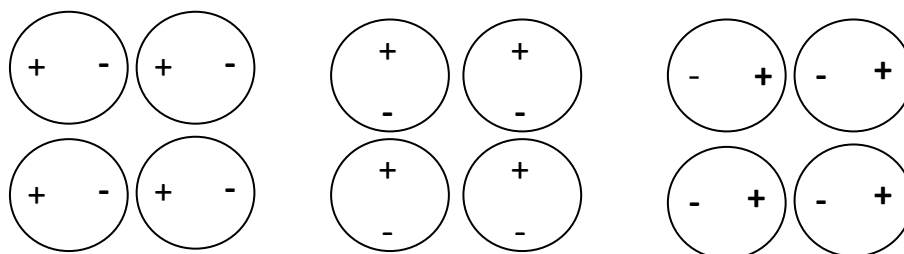
Figure 3: Instantaneous dipoles

Table 1: Attractive energies and dipole moments for some gases

Attractive Energies (kJ/mol)					
Molecule	Dipole 'Moment (D)	Dipole-Dipole	London	Melting Point(K)	Boiling Point (K)
CO	0.12	0.0004	8.74	74	82
HI	0.38	0.025	27.9	222	238
HBr	0.78	0.69	21.9	185	206
HCI	1.03	3.31	16.8	158	183
NH_3	1.49	13.3	14.7	195	240
H_2O	1.84	36.4	9.0	273	373

Since all molecules contain electrons, London forces also exist between polar molecules; in the case of nonpolar molecular substances, London forces are the *only* intermolecular forces that exist. The values listed in Table 1 show that London forces are the principal intermolecular forces for most molecular substances. The hydrogen bond, a special type of dipole-dipole interaction that is discussed in the next section, is responsible for the magnitude of the dipole-dipole energy listed for H_2O, NH_3, and (to a lesser extent) HCI.

The dipole moments of the molecules listed in Table 1 increase in the order given, and the dipole-dipole energies increase in the same order. The London energies, however, depend upon the sizes of the molecules. The largest molecule listed is HI, and it has the strongest London forces. HCI is a more polar molecule than HI; the electronegativity of Cl is 3.2, and the electro negativity of I is 2.7. The dipole-dipole energy of HCI is higher than that of HI. The London energy of HI, however, is so much higher than the London energy of HCI, that the *total* effect causes the molecules of HI to be more strongly attracted to one another than the

molecules of HCI are. The boiling point of HI is 238 K., which is higher than the boiling point of HCI (188 K).

2. The Hydrogen Bond

The intermolecular attractions of certain hydrogen-containing compounds are unusually strong. These attractions occur in compounds in which hydrogen is covalently bonded to highly electronegative elements of small atomic size. In these compounds the atom of the electronegative element exerts such a strong attraction
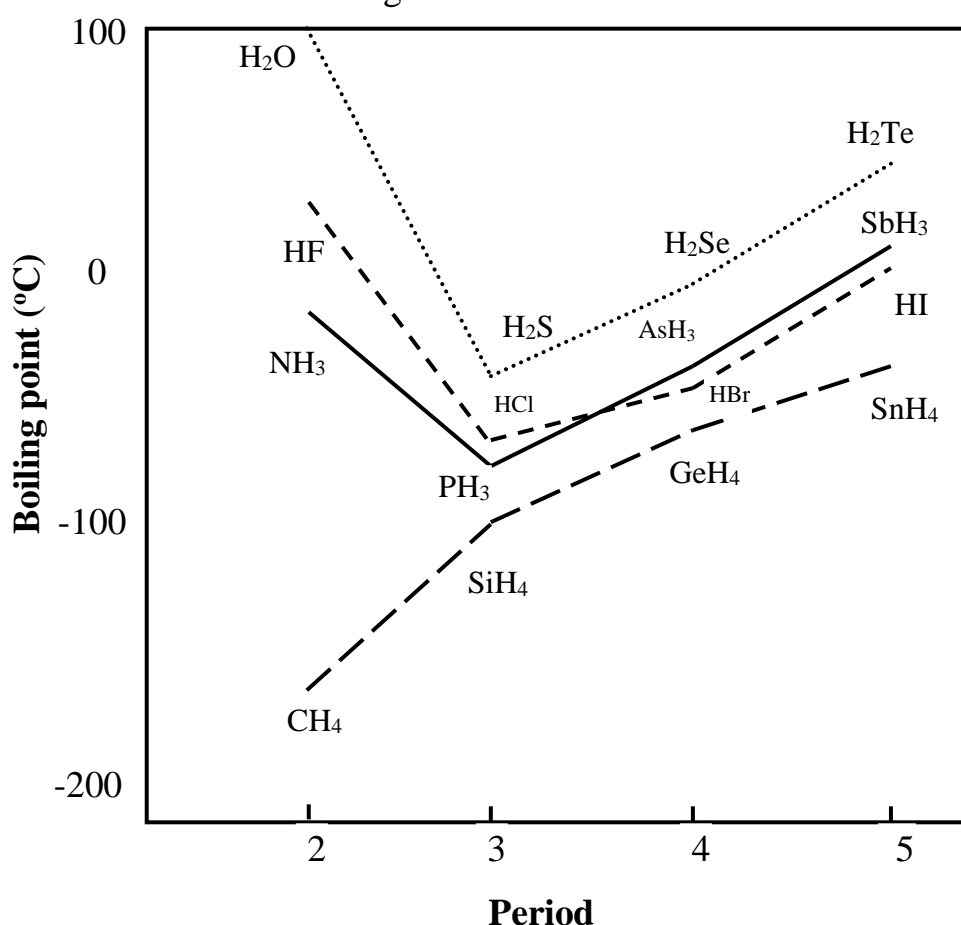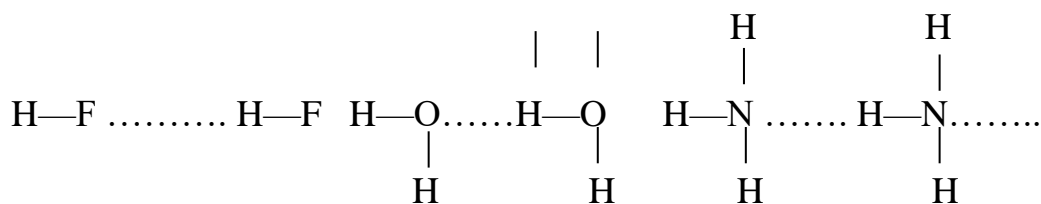
Figure 4: Boiling points of the hydrogen compounds of the elements of groups IVA, VA, VIA and VIIA

on the bonding electrons that the hydrogen atom is left with a significant δ^+ charge. In fact, the hydrogen atom is almost an exposed proton since it has no screening electrons.

The hydrogen atom of one molecule and a pair of unshared electrons on the electronegative atom of another molecule are mutually attracted and form what is called a hydrogen bond. Because of its small size, each hydrogen atom is capable of forming only one hydrogen bond. The association of HF, H_2O, and NH_3 by hydrogen bonds (indicated by dotted lines) can be roughly diagramed as follows:

$$H—F \ldots\ldots H—F \quad H—O\ldots\ldots H—O \quad H—N \ldots\ldots H—N\ldots\ldots$$

with H—O having H below each O, and H—N having H above (on N) and H below each N.

Unusual properties are characteristic of bonding in which hydrogen bonding occurs. In Figure 4 the normal boiling points of the hydrogen compounds of the elements of groups IV A, V A, VI A, and VII A are plotted. The series CH_4, SiH_4, GeH_4, and SnH_4 illustrates the expected trend in boiling point for compounds in which the only intermolecular forces are London forces; the boiling point increases as tri&molecular size increases. The hydrogen compounds of the IV A elements are ncnpolar molecules; the central atom of each molecule has no unshared electron pair.

In each compound of the other three series of Figure (4) however, London forces are aided by dipole-dipole forces in holding the molecules together. Nevertheless, the boiling point of the first member of each series (HF, H_2O, and NH_3) is unusually high in comparison to those of the other members of the series. In each of these three compounds, hydrogen bonding increases the difficulty of separating the molecules from the liquid state. Significant hydrogen bonding is not found in any of the other compounds for which a boiling point is plotted in Figure 4. In addition to high boiling points, compounds that are associated by

hydrogen bonding have abnormally high melting points, heats of vaporization, heats of fusion, and viscosities.

Hydrogen bonding occurs not only between the identical molecules of some pure compounds but also between the different molecules that make up certain solutions. There are two requirements for strong hydrogen bonding:

1. The molecule that supplies the proton for the formation of the hydrogen bond (the *proton donor)* must be highly polar so that the hydrogen atom will have a relatively high positive charge. The increasing strength of the hydrogen bonds N—H …. N < O—H … O < F—H … F parallels the increasing electro-negativity of the atom bonded to hydrogen, N <O < F. The high positive charge on the hydrogen atom attracts the electron pair from another molecule strongly, and the small size of the hydrogen atom permits the second molecule to approach closely.

2. The atom (of *the proton acceptor)* that supplies the electron pair for the hydrogen bond must be relatively small. Really effective hydrogen bonds are formed only by fluorine, oxygen, and nitrogen compounds. Chlorine compounds form weak hydrogen bonds, as evidenced by the slight displacement of the boiling point of HCl (Figure 4). Chlorine has approximately the same electronegativity as nitrogen. A chlorine atom, however, is larger than a nitrogen atom, and the electron cloud of the chlorine atom is, therefore, more diffuse than that of the nitrogen atom.

An examination of (Figure 4) will show that hydrogen bonding has a greater effect on the boiling point of water than on the boiling point of hydrogen fluoride. This effect is observed even though the O—H … O bond is only about two-thirds as strong as the F—H … F bond. There are, *on the average,* twice as many hydrogen bonds *per molecule* in H_2O as

there are per *molecule* in HF. The oxygen atom of each water molecule has two hydrogen atoms and two unshared electron pairs. The fluorine atom of the hydrogen fluoride molecule has three electron pairs that can bond with hydrogen atoms but only one hydrogen atom with which it can form a hydrogen bond.

Other properties of water are affected to an unusual degree by hydrogen bonding. The tetrahedral arrangement of the hydrogen atoms and the unshared electron pairs of oxygen in water cause the hydrogen bonds of the ice crystal to be arranged in this manner and lead to the open structure of the ice crystal. Ice, therefore, has a comparatively low density. In water at the freezing point, the molecules are arranged more closely together; water, therefore, has a higher density than ice   an unusual situation. It should be noted that H_2O molecules are associated by hydrogen bonds in the liquid state but not to the same extent, nor in the rigid manner, as they are associated in ice.

Hydrogen bonding also accounts for the unexpectedly high solubilities of some compounds containing oxygen, nitrogen, and fluorine in certain hydrogen-containing solvents, notably water. Thus, ammonia and methanol dissolve in water through the formation of hydrogen bonds:

```
    H                           H
    |                           |
H—N ……. H—O           H —C—O…. H—O
    |        |                  |   |        |
    H        H                  H   H        H
```

In addition, certain oxygen-containing anions (e.g., the sulfate ion, SO_4^{2-}) dissolve in water through hydrogen-bond formation.

3. The liquid state

In gases, the molecules move rapidly in a completely random manner. In solids, the molecules are held together in the orderly

arrangements typical of crystals. The liquid state is intermediate between the gaseous state and the solid state.

In liquids, the molecules move more slowly than they do in gases. The inter-molecular attractive forces are able, therefore, to hold them together into a definite volume. The molecular motion, however, is too rapid for the attractive forces to fix the molecules into definite positions in a crystal lattice. A liquid, consequently, retains its volume but not its shape. Liquids flow and assume the shapes of their containers.

A change in pressure has almost no effect on the volume of a liquid since there is little free space between the molecules. An increase in temperature, however, increases the volume of most liquids slightly and, consequently, decreases the liquid density. When the temperature of a liquid is increased, the average kinetic energy of the molecules increases, and this increased molecular motion works against the attractive forces. The expansion, however, is much less than that observed for gases, in which the effect of attractive forces is negligible.

Two liquids that are soluble in one another will diffuse into each other when placed together. If one liquid is carefully poured on top of another more dense liquid, the boundary between the two liquids will be sharp and easily seen. This boundary will gradually become less distinct and, in time, will disappear as the molecules of the two liquids diffuse into each other.

The diffusion of liquids is a much slower process than the diffusion of gases. Since the molecules of liquids are relatively close together, a molecule undergoes a tremendous number of collisions in a given time period. The average distance it travels between collisions, the mean free path, is much shorter for a molecule of a liquid than it is for a molecule of a gas. Gases, therefore, diffuse much more rapidly than liquids.

Any liquid exhibits resistance to flow, a property known as viscosity. One way of determining the viscosity of a liquid is to measure the time that it takes for a definite amount of the liquid to pass through a tube of small diameter under a given pressure. Resistance to flow is largely due to the attractions between molecules, and the measurement of the viscosity of a liquid gives a simple estimate of the strength of these attractions. In general, as the temperature of a liquid is increased, the cohesive forces lire less able to cope with increasing molecular motion, and the viscosity decreases. On the other hand, increasing the pressure generally increases the viscosity of a given liquid.

Figure 5. Schematic diagram indicating the unbalanced intermolecular forces on the surface molecules of a liquid as compared to the balanced intermolecular forces on the interior molecules

Surface tension is another property of liquids caused by the intermolecular attractive forces. A molecule in the center of a liquid is attracted equally in all directions by surrounding molecules. Molecules on the surface of a liquid, however, are attracted only toward the interior of the liquid (Figure 5). The surface molecules, therefore, are pulled inward, and the surface area of a liquid tends to be minimized. This behavior accounts forlhe spherical shape of liquid drops. Surface tension is a measure of this inward force on the surface of a liquid, the force which must be overcome to expand the surface area. The surface tension" of a liquid decreases with increasing temperature since the increased

molecular motion tends to decrease the effect of the intermolecular attractive forces.

4. Evaporation

The kinetic energies of the molecules of a liquid follow a Maxwell-Boltzmann distribution similar to the distribution of kinetic energy among gas molecules (Figure 6). The kinetic energy of a given molecule of a liquid is continually changing as the molecule collides with other molecules. At any given instant, however, some of the molecules of the total collection have relatively high energies and some have relatively low energies. The molecules with kinetic energies high enough to overcome the attractive forces of surrounding molecules can escape from the liquid and enter the gas phase if they are close to the surface and are moving in the right direction. They use part of their energy to work against the attractive forces when they escape.

In time, the loss of a number of high-energy molecules causes the average kinetic energy of the molecules remaining in the liquid to decrease, and the temperature of the liquid falls. When liquids evaporate from an open container, heat flows into the liquid from the surroundings to maintain the temperature of the liquid.
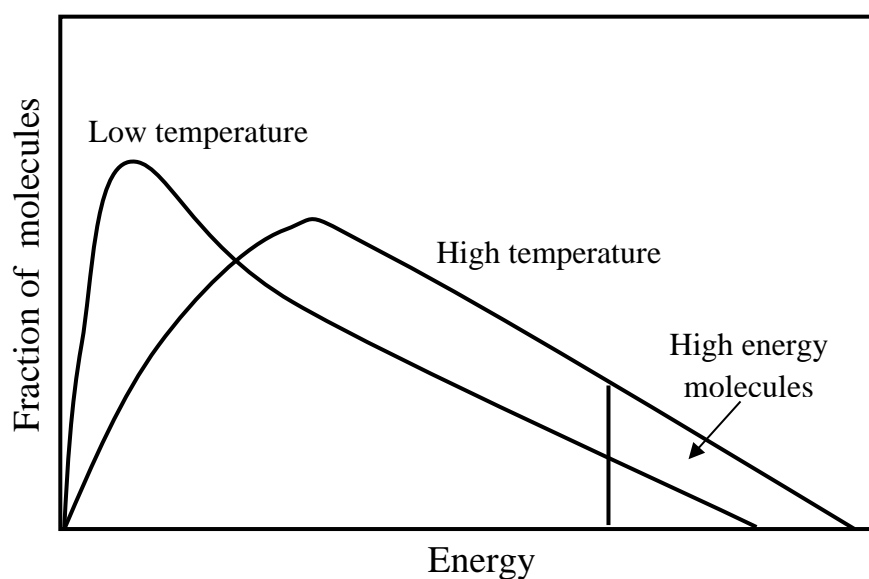

Figure 6: Distribution of kinetic energy among molecules of a liquid

In this way the supply of high-energy molecules is replenished, and the process continues until all of the liquid has evaporated. The total quantity of heat required to vaporize a mole of liquid at a given temperature is called the molar enthalpy of vapori/ation of that liquid. At 25°C, for example,

$$H_2O(1) \rightarrow H_2O(g) \qquad \Delta H_v = +43.8 \text{ kJ}$$

The transfer of heat from the surroundings explains why swimmers emerging from the water become chilled as the water evaporates from their skin. Likewise, the regulation of body temperature is, in part, accomplished by the evaporation of perspiration from the skin. Various cooling devices have made use of this principle. A water cooler of the Middle East consists of a jar of unglazed pottery rilled with water. The water saturates the clay of the pottery and evaporates from the outer surface of the jar, thus cooling the water remaining in the jar.

The rate of .evaporation increases as the temperature of a liquid is raised. When the temperature is increased, the average kinetic energy of the molecules increases, and the number of molecules with energies high enough for them to escape into the vapor phase increases (Figure 6),

5. Vapor Pressure

When a liquid in a closed container evaporates, the vapor molecules cannot escape from the vicinity of the liquid. In the course of their random motion, some of the vapor molecules return to the liquid. We can represent the process for water by using a double arrow:

$$H_2O(l) \rightleftharpoons H_2O(g)$$
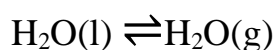
The rate of return of the vapor molecules to the liquid depends upon the concentration of the molecules in the vapor. The more

molecules that there are in a given volume of vapor, the greater the chance that some of them will strike the liquid and be recaptured.

At the start, the rate of return of molecules from the vapor to the liquid is low since there are few molecules in the vapor. The continued vaporization, however, causes the concentration of the molecules in the vapor to increase. The rate of condensation, therefore, also increases. Eventually the system reaches a point in which the rate of condensation equals the rate of vaporization.

This condition, in which the rates of two opposite tendencies are equal, is called a state of equilibrium. At equilibrium, the concentration of molecules in the vapor state is constant because molecules leave the vapor through condensation at the same rate that molecules add to the vapor through vaporization. Similarly, the quantity of liquid is a constant because molecules are returning to the liquid at the same rate that they are leaving it.

It is important to note that a condition of equilibrium does not imply that nothing is going on. In any system, the numbers of molecules present in the liquid and in the vapor are constant because the two opposing changes are taking place at the same rates and *not* because vaporization and condensation have stopped.

Since the concentration of the molecules in the vapor is a constant at equilibrium, the pressure that the vapor exerts is a constant too. The pressure of vapor in equilibrium with a liquid at a given temperature is called the equilibrium vapor pressure of the liquid. The vapor pressure of a given liquid is determined by the temperature and increases when the temperature is increased.

Figure 7 shows the temperature-vapor pressure curves for diethyl ether, ethyl alcohol, and water. The curves show the increase in vapor pressure that accompanies an increase in temperature. The curve for each
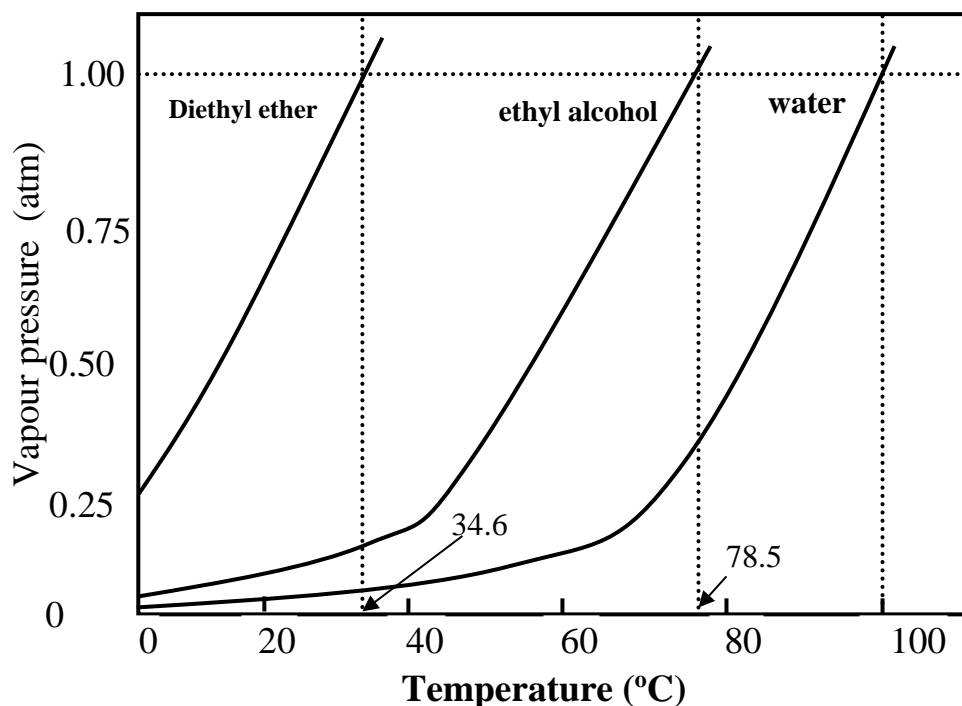
Figure 7: Vapour pressure curves for diethyl ether, ethyl alcohol and water.

substance could be extended to the critical temperature of that substance. At the critical temperature, the vapor pressure equals the critical pressure, and the curves end at this point. Above the critical temperature only one phase can exist—the gas phase.

The magnitude of the vapor pressure of a liquid gives an indication of the strength of the intermolecular attractive forces of that liquid. Liquids that have strong attractive forces have low vapor pressures. At 20^CC, the vapor pressure of water is 0.023 atm, of ethyl alcohol is 0.058 atm, and of diethyl ether is 0.582 atm. The forces of attraction are strongest in water and weakest in diethyl ether. A list of the vapor pressures of water at various temperatures is given in Table 3.

6. Boiling Point

The temperature at which the vapor pressure of a liquid equals the external pressure is called the boiling point of the liquid. At this temperature, vapor produced in the interior of a liquid results in the

bubble formation and turbulence that is characteristic of boiling. Bubble formation is impossible at temperatures below the boiling point. The atmospheric pressure on the surface of the liquid prevents the formation of bubbles with internal pressures that are less than the pressure of the atmosphere.

The temperature of a boiling liquid remains constant until all the liquid has been vaporized. In an open container the maximum vapor pressure that can be attained by any liquid is the atmospheric pressure. This vapor pressure corresponds to the boiling point. Heat must be added to a boiling liquid to maintain the temperature because in the boiling process, the high-energy molecules are lost by the liquid. The higher the rate at which heat is added to a boiling liquid, the taster it boils. The temperature of the liquid, however, does not rise.

The boiling point of a liquid changes with changes in external pressure. Water, for example, will boil at 98.6°C at a pressure of 0.950 atm and at 101.4°C at a pressure of 1.05 atm. Only at a pressure of 1.00 atm will water boil at 100°C. The normal boiling point of a liquid is defined as the temperature at which the vapor pressure of the liquid equals I atm. Boiling points given in reference books ure understood to be normal boiling points.

The normal boiling points of diethyl ether (34.6°C), ethyl alcohol (78.5°C), and water are indicated"on the vapor pressure curves of Figure 9.7. The boiling point of a liquid can be read from its vapor pressure curve by finding the temperature at which the vapor pressure of the liquid equals the prevailing pressure.

The changes in atmospheric pressure at any one geographic location cause a maximum variation of about 2°C in the boiling point of water. The variations from place to place, however, can be greater than this. The

average barometric pressure at sea level is 1 atm. At higher elevations, average barometric pressures are less. At an elevation of 1524 m above sea level, for example, the average barometric pressure is 0.836 atm; at this pressure, water boils at 95.1°C. Water boils at 90.1°C at 0.695 atm, which is the average atmospheric pressure at 3048 m above sea level.

If a liquid has a high normal boiling point or decomposes when heated, it can be made to boil at lower temperatures by reducing the pressure. This procedure is followed in vacuum distillation. Water can be made to boil at 10°C, which is considerably below room temperature, by adjusting the pressure to 0.0121 atm (see Table 8.3). Unwanted water is removed from many food products by boiling it away under reduced pressure. In these procedures, the product is not subjected to temperatures that bring about decomposition or discoloration.

7. Enthalpy of Vaporization

The quantity of heat that must be supplied to vaporize a mole of a liquid at a specified temperature is called the molar enthalpy of vaporization, ΔH_v. Enthalpies of vaporization are usually recorded at the normal boiling point in kilojoules per mole (see Table 2).

Table 2: Enthalpy of vaporization of some liquids

Liquid	Formula	Normal Boiling Point(°C)	Enthalpy(Vaporization) (kJ/mol)
water	H_2O	100.0	40.7
benzene	C_6H_6	80.1	30.8
ethyl alcohol	C_2H_5	78.5	38.6
carbon tetrachloride	CCl_4	76.7	30.0
chloroform	$CHCl_3$	61.3	29.4
diethyl ether	C_2H_5OH	34.6	26.0

The magnitude of the molar enthalpy of vaporization gives an indication of the strength of the intermolecular attractive forces. A high enthalpy of vaporization indicates that these forces are strong. The enthalpy of vaporization of a liquid, however, includes both the energy required to overcome the intermolecular attractive forces and the energy needed to expand the vapor. The volume of a gas is considerably larger than the volume of the liquid from which it is derived. A volume of about 1700 ml of steam, for example, is produced by the vaporization of 1 ml of water at 100°C. Energy must be supplied to do the work of pushing back the atmosphere to make room for the vapor.

When a mole of vapor is condensed into a liquid, energy is released, not absorbed. This enthalpy change is called themolar enthalpy of condensation. It has a negative sign, but it is numerically equal to the molar enthalpy of vaporization at the same temperature.

The enthalpy of vaporization of a liquid decreases as the temperature increases, and it equals zero at the critical temperature of the substance. This trend parallels an increase in the fraction of high-energy molecules. At the critical temperature, all the molecules have sufficient energy to vaporize.

8. The Freezing Point

When a liquid is cooled, the molecules move more and more slowly. Eventually a temperature is reached at which some of the molecules have kinetic energies that are low enough to allow the intermolecular attractions to hold them in crystal lattice. The substance then starts to freeze. Gradually the low-energy molecules assume positions in the crystal lattice. The molecules remaining in the liquid have a higher temperature because of the loss of these low-energy molecules. Heat must be removed from the liquid to maintain the temperature.

The normal freezing point of a liquid is the temperature at which solid and liquid are in equilibrium under a total-pressure of 1 atm. At the freezing point the temperature of the solid-liquid system remains constant until all of the liquid is frozen. The quantity of heat that must be removed to freeze a mole of a substance at the freezing point is called the molar enthalpy of crystallization This quantity represents the difference between the enthalpies of the liquid and the solid.

At times the molecules of a liquid, as they are cooled, continue the random motion characteristic of the liquid state at temperatures below the freezing point. Such liquids are referred to as undercooled or supercooled liquids. These systems can usually be caused to revert to the freezing temperature and the stable solid-liquid equilibrium by scratching the interior walls of the container with a stirring rod or by adding a seed crystal around which crystallization can occur. The crystallization process supplies heat, and the temperature is brought back to the freezing point until normal crystallization is complete.

Some supercooled liquids can exist for long periods, or even permanently, in this state. When these liquids are cooled, molecules solidify in a random arrangement typical of the liquid state rather than in an orderly geometric pattern of a crystal. Substances of this type have complex molecular forms for which crystallization is difficult. They are frequently called amorphous solids, vitreous materials, or glasses; examples include glass, tar, and certain plastics. Amorphous solids have no definite freezing or melting points. These transitions take place over a temperature range. They break into fragments that have curved, shell-like surfaces. Crystalline materials break into fragments that resemble the parent crystals.

Table 3: Enthalpy of fusion of some liquids

Solid	Formula	Melting Point(°C)	ΔH, Enthalpy of fusion (kJ/mol)
water	H_2O	0.0	6.02
benzene	C_6H_6	5.5	9.83
ethyl alcohol	C_2H_5	-117.2	4.60
carbon tetrachloride	CCl_4	-22.9	2.51
chloroform	$CHCl_3$	-63.5	9.20
diethyl ether	C_2H_5OH	116.3	7.26

When a crystalline substance is heated, the temperature at which solid-liquid equilibrium is attained under air at 1 atm pressure is called the melting point. It is. of course, the same temperature as the freezing point of the substance. The quantity of heat that must be *added* to melt a mole of the material at the melting point is called the molar enthalpy of fusion, ΔH, and is numerically equal to the enthalpy of crystallization but opposite in sign (Table 3).

9. Vapor Pressure of a Solid

Molecules in crystal vibrate about their lattice positions. A distribution of kinetic energies exists among these molecules similar to the distribution for liquids and gases but on a lower level. Energy is transmitted from molecule to molecule within a crystal; the energy of any one molecule, therefore, is not constant. High-energy molecules on the surface of the crystal can overcome the attractive forces of the crystal and escape into-the vapor phase. If the crystal is in a closed container, an equilibrium is eventually reached in which the rate of the molecules leaving the solid equals the rate at which the vapor molecules return to

the crystal. The vapor pressure of a solid at a given temperature is a measure of the number of molecules in a given volume of the vapor at equilibrium.

Every solid has a vapor pressure, although some pressures are very low. The size of the vapor pressure is inversely proportional to the strength of the attractive forces. Ionic crystals, therefore, have very low vapor pressures.

Since the ability of molecules to overcome the intermolecular forces of attraction depends upon their kinetic energies, the vapor pressure of a solid increases as the temperature increases. The temperature-vapor pressure curve for ice is illustrated in Figure 9.8. This curve intersects the vapor pressure curve for water at the freezing point. At the freezing point, the vapor pressures of solid and liquid are equal.

In the absence of air, the normal freezing point of water (I atm total pressure) is 0.0025°C. *In air* however, and under a total pressure of I atm, the freezing point of water is 0.0000°C, which is the commonly reported value. The difference in freezing point is caused by the presence of dissolved air in the water. The vapor pressures plotted in Figure 8 are the partial pressures of H_2O in air with the total pressure equal to 1 atm. Freezing points are usually determined in air; however, in any event, any change in freezing point of a given substance caused by the presence of air is generally very small.
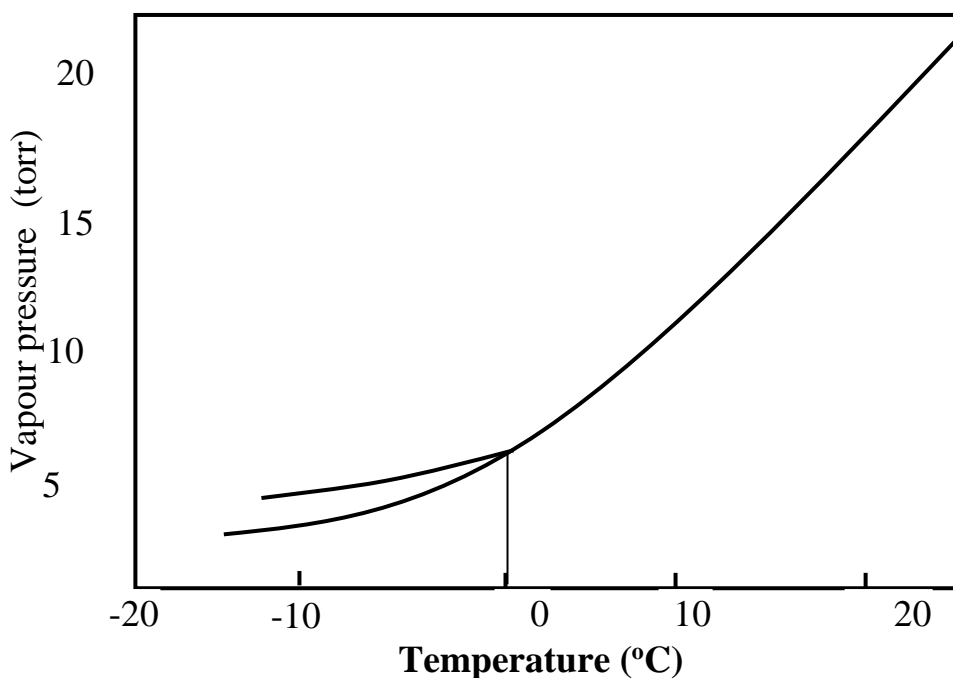
Figure 8: Vapour pressure curves for ice and water near the freezing point. (Vapor pressures are partial pressures of H_2O under air at a total pressure of 1.00 atm.)

10. Phase Diagrams

The temperature-pressure phase diagram for water conveniently illustrates the conditions under which water can exist as solid, liquid, or vapor, as well as the conditions that bring about changes in the state of water. Figure 9 is a schematic representation of the water system. It is not drawn to scale, and some of its features are exaggerated so that important details can be easily seen. Every substance has its own phase diagram, which describes only systems in equilibrium. These diagrams are derived from experimental observations.

The diagram of Figure 9 relates to what is called a one-cornporcenr system: that is, it pertains to the behavior of water in the absence of any other substance. No part of the total pressure of any system described by the diagram is due to the pressure of a gas other than water vapor. The vapor pressure curves plotted in Figure 8 (measured in air under a constant total pressure of 1 atm) therefore deviate slightly, but only very

slightly, from the vapor pressure curves of Figure 9 (for which the vapor pressure of water is the *total* pressure). The easiest way to interpret the phase diagram for water is to visualize the total pressure acting on a system in mechanical terms, for example, as a piston acting on the material of the system contained in cylinder.

In Figure 9 curve OC is a vapor pressure curve for liquid and terminates at the critical point, C. Any point on this line describes a set of temperature and pressure conditions under which liquid and vapor can exist in equilibrium. The extension DO is the curve for supercooled liquid; systems between liquid and vapor described by points on this line are metastable. (The term- metastable is
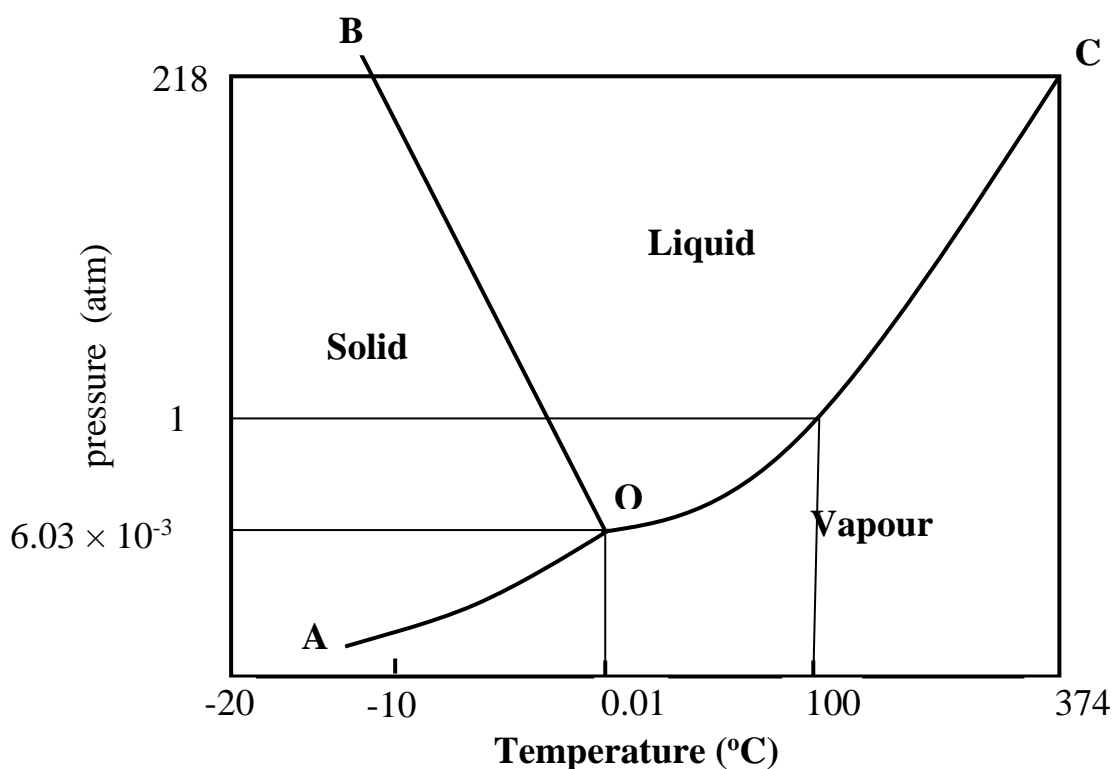
Figure 9: Phase diagram for water.(Not drawn to scale)

applied to systems that are not in the most stable state possible at the temperature in question.) Curve AO is a vapor pressure curve for solid and represents a set of points that describe the possible temperature and

pressure conditions for solid-vapor equilibria. The line BO, the melting point curve, represents conditions for equilibria between solid and liquid.

These three curves intersect at point O, a triple point. Solid, liquid, and vapor can exist together in equilibrium under the conditions represented by this point: 0.01°C (which is 273.16 K) and a pressure of 0.00603 atm (or 4.58 torr).

The phases (solid, liquid, and vapor) that exist in equilibrium under a set of temperature and pressure conditions can be read from the phase diagram. The temperature and pressure define a point on the diagram. The phases can be read from the position of the point. If the point falls

1. *In a region* labeled solid, liquid, or vapor, only *one phase* exists—the phase noted on the diagram

2. *On a line, two phases* exist; the phases are those that are marked in the regions on both sides of the line

3. *On a point,* all *three phases* exist; there is only one such point in the phase diagram given for water—the triple point

The slope of the melting point (or freezing point) curve, BO, shows that the freezing point decreases as the pressure is increased. A slope of this type is observed for only a few substances such as gallium, bismuth, and water. It indicates an unusual situation in which the liquid expands upon freezing. At 0°C a mole of water occupies 18.00cm^3, and a mole of ice occupies 19.63cm^3. The system expands, therefore, when one mole of liquid water freezes into ice. An increase in pressure on the system would oppose this expansion and the freezing process.

Hence, the freezing point of water is lowered when the total pressure is increased. In Figure 9. the slope of the line BO is exaggerated.

Phase changes brought about by temperature changes at constant pressure may be read from a phase diagram by interpreting a horizontal tine drawn at the reference pressure (like the line drawn at 1.00 atm in

Figure 9.). The point where this line intersects curve BO indicates the normal melting point (or freezing point), and the point where the 1.00 atm line intersects curve CO represents the normal boiling point. Beyond this point, only vapor exists.

Phase changes brought about by pressure changes at constant temperature may be read from a vertical line drawn at the reference temperature. If the pressure is increased, for example, at 0.0025°C (Figure 9.), the point where the vertical line crosses AO is the pressure where vapor changes to solid, and the point where the vertical line crosses BO represents the pressure where solid changes to liquid. Above this point, only liquid exists.

For materials that contract upon freezing (that is, the solid phase is more dense than the liquid phase), the freezing-point curve slants in the opposite direction, and the freezing point increases as the pressure is increased. This behavior is characteristic of most substances. The freezing-point curves of most phase diagrams slant to the right as is seen in the phase diagram for carbon dioxide in Figure 10.

The process in which a solid goes directly into a vapor without going through the liquid state is known as sublimation: this process is reversible. The phase diagram for carbon dioxide is typical for substances that sublime at ordinary pressures rather than melt and then boil. The triple point of the carbon dioxide system is -56.6°C at a pressure of 5.11 atm. Liquid carbon dioxide exists only at pressures greater than 5.11 atm. When solid carbon dioxide (dry ice) is heated at 1 atm pressure, it is converted directly into gas at — 78.5°C. This relationship is shown in Figure 9.10. The molar enthalpy of sublimation is the heat that must be added to a mole of solid to convert it directly into a gas.
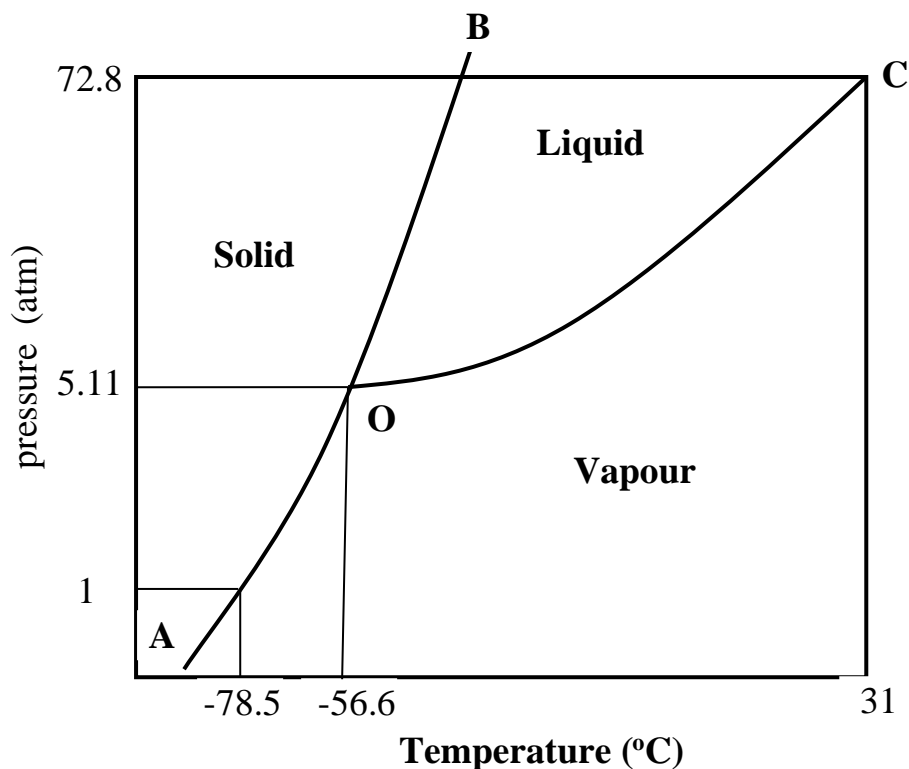
Figure 10: Phase diagram for carbon dioxide.(Not drawn to scale)

11 Types of Crystalline Solids

Crystals are formed by atoms, ions, and molecules. We can classify crystals into four types according to the kind of particles that make up the crystal and the forces that hold them together:

1. Ionic crystals. Positive and negative ions are held in the crystal lattice arrangement by electrostatic attraction. Because these forces are strong, ionic substances have high melting points. Ionic crystals are hard and brittle. Figure 11 shows what happens if an attempt is made to deform an ionic crystal. Because of the movement of one plane of ions over another, ions with the same charge are brought next to one another. The crystal breaks into fragments. Ionic compounds are good conductors of electricity when molten or in solution but not in the crystalline state where the ions are not free to move.

2. Molecular crystals. Molecules occupy lattice positions in crystals of covalent compounds. The intermolecular forces that hold the molecules in the crystal structure are not nearly so strong as the

electrostatic forces that hold ionic crystals together. Molecular crystals, therefore, are soft and have low melting points.

London forces hold nonpolar molecules in the lattice. In crystals of polar molecules, dipole-dipole forces as well as London forces occur. Polar compounds, therefore, generally melt at slightly higher temperatures than nonpolar compounds of *comparable molecular size and shape.*

In general, molecular substances do not conduct electricity in the solid or liquid states. A few molecular compounds, such as water, dissociate to a very slight extent and produce low concentrations of ions; these liquids are poor electrical conductors.

Figure 11 Effect of deformation on (a) a metallic crystal and (b) an ionic crystal

Figure 12 Arrangement of atoms in a diamond crystal

3. Network crystal. In these crystals, atoms occupy lattice positions and they are joined by a network of covalent bonds. The entire crystal can be looked at as one giant molecule. In diamond, an example of this type of crystal, carbon atoms are bonded by covalent bonds into a three-dimensional structure {see Figure 9.12). Materials of this type have high melting points and are extremely hard because of the large number of covalent bonds that would have 10 be broken to destroy the crystal structure. Network crystals do not conduct electricity.

4. Metallic crystals. The outer electrons of metal atoms are loosely held and move freely throughout a metallic crystal. The remainder of the metal atoms, positive ions, occupy fixed positions in the crystal. The negative cloud of the freely moving electrons, sometimes called an electron gas or a sea of electrons, binds the crystal together. This binding force, called a metallic bond, is described more fully in Section 23.1.

The metallic bond is strong. Most metals have high rtfelting points, high densities, and structures in which the positive ions are packed together closely (called close-packed arrangements). Unlike ionic crystals, the positions of the positive ions can be altered without destroying the crystal because of the uniform cloud of negative charge provided by the freely moving electrons (see Figure 11). Most metallic crystals, therefore, are easily deformed, and most metals are malleable and ductile. The freely moving electrons are also responsible for the fact that most metals are good conductors of electricity.

The properties of the four types of crystals are summarized in Table 4.

Table 4: The properties of the four types of crystals.

Type of crystal	Types of charge carriers	Type of attractive forces	Physical properties	Examples
Ionic	positive and negative ions	electrostatic attractions	high m.p. hard, brittle good electrical conductor in fused state	NaCl, BaO, KNO_3
Molecular	polar molecules	London and dipole-dipole	low m.p. soft nonconductor or extremely poor conductor of electricity in liquid state	H_2O, NH_3, SO_2
	nonpolar molecules	London		$H_2CI_2CH_4$
Network	atoms	covalent bonds	very high m.p. very hard nonconductor ofelectricity	C (diamond) SIC. AIN, SiO_2
Metallic	positive ions and mobile electrons	metallic bonds	fairly high m.p. hard or soft malleable and ductile good electrical conductor	Ag, Cu, Na, Fe, K

12. Crystals

A crystal is a symmetrical array of atoms, ions, or molecules arranged in a repeating three-dimensional pattern. If the centers of the material units are replaced with points, the resulting system of points is called a space lattice or crystal lattice. By using a network of lines joining lattice points, a crystal lattice can be divided into identical parts called unit cells (Figure 13). A crystal lattice can be reproduced, in theory, by stacking its unit cells in three dimensions.

The simplest types of unit cells are the cubic unit cells (Figure 14). Notice that it is possible to have points at positions other than the corners of the unit cells. In the body-centered cubic unit cell, a point occurs in the center of the cell. In the face-centered cubic unit cell, a point occurs in the center of each face of the cell.

In crystals of metals, atoms occupy the lattice positions. In counting the number of atoms per unit cell, one must keep in mind that atoms on comers or faces are shared with adjoining cells. Eight unit cells share each corner atom, and two unit cells share each face-centered atom (Figure 15).

Figure 13 Simple cubic space lattice. (A unit cell is shown in color.)

Figure 14 Cubic structures

Figure 15 In cubic crystals, (a) a corner atom is shared by eight unit cells and (b) a face-centered atom is shared by two unit cells.

1. The simple cubic unit cell contains the equivalent of only one atom (8 corners at $\frac{1}{8}$ atom each).

2. The body-centered unit cell contains two atoms (8 corners at $\frac{1}{8}$ atom each and one unshared atom in the center).

3. The face-centered unit cell contains the equivalent of four atoms (8 corners at $\frac{1}{8}$ atom each and 6 face-centered atoms at \ atom each).

Example 1

Nickel crystallizes in a face-centered cubic crystal. The edge of a unit cell is 352 pm. The atomic weight of nickel is 58.7, and its density is 8.94 g/cm^3. Calculate Avogadro's number from these data.

Solution

Since 1 pm = 10^{-10} cm,

    352pm = 3.52 x 10^{-8} cm

The volume of one unit cell is (3.52 x 10^{-8} cm)^3, or 4.36 x 10^{-23} cm^3. Since the unit cell is face-centered, it contains 4 atoms. Therefore,

4 atoms = 4.36 x 10^{-23} cm^3

We derive from the density,

$1 cm^3 = 8.94$ gNi

The number of atoms in 58.7 g of Ni is Avogadro's number:

? atoms = 58.7 g Ni $\left(\frac{1\ cm^3}{8.94gNi}\right)\left(\frac{4\ atoms}{4.36\ x\ 10^{-23}cm^3}\right) = 6.02$ x 10^{23} atoms

Example 2

Sodium crystallizes in a cubic lattice, and the edge of a unit cell is 430 pm. The density of sodium is 0.963 g/cm³, and the atomic weight of sodium is 23.0. How many atoms of sodium are contained in one unit cell? What type of cubic unit cell does sodium form?

Solution

The edge of the unit cell is 4.30 x 10^{-8} cm. The volume of the unit cell, therefore, is (4.30 x 10^{-8} cm)³, or 7.95 x 10^{-23} cm³. We must find the number of Na atoms in this volume.

We derive our conversion factors from the density of Na:

0.963 g Na $= 1$ cm³

and the fact that 1 mol of Na (which is 23.0 g of Na) contains Avogadro's number of Na atoms:

6.02 x 10^{23} atoms Na $= 23.0$ g Na

The solution is

•me iA-23 ₃/0.963gNa\/6.02 x 10^{23}atomsNa

? atoms Na=7.95 x 10^{-23} cm³ $\left(\frac{0.963\ g\ Na}{1\ cm^3}\right) \frac{6.02\ x\ 10^{23}\ atoms\ Na}{23.0\ g\ Na}$

        =2.00 atoms Na

Sodium crystallizes in a body-centered cell since the body-centered cubic unit cell contains 2 atoms.

Crystal data can be used to calculate atomic radii:

1. In the case of a simple cubic unit cell, the atomic radius, *r,* is one-half the length of the edge of the cell, *a* (see Figure 14):

        $r = a/2$

2. In a face-centered cubic unit cell, the atoms that lie along an edge do not touch. We must calculate the length of the face diagonal (see Figure 16a). From the Pythagorean theorem for right triangles,

$$\text{hypotenuse}^2 = \text{side}^2 + \text{side}^2$$

$$(\text{face diagonal})^2 = a^z + a^2$$

$$= 2a^2$$

$$\text{face diagonal} = a \sqrt{2}$$

This diagonal is equal to four radii:

$$4r = a \sqrt{2}$$

$$r = a/\sqrt{8}$$

Figure 9.16 Determination of (a) a face diagonal and (b) a cube diagonal

3. We must determine the length of a cube diagonal to find the atomic radius of an atom that forms a body-centered cubic unit cell (see Figure 16b). From the figure, we see that the diagonal of a cube is the diagonal of a rectangle formed by the edge of the cube, a, and the diagonal of a face, $a \sqrt{2}$. Therefore,

$$(\text{cube diagonal})^2 = a^2 + (a \sqrt{2})^2$$

$$\text{cube diagonal} = a \sqrt{3}$$

This diagonal is equal to four atomic radii:

$$4r = a \sqrt{3}$$

$$r = a \sqrt{3/4}$$

Example 3

Sodium crystallizes in a body-centered cubic unit cell with the length of the edge equal to 430 pm. What is the atomic radius of Na?

Solution

The cube diagonal of the unit cell is

cube diagonal $= a \sqrt{3}$

$$= (430 \text{pm}) \ \sqrt{3}$$

$$= 745 \text{ pm}$$

This length is four atomic radii:

4r $= 745$ pm

$r = 186$ pm

Figure 17 Derivation of the Bragg equation

13 X-ray Diffraction of Crystals

Much of what is known about the internal structure of crystals has been learned from X-ray diffraction experiments. When two X rays that have the same wavelength are in phase, they reinforce each other and produce a wave that is stronger than either of the original waves. Two waves that are completely out of phase cancel each other (see Figure 8).

Figure 17 illustrates the way that crystal spacings can be determined by use of X rays of a single wavelength, A. The rays strike the parallel planes of the crystal at an angle 6. Some of the rays are reflected from the upper plane, some from the second plane, and some

from the lower planes. A strong reflected beam will result only if all the reflected rays are in phase.

In Figure 17 the lower ray travels farther than the upper ray by an amount equal to EF + FG. The rays will be in phase at BG only if the difference is equal to a whole number of wavelengths:

EF + FG = $n\lambda$.

where n is a simple integer.

Since angle ABE is a right angle,

$\theta + a = 90°$

Angle JBF is also a right angle, and

$\theta' + a = 90°$

The angle θ' therefore is equal to θ. The sine of angle θ' is equal to EF/BF (the ratio of the side opposite the angle to the hypotenuse). Since line BF is equal to d.

$\sin \theta' = \dfrac{EF}{d}$

or

EF = d sin θ

The expression

FG = d sin θ

Can be derived in the same way. Therefore.

EF + FG = *2d sin θ*

Since EF + FG is equal to $n\lambda$,

$n\lambda$ = *2d sin d θ*

This equation, derived by William Henry Bragg and his son William Lawrence Bragg in 1913, is called the Bragg equation.

With X rays of a definite wavelength, reflections at various angles will be observed for a given set of planes separated by a given distance, *d.*

These reflections correspond to $n = 1, 2. 3$, and so on, and are spoken of as first order, second order, third order, and so on. With each successive order, the angle 9 increases, and the intensity of the reflected beam weakens.

Figure 9.18 is a schematic representation of an X-ray spectrometer. An X-ray beam defined by a slit system impinges upon a crystal that is mounted on a turntable. A detector (photographic plate, ionization chamber, or Geiger counter) is positioned as shown in the figure. As the crystal is rotated, strong signals flash out as angles are passed that satisfy the Bragg equation. Any set of regularly positioned planes that contain atoms can give rise to reflections not only those that form the faces of the unit cells. Thus, the value of d is not necessarily the edge of the unit cell, although the two are always mathematically related.

Figure 18 X-ray diffraction of crystals. (Schematic.)

Example 4

The diffraction of a crystal of barium with X radiation of wavelength 229 pm gives a first-order reflection at 27" 8'. What is the distance between the diffracted planes?

Solution

Substitution into the Bragg equation gives

$n't. = 2d\sin 8$ 1 (229pm) = 240,456] d = 251 pm

Chapter 3
Thermochemistry

In the course of a chemical reaction, energy is either liberated or absorbed. Calculations relating to these energy changes are as important as those concerned with the masses of reacting substances. Thermochemistry is the study of the heat released or absorbed by chemical and physical changes. In succeeding chapters, calculations involving these energy changes will be frequently encountered. In this chapter, this type of calculation will be introduced.

3.1 Energy Measurement

It is common to think offeree as the application of physical strength—as pushing. If the effects of friction are neglected, a body in motion remains in motion at a constant velocity, and a body at rest stays at rest (its velocity is zero). If these bodies are pushed, there will be a change in their velocities. The increase in velocity per unit time is called the acceleration.

Suppose, for example, that we have a body moving at a velocity of I m/s. Assume that this body is acted on by a constant force, that is, given a sustained push. The body will move faster and faster. At the end of 1 second it may be moving at the rate of 2 m/s. At the end of 2 s, its speed may be 3 m/s. If the body picks up speed at the rate of one meter per second in a second, its acceleration is said to be I m/s^2.

A force that gives a *one gram* body an acceleration of I m/s^2 is not so large as a force that gives a *one kilogram* body the same acceleration. The magnitude of a force *(F),* therefore, is proportional to the mass of the body *(m)* as well as to the acceleration *(a)* that the force produces:

$F = ma$

The SI unit of force is called the newton (symbol, N) and is derived from the base units of mass (the kilogram), length (the meter), and time (the second):

$$F = ma \tag{3.1}$$
$$IN = (1 \text{ kg})(Im/s^2)$$
$$I\,N = I \text{ kg.m/s}^2$$

Work *(W)* is defined as the force times the distance through which the force acts (d).

$$W = Fd \tag{3.2}$$

In the International System, the unit of work is the joule (symbol, J). The joule is defined as the work done when a force of one newton acts through a distance of one meter:

$$W = Fd$$
$$1\text{ J} = (1 \text{ N})(1 \text{ m})$$
$$= 1 \text{ N.m}$$
$$= 1 \text{ kg.m}^2/s^2$$

Energy may be defined as the capacity to do work. There are many forms of energy, such as heat energy,-electrical energy, and chemical energy, When one form of energy is converted into another form, energy is neither created nor destroyed. The SI unit of work, the joule, is the unit used for all energy measurements, including heat measurements. The unit is named in honor of James Joule (1818-1889), a student of John Dalton, who demonstrated that a given quantity of work always produces the same quantity of heat.

3.2 Temperature and Heat

Most liquids expand as the temperature increases. The mercury thermometer is designed to use the expansion of mercury to measure

temperature. The thermometer consists of a small bulb sealed to a tube that has a narrow bore (called a capillary tube). The bulb and part of the tube contain mercury, the space above the mercury is evacuated, and the upper end of the tube is sealed. When the temperature increases, the mercury expands and rises in the capillary tube.

The Celsius temperature scale, named for Anders Celsius, a Swedish astron-omer, is employed in scientific studies and is part of the International System. The scale is based on the assignment of 0°C to the normal freezing point of water and 100°C to the normal boiling point of water. When a thermometer is placed in a mixture of ice and water, the mercury will stand at a height that is marked on the tube as 0°C. When the thermometer is placed in boiling water under standard atmospheric pressure, the mercury will rise to a position that is marked 100°C. The tube is marked between these two fixed points to indicate 100 equal divisions, each of which represents one degree. The thermometer is calibrated below 0°C and above 100°C by marking off degrees of the same size. The Celsius scale was formerly called the centigrade scale, derived from the Latin words *centum* (a hundred) and *gradus* (a degree).

On the Fahrenheit temperature scale (named for G. Daniel Fahrenheit, a German instrument maker) the normal freezing point of water is 32°F and the normal boiling point of water is 212°F. Since there arc 100 Celsius degrees and 180 (212 minus 32) Fahrenheit degrees between these two fixed points, 5 Celsius degrees equal 9 Fahrenheit degrees.

The Fahrenheit temperature scale is not used in scientific work. Conversion of a temperature from the Fahrenheit scale (T_f) to the Celsius scale (t_c) can be accomplished in the following way:

1. Subtract 32 from the Fahrenheit reading. The value obtained tells how many Fahrenheit degrees the temperature is above the freezing point of water.

Figure 1 Comparison of the Celsius (centigrade) and Fahrenheit temperature scalss

2. Since 5 Celsius degrees equal 9 Fahrenheit degrees, 5/9 of the value obtained is the number of Celsius degrees above the freezing point of water, which is 0°C.

Hence,

$$t_c = \frac{5^0 C}{9^0 C} (t_F - 32°F) \tag{3.3}$$

In Figure 3.1, the two temperature scales are compared. The thermodynamic temperature scale, called the Kelvin scale, is described in Section 8.3,

Temperature is defined as the degree of hotness. Heat, on the other hand, is a form of energy. In the past, chemists have customarily measured heat in calories. The specific bent of a substance is denned as the amount of heat required to raise the temperature of 1 g of the substance by 1°C. The calorie was originally defined in terms of the specific heat of water. The one-degree temperature interval had to be specified, however, since the specific heat of water changes slightly as the temperature changes. For many years, the calorie was defined as the

amount of heat required to raise the temperature of I g of water from 14.5°C to 15.5°C.

Very precise determinations of heat energy, in joules, can be made by electrical measurements. The joule, therefore, is a better primary standard of heat than the specific heat of water. The caloric is now defined by its joule equivalent:

1 cal = 4.184J (exactly)

Several points should be noted:

1. The joule and the calorie are relatively small units for measurement of ther-mochemical values. Such values are frequently reported in kilojoules (a kJ is 1000 J) and kilocalories (a kcal is 1000 cal).

2. The International Committee of Weights and Measures recommends that all energy measurements be based on the joule and that the calorie no longer be used, In the past, however, thermochemical values have customarily been recorded in calorie's and'kilocalories.

   a. To convert a value given in *calories to joules,* multiply by (4.184J/1 cal).

   b. To convert a value given in *kilocalories to kilojoules,* multiply by (4.184 kJ/1 kcal).

   3. For our purposes, the specific heat of water can be considered to be a constant, 4.184J/(g°C) or 1.000cal/(g°C), over any temperature interval between the freezing point and boiling point of water.

Figure 2: Bomb calorimeter

3.3 Calorimetry

The heat capacity (C) of a given mass of a substance is the amount of heat required to raise the temperature of the mass by 1.°C. Specific heat is the heat capacity of *one gram* of a substance the amount -of heat required to raise the temperature of 1 g of the substance by 1°C Therefore,

$$C = \text{(mass) (specific heat)} \tag{3.4}$$

Since the specific heat of water is 4.184 J/(g°C), the heat capacity of 500 g of water is

C=[500g][4.18J/(g°C)]

- 2090 J/°C = 2.09 kJ/°C

This sample absorbs 2.09 kJ of heat for each degree that the temperature increases. Twice this amount of heat would be required to raise the temperature by 2°C. In general,

$$q = C(t_2 - t_1)$$

where *q* is the heat absorbed by the sample, C is the heat capacity of the sample, t_2 is the final temperature, and t_1 is the initial temperature. The heat absorbed by a 500-g sample of water when it is heated from 20.00°C to 25.00°C can be calculated in the following way:

$$q = C(t_2 - t_1) \tag{3.5}$$

$$= (2.09 \text{ kJ/°C})(25.00°C - 20.00°C)$$

$$= (2509 \text{ kJ/°C})(5.00°C)$$

$$= 10.4 \text{ kJ}$$

A device called a calorimeter is used to measure the heat changes that accompany chemical reactions. A calorimeter consists of a vessel, in which the reaction is conducted, submerged in a weighed quantity of water in a well-insulated container. The reaction is run using known quantities of reactants, and the heat evolved by the reaction increases the temperature of the water and the calorimeter. The amount of heat

liberated by the reaction can be calculated from the increase in temperature if the total heat capacity of the calorimeter and its contents is known.

Example 3.1

A bomb type of calorimeter (Figure 3.2) is used to measure the heat evolved by the combustion of glucose, $C_6H_UO_6$:

$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O \ (1)$$
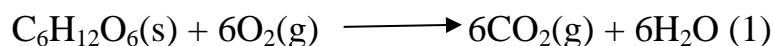
A 3.00-g sample of glucose is placed in the bomb, which is then filled with oxygen gas under pressure. The bomb is placed in a well-insulated calorimeter vessel that is filled with 1.20 kg of water. The initial temperature of the assembly is 19.00°C. The reaction mixture is ignited by the electrical heating of a wire within the bomb. The reaction causes the temperature of the calorimeter and its contents to increase to 25.50°C. The heat capacity of the calorimeter is 2.21 kJ/°C. The molecular weight of glucose is 180. How much heat is evolved by the combustion of I mol of glucose?

Solution

Since 1200 g of water is employed and the specific heat of water is 4.13 J/(g°C), the heat capacity of the water in the calorimeter, C_{H2O}, is

$$C = (mass)(specific\ heat)$$

$$C_{H2O} = [1200g][4.18J/(g°C)]$$

$$= 5016\ J/°C = 5.02\ kJ/°C$$

The heat capacity of the calorimeter, C_{cat}, is 2.21 kJ/°C. The total heat capacity, C_{total} is . .

$$C_{total} = C_{H2O} + C_{cal}$$

$$= 5.02kJ/°C + 2.21\ kJ/°C$$

$$= 7.23\ kJ/°C$$

Thus, 7.23 kJ of heat is needed to raise the temperature of the assembly by 1°C. The amount of heat *absorbed* by the calorimeter and the water is

$q = C(t_2 - t_1)$

$= (7.23 \text{ kJ/°C})(25.50°C - 19.00°C)$

$= (7.23 \text{ kJ/°C})(6.50°C)$

$= 47.0 \text{ kJ}$

This quantity (47.0 kJ) is also the amount of heat *evolved* by the combustion of 3,00 g of glucose. Therefore,

$47.0 \text{ kJ} = 3.00\text{g } C_6H_{12}O_6$

For a mol of glucose (180 g of glucose), the quantity of heat evolved is

$?\text{kJ} = 180\text{g}C_6H_{12}O_6 \left(\dfrac{47.0 \, kJ}{3.00 g\, C_6 H_{12} O_6} \right. = 2.82 \times 10^3 \text{ kJ}$

3.4 Thermochemical Equations

If a reaction that produces a gas is run in a closed container, the pressure inside the container will increase. Most reactions, however, are run in containers that are open to the atmosphere. For these reactions, the pressure is constant whether gases are produced or not.

The heat liberated or absorbed by reactions that are conducted under constant pressure can be related to a property that is called enthalpy and is given the symbol *H,* Every pure substance is assumed to have an enthalpy (which is also called a heat content). A given set of reactants, therefore, has a definite total enthalpy, $H_{reactants}$ The corresponding set of products also has a definite total enthalpy, $H_{products}$- The heat of reaction is the difference between these enthalpies and is therefore given.the symbol ΔH. The upper case Greek delta, A, is used to indicate a difference:

$\Delta H = H_{products} - H_{reactants}$

Reactions that liberate heat are called exothermic reactions. For reactions of this type, the products have a lower enthalpy than the reactants; ΔH is a negative value. When the reaction occurs, the products replace the reactants **in** the system. The enthalpy of the reaction system declines (ΔH is negative), and the difference is given off as heat (see Figure 3).

Reactions that absorb heat are called endothermic reactions. For reactions of this type, the enthalpy of the products is higher than the enthalpy of the reactants, and ΔH is positive. When the reaction occurs, heat must be supplied in order to raise the enthalpy of the system (see Figure 4).

The enthalpies of chemical substances depend upon temperature and pressure. By convention, ΔH values are usually reported for reactions run at 25°C and standard atmospheric pressure. If any other conditions are employed, they are noted.

Thermochemical data may be given by writing a chemical equation for the reaction under consideration and listing beside it the ΔH value for the reaction *as it is written.* The appropriate value of ΔH is the one required when the equation is read in molar quantities. Contrary to usual practice, fractional coefficients may be used to balance the chemical equation. A fractional coefficient simply indicates a fraction of a mole of a substance. Thus,

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(1) \quad \Delta H = -286 \text{ kJ}$$

When 1 mol of hydrogen gas reacts with 1 mol of oxygen gas to produce I mol of liquid water, 286 kJ of heat is evolved.

The state of each substance in the reaction must be indicated in the equation. A designation, such as (g) for gas, (s) for solid, (1) for liquid, or(aq) for "in aqueous solution," is placed after each formula. The need

for this convention can be demonstrated by comparing the following equation with the preceding one:

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$ $\Delta H = -242kJ$. ;
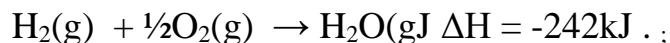
Notice that 44 kj less heat is liberated by the second reaction than by the first reaction. This quantity of heat is used to convert 1 mol of H_2O (1) to 1 mol of $H_2O(g)$.

When an equation is reversed, the sign of ΔH is changed. A reaction that is endothermic in one direction is exothermic in the opposite direction:

$\frac{1}{2}H_2(g) + \frac{1}{2}I_2(s) \rightarrow HI(g)$ $\Delta H = +25.9$ kJ

$HI(g) \rightarrow \frac{1}{2}H_2(g) + \frac{1}{2}I_2(s)$ $\Delta H = -25.9kJ$

If the coefficients of the substances in a chemical equation are multiplied by a factor, the ΔH value nuisl he multiplied by the sume factor. For example, if the

Figure 3: Enthalpy diagram for an exothermic reaction

Figure 4: Enthalpy diagram (or an endothermic reaction

Last equation is multiplied through by 2, the ΔH value must also be multiplied by 2:

$$2HI(g) \rightarrow H_2(g) + I_2(s) \qquad \Delta H = 2(-25.9 \text{ kJ}) = -51.8 \text{kJ}$$

In like manner, the coefficients of an equation and the ΔH value can be divided by the same number.

The conventions for writing thermochemical equations can be summarized as follows:

1. For exothermic reactions (the reaction system loses heat), ΔH is negative. For endothermic reactions (the reaction system absorbs heat), ΔH is positive.

2. Unless otherwise noted, ΔH values are given for reactions run at 25°C and standard atmospheric pressure.

3. Designations such as (g), (s), (I), and (aq) are placed behind the formulas in the equation to indicate the physical state of each substance.

4. The coefficients of the substances of the chemical equation indicate the number of moles of each substance involved in the reaction (fractions may be used), and the ΔH value given corresponds to these quantities of materials.

5. If the coefficients in the chemical equation are multiplied or divided by a factor, the ΔH value must be multiplied or divided by the same factor,

6. When a chemical equation is reversed, the sign but not the magnitude of the ΔH value is changed.

Thermochemical problems are solved in much the same way that simple stoichiometric problems are solved.

Example 3.2

The thermite reaction is highly exothermic:

$$2 \text{ Al}(s) + Fe_2O_3(s) \rightarrow 2 \text{ Fe}(s) + Al_2O_3(s) \qquad \Delta H = -848 \text{ kJ}$$
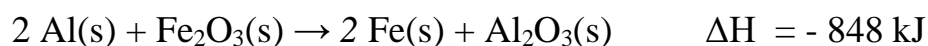
How much heat is liberated when 36,0 g of Al reacts with excess Fe_2O_3?

Solution

The equation and ΔH value show that

-848 kJ = 2mol Al

Since the atomic weight of Al is 27.0,

? kJ = 36.0 g Al $\left(\left(\dfrac{1\ mol\ Al}{27.0\ g\ Al}\right)\left(\dfrac{-848\ kJ}{2\ mol\ Al}\right)\right)$ = - 565 kJ
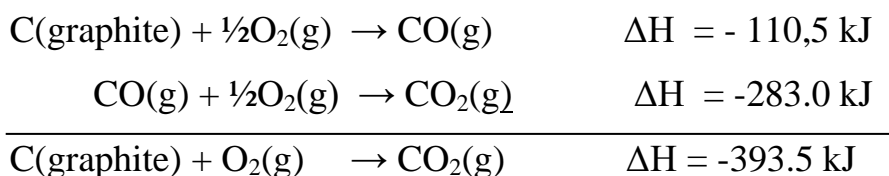
3.5 The Law of Hess

The basis of many thermochemical calculations is the law of constant he;it summation, which was established experimentally by G. H. Hess in 1840. This law of Hess states that the change in enthalpy for any chemical reaction is constant, whether the reaction occurs in one step or in several steps. Thermochemical data, therefore, may be treated algebraically.

Consider, for example, the reaction of graphite with oxygen that produces carbon dioxide gas:

$C(graphite) + O_2(g) \rightarrow CO_2(g)$ ΔH = -393.5 kJ
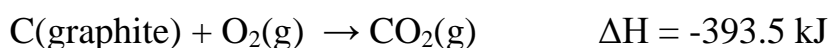
This transformation also can occur in two steps: the reaction of graphite with O_2 that forms CO followed by ihc reaction of the CO with O_2 that forms CO_2, Addition of the equations for the steps gives a result that is identical with the equation for the direct reaction (see Figure 3.5).

$\underline{\begin{array}{lll} C(graphite) + ½O_2(g) \rightarrow CO(g) & \Delta H = -110,5\ kJ \\ \quad CO(g) + ½O_2(g) \rightarrow CO_2(g) & \Delta H = -283.0\ kJ \end{array}}$

$C(graphite) + O_2(g) \quad \rightarrow CO_2(g)$ ΔH = -393.5 kJ

Since thermochemical data can be treated algebraically, it is possible to derive an enthalpy of reaction from measurements made on other reactions Suppose, for example, thai the following thermochemical equations are given:

Figure 5 Enthalpy diagram to illustrate the law o(Hess law)

$$C(graphite) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H = -393.5 \text{ kJ } (3.7)$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(I) \qquad \Delta H = -285.9 \text{ kJ } (3.8)$$

$$CO_2(g) \, H_2O(g) \rightarrow CO_2(g) + H_2O(I) \qquad \Delta H = -890.4 \text{ kJ } \quad (3.9)$$

These relations can be used to find the ΔH for the reaction in which methane, CH_4, is prepared from carbon.and hydrogen. This enthalpy change cannot be measured directly:

$$C(graphite) + H_2(g) \rightarrow CH_4(g) \qquad \Delta H = ?$$
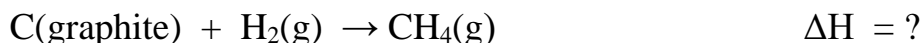
Since 1 moi of C(graphite) appears on the left of equation (3.7) and *also* on the left of the desired equation, equation (3.7) is written as previously given:

$$C(graphite) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H = -393.5 \text{ kJ} \qquad (3.7)$$

Two moles of $H_2(g)$ appear on the left of the desired equation and only 1 moi of $H_2(g)$ appears on the left of equation (3.8). Equation (3.8), therefore, is multiplied through by 2, and the ΔH value is multiplied by 2:

$$2H_2(g) + O_2(g) \rightarrow H_2O(I) \qquad \Delta H = -571.8 \text{ kJ } (3.10)$$

One mole of $CH_4(g)$ appears on the *right* side of the desired equation. Therefore, equation (3.9) is reversed, and the sign of the ΔH value is changed:

$$CO_2(g) + 2H_2O(1) \rightarrow CH_4(g) + 2O_2(g) \qquad \Delta H = +890.4 \text{ kJ } \quad (3.11)$$

Equations (3,7), (3.10), and (3.11) are added. Terms common to both sides of the final equation ($2O_2$, CO_2, and 2 H_2O) are canceled.

Qgraphile) + 2 $H_2(g) \rightarrow CH_4(g)$ ΔH = - 74.9 kJ
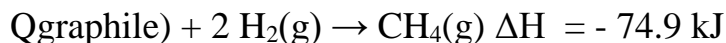
The resulti0opp-00png ΔH value is the enthalpy of reaction that was sought.

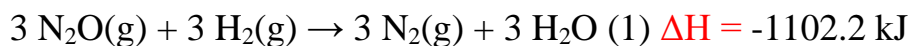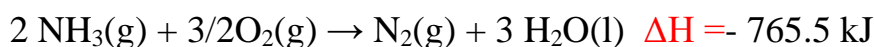**Example 3.3**

Given the following thermochemical equations:

$4NH3(g) + 3O_2(g) \rightarrow 2N_2(g) + 6H_2O(I)$ ΔH = - 1531 kJ   (3.12)

$N_2O(g) + H_2(g) \rightarrow N_2(g) + H_2O(l)$ ΔH = - 367.4 kJ   (3.13)

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(1)$ ΔH = -285.9 kJ   (3.14)

Find the value of ΔH for the reaction

$2NH_3(g\} + 3N_2O(g) \rightarrow 4N_2(g) + 3H_2O(I)$
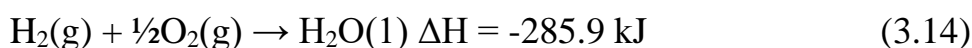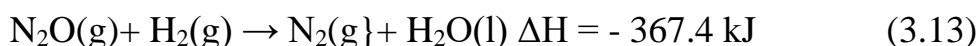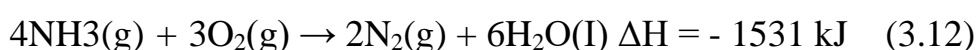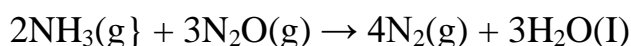
Solution

Since the desired equation has 2 mol of NH_3 on the left, we divide equation (3.12) by 2 and the ΔH value by 2. We multiply equation (3.13) and the corresponding ΔH value by 3 so that the coefficient of N_2O in the final equation will be 3. To eliminate the 3 $H_2(g)$ added to the left by the last step, we reverse equation (3.14) and multiply it by 3; the ΔH value is multiplied by 3 and its sign changed:

2 $NH_3(g) + 3/2O_2(g) \rightarrow N_2(g) + 3 H_2O(l)$ ΔH =- 765.5 kJ

3 $N_2O(g) + 3 H_2(g) \rightarrow 3 N_2(g) + 3 H_2O (1)$ ΔH = -1102.2 kJ

$3H_2O(1) \rightarrow 3H_2(g) + 3/2O_2(g)$ AH = +857.7 kJ

The equations and A// values are added. Terms common to both sides of the final equation ($3/2O_2$, 3 H_2, and 3 H_2O) are canceled:

2 $NH_3(g) + 3 N_2O(g) \rightarrow 4 N_2(g) + 3 H_2O (1)$ ΔH = - 1010.0 kJ
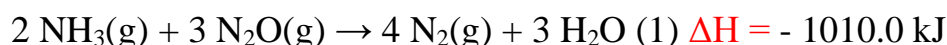
3.6 Enthalpies of Formation

The enthalpy of an element or compound depends upon the temperature and pressure. If we wish to compare ΔH values, the conditions under which they have been measured must be identical. The standard state of a substance is the state in which the substance is stable at 1 atm pressure and 25°C. The symbol ΔH is used to indicate standard enthalpy changes, which apply to reactions involving only materials in their standard states.

The standard enthalpy of formation, $\Delta H°_f$ of a compound is the enthalpy change for the reaction in which 1 mol of the compound in its standard state is made from its elements in their standard states. Enthalpy of formation, therefore, is a specific type of enthalpy change. The ΔH values for the reactions shown in Figures 3 and 4 are in reality the ΔH values of $H_2O(l)$ and $HI(g)$, respectively:

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O\,(l) \qquad \Delta H_f^{\circ} = -2K5.9\,kJ$$

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}I_2(s) \rightarrow HI(g) \qquad \Delta H_f^{\circ} = +25.9\,kJ$$

Enthalpies of formation are either measured directly or calculated from other thermochemical data by applying the law of Hess. The result of the calculation of this type given in Section 3.5,

$$C\,(graphite) + 2H_2(g) \rightarrow CH_4(g) \qquad \Delta H_f^{\circ} = -74.9\,kJ$$
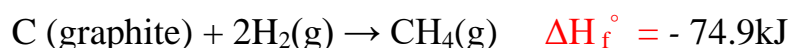
is the enthalpy of formation of $CH_4(g)$. Some enthalpies of formation are listed in Table 3.1

Table 1: Enthalpies of formation of some compounds.

Compound	ΔH_f° (kJ/mol)	Compound	ΔH_f° (kJ/mol)
$H_2O(g)$	-241.8	$COCl_2(g)$	-223.
$H_2O(l)$	-285.9	$SO_2(g)$	-296.9
$HF(g)$	-269	$CO(g)$	-110.5
$HCl(g)$	-92.30	$CO_2(g)$	-393.5
$HBr(g)$	-36.2	$NO(g)$	+ 90.37
$Hl(g)$	+ 25.9	$NO_2(g)$	+ 33.8
$H_2S(g)$	-20.2	$HNO_3(I)$	-173.2
$HCN(g)$	+ 130.5	$NH_4NO_3(s)$	-365.1
$NH_3(g)$	-46.19	$NaCl(s)$	-411.0
$PH_3(g)$	+ 9.25	$MgO(s)$	-601.83
$CH_4(g)$	-74.85	$CaO(s)$	-635.5
$C_2H_6(g)$	-84.68	$Ca(OH)_2(s)$	-986.59
$C_2H_4(g)$	+ 52.30	$CaCO_3(s)$	-1206.9
$C_2H_2(g)$	+ 226.7	$Ca_3P_2(s)$	-504.17
$C_6H_6(1)$	+ 49.04	$BaO(s)$	-583.1
$CH_3OH(g)$	-201.2	$BaCO_3(s)$	-1218.
$CH_3OH(l)$	-238.6	$Al_2O_3(s)$	- 1669.8
$CH_3NHjtg)$	-28	$Fe_2O_3(s)$	-822.2
$NF_3\{H\}$	-113	$AgC(s)$	- 127.0
$CF_4(g)$	-913.4	$HgBr_2(s)$	-169
$CHCl_3(I)$	-132	$ZnO(s)$	-348.0

The enthalpy change for a reaction can be calculated from the enthalpies of formation of the compounds involved in the reaction. For example, the enthalpy change for the reaction

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g) \; \Delta H_f^\circ = ?$$
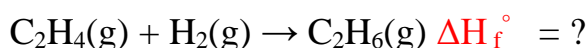
can be calculated from the enthalpies of formation of ethylene, $C_2H_4(g)$, and ethane, $C_2H_6(g)$:

$$2C(graphite) + 2 H_2(g) \rightarrow C_2H_4(g) \qquad \Delta H_f^\circ = + 52.30 \text{ kJ} \quad (3.15)$$

$$2C(graphite) + 3H_2(g) \rightarrow C_2H_6(g) \qquad \Delta H_f^\circ = - 84.68 \text{ KJ} \quad (3.16)$$
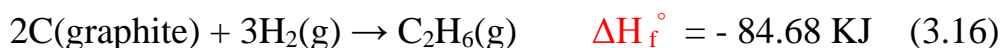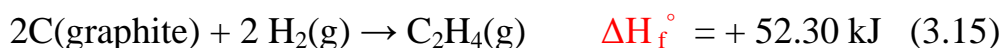
The reverse of equation (3.15) indicates a transformation in which $C_2H_4(g)$ breaks down into its elements. The appropriate value of the enthalpy change for the reversed reaction is ΔH_f° (C_2H_4) or -52.30 kJ. The elements from the decomposition of $C_2H_4(g)$ plus an additional mole of $H_2(g)$ can be imagined to form $C_2H_6(g)$; equation (3.16) is written as shown. When these two equations are added, the desired thermochemical expression is obtained:

$$C_2H_4(g) \rightarrow 2C(graphite) + 2H_2(g) \qquad \Delta H_f^\circ = - 52.30 \text{ kJ}$$

$$\underline{2C(graphite) + 3H_2(g) \rightarrow C_2H_6(g) \qquad \Delta H_f^\circ = - 84.68 \text{ kJ}}$$

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g) \qquad \Delta H_f^\circ = - 136.98 \text{ kJ}$$
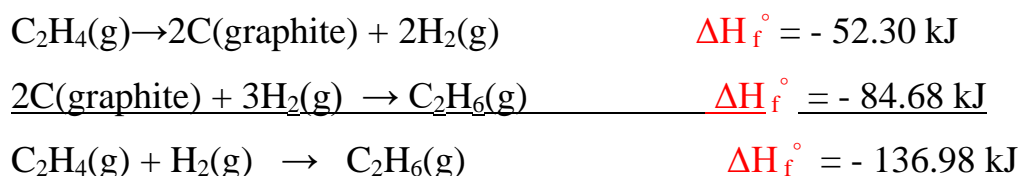
The ΔH of the reaction is, therefore, ΔH_f° (C_2H_6) - ΔH_f° (C_2H_4).

In general, a $\Delta H\circ$ value for a reaction may be obtained by subtracf.ing the sum of the enthalpies of formation of the reactants from the sum of the enthalpies of formation of the products:

$$\Delta H\circ = \Sigma\Delta H_f^\circ \text{ (products) - } \Sigma\Delta H_f^\circ \text{ (reactants)}$$

The uppercase Greek sigma, Σ, indicates a sum. By reversing the sign of (reactants), we indicate a process in which the reactants are broken down into the elements. The formation of the products from these elements is indicated by the term $\Sigma\Delta H_f^\circ$ (products).

Two factors frequently cause trouble in the use of this approach for the calculation of $\Delta H\circ$ values.

1. Enthalpies of formation are given in kilojoules per *mole.* The chemical equation that corresponds to a value listed in Table 3.1 pertains to the formation of only *one* mole of the compound. If more than one mote (or less than one mole) of the compound is involved in the reaction being studied, the ΔH_f° value must be multiplied by the number of moles involved.

2. The enthalpy of formation of an *element* in its standard state is zero (the enthalpy change when an element is prepared from itself). No terms for elements are added into the sums $\Sigma\Delta H\circ$ (products) and $\Sigma\Delta H\circ$ (reactants),

Consider the reaction

$2 NH_3(g) + 3 Cl_2(g) \rightarrow N_2(g) + 6 HCl(g)$ $\Delta H =$?
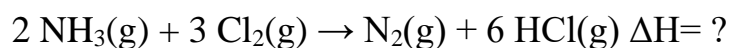
The enthalpy change for the reaction can be calculated in the following way:

$\Delta H^\circ = \Sigma\Delta H_f^\circ$ (Products) - $\Sigma\Delta H_f^\circ$ (reactants)

$= 6 \Delta H_f^\circ(HC1) - 2 \Delta H_f^\circ(NH_3)$

$= 6(-92.30kJ) - 2(- 46.19 kJ)$

$= -553.80kJ + 92.38 kJ = -461.42kJ$

This calculation may be checked by the addition of the appropriate thermo-crTemical equations. Since 6 mol of HCl(g) are prepared, the equation for the formation of HCI(g) is multiplied through by 6 and the enthalpy of formation of HCl(g) is multiplied by 6. -Two moles of NH_3(g) are *consumed* in the reaction. The equation for *the formation* of NH_3(g) is multiplied through by 2 and *reversed;* the value of ΔH° is multiplied by 2 and the sign changed. These two thermochemical expressions are added. No separate equations are introduced for the elements thai are involved in the reaction ($C1_2$ and N_2):

$3H_2(g) + 3Cl_2(gJ) \rightarrow 6HCl(g)$ $\qquad \Delta H^\circ = 6 \Delta H_f^\circ = -553.80kJ$

$\underline{\qquad 2NH_3(g) \rightarrow N_2(g) + 3H_2(g) \quad \Delta H^\circ = -2 \Delta H_f^\circ = +92.38 \text{ kJ}}$

$2NH_3(g) + 3Cl_2(g)\text{------}N_2(g) + 6HCl(g)$ $\qquad \Delta H^\circ = -461.42 \text{ kj}$
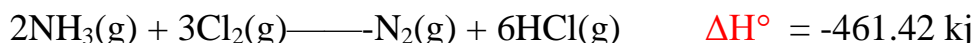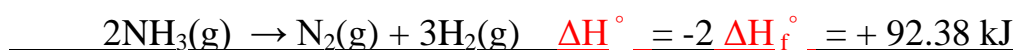
The terms "$3H_2(g)$" cancel in the addition. Notice that "$3Cl_2(g)$" and "$N_2(g)$" appear in the final equation even though no special provision was made for their introduction.

Example 3.4

Use enthalpies of formation to calculate the ΔH° of the reaction

$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$

Solution

The values needed can be found in Table 3.1

$\Delta H^\circ = \Sigma \Delta H_f^\circ \text{ (Products)} - \Sigma \Delta H_f^\circ \text{ (reactants)}$

$= 3\Delta H^\circ (CO_2) - [3\Delta H^\circ(Fe_2O_3) + 33\Delta H^\circ (CO)]$

$= 3(-393.5 \text{ kJ}) - [(-822.2 \text{ U}) + 3(-110.5 \text{ kJ})]$

$= -1180.5 \text{ kJ} + 11 \ 53.7 \text{ kJ} = -26.8 \text{ kJ}$

Example 3.5

Given the following data;

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(1) \quad \Delta H^\circ = -890.4 \text{ kJ}$
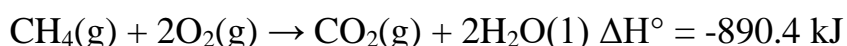
the enthalpy of formation of $CO_2(g)$ is - 393.5 kJ/mol, the enthalpy of formation of $H_2O(1)$ is -285,9 kj/mol. Calculate the enthalpy of formation of $CH_4(g)$.

Solution

In this case, the value of ΔH for a reaction is known and a ΔH° value for one of the reactants is sought.

$\Delta H^\circ = \Sigma \Delta H_f^\circ \text{ (products)} - \Sigma \Delta H_f^\circ \text{ (reactants)}$

$\Delta H^\circ = \Delta H_f^\circ (CO_2) + 2\Delta H_f^\circ (H_2O) - \Delta H_f^\circ (CH_4)$

$$-890.4 \text{ kJ} - (-393.5 \text{ kJ}) + 2(-285.9\text{kJ}) - \Delta H_f^\circ \text{ (CH}_4)$$

$$- 890.4 \text{ kJ} = -965.3 \text{ kJ} - \Delta H^\circ \text{ (CH}_4)$$

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

Using Enthalpies of Formation to derive AH Values

1. Write the chemical equation for the reaction.

2. Substitute in the equation:

$$\Delta H^\circ = \Sigma \Delta H_f^\circ \text{ (products) } -\Sigma \Delta H_f^\circ \text{ (reactants)}$$

(a) The term $\Sigma \Delta H^\circ$ (products) is the sum of the enthalpies of formation , .of the *compounds* that appear on the *right* side of the chemical equation..

(b) The term $\Sigma \Delta H^\circ$ (reactants) is the sum of the enthalpies of formation of *the compounds* that appear on the *left* side of the chemical equation.

To obtain either of these sums, multiply the enthalpy of formation of each compound by the number of moles of that compound involved in the reaction (given by the appropriate coefficient of the chemical equation). No enthalpy terms are introduced for *elements* that appear in the chemical

3.7 Bond Energies

Atoms are held together in molecules by chemical bonds. The energy required to *break* the bond that holds two atoms together in a diatomic molecule is called the bond dissociation energy. These values are reported in kilojoules per mole of bonds. In the following equations, which illustrate this process, dashes are used to represent the bonds between atoms; H_2, for example, appears as H—H:

$$\text{H - H(g)} \rightarrow 2 \text{ H(g)} \qquad \Delta H = +435 \text{ kJ}$$

$$\text{Cl - Cl(g)} \rightarrow 2\text{Cl(g)} \qquad \Delta H = +243 \text{ kJ}$$

$$\text{H-Cl(g)} \rightarrow \text{H(g)} + \text{CI(g)} \qquad \Delta H = +431 \text{ kJ}$$
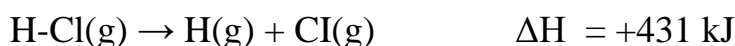
Each of these ΔH values is *positive,* which indicates that energy is *absorbed* in each process. The bond in the H_2 molecule is the strongest of

the three. It takes the most energy to pull the atoms of the H_2 molecule apart.

If one of these equations is reversed, the sign of the ΔH value must be changed;

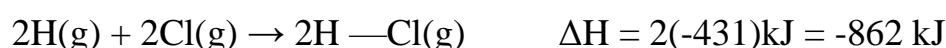$H(g) + Cl(g) \rightarrow H\text{—}Cl(g)$ $\Delta H = -431$ kJ

When a bond forms, energy is *released* the same amount that is *required* to break the bond.

Bond energies may be used to determine ΔH values. Consider the reaction

$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$ $\Delta H = 2\Delta H° = -184.6$ kJ
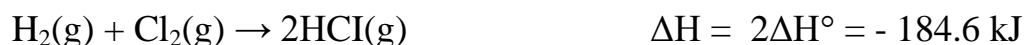
The ΔH for this reaction is twice the enthalpy of formation of $HCl(g)$ since the equation indicates the formation of two moles of $HCl(g)$. We can derive this ΔH value from bond energies in the following way. The enthalpy change is the sum of the energy *required* to break 1 mol of H— H bonds, the energy *required* to break 1 mol of Cl—Cl bonds, and the energy *evolved'by* the formation of 2 mol of H—Cl bonds.

$\text{H-H}(g) \rightarrow 2H(g)$ $\Delta H = +435$kJ

$Cl\text{—}Cl(g) \rightarrow 2Cl(g)$ $\Delta H = +243$kJ

$2H(g) + 2Cl(g) \rightarrow 2H\text{—}Cl(g)$ $\Delta H = 2(-431)$kJ $= -862$ kJ

The sum of these equations is

$H\text{—}H(g) + Cl\text{—}Cl(g) \rightarrow 2H - Cl(g)$ $\Delta H = -184$ kJ

A molecule that contains more than two atoms, such as H_2O, is called a polyatomic molecule. Molecules of this type contain more than one bond. There are, for example, two H—O bonds in the H_2O molecule. The AH for

$H\text{—}O\text{—}H(g) \rightarrow 2\,H(g) + O(g)$ $\Delta H = +926$ kJ
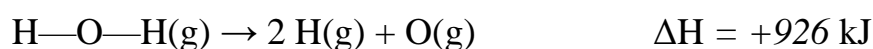
refers to a process in which *two* moles of H—O bonds are broken. The average bond energy of the H—O bond, therefore, is +926 kJ/mol, or +463 kJ/mol.

In the H_2O molecule, the H—O bonds are equivalent. If the bonds were broken one at a time, however, the AH values would not be the same.

H- O—H(g) → H(g) + O—H(g) $\Delta H = +501$ kJ

O—H(g) → O(g) + H(g) $\Delta H = +425$ kJ
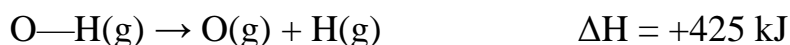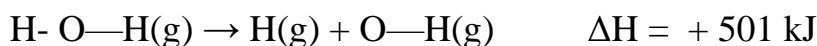
The average of the AH values for the steps is + 463 kJ/mol, which is the average bond energy. In general, the second .bond of a molecule such as H_2O is easier .to break than the first. The fragment remaining after one H has been removed (0—H) is not as stable as the original molecule (H—O—H).

The bond energy of.a given type of bond is not the same in all molecules containing that bond. The H—O bond energy in H—O—H is different from the H—O bond energy in H—O—Cl. The values listed in Table 3.2 for diatomic molecules are bond dissociation energies. The other values listed are average bond energies, and each of these values is an average derived from a large number of cases. Since average bond energies are approximations, a ΔH value obtained by use of these values must be regarded as an estimate.

In some molecules, two atoms are bonded together by more than one bond. Two nitrogen atoms, for example, can be joined by a single bond (N—N), a double bond (N=N), or a triple bond (N≡N), depending on the molecule. Multiple bonds are indicated in Table 3.2.

Example 3.6

Use average bond energies to calculate the value of ΔH for the reaction

$$\begin{array}{c} \text{H} \\ | \\ 2\text{H}{-}\text{N}{-}\text{H}(g) + 3\text{C1}{-}\text{Cl}(g) \rightarrow \text{N}{\equiv}\text{N}(g) + 6\text{H}{-}\text{Cl}(g) \end{array}$$
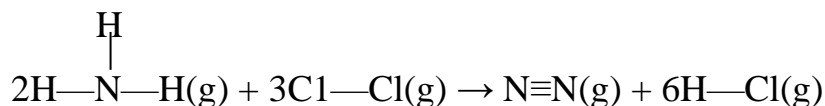
Solution

We can imagine the reaction to take place by a series of steps. Energy is absorbed (ΔH is positive) when a bond is broken, and energy is evolved (ΔH is negative) when a bond is formed.
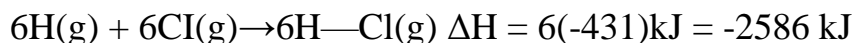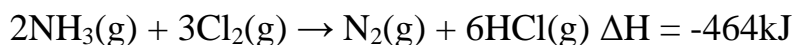
Six N—H bonds are broken:

$$\begin{array}{c} \text{H} \\ | \\ 2\,\text{H}{-}\text{N}{-}\text{H}(g) \rightarrow 2\,\text{N}(g) + 6\,\text{H}(g) \end{array} \qquad \Delta H = 6(+389)\text{kJ} = +2334\text{kJ}$$
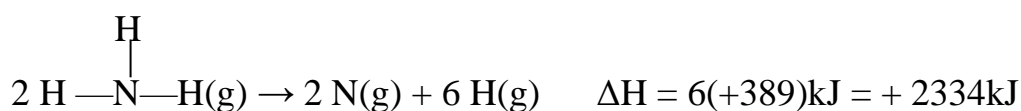
Three Cl—Cl bonds are broken:

$$3\text{C1}{-}\text{Cl}(g) \underline{\hspace{1cm}} 6\text{Cl}(g) \qquad \Delta H = 3(+243)\text{kJ} = +729\text{kJ}$$

One N≡N bond is formed: .

$$2\,\text{N}(g) \rightarrow \text{N}{\equiv}\text{N}(g) \qquad\qquad \Delta H = -941 \text{ kJ}$$

Six H—Cl bonds are formed:

$$6\text{H}(g) + 6\text{CI}(g) \rightarrow 6\text{H}{-}\text{Cl}(g) \quad \Delta H = 6(-431)\text{kJ} = -2586 \text{ kJ}$$

The sum of these steps is the answer to the problem:

$$2\text{NH}_3(g) + 3\text{Cl}_2(g) \rightarrow \text{N}_2(g) + 6\text{HCl}(g) \quad \Delta H = -464\text{kJ}$$

In Section 3.6, enthalpies of formation were used to calculate the value of ΔH for this reaction. The value obtained in this way (— 461 kj) is a more reliable value than the one derived from bond energies (— 464 kJ).

Table 2: Average bond energy for various bonds.

Bond	Average Bond Energy (kJ/mol)	Bond	Average Bond Enprgy
H— H	435	P— H	318
H—F	56S	N— Cl	20
H— Cl	431	P— Cl	329
H— Br	364	C— C	347
H— I	297	C=C	619
F — F	155	C≡C	812
Cl— Cl	243	C— H	414
Br— Br	193	C— 0	335
I— I	151	C=O	707
0—0	138	C— F	485
O_2^b	494	C— C	326
0 — H	463	C— N	2S3
0— F	184	C=N	616
O—CI	205	C≡N	879
N— N	159	S— H	339
N=N	418	S— S	213
N≡N	941	S— Cl	276
N— H	389		

* Reactants and products in gaseous state.

* Double bond of molecular oxygen.

Chapter

Electrochemistry

All chemical reactions are fundamentally electrical in nature since electrons are involved (in various ways) in all types of chemical bonding. Electrochemistry, however, is primarily the study of oxidation-reduction phenomena.

The relations between chemical change and electrical energy have theoretical as well as practical importance. Chemical reactions can be used to produce electrical energy (in cells that are called either voltaic or galvanic cells). Electrical energy can be used to bring about chemical transformations (in electrolytic cells). In addition, the study of electrochemical processes leads to an understanding, as well as to the systemization, of oxidation-reduction phenomena that take place outside cells.

1 Metallic Conduction

An electric current is the flow of electric charge. In metals this charge is carried by electrons, and electrical conduction of this type is called metallic conduction. The current results from the application of an electric force supplied by a battery or some other source of electrical energy. A complete circuit is necessary to produce a current.

Metallic crystals may be described in terms of mobile electron clouds permeating relatively fixed lattices of positive metal ions. When electrons are forced into one end of a metal wire, the impressed electrons displace other electrons of the cloud at the point of entry. The displaced electrons, in turn, assume new positions by pushing neighboring electrons ahead, and this effect is transmitted down the length of the wire until

electrons are forced out of the wire at the opposite end. The current source may be regarded as an electron pump, for it serves to force electrons into one end of the circuit and drain them off from the other end. At any position in the wire, electrical neutrality is preserved, since the rate of electrons in equals the rate of electrons out.

The analogy between the flow of electricity and the flow of a liquid is an old one. In earlier times electricity was described in terms of a current of "electric fluid." Conventions of long standing, which may be traced back to Benjamin Franklin (1747) and which were adopted before the electron was identified, ascribe a positive charge to this current. We shall interpret electrical circuits in terms of the movement of electrons. Remember, however, that conventional electric current is arbitrarily described as positive and as flowing in the opposite direction.

Electric current is measured in amperes (A). Quantity of electric charge is measured in coulombs (C); the coulomb is defined as the quantity of electricity carried in one second by a current of one ampere. Therefore,

1 A = 1 C/s and

and

1 C = 1 A-s

The current is forced through the circuit by an electrical potential difference, which is measured in volts (V). It takes one joule of work to move one coulomb from a lower to a higher potential when the potential difference is one volt. One volt, therefore, equals one joule/coulomb, and one volt-coulomb is a unit of energy and equals one joule:

1 V = 1 J/C

1 V.C = I J

The higher the potential difference between two points in a given wire, the more current the wire will carry between those two points. George Ohm in 1826 expressed the quantitative relation between potential difference, $ in volts, and current, *I*, in amperes, as

I= E /R or E = IR

Where the proportionality constant, *R,* of Ohm's law is called the resistance. Resistance is measured in ohms (Ω). One volt is required to force a current of one ampere through a resistance of one ohm.

Resistance to the flow of electricity in metals is probably caused by the vibration of the metal ions about their lattice positions. These vibrations interfere with the motion of the electrons and retard the current. As the temperature is increased, the thermal motion of the metal ions is increased. Hence, the resistance of metals increases and the metals become poorer conductors.

2 Electrolytic Conduction

Electrolytic conduction, in which the charge is carried by ions, will not occur unless the ions of the electrolyte are free to move. Electrolytic conduction, therefore, is exhibited principally by molten salts and by aqueous solutions of electrolytes. Furthermore, a sustained current through an electrolytic conductor requires that chemical change accompany the movement of ions.

These principles of electrolytic conduction are best illustrated by reference

Figure 1 : Electrolysis of molten sodium chloride

an electrolytic cell such as the one diagrammed in Figure 1 for the electrolysis of molten NaCl between inert electrodes. The current source pumps electrons into the left-hand electrode, which therefore may be considered to be negatively charged. Electrons are drained from the right-hand, positive electrode. In the electric field thus produced, sodium ions (cations) are attracted toward the negative pole (cathode), and chloride ions (anions) are attracted toward the positive pole (anode). Electric charge in electrolytic conduction is carried by cations moving toward the cathode and anions moving in the opposite direction, toward the anode.

For a complete circuit, electrode reactions must accompany the movement of ions. At the cathode some chemical species (not necessarily the charge carrier) must accept electrons and be reduced. At the anode, electrons must be removed from some chemical species, which as a consequence is oxidized. The conventions relating to the terms anode and cathode are summarized in Table 18.1.

In the diagrammed cell, sodium ions are reduced at the cathode:

$Na^+ + e^- \rightarrow Na$
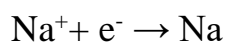
and chloride ions are oxidized at the anode:

$2Cl^- \rightarrow Cl_2 + 2e^-$
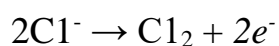
Table 1: The conventions relating to anode and cathode electrodes

	Cathodes	**Anodes**
Ions attracted	Cations	Anions
Direction of electron movement	Into cell	Out of cell
Half-reaction	Reduction	Oxidation
Sign		
Electrolysis cell	Negative	Positive
Galvanic cell	Positive	Negative

Proper addition of these two partial equations gives the reaction for the entire cell:

$$2\text{Na Cl (l)} \xrightarrow{\textit{electrolysis}} 2\text{ Na (l)} + \text{Cl}_2\text{ (g)}$$
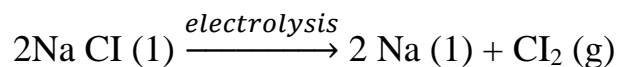
the actual operation of the commercial cell used to produce metallic sodium, calcium chloride is added to lower the melting point of sodium chloride, and the cell is operated at a temperature of approximately 600°C. At this temperature, sodium metal is a liquid.

We can trace the flow of negative charge through the circuit of Figure 18.1 as follows. Electrons leave the current source and are pumped into the cathode where they are picked up by and reduce sodium ions that have been attracted to this negative electrode. Chloride ions move away from the cathode toward the anode and thus carry negative charge in this direction. At the anode, electrons are removed from the chloride ions, thus oxidizing them to chlorine gas. These electrons are pumped out of the cell by the current source. In this manner the circuit is completed.

Electrolytic conduction, then, rests on the mobility of ions, and anything that inhibits the motion of these ions causes resistance to the current. Factors that influence the electrical conductivity of solutions of electrolytes include interionic attractions, solvation of ions, and viscosity of the solvent. These factors rest on solute-solute attractions, solute-solvent attractions, and solvent-solvent attractions, respectively. The average kinetic energy of the solute ions increases as the temperature is raised, and therefore, the resistance of electrolytic conductors generally decreases as the temperature is raised (that is, conduction increases). Furthermore, the effect of each of the three previously mentioned factors decreases as the temperature is increased.

At all times the solution is electrically neutral. The total positive charge of all of the cations equals the total negative charge of all of the anions.

3. Electrolysis

The electrolysis of molten sodium chloride serves as a commercial source of sodium metal and chlorine gas. Analogous procedures are used to prepare other very active metals (such as potassium and calcium). When certain aqueous solutions are electrolyzed, however, water is involved in the electrode reactions rather than the ions derived from the solute. Hence, the current-carrying ions are not necessarily discharged at the electrodes.

Figure 2: Electrolysis of aqueous sodium sulphate

In the electrolysis of aqueous sodium sulfate, sodium ions move toward the cathode and sulfate ions move toward the anode (see Figure 18.2). Both these ions are difficult to discharge. When this electrolysis is conducted between inert electrodes, hydrogen gas is evolved at the cathode, and the solution surrounding the electrode becomes alkaline. Reduction occurs at the cathode; but rather than the reduction of the sodium ion:

$$e^- + Na^+ \rightarrow Na$$
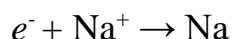
the *net change* that occurs is the reduction of water:

$$2e + 2H_2O \rightarrow H_2(g) + 2OH^-$$
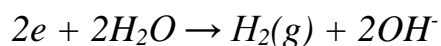
Water is an extremely weak electrolyte. Pure water is approximately 2 x 10^{-7} % ionized at 25°C:

$$2H_2O \rightarrow H_3O^3 + OH^-$$

or, more briefly,

$$H_2O \rightarrow H^2 + OH^-$$
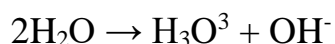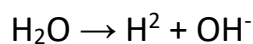
The exact mechanism of the cathode reaction in the electrolysis of aqueous Na_2SO_4 is not known. It may be that the hydrogen ions from water are discharged and that the reaction proceeds as follows:

$$H_2O \leftrightharpoons H^+ + OH^-$$

$$2e^- + 2H^+ \rightarrow H_2 \text{ (g)}$$
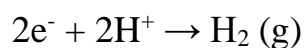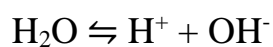
Multiplication of the first equation by 2 followed by addition of the two equations gives the net change

$2e^- + 2H_2O \rightarrow H_2(g) + 2OH^-$
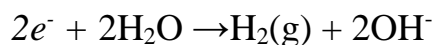
In general, water is reduced at the cathode (producing hydrogen gas and hydroxide ions) whenever the cation of the solute is difficult to reduce.

Oxidation occurs at the anode, and in the electrolysis of aqueous Na_2SO_4 the anions (SO_4^{2-}) that migrate toward the anode are difficult to oxidize:

$$SO_4^{2-} \rightarrow S_2O_8^{2-} \ 2e^-$$
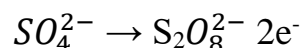
Therefore, the oxidation of water occurs preferentially. The mode of this reaction may be

$$H_2O \rightarrow H^+ + OH^-$$

$$4 OH^- \rightarrow O_2 \text{ (g)} + 2H_2O + 4e^-$$
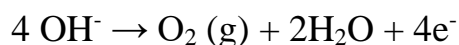
Multiplying the first equation by 4 and adding the equations, we get the net change

$$2 H_2O \rightarrow O_2 \text{ (g)} + 4H^- + 4e^-$$
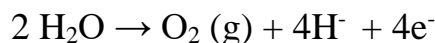
At the anode the evolution of oxygen gas is observed, and the solution surrounding the pole becomes acidic. In general, water is oxidized at the anode (producing oxygen gas and hydrogen ions) whenever the anion of the solute is difficult to oxidize.

The complete reaction for the electrolysis of aqueous Na_2SO_4 may be obtained by adding the cathode and anode reactions:
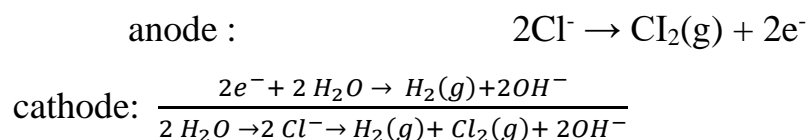
$$2 \, [2e^- + 2H_2O \rightarrow H_2(g) + 2OH^-]$$
$$\underline{2H_2O \rightarrow O_2(g) + 4H^- + 4e^-}$$
$$6 \, H_2O \rightarrow 2 \, H_2(g) + O_2(g) + 4H^+ \, 4OH^-$$
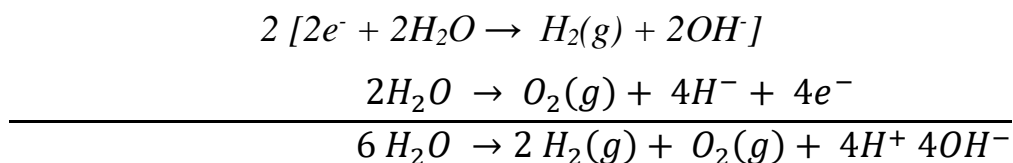
If the solution is mixed, the hydrogen and hydroxide ions that are produced neutralize one another, and the net change

$$2H_2O \xrightarrow{\text{electrolysis}} 2H_2\text{ (G)} + O_2\text{(G)}$$
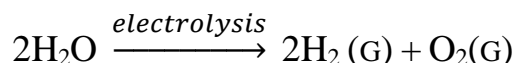
is merely the electrolysis of water. In the course of the electrolysis, the hydrogen ions migrate away from the anode, where they are produced, toward the cathode. In like manner, the hydroxide ions move toward the anode. These ions neutralize one another in the solution between the two electrodes.

The electrolysis of an aqueous solution of NaCl between inert electrodes serves as an example of a process in which the anion of the electrolyte is discharged, but the cation is not:

anode : $\qquad\qquad 2Cl^- \rightarrow Cl_2(g) + 2e^-$

cathode: $\dfrac{2e^- + 2\,H_2O \rightarrow H_2(g) + 2OH^-}{2\,H_2O \rightarrow 2\,Cl^- \rightarrow H_2(g) + Cl_2(g) + 2OH^-}$

Since the sodium ion remains unchanged in the solution, the reaction may be indicated

$$2H_2O + 2Na^+ + 2Cl^- \xrightarrow{\text{electrolysis}} H_2 \text{ (g)} + Cl_2\ 2Na^+ + 2OH^-$$
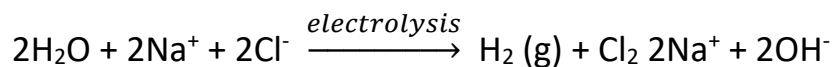
This process is a commercial source of hydrogen gas, chlorine gas, and, by evaporation of the solution left after electrolysis, sodium hydroxide,

In the electrolysis of a solution of $CuSO_4$ between inert electrodes (see right portion of Figure 18.4, given subsequently), the current is carried by the Cu^{2+} and SO_4^{2-} ions. The current-carrying cations are discharged, but the anions are not:

anode: $2\ H_2O \rightarrow O_2 \text{ (g)} + 4H^+ + 4e^-$

cathode: $$\frac{2[2e^- + Cu^{2+} \rightarrow Cu(s)]}{2Cu^{2+} + 2H_2O \rightarrow O_2\ (g) + 2Cu\ (s) + 4H^-}$$
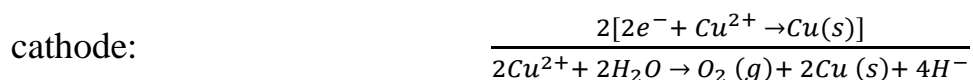
Figure3   Electrolysis of aqueous cupric sulfate between copper electrodes
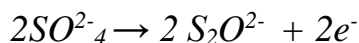
It is, of course, possible to have both ions of the solute discharged during the electrolysis of an aqueous solution. An example is the electrolysis of **CuCl₂** between inert electrodes;

anode: $\qquad\qquad\qquad\qquad$ $2Cl^- \rightarrow Cl_2\ (g) + 2e^-$

cathode: $\dfrac{2e^- + Cu^{2+} \rightarrow Cu(s)}{cu^{2+} + 2Cl^- \rightarrow Cu\ (s) + Cl_2(g)}$
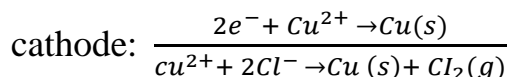
It is also possible to have the electrode itself enter into an electrode reaction. If aqueous $CuSO_4$ is electrolyzed between copper electrodes (see Figure 18.3), Cu^{2+} ions are reduced at the cathode:

$$2e^- + Cu^{2+} \rightarrow Cu$$
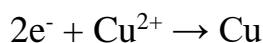
but of the *three* possible anode oxidations:

$$2SO^{2-}_{\ 4} \rightarrow 2\ S_2O^{2-}\ + 2e^-$$

$$2H_2O \rightarrow O_2(g)\ + 4H^+ + 4e^-$$

$$Cu(s) \rightarrow Cu^{2+} + 2e^-$$
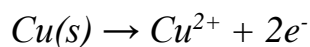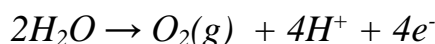
the oxidation of the copper metal of the electrode is observed to occur. Hence, at the anode, copper from the electrode goes into solution as Cu^{2+} ions, and at the cathode, Cu^{2+} ions plate out as Cu(s) on the electrode. This process is used to refine copper. Impure copper is used as the anode of an electrolytic cell, and a solution of $CuSO_4$ is electrolyzed. Pure copper plates out on the cathode. Active electrodes are also used in electroplating processes. In silver plating, silver anodes are employed.

4 Stolchiometry of Electrolysis

The quantitative relationships between electricity and chemical change were first described by Michael Faraday in 1 832 and 1 833. Faraday's work is best understood • by reference to the half- reactions

that occur during electrolysis. The change at the cathode in the electrolysis of molten sodium chloride:

$$Na^+ + e^- \rightarrow Na$$
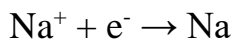
shows that one electron is required to produce one sodium atom. One mole of electrons (Avogadro's number of electrons) is required to produce one mole of sodium metal (22.9898 g Na). The quantity of charge equivalent to one mole of electrons is called the farad?) (F) and has been found to equal 96,485 coulombs (C), which for ordinary problem work is customarily rounded off to 96,500 C:

1 F = 96,500 C

If 2 F of electricity were used, 2 mol of Na would be produced.

In the same time that electrons equivalent to 1 F of electricity are added to the cathode, that same number of electrons is removed from the anode:

The removal of 1 mol of electrons (1 F) from the anode would result in the discharge of 1 mol of Cl^- ions and the production of 0.5 mol of chlorine gas. If 2 F of electricity flow through the cell, 2 mol of CP ions are discharged and 1 mol of Cl_2 gas liberated.

Electrode reactions, therefore, may be interpreted in terms of moles and faradays. The anode oxidation of the hydroxide ion, for example,

$$4OH^- \rightarrow O_2(g) + 2H_2O + 4e^-$$
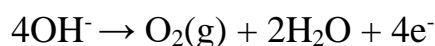
may be read as stating that 4 mol of OH ~ ion produce 1 mol of O_2 gas and 2 mol of H_2O when 4 F of electricity are passed through the cell.

The relationships between moles of substances and faradays of electricity are the basis of stoichiometric calculations that involve electrolysis. Remember that one ampere (1A) is equal to a current rate of one coulomb (1 C) per second:

$$1 \text{ A} = 1 \text{ C/s}$$

Example 1

The charge on a single electron is 1.6022 x 10⁻¹⁹ C. Calculate Avogadro's number from the fact that 1 F = 96,485 C.

Solution

? electrons = 9.6485 x 10^4 C $\dfrac{1\ \text{electron}}{1.6022\ x\ 10^{-19}C}$

= 6.0220 x 10^{23} electrons

Example ,2

In the electrolysis of $CuSO_4$, how much copper is plated out on the cathode by a current of 0.750 A in 10.0 min?

Solution

The number of faradays used may be calculated as follows:

? F = 10.0 min ($\dfrac{60s}{1\ min}$) ($\dfrac{0.75}{I\ s}$) ($\dfrac{I\ F}{96,500\ C}$)

= 0.00466 F

The cathode reaction is $Cu^{2+} + 2e^- \rightarrow Cu(s)$, and therefore 2 F plate out 63.5 g ofCu(s):

? g Cu = 0.00466 F ($\dfrac{63.5g\ Cu\ (s)}{2F}$) = 0.148g Cu(s)

Example 3

(a) What volume of $O_2(g)$ at STP is liberated at the anode in the electrolysis of $CuSO_4$ described in Example 18.2? (b) If 100 ml of 1.00 M $CuSO_4$ is employed in the cell, what is the H^+ (aq) concentration at the end of the electrolysis? Assume that there is no volume change for the solution during the experiment and that the anode reaction is

2HO

$$2H_2O \rightarrow 4H^+ (aq) + O_2(g) + 4e^-$$
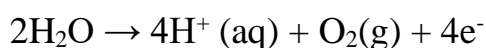
Solution

(a) Four faradays produce 22.4 liter of O_2fg) at STP:

? liter $O_2(g)$ = 0.00466 F $(\frac{22.4\ liter\ O_2(g)}{4F})$

$\qquad$ = 0.0261 liter O_2 (g)

(b) Four faradays also produce 4 mol of H^+ (aq):

? mol H^+(aq) = 0.00466 F $(\frac{1\ mol\ H^+\ (aq)}{1F})$

$\qquad$ =0.00466 mol H^+ (aq)

$\qquad$ The small contribution of H^+ (aq) from the ionization of water may be ignored, and we may assume that there are 0.00466 mol H^+(aq) in 100 ml of solution:

? mol H^+ (aq) $=$ 1000 ml solution $(\frac{.00466\ mol\ H^+\ (aq)}{100ml\ solution})$ $\qquad$ 100 ml solution

$\qquad$ = 0.0466 mol H^+(aq)

The solution is therefore 0.0466 *M* in hydrogen ion.

In Figure 18.4, two electrolytic cells are set up in series. Electricity passes through one cell first and then through the other before returning to the current source. If silver nitrate is electrolyzed in one of the cells, the cathode reaction is

$Ag^+ + e \rightarrow Ag(s)$
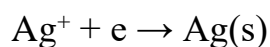
and metallic silver is plated out on the electrode used. By weighing this electrode before and after the electrolysis, one can determine the quantity of silver plated out and hence the number of coulombs that have passed through the cell. One faraday would plate out 107.868 g of silver. One coulomb, therefore, is equivalent to

(107.868 g Ag)/ (96.485 C) = 1.1180 x 10^{-3} g Ag/C

Figure 4: Silver Coulometer in series with a cell for electrolysis

The same number of coulombs pass through both cells in a given time when these cells are arranged in series. The number of coulombs used in an electrolysis, therefore, can be determined by the addition, in series, of this silver coulometer to the circuit of the experimental cell.

Example 4

(a) What mass of copper is plated out in the electrolysis of $CuSO_4$ in the same time that it takes to deposit 1.00 g of Ag in a silver coulometer that is arranged in series with the $CuSO_4$ cell? (b) If a current of 1 .00 A is used, how many minutes are required to plate out this quantity of copper?

Solution

(a) From the electrode reactions we see that 2 F deposit 63.5 g Cu and 1 F deposits   107.9 g Ag:

$$? \text{ g Cu} = 100\text{g Ag} \left(\frac{1 F}{107.9 \, g \, Ag}\right) \left(\frac{63.5g \, Cu}{2F}\right) = 0.294\text{g Cu}$$

(b) $? \text{ min} = 1.00 \text{ g Ag} \left(\frac{96,500 \, C}{107.9 \, g \, Ag}\right) \left(\frac{1 \, S}{1 \, C}\right) \left(\frac{1 \, min}{60 \, s}\right)$

$= 14.9 \text{ min}$

5. Voltaic Cells

A cell that is used as a source of electrical energy is called a voltaic cell or a galvanic cell after Alessandro Volta (1800) or Luigi Galvani (1780), who first experimented with the conversion of chemical energy into electrical energy.

The reaction between metallic zinc and copper(II) ions in solution is illustrative of a spontaneous change in which electrons are transferred:

$Zn(s) + Cu^{2+}(aq)$ —— $Zn^{2+}(aq) + Cu(s)$
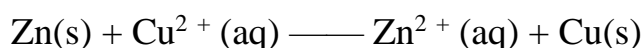
The exact mechanism by which electron transfer occurs is not known. We may, however, represent the above reaction as a combination of two half-reactions:

$Zn(s)$——$-Zn^{2+},(aq) + 2e^{-}$

$2e^{-} + Cu^{2+}(aq) \rightarrow Cu(s)$
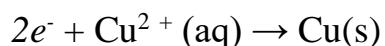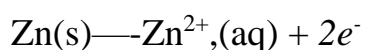
In a voltaic cell these half-reactions are made to occur at different electrodes so that the transfer of electrons takes place through the external electrical circuit rather than directly between zinc metal and copper (II) ions.

Figure 5   The Dantell cell

The cell diagrammed in Figure 18.5 is designed to make use of this reaction to produce an electric current. The half-cell on the left contains a

zinc metal electrode and $ZnSO_4$ solution. The half-cell on the right consists of a copper metal electrode in a solution of $CuSO_4$. The half-cells are separated by a porous partition that prevents the mechanical mixing of the solutions but permits the passage of ions under the influence of the flow of electricity. A cell of this type is called a Daniell cell.

When the zinc and copper electrodes are joined by a wire, electrons flow from the zinc electrode to the copper electrode. At the zinc electrode the zinc metal is *oxidized* to zinc ions. This electrode is the anode, and the electrons that are the product of the oxidation *leave* the cell from this pole (see Table 18.1). The electrons travel the external circuit to the copper electrode where they are used in the reduction of copper (II) ions to metallic copper. The copper thus produced plates out on the electrode. The copper electrode is the cathode. Here, the electrons *enter* the cell and *reduction* occurs.

Since electrons are produced at the zinc electrode, this anode is designated as the negative pole. Electrons travel from the negative pole to the positive pole in the external circuit of any voltaic cell when the cell is operating. The cathode, where electrons are used in the electrode reaction, is therefore the positive pole. Within the cell the movement of ions completes the electric circuit. At first glance, it is surprising that anions, which are negatively charged, should travel toward an anode that is the negative electrode. Conversely, cations, which carry a positive charge, travel toward the cathode, which is the positive pole.

Careful consideration of the electrode reactions provides the answer to this problem. At the anode, zinc ions are being produced and electrons left behind in the metal. At all times the electrical neutrality of the solution is maintained. In the solution surrounding the electrode there must be as much negative charge from anions as there is positive charge from cations. Hence, SO_4^{2-} ions move toward the anode to neutralize the

effect of the Zn^{2+} ions that are being produced. At the same time, zinc ions move away from the anode toward the cathode. At the cathode, electrons are being used to reduce Cu^{2+} ions to copper metal. While the Cu^{2+} ions are being discharged, more Cu^{2+} ions move into the region surrounding the cathode to take the place of the ions being removed. If this did not occur, a surplus of SO^{2-} ions would build up around the cathode.

The porous partition is added to prevent mechanical mixing of the solutions of the half-cells. If Cu^{2+} ions came into contact with the zinc metal electrode, electrons would be transferred directly rather than through the circuit. In the normal operation of the cell, this "short circuit" does not occur because the Cu^{2+} ions move in a direction away from the zinc electrode.

Actually this cell would work if a solution of an electrolyte other than $ZnSO_4$ were used in the anode compartment, and if a metal other than copper were used for the cathode. The substitutes, however, must be chosen so that the electrolyte in the anode compartment does not react with the zinc electrode and the cathode does not react with Cu^{2+} ions.

6. Electromotive Force

If 1 *M* $ZnSO_4$ and 1 *M* $CuSO_4$ solutions are employed in the Daniell cell, the cell may be represented by the notation

$$Zn(s) \, Zn^{2+} \, (1M)/Cu^{2+} \, (1M)/Cu(s)$$
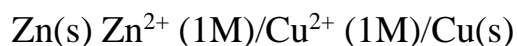
in which the vertical lines represent phase boundaries. By convention, the substance forming the anode is listed first. The other materials of the cell are then listed in the order that one would encounter them leading from the anode to the cathode. The composition of the cathode is given last.

Electric current is produced by a voltaic cell as a result of the electromotive force (emf) of the cell, which is measured in volts. The greater the tendency for the cell reaction to occur, the higher the emf of

the cell. The emf of a given cell, however, also depends upon the Concentrations of the substances used to make the ceil.

A standard emf, pertains to the electromotive force of a cell, at 25°C, in which all reactants and products are present in their standard states. The standard state of a solid or a liquid is, of course, the pure solid or pure liquid itself. The standard state of a gas or a substance in solution is a defined state of *ideal unit activity* — that is, corrections are applied for deviations from ideality caused by intermolecular and interionic attractions. For our discussion we shall make the assumption that the activity of ions may be represented by their molar concentrations and the activity of gases by their pressures in atmospheres. Hence, according to this approximation, a standard cell would contain ions at 1 *M* concentrations and gases at 1 atm pressures. In the cell notations that follow, concentrations will be indicated only if they deviate from standard.

If the emf of a cell is to be used as a reliable measure of the tendency for the cell reaction to occur, the voltage must be the maximum value obtainable for the particular cell under consideration. If there is an appreciable flow of electricity during measurement, the voltage measured, *&,* will be reduced because of the internal resistance of the cell. In addition, when the cell delivers current, the electrode reactions produce concentration changes that reduce the voltage.

The emf of a cell, therefore, must be measured with no appreciable flow of electricity through the cell. This measurement is accomplished by the use of a potentiometer. The circuit of a potentiometer includes a current source of variable voltage and a means of measuring this voltage. The cell being studied is connected to the potentiometer circuit in such a

way that the emf of the cell is opposed by the emf of the potentiometer current source.

If the emf of the cell is larger than that of the potentiometer, electrons will flow in the normal direction for a spontaneously discharging cell of that type. On the other hand, if the emf of the potentiometer current source is larger than that of the cell, electrons will flow in the opposite direction, thus causing the cell reaction to be reversed. When the two emf's are exactly balanced, no electrons flow. This voltage is the reversible emf of the cell. The emf of a standard Daniell cell is 1.10 V.

Faraday's laws apply to the cell reactions of voltaic, as well as electrolytic, cells. One precaution must be observed, however. Electricity is generated by the simultaneous oxidation and reduction half-reactions that occur at the anode and cathode, respectively. Both must occur if the cell is to deliver current. Two faradays of electricity will be produced, therefore, by the oxidation of 1 mof of zinc at the anode *together with* the reduction of 1 mol of Cu^{2+} ions at the cathode. The partial equations

anode: $Zn \rightarrow Zn^{2+} + 2e^{-}$

cathode: $2e^{-} + Cu^{2+} \rightarrow Cu$
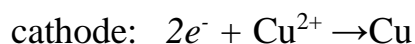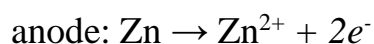
when read in terms of moles, represent the flow of two times Avogadro's number of electrons or the production of 2 F of electricity.

The quantity of electrical energy, in joules, produced by a cell is the product of the quantity of electricity delivered, in coulombs, and the emf of the cell, in volts (see Section 18.1). The electrical *energy produced by* the reaction between 1 mol of zinc metal and 1 mol of copper(II) ions may be calculated as follows:

$2(96,500 \, Q(UOV) = 212,000 \, J = 212 \, kJ$

One volt-coulomb is a joule.

The emf used in the preceding calculation is the reversible emf of the standard Daniell cell and hence the maximum voltage for this cell. Therefore, the value secured (212 kJ) is the maximum work that can be obtained from the operation of this type of cell. The maximum *net* work* that can be obtained from a chemical reaction conducted at a constant temperature and pressure is a measure of the *decrease* in the Gibbs free energy (see Section 17.4) of the system. Hence,

$$\Delta G = -nF\$$$

where *n* is the number of moles of electrons transferred in the reaction (or the number of faradays produced), *F* Is the value of the faraday in appropriate units, and *$* is the emf in volts. If .F is expressed as 96,487 C, ΔG is obtained in joules. A change in free energy derived from a standard emf, , is given the symbol ΔG. The free energy change of a reaction is a measure of the tendency of the reaction to occur. If work must be done on a system to bring about a change, the change is not spontaneous. At constant temperature and pressure a spontaneous change is one from which net work can be obtained. Hence, for any spontaneous reaction the free energy of the system decreases; ΔG is negative. Since $AG = -nF\$$, only *if $* is positive will the cell reaction be spontaneous and serve as a source of electrical energy.