



Engineering Chemistry

(BMS022)

by
Prof. Dr. Shaimaa Khalaf

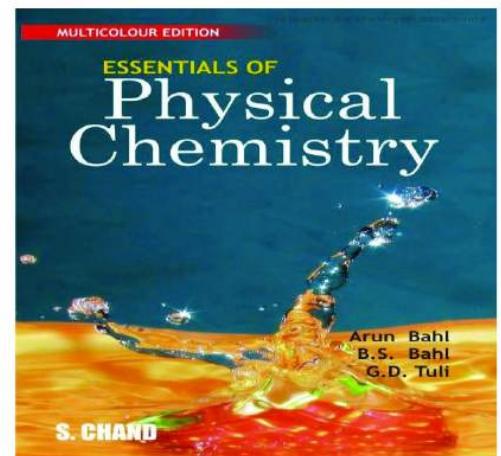


Physical Chemistry

- The branch of chemistry dealing with the relations between the physical properties of substances and their chemical composition and transformations.
- Physical Chemistry is the application of physical principles and measurements to understand the properties of matter, as well as for the development of new technologies for the environment, energy and medicine.
- Why does it happen?

Contents

1. States of Matter
 2. Solutions and Their Properties
 3. Thermochemistry
 4. Electrochemistry and Applications
 5. Chemical Industry: Chemistry of cement
 6. Chemical Thermodynamics
- **Reference:**
 - *Essentials of Physical Chemistry*
 - *by B.S. Bahl.*

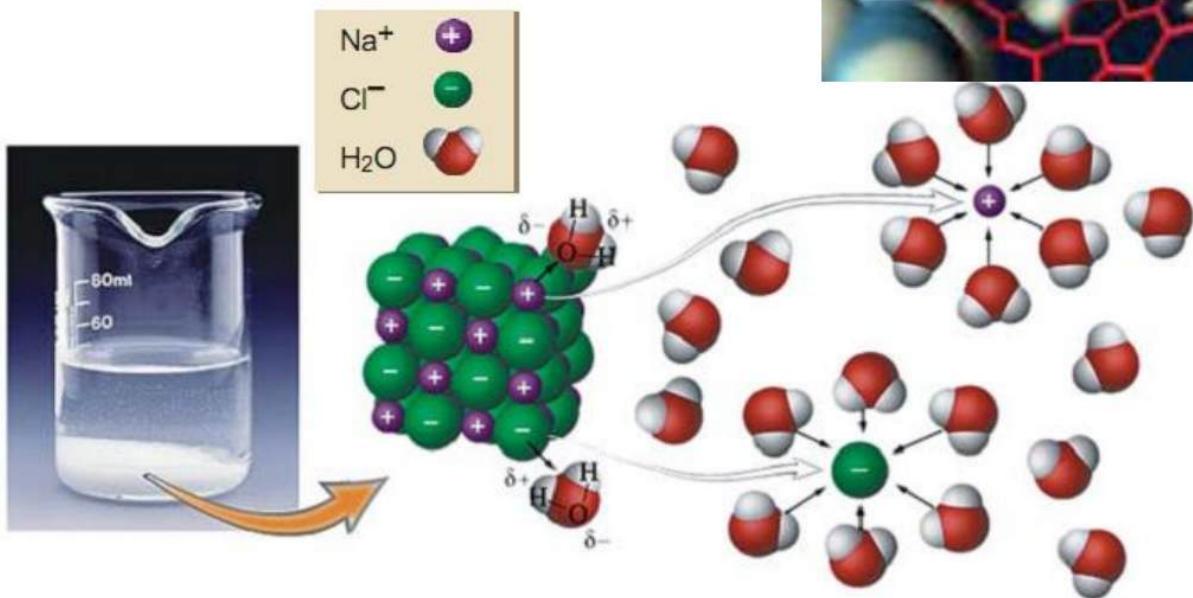
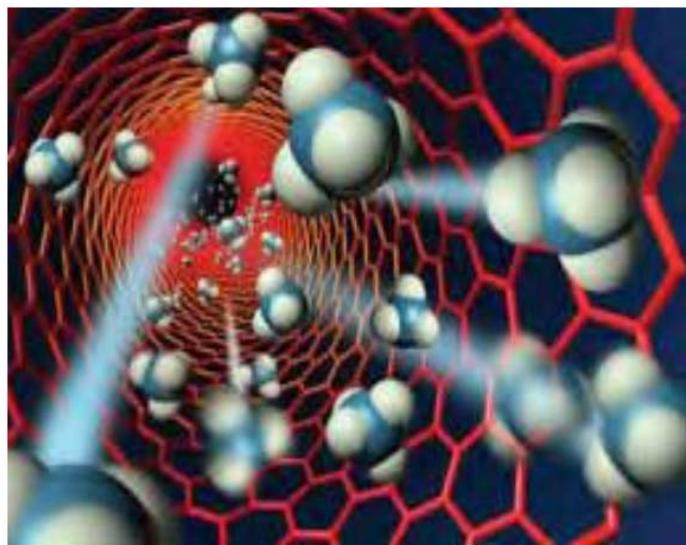




States of Matter

Gases

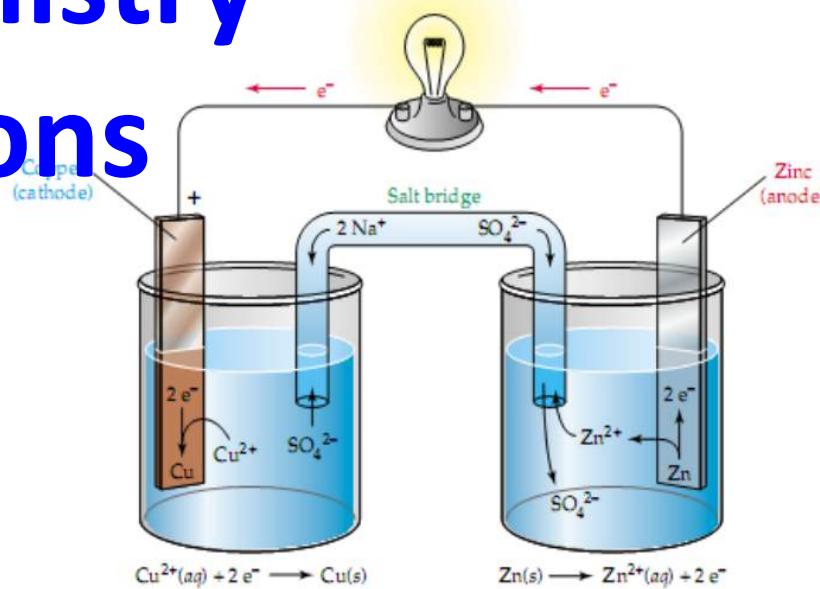
2. Solutions and Their Properties



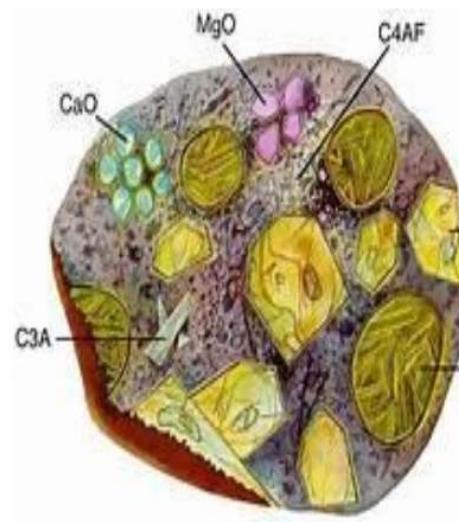
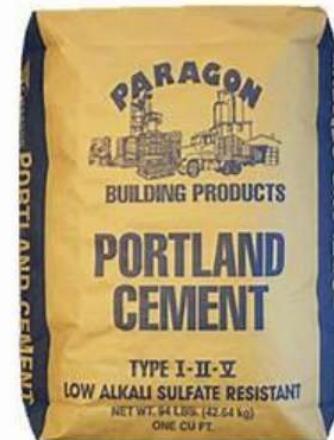
3. Thermochemistry



4. Electrochemistry and Applications



5. Chemistry of cement



Portland cement

6. Chemical thermodynamics



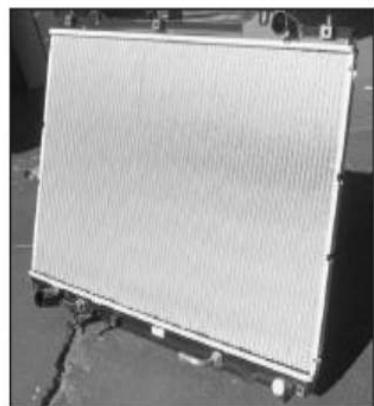
The human body



Air conditioning systems



Airplanes



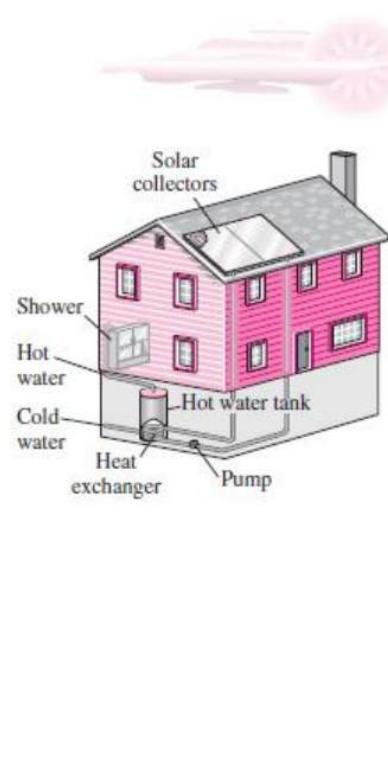
Car radiators



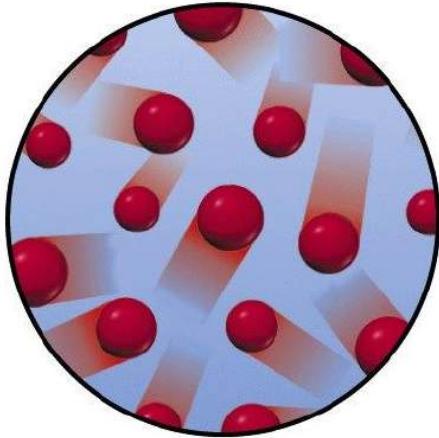
Power plants



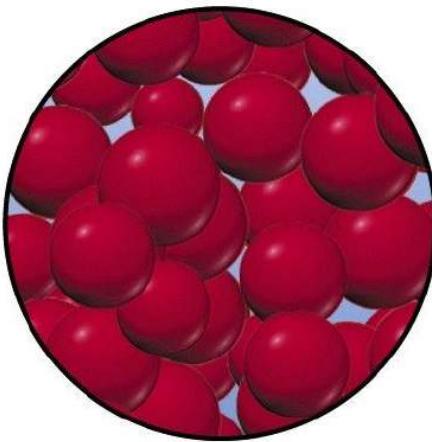
Refrigeration systems



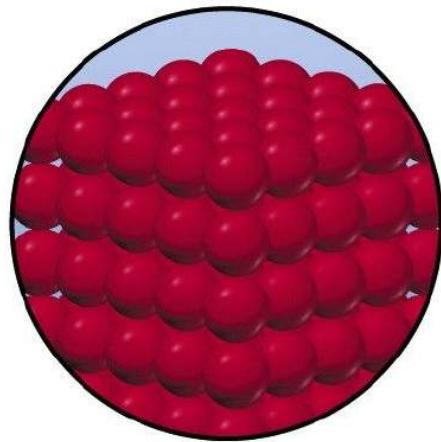
State of Matter



In gases, the particles feel little attraction for one another and are free to move about randomly.



In liquids, the particles are held close together by attractive forces but are free to move over one another.



In solids, the particles are rigidly held in an ordered arrangement.

Figure 10-1 Chemistry, 5/e
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A molecular comparison of gases, liquids, and solids.

Gaseous State

Gases: Their Properties
and Behavior

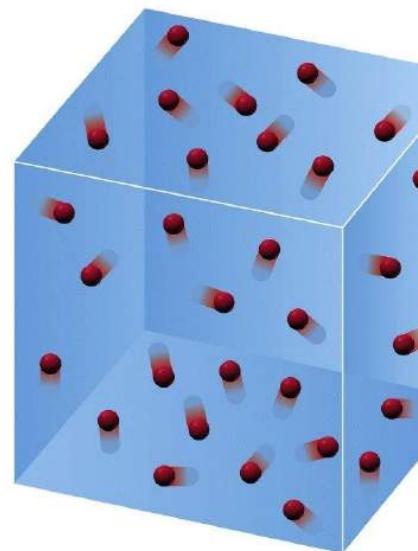
General characteristics of gases

- 1- Expansibility
- 2- Compressibility
- 3- Diffusibility
- 4- Pressure

Parameters of a gas

- The physical properties of a gas can be defined by four variables:

- P pressure
- T temperature
- V volume
- n number of moles



A gas is a large collection of particles moving at random through a volume that is primarily empty space.

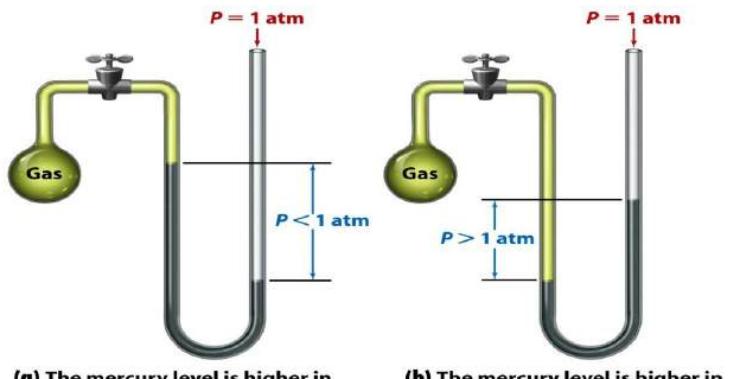
Figure 9-1 Chemistry, 5/e
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Gas Pressure (P)

Is defined as the force exerted by the impacts of its molecules per unit surface area in contact.

$$\text{Pressure: } \frac{\text{Force}}{\text{Unit area}}$$

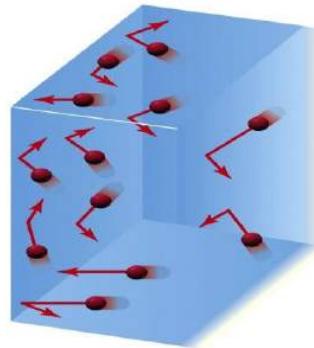
Atmospheric pressure is measured with a barometer; the pressure of any gas is measured with a manometer.



(a) The mercury level is higher in the arm open to the bulb because the pressure in the bulb is lower than atmospheric.

(b) The mercury level is higher in the arm open to the atmosphere because the pressure in the bulb is higher than atmospheric.

Figure 9-4 Chemistry, 5/e
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Collisions of randomly moving particles with the walls of the container exert a force per unit area that we perceive as gas pressure.

The empty space above the mercury in the sealed end of the tube is a vacuum.

The downward pressure of the mercury in the column is exactly balanced by the outside atmospheric pressure that presses down on the mercury in the dish and pushes it up the column.

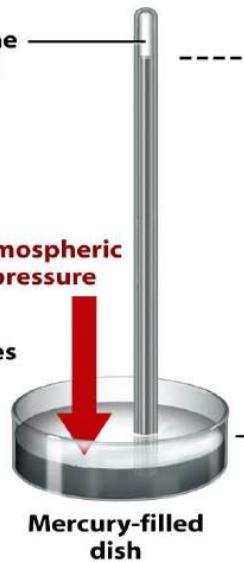


Figure 9-3 Chemistry, 5/e
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Gas volume (V)

- The volume of the container is the volume of gas. Expressed as liter or ml.

Gas temperature (T)

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

Moles of gas sample (n)

$$n = m / M$$

m = mass of gas samples

M = molar mass(weight) of sample

- Calculate the number of moles in each of the following : (C=12, H=1, O=16, N= 14)
- 16 gram of methane (CH_4)

$$n = m / M$$

$$= 16 / (12 + 4 \times 1) = 1 \text{ mole}$$

- 32 gram of NH_3

$$= 32 / (14 + 3 \times 1)$$

- 40 gram of O_2

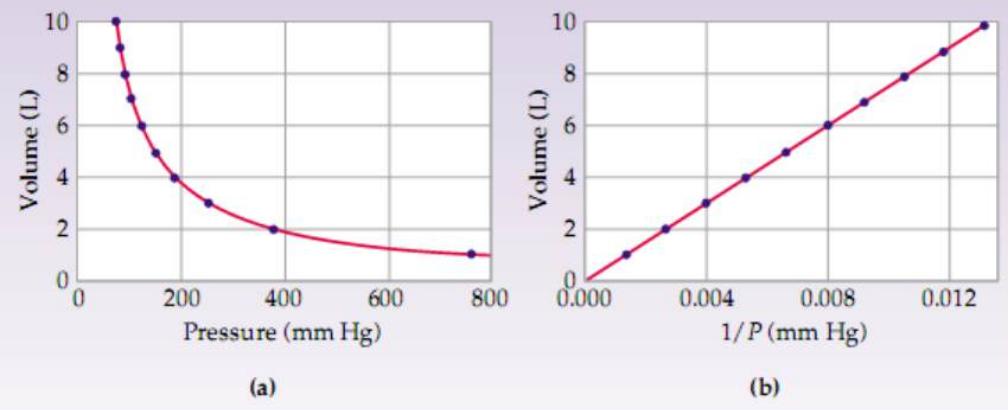
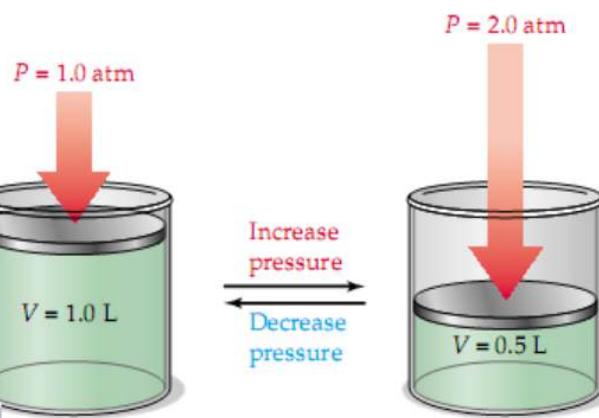
The Gas Laws

- **Boyle's Law** : The Relationship Between Volume and Pressure

$$\text{Volume} \propto \frac{1}{\text{Pressure}}$$

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

For the same gas: $P_1 V_1 = P_2 V_2 = k$

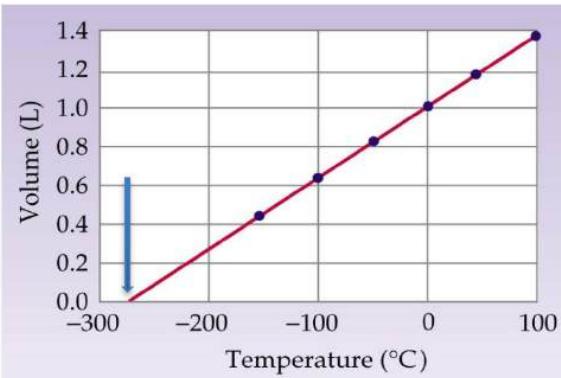
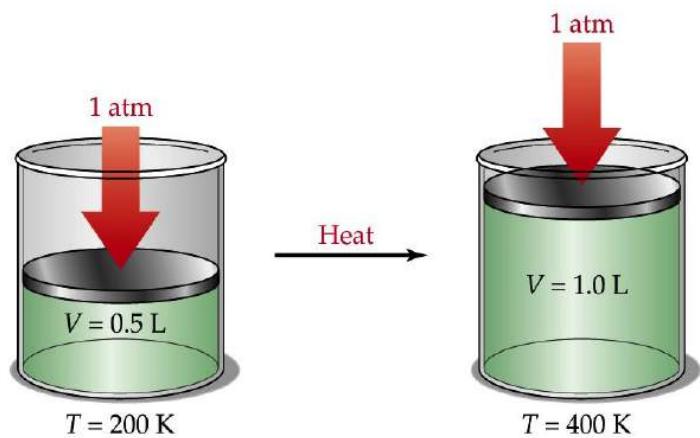


- **Charles' Law**: The Relationship Between Volume and Temperature

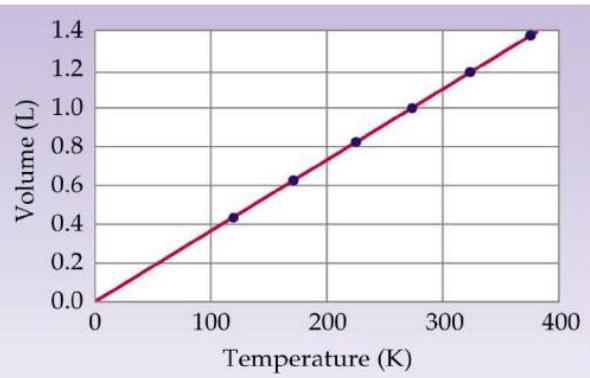
$$V \propto T$$

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

For the same gas : $\frac{V_1}{T_1} = \frac{V_2}{T_2} = k$



(a)



(b)

Combined Gas Law

Boyle's Law	$V \propto \frac{1}{P}$	(T, n constant)
Charles' Law	$V \propto T$	(P, n constant)
Therefore,	$V \propto \frac{T}{P}$	(n constant)

$$\frac{P_1 \cdot V_1}{T_1} = \frac{P_2 \cdot V_2}{T_2}$$

➤ 25.8 liter of a gas has a pressure of 690 torr and a temperature of 17°C. What will be the volume if the pressure is changed to 1.85 atm and the temperature to 345 K.

Initial conditions :

$$V_1 = 25.8 \text{ litres}$$

$$P_1 = \frac{690}{760} = 0.908 \text{ atm}$$

$$T_1 = 17 + 273 = 290 \text{ K}$$

Final Conditions :

$$V_2 = ?$$

$$P_2 = 1.85 \text{ atm}$$

$$T_2 = 345 \text{ K}$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\frac{0.908 \text{ atm} \times 25.8 \text{ litre}}{290 \text{ K}} = \frac{1.85 \text{ atm} \times V_2}{345 \text{ K}}$$

$$V_2 = \frac{0.908 \times 25.8 \times 345}{290 \times 1.85} = 15.1 \text{ litres}$$

- Oxygen gas is normally sold in 49.0 L steel containers at a pressure of 150.0 atm. What volume would the gas occupy if the pressure was reduced to 1.02 atm and the temperature raised from 20°C to 35°C?

$$V_2 = 7.575 \times 10^3 \text{ L}$$

GAY LUSSAC'S LAW

In 1802 Joseph Gay Lussac as a result of his experiments established a general relation between the pressure and temperature of a gas. This is known as Gay Lussac's Law or Pressure-Temperature Law. It states that : at constant volume, the pressure of a fixed mass of gas is directly proportional to the Kelvin temperature or absolute temperature.

The law may be expressed mathematically as

$$P \propto T \quad (\text{Volume, } n \text{ are constant})$$

or

$$P = kT$$

or

$$\frac{P}{T} = k$$

For different conditions of pressure and temperature

$$\frac{P_1}{T_1} = k = \frac{P_2}{T_2}$$

or

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

Knowing P_1 , T_1 , and T_2 , P_2 can be calculated.

Avogadro's Law The Volume–Amount Law

At constant pressure and temperature, the volume of a gas is directly proportional to the number of moles of the gas.

$$V \propto n$$

(T and P constant)

or

$$V = An$$

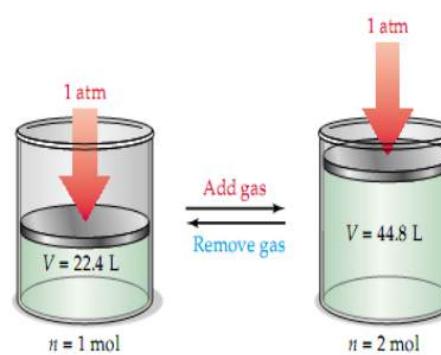
where A is constant of proportionality.

$$\text{or } \frac{V}{n} = A$$

For any two gases with volumes V_1 , V_2 and moles n_1 , n_2 at constant T and P,

$$\frac{V_1}{n_1} = A = \frac{V_2}{n_2}$$

If $V_1 = V_2$, $n_1 = n_2$



The Molar Gas Volume.

- It follows as a corollary of Avogadro's Law that one mole of any gas at a given temperature (T) and pressure (P) has the same fixed volume. It is called the molar gas volume or molar volume. In order to compare the molar volumes of gases, chemists use a fixed reference temperature and pressure. This is called **standard temperature and pressure** (abbreviated, STP). The standard temperature used is 273 K (0°C) and the standard pressure is 1 atm (760 mm Hg). At STP we find experimentally that one mole of any gas occupies a volume of 22.4 liters. To put it in the form of an equation, we have
- **1 mole of a gas at STP= 22.4 liters**

The Ideal Gas Law

Ideal gases obey an equation incorporating the laws of Charles, Boyle, and Avogadro.

$$P \cdot V = n \cdot R \cdot T$$

1 mole of an ideal gas occupies **22.414 L** at **STP**

STP = **Standard Temperature Pressure**

STP conditions are **273.15 K** and **1 atm** pressure

The gas constant $R = \mathbf{0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}$

$$R = \frac{P \cdot V}{n \cdot T} = \frac{(1 \text{ atm})(22.414 \text{ L})}{(1 \text{ mol})(273.15 \text{ K})} = 0.082\ 058 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} = 8.3145 \text{ J}/(\text{K} \cdot \text{mol})$$

In fact, there is no such thing as an ideal gas that obeys the equation perfectly under all circumstances; all real gases deviate slightly from the behavior predicted by the law

- How many moles of air are in the lungs of an average adult with a lung capacity of 3.8 L? Assume that the person is at 1.00 atm pressure and has a normal body temperature of 37°C.

$$n = \frac{PV}{RT} = \frac{(1.00 \text{ atm})(3.8 \text{ L})}{\left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}}\right)(310 \text{ K})} = 0.15 \text{ mol}$$

- In a typical automobile engine, the mixture of gasoline and air in a cylinder is compressed from 1.0 atm to 9.5 atm. If the uncompressed volume of the cylinder is 410 mL, what is the volume (in milliliters) when the mixture is fully compressed?

This is a Boyle's law problem because only P and V are changing, while n and T remain fixed. We can therefore set up the following equation and solve for V_{final} .

$$(PV)_{\text{initial}} = (PV)_{\text{final}} = nRT$$

SOLUTION

$$V_{\text{final}} = \frac{(PV)_{\text{initial}}}{P_{\text{final}}} = \frac{(1.0 \text{ atm})(410 \text{ mL})}{9.5 \text{ atm}} = 43 \text{ mL}$$

Density and Molar Mass Calculations:

$$d = \frac{\text{mass}}{\text{volume}} = \frac{n \cdot M}{V} = \frac{P \cdot M}{R \cdot T}$$

You can calculate the **density or molar mass (M)** of a gas. The density of a gas is usually very low under atmospheric conditions

Units of density: g/ L

To identify the contents of an unlabeled cylinder of gas, a sample was collected and found to have a density of 5.380 g/L at 15°C and 736 mm Hg pressure.

What is the molar mass of the gas?

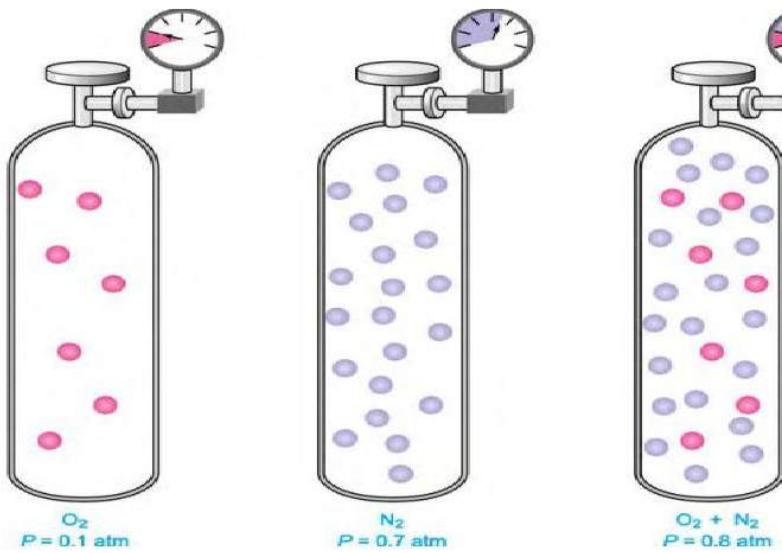
Dalton's Law of Partial Pressures

- In a mixture of gases the **total pressure**, P_{tot} , is the sum of the **partial pressures** of the gases:
- $P_{\text{Total}} = P_1 + P_2 + P_3 + \dots$. At constant V and T

$$P_1 = n_1 \left(\frac{RT}{V} \right) \quad P_2 = n_2 \left(\frac{RT}{V} \right) \quad P_3 = n_3 \left(\frac{RT}{V} \right)$$

$$P_{\text{total}} = (n_1 + n_2 + n_3 + \dots) \left(\frac{RT}{V} \right)$$

$$P_{\text{total}} = \frac{RT}{V} \sum n$$



- **the total pressure exerted by a mixture of gases in a container at constant V and T equals the sum of the pressures of each individual gas in the container**

- **Mole Fraction (x)** : Number of moles of the component divided by the total number of moles in the mixture.

The mole fraction of component 1, for example, is

$$X_1 = \frac{n_1}{n_1 + n_2 + n_3 + \dots} = \frac{n_1}{n_{\text{total}}}$$

But because $n = PV/RT$, we can also write

$$X_1 = \frac{P_1 \left(\frac{V}{RT} \right)}{P_{\text{total}} \left(\frac{V}{RT} \right)} = \frac{P_1}{P_{\text{total}}}$$

$$P_1 = X_1 \cdot P_{\text{total}}$$

- **Partial pressure exerted by each component in a gas mixture is equal to the mole fraction of that component times the total pressure**

- For a two-component system, the moles of components A and B can be represented by the **mole fractions** (X_A and X_B)

$$X_A = \frac{n_A}{n_A + n_B} \quad X_B = \frac{n_B}{n_A + n_B} \quad X_A + X_B = 1$$

- What is the mole fraction of each component in a mixture of 12.45 g of H_2 , 60.67 g of N_2 , and 2.38 g of NH_3 ?

SOLVED PROBLEM 1. What pressure is exerted by a mixture of 2.00 g of H₂ and 8.00 g of N₂ at 273 K in a 10 litre vessel?

SOLUTION

Applying the ideal-gas equation

$$P = n \frac{RT}{V}$$

we can find the partial pressure of H₂ and N₂

$$\text{Moles of H}_2 = \frac{2.00}{2.02} = 0.990$$

$$\text{Moles of N}_2 = \frac{8.00}{28} = 0.286$$

$$\therefore P_{H_2} = \frac{0.990 \text{ mole} \times 0.0821 \text{ atm. litre K}^{-1} \text{ mol}^{-1} \times 273 \text{ K}}{10.0 \text{ litre}}$$
$$= 2.20 \text{ atm.}$$

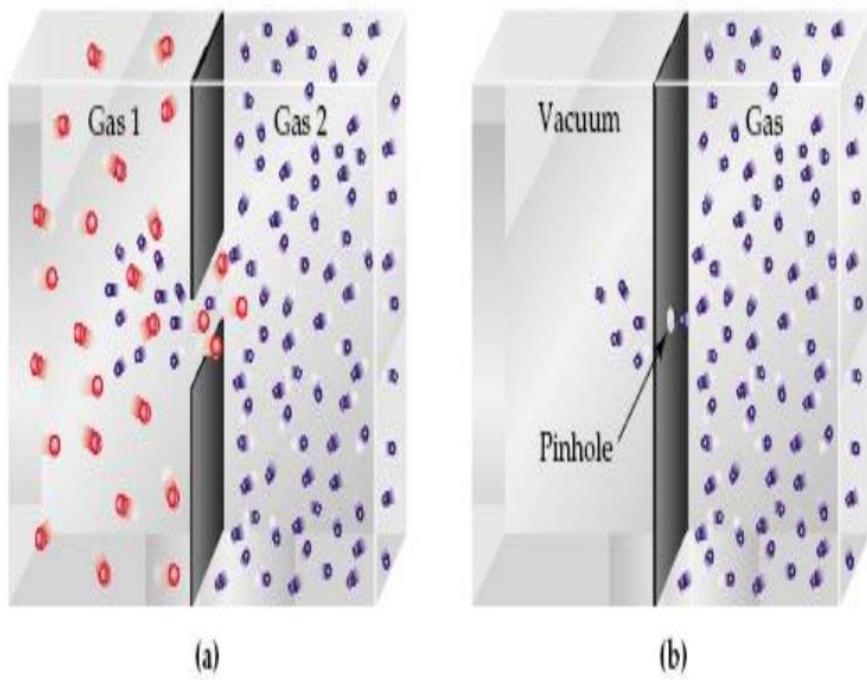
$$\text{and } P_{N_2} = \frac{0.286 \text{ mole} \times 0.0821 \text{ atm. litre K}^{-1} \text{ mol}^{-1} \times 273 \text{ K}}{10.0 \text{ litre}}$$
$$= 0.64 \text{ atm}$$

$$\text{Thus } P_{\text{total}} = P_{H_2} + P_{N_2}$$
$$= 2.20 \text{ atm} + 0.64 \text{ atm}$$
$$= \mathbf{2.84 \text{ atm}}$$

Thus the pressure exerted by the mixture of H₂ and N₂ is **2.84 atm**.

Diffusion & Effusion

FIGURE 9.13 (a) Diffusion ► is the mixing of gas molecules by random motion under conditions where molecular collisions occur. (b) Effusion is the escape of a gas through a pinhole without molecular collisions.



Diffusion is the process of mixing of different gases by random molecular motion with frequent collisions.

Effusion

A process in which gas molecules escape without collisions through a tiny hole into a vacuum

Graham's Law

- the rate of effusion of a gas is inversely proportional to the square root of its mass. In other words, the lighter the molecule, the more rapidly it effuses.



Figure 10.11

A light molecule diffuses quicker than a heavy molecule.

under the same conditions of temperature and pressure, the rates of diffusion of different gases are inversely proportional to the square roots of their molecular masses.

Mathematically the law can be expressed as

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

Which gas in each of the following pairs diffuses more rapidly, and what are the relative rates of diffusion?

Kr = 83.8 O = 16 N=14 C=12

(a) Kr and O₂

(b) N₂ and acetylene (C₂H₂)

The Kinetic-Molecular Theory of Gases

1. A gas consists of tiny particles, either atoms or molecules, moving about at random.
2. The volume of the particles themselves is negligible compared with the total volume of the gas; most of the volume of a gas is empty space.
3. The gas particles act independently of one another; there are no attractive or repulsive forces between particles.
4. Collisions of the gas particles, either with other particles or with the walls of a container, are elastic . *There is no loss in the Kinetic energy.*
5. The average kinetic energy of the gas particles ($\frac{1}{2} m u^2$)is proportional to the Kelvin temperature of the sample.

the total kinetic energy of a number of moles of gas particles equals

$$E_K = \frac{3}{2} nRT$$

it possible to calculate the average speed (velocity) u of a gas particle

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

SOLVED PROBLEM 2. Calculate the kinetic energy of two moles of N₂ at 27°C. (R = 8.314 JK⁻¹ mol⁻¹)

SOLUTION

We know

$$E = \frac{3}{2} nRT$$

Here,

$$T = 27 + 273 = 300 \text{ K}; n = 2; R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

Substituting these values, we have

$$E = \frac{3}{2} \times 2 \times 8.314 \times 300 = 7482.6 \text{ J}$$

Therefore the kinetic energy of two moles of N₂ is 7482.6 J.

➤ The heavier the molecule, the slower the average speed

TABLE 9.5 Average Speeds (m/s) of Some Molecules at 25 °C

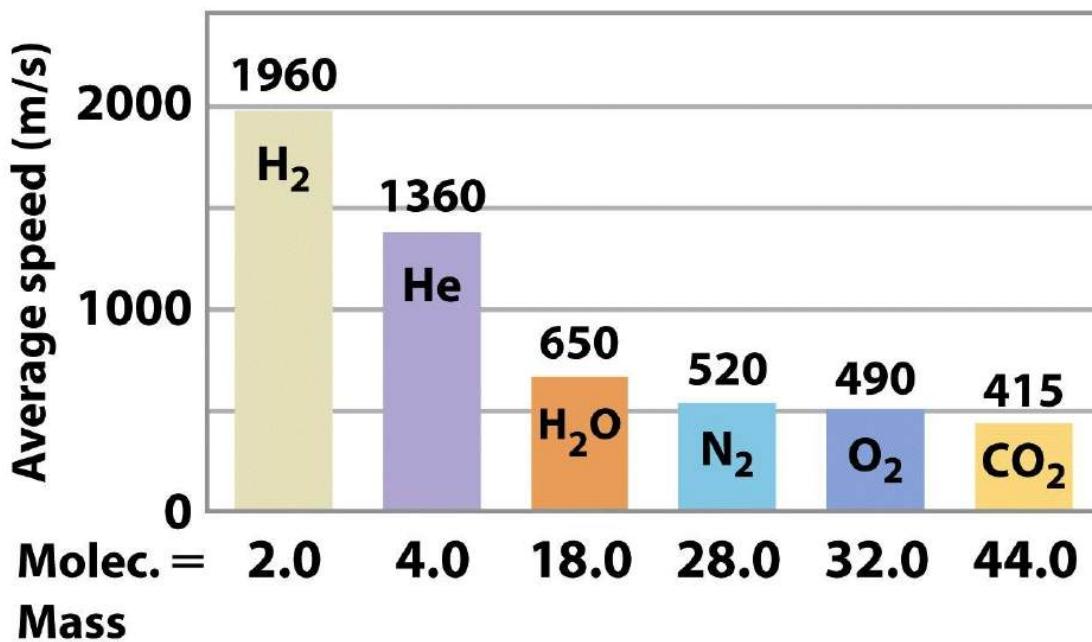


Table 9-5 Chemistry, 5/e
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Because temperature is a measure of average kinetic energy and is independent of the gas's chemical identity, different gases at the same temperature have the same average kinetic energy but not the same speed

$$\left(\frac{1}{2}mu^2\right)_{\text{gas 1}} = \left(\frac{1}{2}mu^2\right)_{\text{gas 2}} \text{ at the same } T$$

$$\frac{u_1}{u_2} = \sqrt{\frac{M_2}{M_1}}$$

mixtures of gases can be separated into their pure components by taking advantage of the different rates of diffusion of the components.



The uranium-235 used as a fuel in nuclear reactors is obtained by gas diffusion of UF₆ in these cylinders.

$$\text{For } {}^{235}\text{UF}_6, m = 349.03 \text{ amu}$$

$$\text{For } {}^{238}\text{UF}_6, m = 352.04 \text{ amu}$$

$$\text{so } \frac{\text{Rate of } {}^{235}\text{UF}_6 \text{ diffusion}}{\text{Rate of } {}^{238}\text{UF}_6 \text{ diffusion}} = \sqrt{\frac{352.04 \text{ amu}}{349.03 \text{ amu}}} = 1.0043$$

How Does an Ideal Gas Differ from Real Gases ?

- A gas that confirms to the assumptions of the kinetic theory of gases is called an ideal gas. It obeys the basic laws strictly under all conditions of temperature and pressure.
- The real gases as hydrogen, oxygen, nitrogen etc., are opposed to some assumptions. Thus :
 - (a) The actual volume of molecules in an ideal gas is negligible, while in a real gas it is appreciable.
 - (b) There are no attractive forces between molecules in an ideal gas while these exist in a real gas.
 - (c) Molecular collisions in an ideal gas are perfectly elastic while it is not so in a real gas.
- For the reasons listed above, real gases obey the gas laws under moderate conditions of temperature and pressure. At very low temperature and very high pressure, the real gases show considerable deviations from the ideal gas behavior.

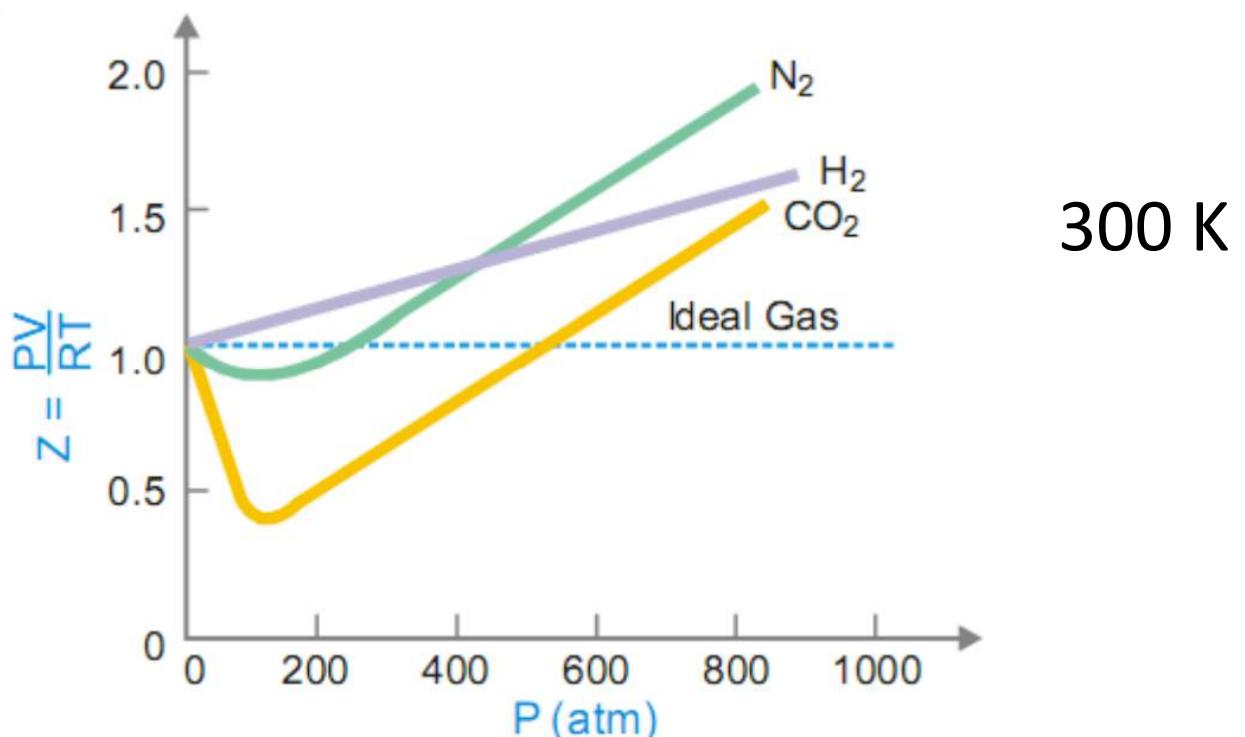
DEVIATIONS FROM IDEAL BEHAVIOR

- An ideal gas is one which obeys the gas laws or the gas equation $PV = RT$ at all pressures and temperatures.
- However no gas is ideal. Almost all gases show significant deviations from the ideal behavior. Thus the gases H_2 , N_2 and CO_2 which fail to obey the ideal-gas equation are termed non-ideal or real gases.
- Compression Factor
- The extent to which a real gas departs from the ideal behavior may be depicted in terms of a new function called the Compression factor, denoted by Z. It is defined as

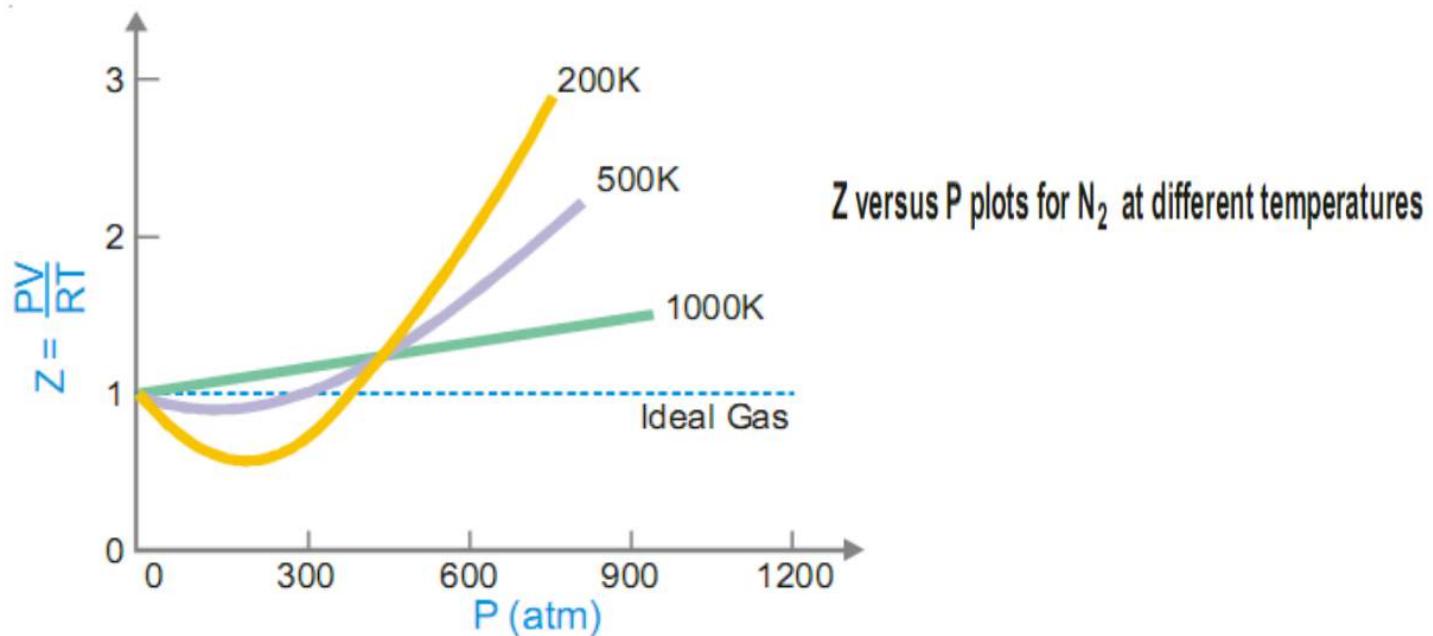
$$Z = \frac{PV_m}{RT}$$

For an ideal gas, $Z = 1$ and it is independent of temperature and pressure.

- For a real gas, the deviations from ideal behavior depend on (i) pressure; and temperature.
- Effect of Pressure Variation on Deviations



Effect of Temperature on Deviations



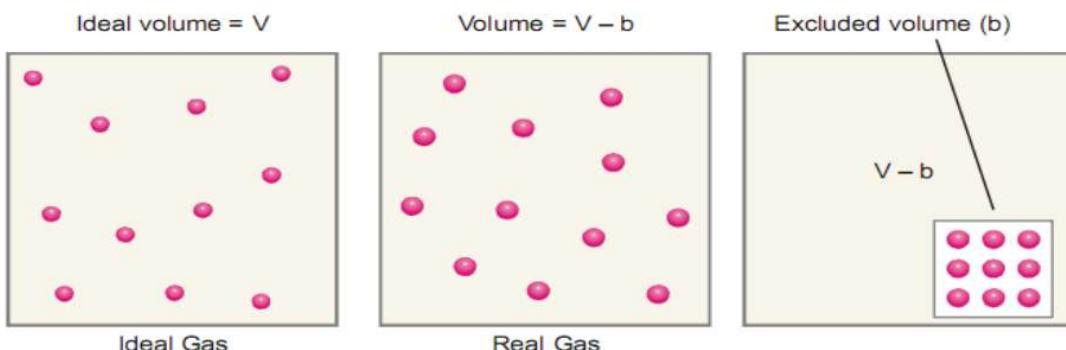
- (1) At low pressures and fairly high temperatures, real gases show nearly ideal behavior and the ideal-gas equation is obeyed.
- (2) At low temperatures and sufficiently high pressures, a real gas deviates significantly from ideality and the ideal-gas equation is no longer valid.

EXPLANATION OF DEVIATIONS–VAN DER WAALS EQUATION

- van der Waals (1873) attributed the deviations of real gases from ideal behavior to two erroneous postulates of the kinetic theory. These are :
 - (1) the molecules in a gas are point masses and possesses no volume.
 - (2) there are no intermolecular attractions in a gas.
- Therefore, the ideal gas equation $PV = nRT$ derived from kinetic theory could not hold for real gases.
- van der Waals pointed out that both the pressure (P) and volume (V) factors in the ideal gas equation needed correction in order to make it applicable to real gases.

Volume Correction

- The volume of a gas is the free space in the container in which molecules move about.
- Volume V of an ideal gas is the same as the volume of the container. The dot molecules of ideal gas have zero-volume and the entire space in the container is available for their movement.
- However, van der Waals assumed that molecules of a real gas are rigid spherical particles which possess a definite volume.



■ **Figure 10.25**
Volume of a Real gas.

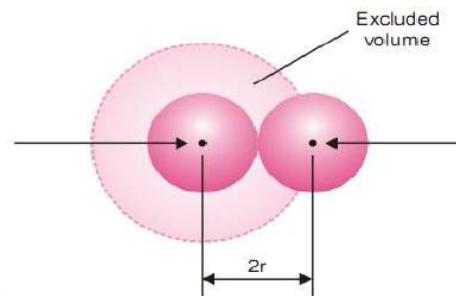
The volume of a real gas is, therefore, ideal volume minus the volume occupied by gas molecules

equation is corrected as :

$$(V - b)$$

For n moles of the gas, the corrected volume is :

$$(V - nb)$$



■ **Figure 10.26**
Excluded volume for a pair of gas molecules.

where b is termed the **excluded volume** which is constant and characteristic for each gas.

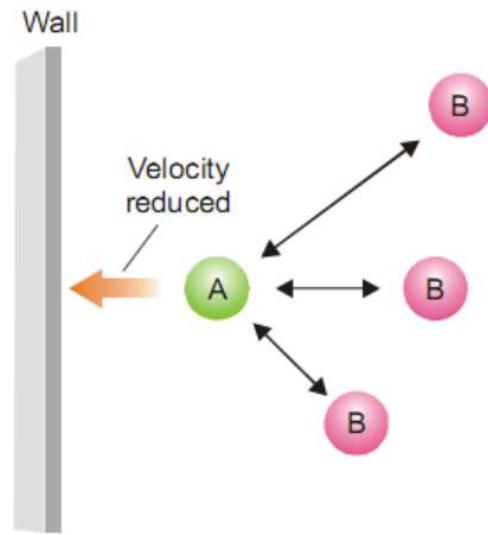
Pressure Correction

- A molecule in the interior of a gas is attracted by other molecules on all sides. These attractive forces cancel out.
- But a molecule about to strike the wall of the vessel is attracted by molecules on one side only. Hence it experiences an inward pull. Therefore, it strikes the wall with reduced velocity and the actual pressure of the gas, P , will be less than the ideal pressure.

If the actual pressure P , is less than P_{ideal} by a quantity p , we have

$$P = P_{\text{ideal}} - p$$

$$P_{\text{ideal}} = P + p$$



- p is determined by the force of attraction between molecules (A) striking the wall of container and the molecules (B) pulling them inward. The net force of attraction is, therefore, proportional to the concentration of (A) type molecules and also of (B) type of molecules. That is,

$$p \propto C_A \times C_B$$

$$p \propto \frac{n}{V} \times \frac{n}{V}$$

$$p = \frac{an^2}{V^2}$$

where n is total number of gas molecules in volume V and a is proportionality constant characteristic of the gas. Thus the pressure P in the ideal gas equation is corrected as :

$$\left(P + \frac{an^2}{V^2} \right)$$

The Behavior of Real Gas (van der Waals equation)

Correction for
intermolecular attractions.

Correction for
molecular volume.

van der Waals equation:
$$\left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

or
$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

Constant a and b in van der Waals equation are called van der Waals constants. These constants are characteristic of each gas.

Calculate the pressure exerted by 1.00 mole of methane (CH_4) in a 250 mL container at 300 K using van der Waals equation. What pressure will be predicted by ideal gas equation?

$a = 2.253 \text{ L}^2 \text{ atm mol}^{-2}$, $b = 0.0428 \text{ L mol}^{-1}$; $R = 0.0821 \text{ L atm mol}^{-1} \text{ K}$.

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

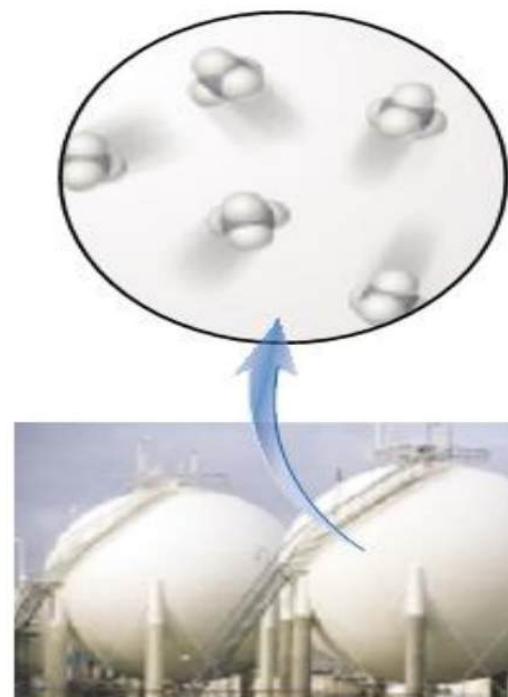
$$P = \frac{1 \times 0.0821 \times 300}{0.250 - (1 \times 0.0428)} - \frac{1^2 \times 2.253}{(0.250)^2}$$
$$= 82.8 \text{ atm}$$

LIQUEFACTION OF GASES – CRITICAL PHENOMENON

A gas can be liquefied by lowering the temperature and increasing the pressure. At lower temperature, the gas molecules lose kinetic energy. The slow moving molecules then aggregate due to attractions between them and are converted into liquid. The same effect is produced by the increase of pressure. The gas molecules come closer by compression and coalesce to form the liquid.

Which has a higher average speed, H₂ at 150 K or He at 375°C?

- How many moles of methane gas, are in a storage tank with a volume of 1×10^5 L at STP? How many grams?





helium–oxygen mixture is used in diving gas instead of compressed air (nitrogen– oxygen). If air were used, nitrogen would dissolve in the diver’s blood at the high underwater pressures and would be released as painful bubbles when the diver returned to the surface.

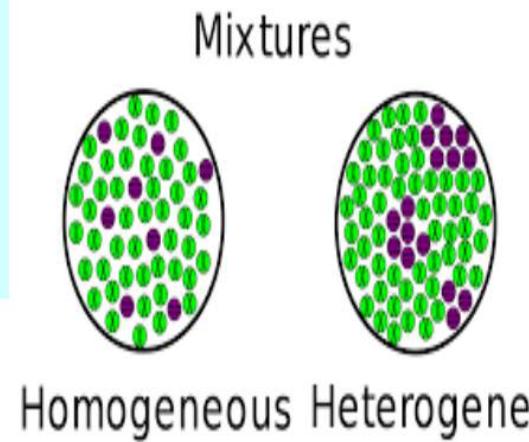


Solutions and Their Properties

1



- **Solutions** are homogeneous mixtures, contain particles with diameters in the range 0.1–2 nm—the size of a typical ion or small molecule. They are transparent, although they may be colored, and they do not separate on standing.
- **Homogeneous mixtures** are those in which the mixture is uniform, at least to the naked eye, and which therefore have the same composition throughout.



- **Solvent**: The major component.
- **Solute**: A minor component.

TABLE 11.1 Some Different Kinds of Solutions

Kind of Solution	Example
Gas in gas	Air (O_2N_2), Ar, and other gases)
Gas in liquid	Carbonated water (CO_2 in water)
Gas in solid	H_2 in palladium metal
Liquid in liquid	Gasoline (mixture of hydrocarbons)
Liquid in solid	Dental amalgam (mercury in silver)
Solid in liquid	Seawater ($NaCl$ and other salts in water)
Solid in solid	Metal alloys, such as sterling silver (92.5% Ag, 7.5% Cu)

Table 11-1 Chemistry, 5/e
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Concentration



- **Concentration:** The amount of solute present in a given amount of solution.
- **Percent by Mass (weight percent):** The ratio of the mass of a solute to the mass of a solution, multiplied by 100%.

$$\% \text{ by mass of solute} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100$$

mass of solution = mass of solute + mass of solvent

For example, if a solution of HCl contains 36 per cent HCl by weight, it has 36 g of HCl for 100 g of solution.

SOLVED PROBLEM. What is the per cent by weight of NaCl if 1.75 g of NaCl is dissolved in 5.85 g of water.

SOLUTION

$$\text{Wt. of solute (NaCl)} = 1.75 \text{ g}$$

$$\text{Wt. of solvent (H}_2\text{O)} = 5.85 \text{ g}$$

$$\therefore \text{Wt. of solution} = 1.75 + 5.85 = 7.60 \text{ g}$$

Hence concentration of NaCl % by weight

$$= \frac{1.75}{7.60} \times 100 \\ = 23.0$$

Units of Concentration

- **Mole Fraction (X):** $X_A = \frac{\text{Moles of A}}{\text{Total number of moles}} = \frac{n_A}{n_{\text{total}}}$
No units
- **Molarity (M):** Molarity = $\frac{\text{Moles of solute}}{\text{Liters of SOLUTION}} = \frac{\text{mol}}{\text{Liter}}$
- **Molality (m):** Molality = $\frac{\text{Moles of solute}}{\text{Kilograms of SOLVENT}} = \frac{\text{mol}}{\text{Kg}}$

SOLVED PROBLEM 1. What is the molarity of a solution prepared by dissolving 75.5 g of pure KOH in 540 ml of solution.

$$K= 39, O=16, H=1$$

$$M = \frac{m(g)}{Molar\ mass} \times \frac{1000}{V(ml)}$$

SOLVED PROBLEM. What is the molality of a solution prepared by dissolving 5.0 g of toluene (C_7H_8) in 225 g of benzene (C_6H_6)?

$$m = \frac{\text{mass (solute)}_{(g)}}{\text{Molar mass solute}} \times \frac{1000}{\text{mass (solvent)}_{(g)}}$$

SOLVED PROBLEM. What is the molality of a solution prepared by dissolving 5.0 g of toluene (C_7H_8) in 225 g of benzene (C_6H_6)?

SOLUTION

Calculation of number of moles of solute :

$$\text{Molecular mass of toluene} = 12 \times 7 + 1 \times 8 = 92$$

$$\text{No. of moles of 5 g of toluene} = \frac{5}{92} = 0.0543$$

$$\text{Mass of solvent in kg} = \frac{225\text{g}}{1000} = 0.225\text{kg}$$

$$\begin{aligned}\text{Molality} &= \frac{\text{No. of moles of solute}}{\text{Mass of solvent in kg}} = \frac{0.0543}{0.225} \\ &= 0.24\text{m}\end{aligned}$$

TABLE 11.3 A Comparison of Various Concentration Units

Name	Units	Advantages	Disadvantages
Molarity (M)	<u>mol solute</u> L solution	Useful in stoichiometry; measure by volume	Temperature-dependent; must know density to find solvent mass
Mole fraction (X)	none	Temperature-independent; useful in special applications	Measure by mass; must know density to convert to molarity
Mass %	%	Temperature-independent; useful for small amounts	Measure by mass; must know density to convert to molarity
Molality (m)	<u>mol solute</u> kg solvent	Temperature-independent; useful in special applications	Measure by mass; must know density to convert to molarity

Table 11-3 Chemistry, 5/e
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Types of solutions

1- Solution of gas in gas

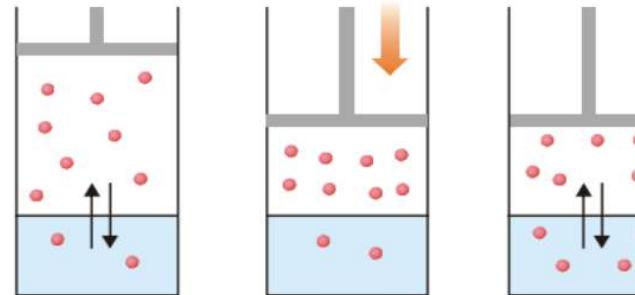
- Complete miscibility
- Dalton's law of partial pressure

2- Solution of gas in liquid

• The solubility of a gas in a solvent depend on temperature and pressure.

Effect of pressure

According to **Henry's law**, the solubility of a gas in a liquid at a given temperature is directly proportional to the partial pressure of the gas over the solution:



$$\text{Solubility, } c \propto P$$

$$C = k \cdot P$$

$$k = \text{mol/(L.atm)}$$

The constant k in this expression is characteristic of a specific gas, and P is the partial pressure of the gas over the solution.

The Henry's-law constant of methyl bromide (CH_3Br), a gas used as a soil fumigating agent, is $k = 0.159 \text{ mol}/(\text{L} \cdot \text{atm})$ at 25°C . What is the solubility (in mol/L) of methyl bromide in water at 25°C and a partial pressure of 125 mm Hg?

$$\text{Solubility} = k \cdot P = 0.159 \frac{\text{mol}}{\text{L} \cdot \text{atm}} \times 0.164 \text{ atm} = 0.0261 \text{ M}$$

Effect of Temperature on Solubility of Gases

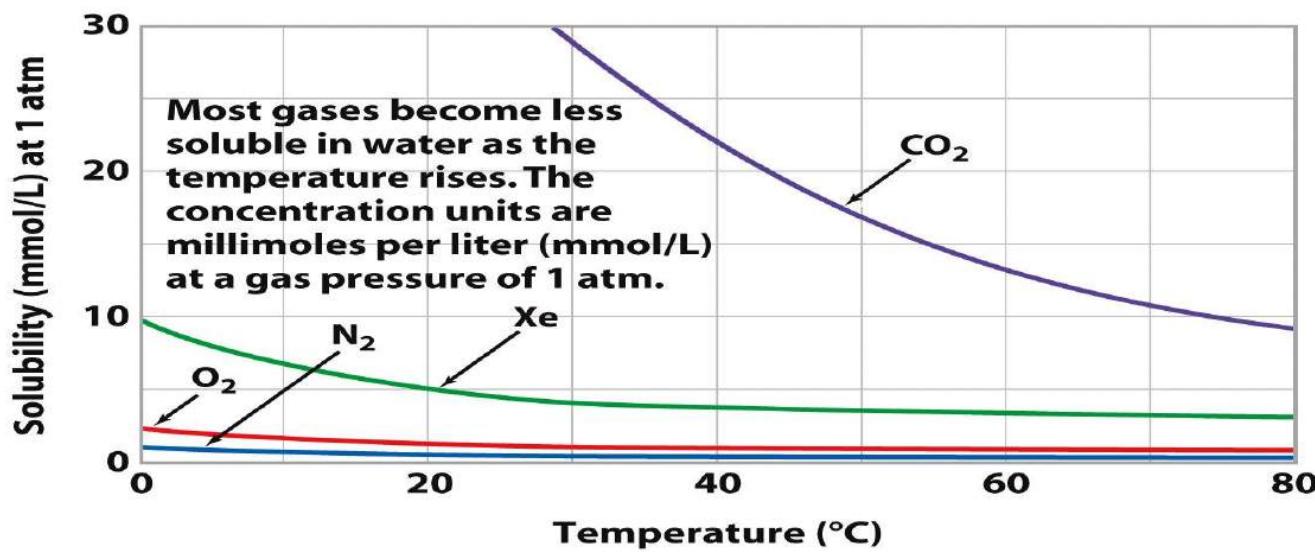
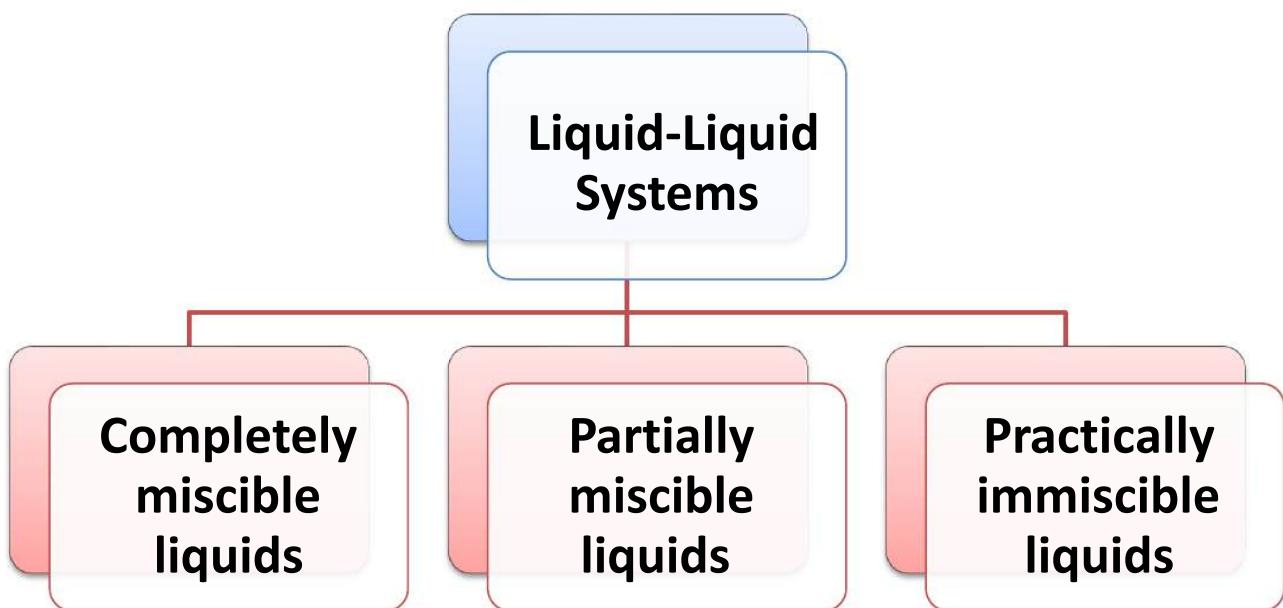


Figure 11-7 Chemistry, 5/e

3- SOLUTIONS OF LIQUIDS IN LIQUIDS

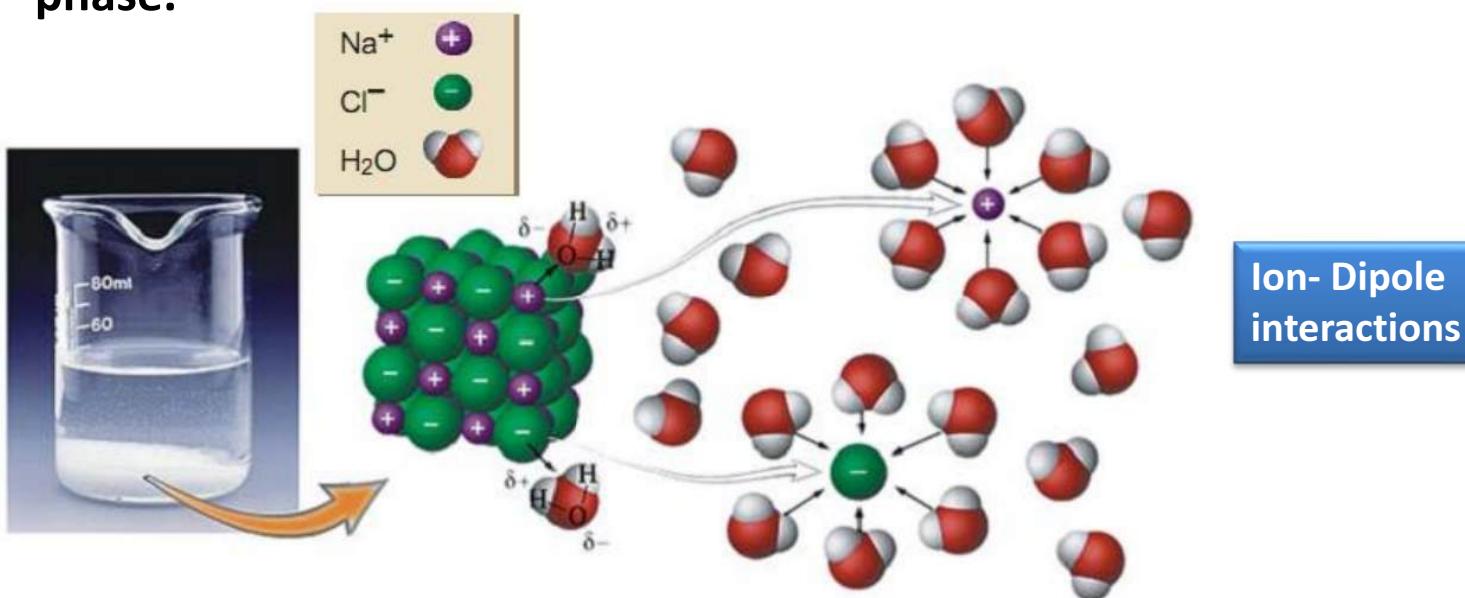
- The solutions of liquids in liquids may be divided into three classes as follows :
- *Like dissolve like*



4- SOLUTIONS OF SOLIDS IN LIQUIDS

- The process of solution of a solid substance in a solvent is explained by the electrical forces operating between the molecules or ions of the solute and the molecules of the solvent.
- *Like dissolve like*
 - polar solutes dissolve easily in polar solvents
 - a non-polar solute does not dissolve in a polar solvent

- An ionic substance, when placed in water furnishes cations (+) and anions (-). These ions are surrounded by solvent molecules with their oppositely charged ends directed towards the ion. The ion enveloped by a layer of the solvent molecules in this manner, is called a **Solvated ion** or **Hydrated ion** in case water is the solvent.
- the hydrated sodium and chloride ions as Na^+ (aq) and Cl^- (aq). This representation indicates that the ions are in the aqueous phase.



lattice Energy: energy required to break bonds in the crystal lattice ($\Delta H_{\text{latt}} = +\text{ve}$)

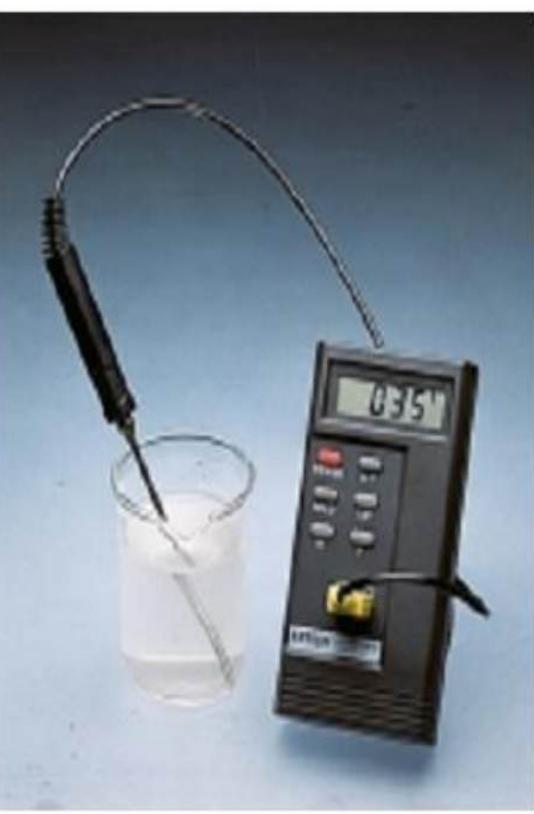
Hydration Energy: energy released when an ion is surrounded by water molecules ($\Delta H_{\text{Hyd}} = -\text{ve}$)

Solution Formation

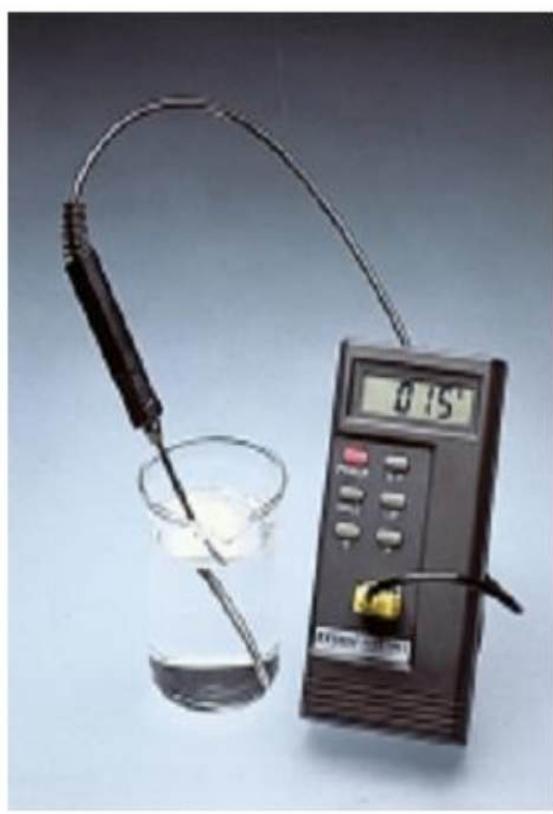
$$\Delta H_{\text{Soln}} = \Delta H_{\text{latt}} + \Delta H_{\text{hyd}}$$

- **Exothermic ΔH_{soln} ($\Delta H = -\text{ve}$):**
 - The solute–solvent interactions are stronger than solute–solute or solvent–solvent.
 - Ex: LiCl, NaBr, KOH etc
- **Endothermic ΔH_{soln} ($\Delta H = +\text{ve}$):**
 - The solute–solvent interactions are weaker than solute–solute or solvent–solvent.
 - Ex: NaCl, KCl, KBr etc

◀ FIGURE 11.3 (a) Dissolution of CaCl_2 in water is exothermic, causing the temperature of the water to rise from its initial value of 25°C. (b) Dissolution of NH_4NO_3 is endothermic, causing the temperature of the water to fall from its initial value.



(a)



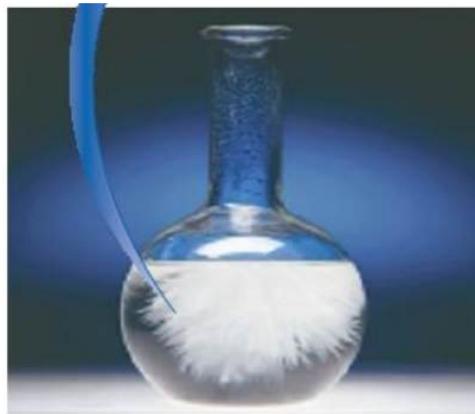
(b)

Some Factors Affecting Solubility

- **Saturated Solution:** A solution containing the maximum possible amount of dissolved solute at equilibrium.
- **Unsaturated Solution:** A solution containing amount of dissolved solute lower-than-equilibrium amount.
- **Supersaturated Solution:** A solution containing amount of dissolved solute greater-than-equilibrium amount.



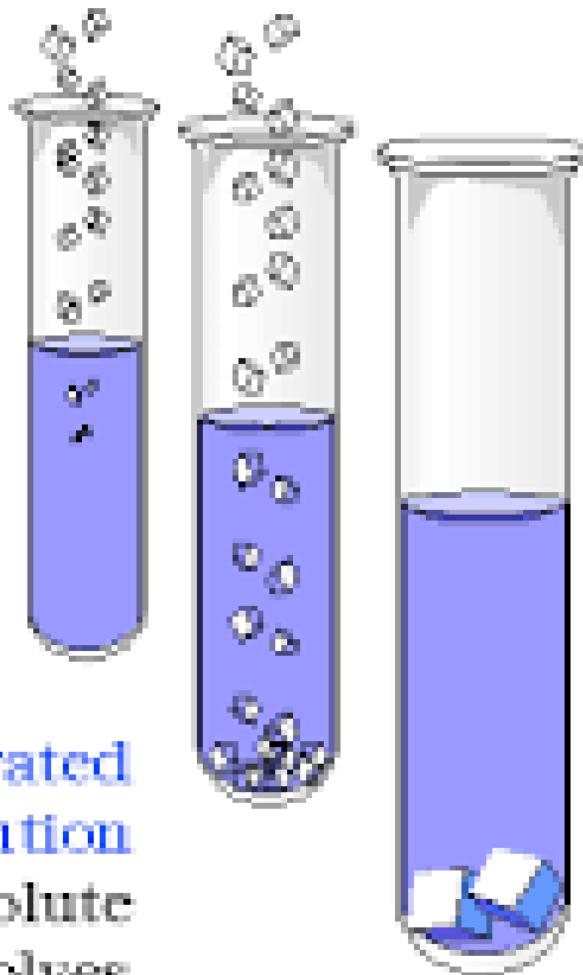
(a)



(b)

A supersaturated solution of sodium acetate in water. When a tiny seed crystal is added, larger crystals begin to grow and precipitate from the solution until equilibrium is reached.

**unsaturated
solution**
more solute
dissolves



**supersaturated
solution**
added crystals
grow

- Each substance has a characteristic solubility in a given solvent.
- **The solubility of a substance:**
- the number of grams of solute that can be dissolved in 100 grams of the solvent to give saturated solution at a particular temperature.
- For example, a saturated solution of sodium chloride in water at 0°C contains 35.7 g of NaCl in 100 g of H₂O. That is, the solubility of NaCl in water at 0°C is 35.7 g/100 g.
- **SOLUBILITY CURVES**
- A curve drawn between solubility and temperature is termed Solubility Curve. It shows the effect of temperature on the solubility of a substance.

Effect of Temperature on Solubility

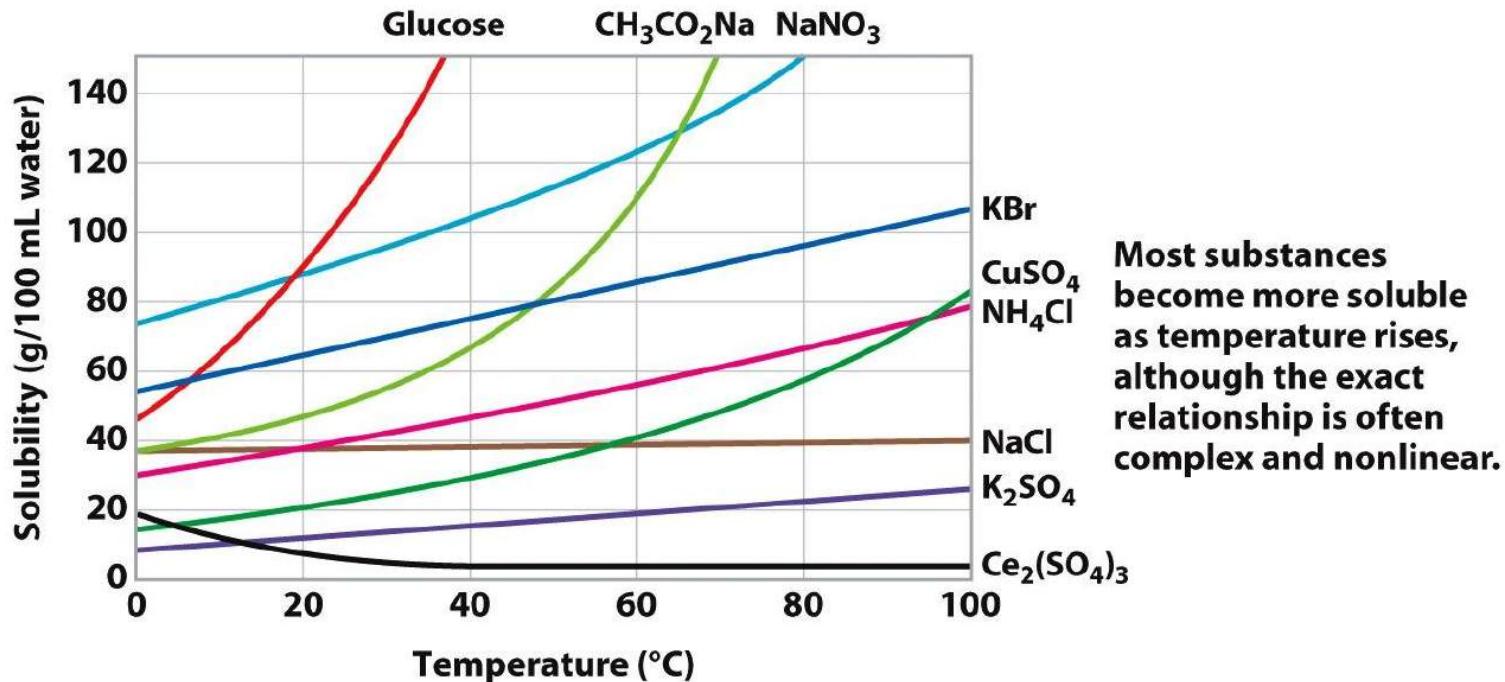


Figure 11-6 Chemistry, 5/e
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Physical Behavior of Solutions : COLLIGATIVE PROPERTIES

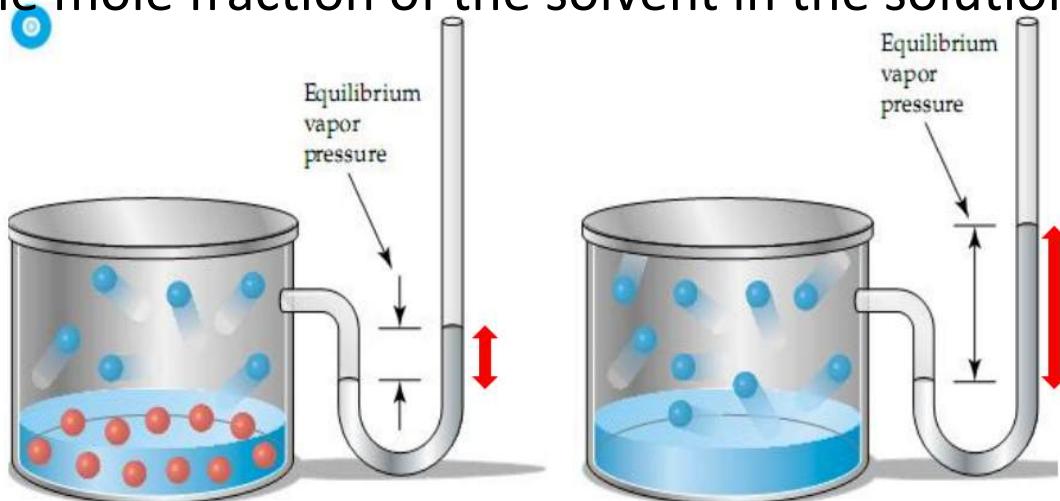
- **Colligative Properties:** Properties that depend on the amount of a dissolved solute but not on its chemical identity.
- Pure water boils at 100.0°C and freezes at 0.0°C, for example, but a 1.00 m solution of NaCl in water boils at 101.0°C and freezes at -3.7°C
- **In comparing the properties of a pure solvent with those of a solution...**
 1. Lowering of the Vapor Pressure
 2. Elevation of the Boiling Point
 3. Depression of the Freezing Point
 4. Osmosis

Vapor-Pressure Lowering of Solutions:

- If the solute is **non-volatile** and has no appreciable vapor pressure of its own, as occurs when a solid is dissolved, then the vapor pressure of the solution is always lower than that of the pure solvent.
- If the solute is **volatile** and has a significant vapor pressure of its own, as often occurs in a mixture of two liquids, then the vapor pressure of the mixture is intermediate between the vapor pressures of the two pure liquids.

Solutions with a Nonvolatile Solute

- According to Raoult's law, the vapor pressure of a solution containing a non-volatile solute is equal to the vapor pressure of the pure solvent times the mole fraction of the solvent.
- RAOULT'S LAW**
- $P_{\text{soln}} = P^{\circ}_{\text{solv}} \cdot X_{\text{solv}}$
- where P_{soln} is the vapor pressure of the solution, P°_{solv} is the vapor pressure of pure solvent at the same temperature, and X_{solv} is the mole fraction of the solvent in the solution.



- Take a solution of 1.00 mol of glucose in 15.0 mol of water at 25°C. The vapor pressure of pure water at 25°C is 23.76 mm Hg. What is the lowering in vapor pressure.

$$P_{\text{soln}} = P_{\text{solv}} \times X_{\text{solv}} = 23.76 \text{ mm Hg} \times \frac{15.0 \text{ mol}}{1.00 \text{ mol} + 15.0 \text{ mol}} = 22.3 \text{ mm Hg}$$

$$\Delta P_{\text{soln}} = P_{\text{solv}} - P_{\text{soln}} = 23.76 \text{ mm Hg} - 22.3 \text{ mm Hg} = 1.5 \text{ mm Hg}$$

- A solution of 1.00 mol NaCl in 15.0 mol water at 25°C. The vapor pressure of pure water at 25°C is 23.76 mm Hg. What is the lowering in vapor pressure.

$$X_{\text{water}} = \frac{15.0 \text{ mol H}_2\text{O}}{1.00 \text{ mol Na}^+ + 1.00 \text{ mol Cl}^- + 15.0 \text{ mol H}_2\text{O}} = 0.882$$

$$P_{\text{sln}} = P_{\text{solv}} \times X_{\text{solv}} = 23.76 \text{ mm Hg} \times 0.882 = 21.0 \text{ mm Hg}$$

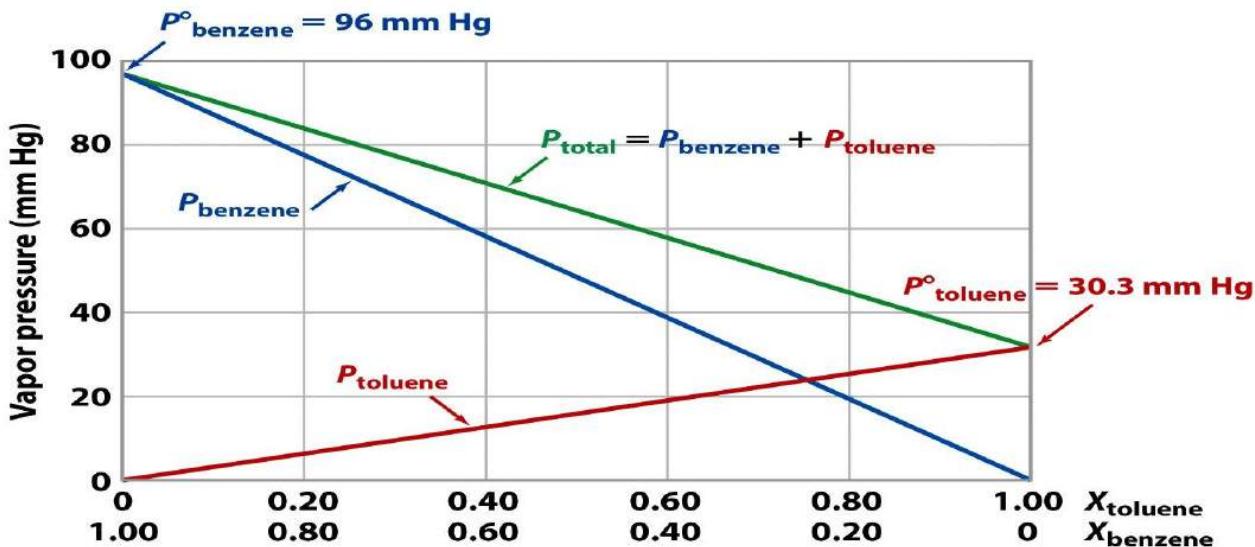
Solutions with a volatile Solute

- from Dalton's law, the overall vapor pressure of a mixture of two volatile liquids A and B is the sum of the vapor-pressure contributions of the individual components, P_A and P_B :

$$P_{\text{total}} = P_A + P_B$$

The individual vapor pressures P_A and P_B are calculated by Raoult's law. That is, the vapor pressure of A is equal to the mole fraction of A (X_A) times the vapor pressure of pure A (P°_A), and the vapor pressure of B is equal to the mole fraction of B (X_B) times the vapor pressure of pure B (P°_B). Thus, the total vapor pressure of the solution is

$$P_{\text{total}} = P_A + P_B = (P^\circ_A \cdot X_A) + (P^\circ_B \cdot X_B)$$



- Two miscible liquids, A and B, have vapor pressures of 250 mm Hg and 450 mm Hg, respectively. They were mixed in equal molar amounts. What is the total vapor pressure of the mixture?

Boiling-Point Elevation and Freezing-Point Depression of Solutions

- Because a solution of a nonvolatile solute has a lower vapor pressure than a pure solvent has at a given temperature, the solution must be heated to a higher temperature to cause it to boil.

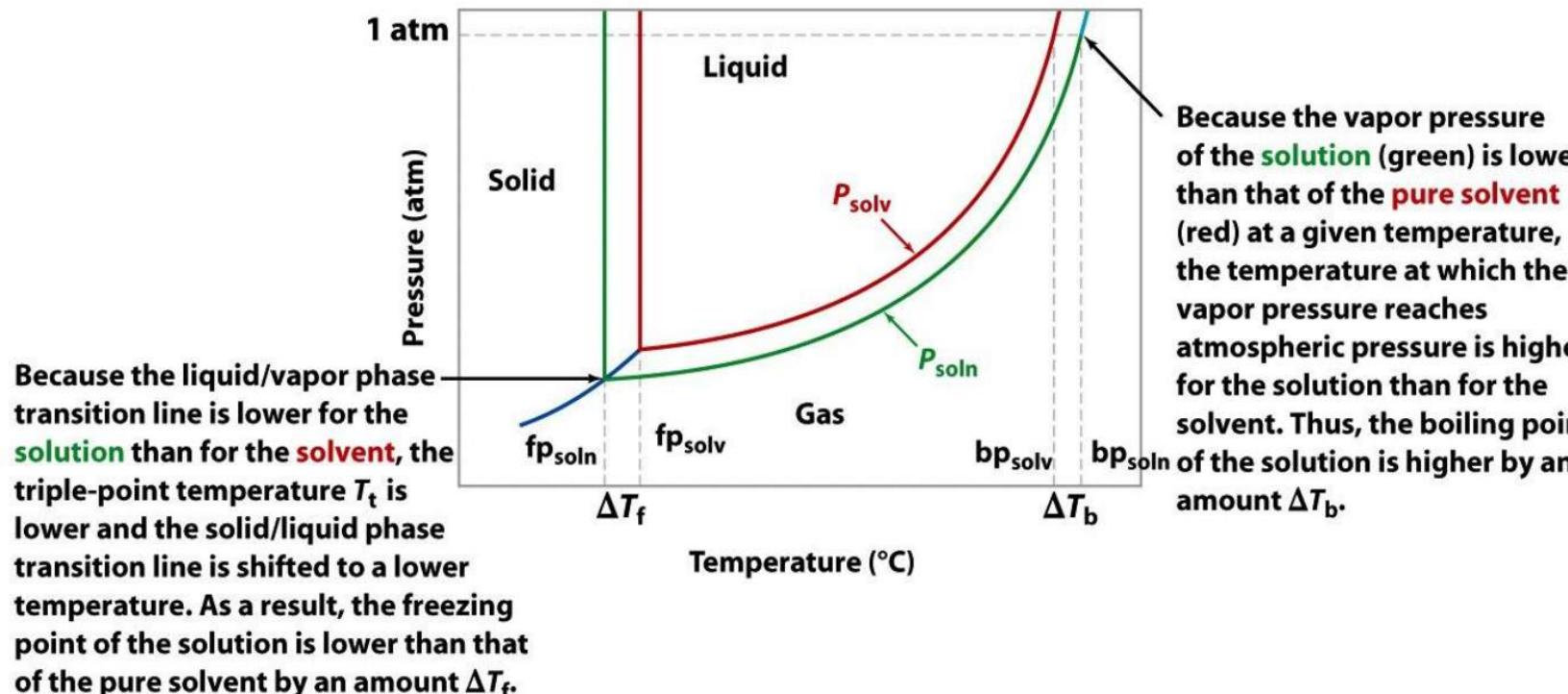


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- **Boiling-Point Elevation (ΔT_b):** The boiling point of the solution (T_b) minus the boiling point of the pure solvent (T_b°):

$$\Delta T_b = T_b - T_b^{\circ} = +\text{ve value}$$

For water: $\Delta T_b + 100^{\circ}\text{C} = T_b(\text{solution})$

- We can express the relationship between ΔT_b and concentration as follows:
- $\Delta T_b = m K_b$
- where m is the concentration of the solute expressed in **molality**, and K_b is the ***molal boiling point elevation constant*** of the solvent, which has units of $^{\circ}\text{C}/m$.

- **Freezing-Point Depression (ΔT_f):** The freezing point of the pure solvent (T_f°) minus the freezing point of the solution (T_f).

$$\Delta T_f = T_f^\circ - T_f = +\text{ve value}$$

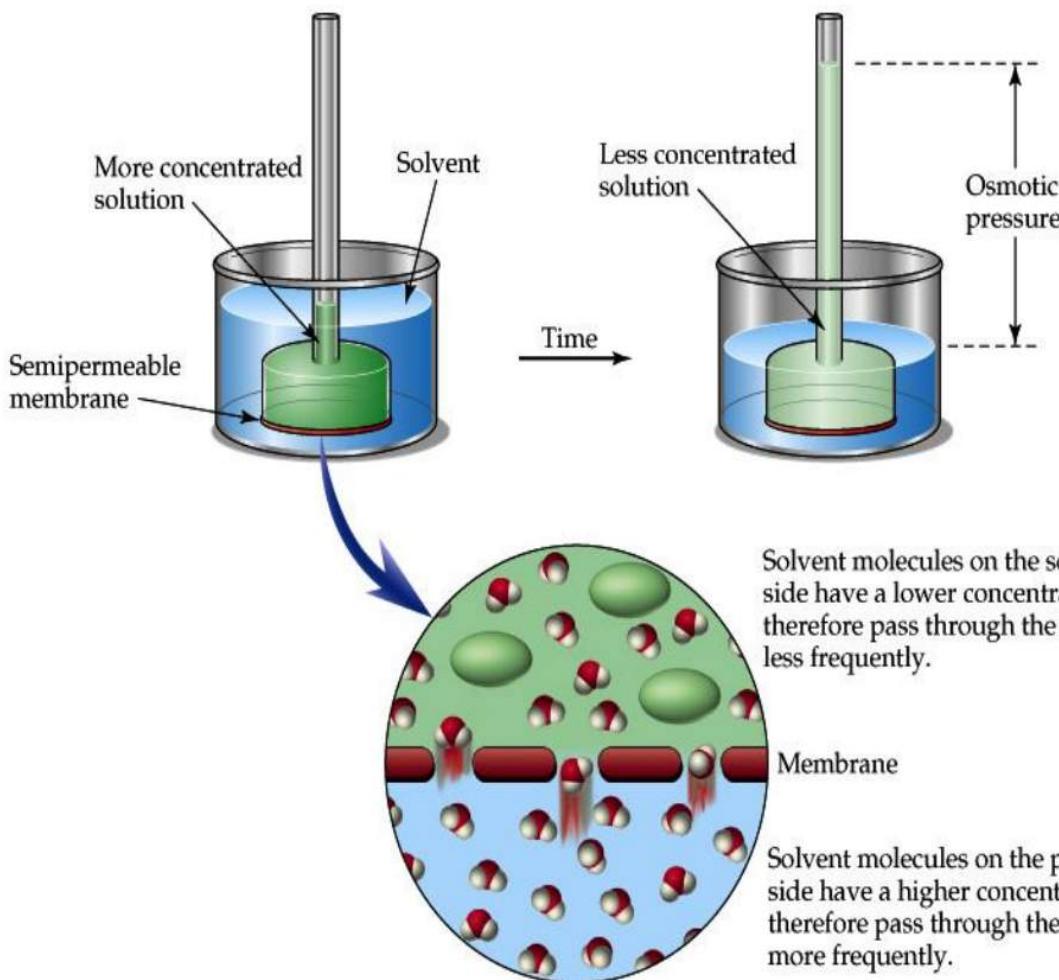
For water: $\Delta T_f = 0^\circ\text{C} - T_f$ (solution)

- The relationship between (ΔT_f) and the solute concentration is given by
 - $\Delta T_f = m K_f$

Osmosis and Osmotic Pressure

Semi-permeable membrane. they allow water or other small molecules to pass through, but they block the passage of large solute molecules or ions.

Osmosis: The passage of solvent through a semi-permeable membrane from the less concentrated side to the more concentrated side.



- **Osmotic Pressure (π):** The amount of pressure necessary to cause osmosis to stop.
- Amount of osmotic pressure depends on concentration of solute in solution

$$\pi = i \cdot MRT$$

R = gas constant = 0.08206 (L·atm)/(mol·K)

M = molar concentration of solute particles (mol/L)

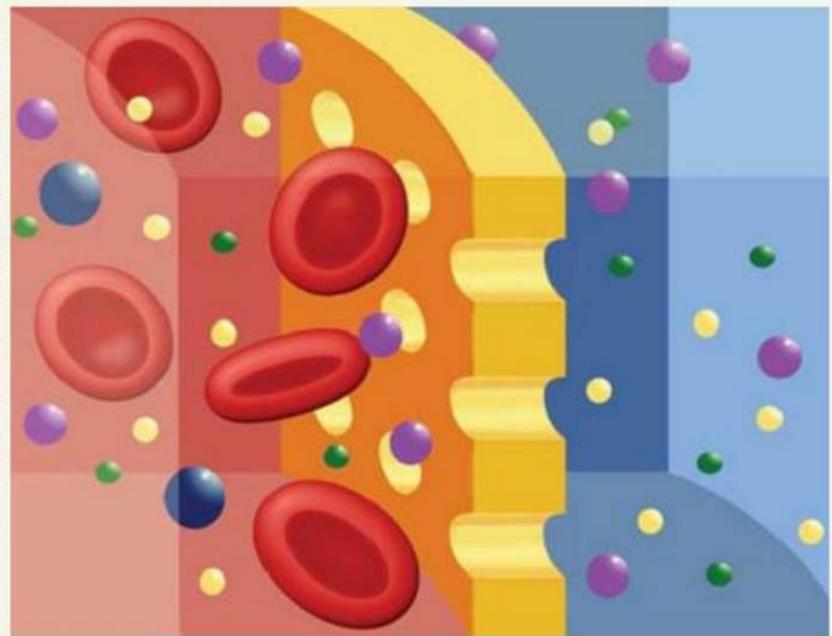
T = Temperature in Kelvins

i = van't Hoff factor

- Osmotic pressure can be extremely high for dilute solutions

What is the osmotic pressure (in atm) of a 0.884 M sucrose solution at 16°C?

KIDNEY DIALYSIS



A hospital patient whose kidneys have ceased to function receives dialysis. In this process, the patient's blood is pumped through a dialysis machine, where it is filtered to remove waste products, then returned to the patient's body through a vein.

Scheme of semipermeable membrane during kidney dialysis, where red is blood, blue is the dialysing fluid, and yellow is the membrane.

Questions on chapter 2

Solutions and Their Properties

1. Calculate the mole fraction of HCl in a solution of hydrochloric acid in water, containing 36 per cent HCl by weight

Solution: Suppose that the mass of solution = 100 g

- The solution contain 36 g of HCl (solute)
and 64 g of H₂O (solvent)
- Number of moles of HCl = mass/molar mass
 $= 36 / 36.5 = 0.99$

- Number of moles of H₂O = 64 / 18 = 3.55

$$X_{\text{HCl}} = \frac{\text{moles of HCl}}{\text{moles of HCl} + \text{moles of H}_2\text{O}}$$
$$= \frac{0.99}{3.55 + 0.99} = 0.218$$

2- What is the molarity of a solution prepared by dissolving 80 g of pure NaOH in 500 ml of solution.

Solution:

- Mass (wt.) = 80 g
- Molar mass (M.wt) = $23+16+1=40$
- Volume of solution = 500 ml

$$M = \frac{wt\ (g)}{M.wt} \times \frac{1000}{Volume\ (ml)}$$

- $M = 4 \text{ mol/L}$

3- What is the molality of a solution made by dissolving 1.45 g of table sugar (sucrose, C₁₂H₂₂O₁₁) in 30.0 mL of water? The molar mass of sucrose is 342.3 g/mol.

Solution:

$$\text{Mass of solute} = 1.45 \text{ g} \quad \text{Molar mass of solute} = 342.3$$

$$\text{Mass of solvent} = 30 \text{ g} \text{ (because density of water} = 1 \text{ then volume} = \text{mass})$$

$$m = \frac{\text{mass (solute)}_{(\text{g})}}{\text{Molar mass solute}} \times \frac{1000}{\text{mass (solvent)}_{(\text{g})}}$$

4 - Take a solution of 1.00 mol of glucose in 15.0 mol of water at 25°C. The vapor pressure of pure water at 25°C is 23.76 mm Hg. What is the lowering in vapor pressure.

$$P_{\text{solv}} = P_{\text{pav}} \times X_{\text{solv}} = 23.76 \text{ mm Hg} \times \frac{15.0 \text{ mol}}{1.00 \text{ mol} + 15.0 \text{ mol}} = 22.3 \text{ mm Hg}$$

$$\Delta P_{\text{solv}} = P_{\text{pav}} - P_{\text{solv}} = 23.76 \text{ mm Hg} - 22.3 \text{ mm Hg} = 1.5 \text{ mm Hg}$$

5 - A solution of 1.00 mol NaCl in 15.0 mol water at 25°C. The vapor pressure of pure water at 25°C is 23.76 mm Hg. What is the lowering in vapor pressure.

$$X_{\text{water}} = \frac{15.0 \text{ mol H}_2\text{O}}{1.00 \text{ mol Na}^+ + 1.00 \text{ mol Cl}^- + 15.0 \text{ mol H}_2\text{O}} = 0.882$$

$$P_{\text{soln}} = P_{\text{solv}} \times X_{\text{solv}} = 23.76 \text{ mm Hg} \times 0.882 = 21.0 \text{ mm Hg}$$

$$\Delta P = P^\circ - P_{\text{soln}} = 23.76 - 21 = 2.76$$

6 - Two miscible liquids, A and B, have vapor pressures of 250 mm Hg and 450 mm Hg, respectively. They were mixed in equal molar amounts. What is the total vapor pressure of the mixture?

- Solution:

$$P^o_A = 250 \text{ mmHg} \quad P^o_B = 450 \text{ mmHg}$$

they mixed in 1:1 ratio (both have the same number of moles)

Suppose the number of moles of A = the number of moles of B = 1

$$\begin{aligned} P &= P^o_A \cdot X_A + P^o_B \cdot X_B \\ &= 250 * 0.5 + 450 * 0.5 = 350 \text{ mmHg} \end{aligned}$$

7 - Two miscible liquids, A and B, have vapor pressures of 250 mm Hg and 450 mm Hg, respectively. They were mixed in A : B ratio equal 1 : 2 . What is the total vapor pressure of the mixture?

- **Solution:**

$$P^o_A = 250 \text{ mmHg} \quad P^o_B = 450 \text{ mmHg}$$

Suppose the number of moles of A = 1

the number of moles of B = 2

$$\begin{aligned} P &= P^o_A \cdot X_A + P^o_B \cdot X_B \\ &= 250 * \frac{1}{3} + 450 * \frac{2}{3} = 383.3 \text{ mmHg} \end{aligned}$$

8- Assume that a tablespoon (50.00 g) of NaCl is added to 500 mL of water at 20.0 °C.

At what temperature will the water boil?

What is the freezing point of the solution ?

$$K_b = 0.51 \text{ } ^\circ\text{C}/m. \quad K_f = 1.86 \text{ } ^\circ\text{C}/m.$$

Solution:

Find the molality of the solution

Mass of solute = 50 g

Mass of solvent = 500 g

Molar mass of solute = 23 + 35.5 = 58.5

$$m = \frac{\text{mass (solute)}_{(g)}}{\text{Molar mass solute}} \times \frac{1000}{\text{mass (solvent)}_{(g)}}$$

Molality = 1.71 mol / kg

The boiling point of solution

$$\Delta T_b = m K_b$$

$$= 2 * 1.71 * 0.51 = 1.74^\circ\text{C}$$

- $\Delta T_b = T_b - T_b^o = +ve \text{ value}$

For water: $\Delta T_b + 100^\circ\text{C} = T_b(\text{solution})$

$$= 1.74 + 100 = 101.74^\circ\text{C}$$

The freezing point of solution

$$\Delta T_f = m K_f$$

$$= 2 * 1.71 * 1.86 = 6.36^\circ\text{C}$$

- $\Delta T_f = T_f^\circ - T_f = +\text{ve value}$

For water:

$$\Delta T_f = 0^\circ\text{C} - T_f(\text{solution})$$

$$T_f = 0 - 6.36 = -6.36^\circ\text{C}$$

9. What is the osmotic pressure (in atm) of a 0.884 M sucrose solution at 16°C?

Solution:

- $\Pi = i \cdot MRT$
= $1 * 0.884 * 0.082 * (16+273)$
= 20.949 atm

10- Which one of the following solutions would produce maximum elevation in boiling point?

(a) 0.1 M glucose

b) 0.2 M NaCl

(c) 0.1 M Ba(NO₃)₂

(d) 0.1 M MgSO₄

• The concentration of particles:

(a) 0.1 M

(b) 0.4 M

(c) 0.3 M

(d) 0.2 M

the answer is (b)

- 11- Which one of the following solutions would produce maximum depression in the freezing point?
 - (a) 0.4 M sucrose
 - (c) 0.1 M $\text{Ba}(\text{NO}_3)_2$
 - (b) 0.1 M NaCl
 - (d) 0.02 M CaCl_2
- The concentration of particles:
 - (a) 0.4 M
 - (b) 0.2 M
 - (c) 0.3 M
 - (d) 0.06 M

the answer is (a)

3. Thermochemistry



nb

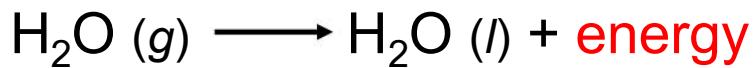


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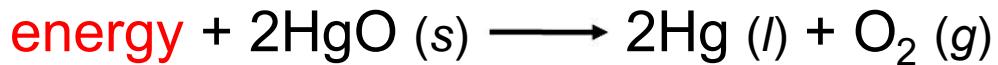
Thermochemistry

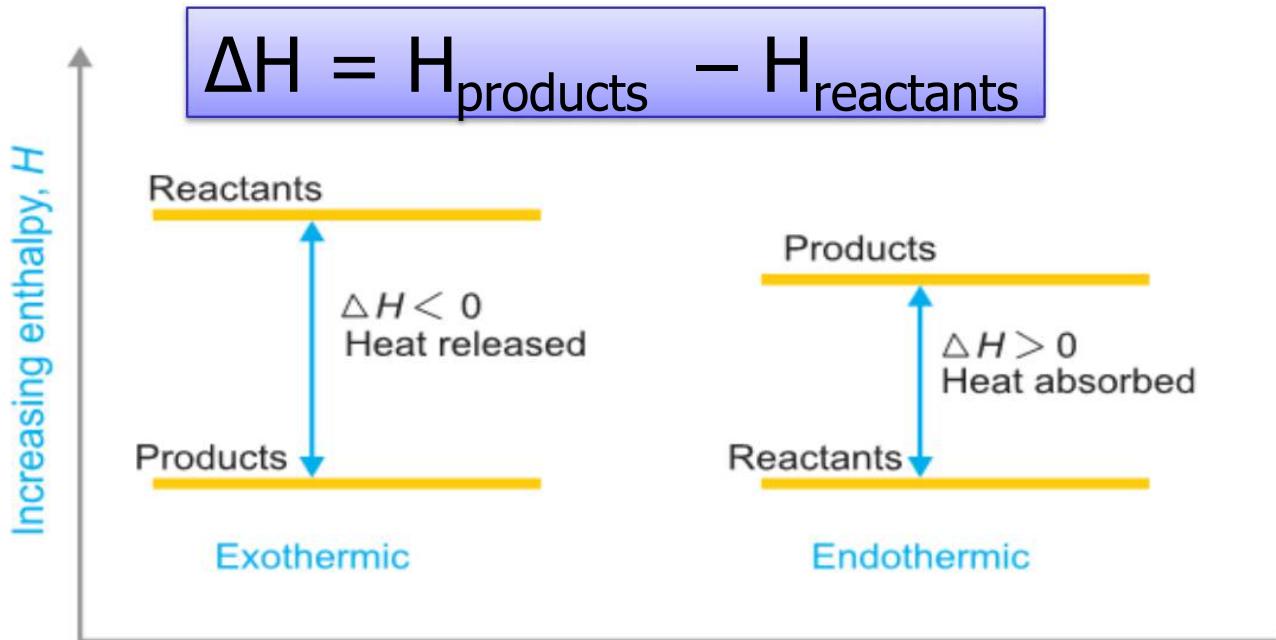
- Thermochemistry is the branch of physical chemistry which deals with the thermal or heat changes caused by chemical reactions.
- **Heat** is the thermal energy transferred between two objects as the result of a temperature difference
- **Temperature** is a measure of the kinetic energy of molecular motion.
- **Enthalpy (heat inside)H**
- ΔH =Heat change in a reaction at constant pressure

Exothermic process is any process that gives off heat – transfers thermal energy from the system to the surroundings.



Endothermic process is any process in which heat has to be supplied to the system from the surroundings.





■ **Figure 8.1**
Enthalpy diagram for an exothermic and endothermic reaction.

Melting ice cubes

Nuclear fission

Evaporation of water

Cooking an egg

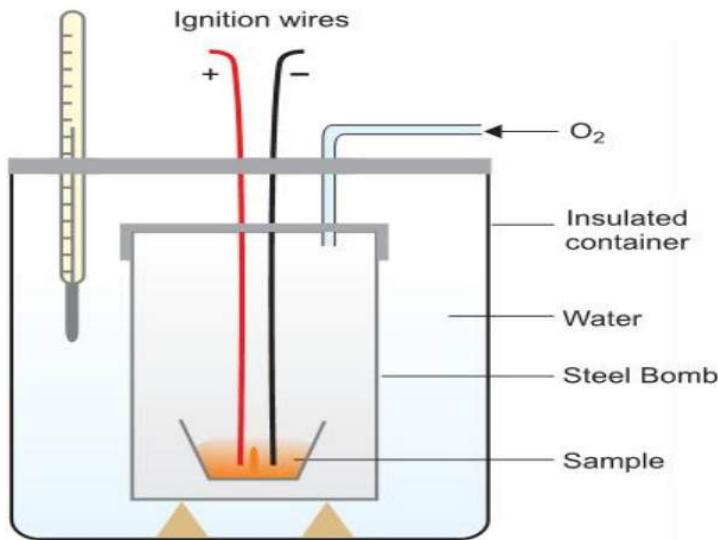
Mixing water and strong acids

Experimental Determination of ΔH

The heat given out or absorbed in a chemical reaction is measured in a suitable apparatus called a **calorimeter**

The energy changes are usually expressed as the calorie (cal.), and Joule (J). It may be noted that

$$1 \text{ cal} = 4.18 \text{ J}$$



■ **Figure 8.4**
Bomb Calorimeter.

Thermochemical Equations

- The stoichiometric coefficients always refer to the number of moles of a substance.
- The physical states of all reactants and products must be specified in thermochemical equations



- If you reverse a reaction, the sign of ΔH changes



- If you multiply both sides of the equation by a factor n , then ΔH must change by the same factor n .



HEAT OF REACTION OR ENTHALPY OF REACTION

- Heat of reaction may be defined as the amount of heat absorbed or evolved in a reaction when the number of moles of reactants as represented by the balanced chemical equation change completely into the products.
- ΔH° = the enthalpy of a reaction carried out at 1 atm.
- HEAT OF COMBUSTION HEAT OF SOLUTION
- HEAT OF NEUTRALISATION

- Enthalpies of Physical Change:
- HEAT OF FUSION
- HEAT OF VAPOURISATION

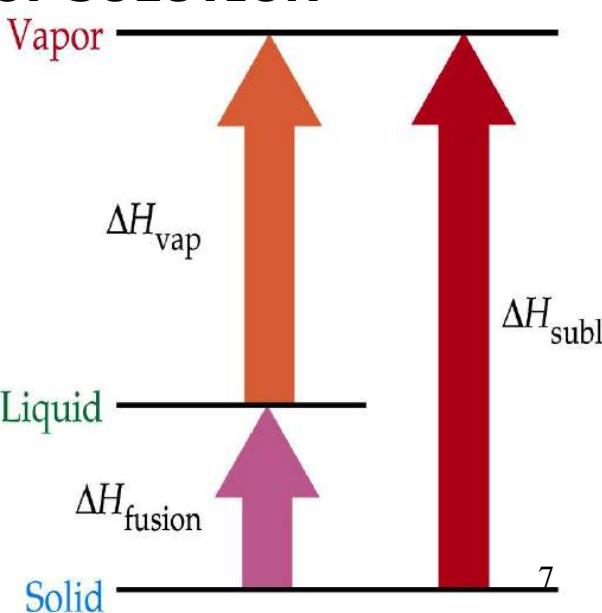


Table 6.2 Heats of Some Typical Reactions Measured at Constant Pressure

Type of Reaction	Example	ΔH (kJ)
Heat of neutralization	$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$	-56.2
Heat of ionization	$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq)$	56.2
Heat of fusion	$H_2O(s) \longrightarrow H_2O(l)$	6.0
Heat of vaporization	$H_2O(l) \longrightarrow H_2O(g)$	44.0
Heat of reaction	$MgCl_2(s) + 2Na(l) \longrightarrow 2NaCl(s) + Mg(s)$	-180.2

* Measured at 25°C. At 100°C, the value is 40.79 kJ.

HEAT OF FORMATION

- The change in enthalpy that takes place when one mole of the compound is formed from its elements.



- the standard heat of formation of all elements is assumed to be zero.

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



$$\Delta H^0 = [c\Delta H_f^0 \text{ (C)} + d\Delta H_f^0 \text{ (D)}] - [a\Delta H_f^0 \text{ (A)} + b\Delta H_f^0 \text{ (B)}]$$

Calculate ΔH° for the reaction



given that ΔH_f° for $\text{CO}_2(\text{g})$, $\text{CO}(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ are -393.5 , -111.31 and $-241.80 \text{ kJ mol}^{-1}$ respectively.

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

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

$$= [-111.3 + (-241.8)] - [-393.5 + 0]$$

$$= -353.1 + 393.5$$

$$= 40.4 \text{ kJ}$$

Benzene (C_6H_6) burns in air to produce carbon dioxide and liquid water. How much heat is released per mole of benzene combusted? The standard enthalpy of formation of benzene is 49.04 kJ/mol.



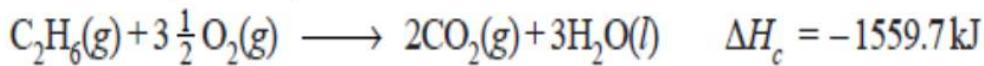
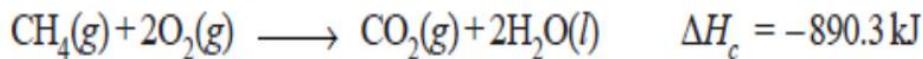
$$\Delta H^0 = [12\Delta H_f^0(CO_2) + 6\Delta H_f^0(H_2O)] - [2\Delta H_f^0(C_6H_6)]$$

$$\Delta H^0 = [12(-393.5) + 6(-187.6)] - [2(49.04)] = -5946 \text{ kJ}$$

$$\frac{-5946 \text{ kJ}}{2 \text{ mol}} = -2973 \text{ kJ/mol } C_6H_6$$

HEAT OF COMBUSTION

- The heat of combustion of a substance is defined as : **the change in enthalpy of a system when one mole of the substance is completely burnt in excess of air or oxygen.**



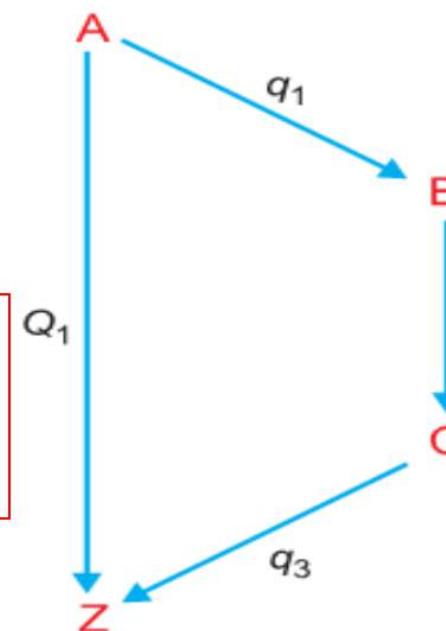
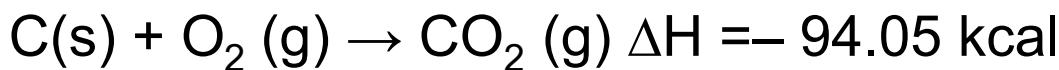
In case of methane heat produced per gram is $890.3/16 = 55.64 \text{ kJ g}^{-1}$ while for ethane it is $-1559.7/30 = 51.90 \text{ kJ g}^{-1}$. Thus methane has better fuel efficiency than ethane as it produces more heat per gram.

It should be noted clearly that the **heat of combustion of a substance (ΔH_c) is always negative**. Heat energy is evolved during the process of combustion i.e., $\Delta H_c = -$ ve.

HESS'S LAW OF CONSTANT HEAT SUMMATION

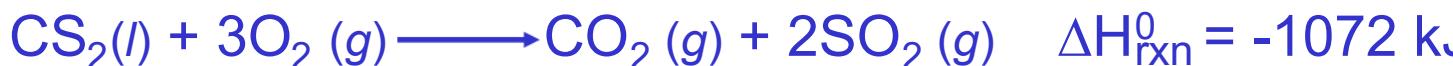
- When reactants are converted to products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps.

Burning of carbon to CO₂





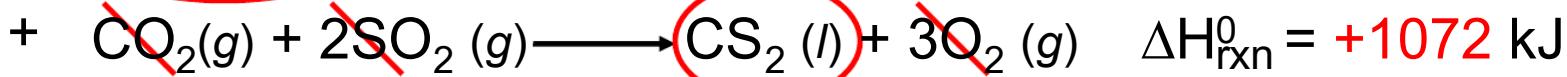
Calculate the standard enthalpy of formation of CS_2 (l) given that:



1. Write the enthalpy of formation reaction for CS_2



2. Add the given rxns so that the result is the desired rxn.

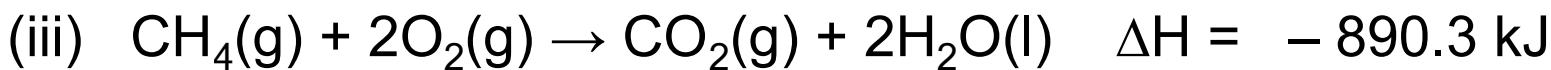
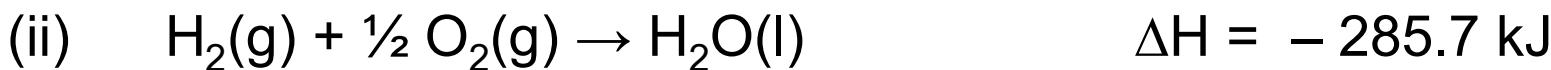


$$\Delta H_{\text{rxn}}^0 = -393.5 + (2 \times -296.1) + 1072 = 86^{14} \text{ kJ}$$

Determine ΔH of the reaction



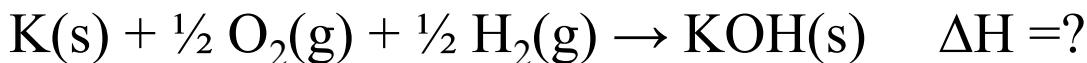
from the following data :



Calculate the heat of formation of potassium hydroxide from the following data.



SOLUTION



Adding equations (i) and (ii) and subtracting equation (iii) will give

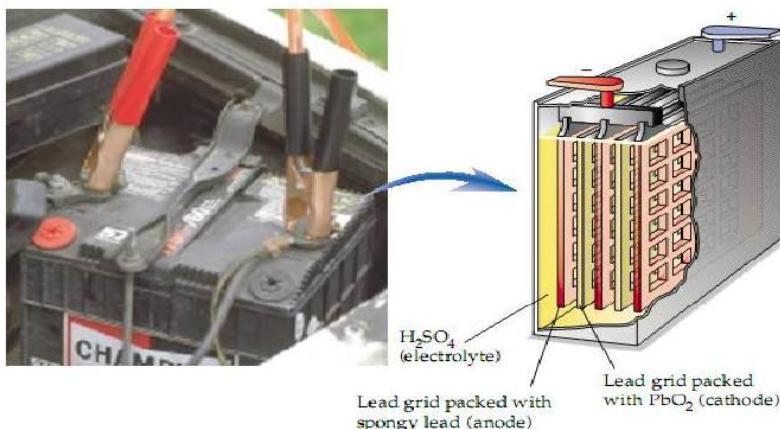
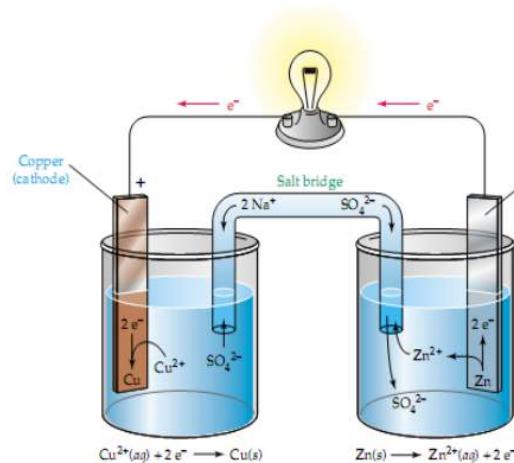
$$\Delta H = - 48.0 + (- 68.5) - (- 14.0) = - 102.5 \text{ kcal}$$

- Task:

Report about:

Fuels combustion

4. Electrochemistry and Applications



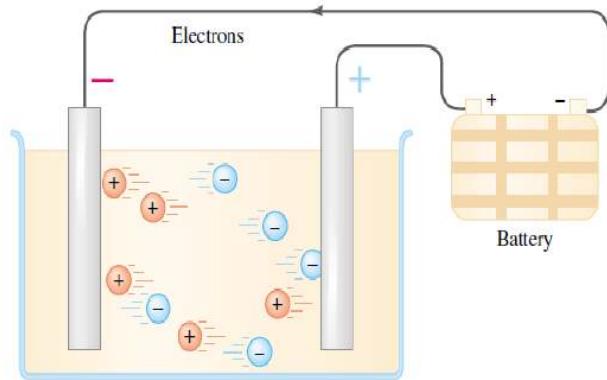
Electrochemistry

- **Electrochemistry** deals with the chemical changes produced by electric current and with the production of electricity by chemical reactions.
- In most applications the reacting system is contained in a **cell**, and an electric current enters or exits by **electrodes**.
- **Electrodes** are surfaces on which oxidation or reduction half-reactions occur. They may or may not participate in the reactions. Those that do not react are called **inert electrodes**.
- **The cathode** is defined as the electrode at which reduction occurs as electrons are gained by some species. **The anode** is the electrode at which oxidation occurs as electrons are lost by some species.
- We classify electrochemical cells into two types.
 1. **Electrolytic cells** are those in which electrical energy from an external source causes non-spontaneous chemical reactions to occur.
 2. **Voltaic cells (Galvanic)** are those in which spontaneous chemical reactions produce electricity and supply it to an external circuit.

ELECTRICAL CONDUCTION

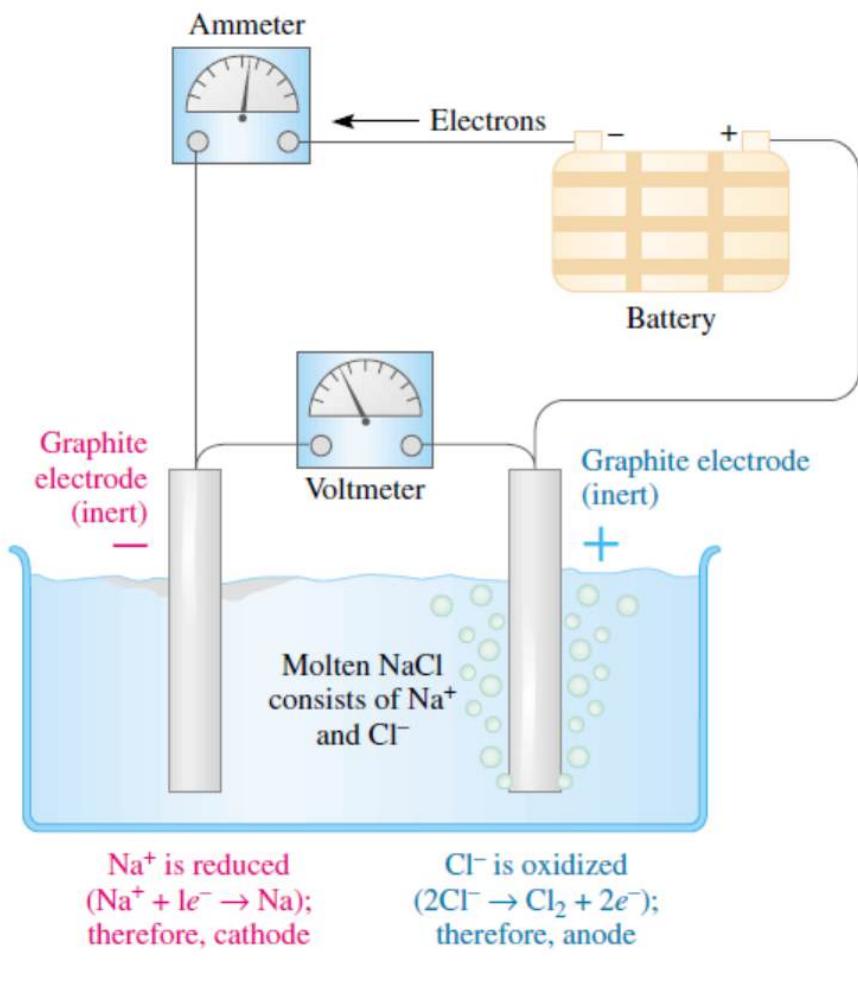
- Electric current represents transfer of charge.
- Charge can be conducted through metals and through pure liquid electrolytes (that is, molten salts) or solutions containing electrolytes.
- The former type of conduction is called **metallic conduction**. It **involves the** flow of electrons with no similar movement of the atoms of the metal and no obvious changes in the metal.

➤ **Ionic, or electrolytic, conduction is the conduction** of electric current by the motion of ions through a solution or a pure liquid. Positively charged ions migrate toward the negative electrode while negatively charged ions move toward the positive electrode. Both kinds of conduction, ionic and metallic, occur in electrochemical cells

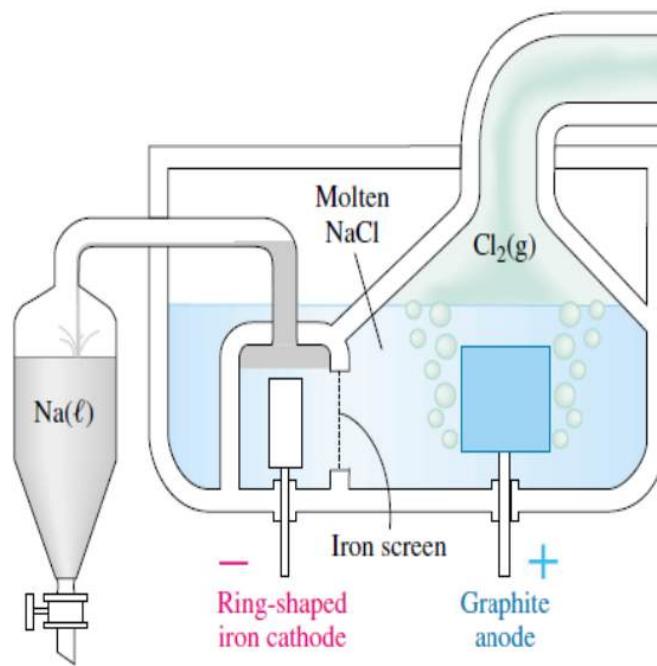


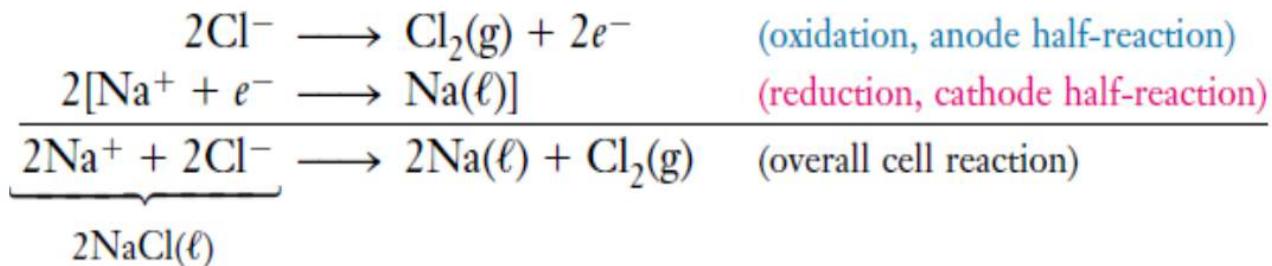
ELECTROLYTIC CELLS

- In some electrochemical cells *nonspontaneous chemical reactions are forced to occur by the input of electrical energy*. This process is called **electrolysis**.
 - An electrolytic cell consists of a container for the reaction material with electrodes immersed in the reaction material and connected to a source of direct current. **Inert electrodes** are often used so that they do not react.
-
- **THE ELECTROLYSIS OF MOLTEN SODIUM CHLORIDE**
 - Solid sodium chloride does not conduct electricity. Its ions vibrate about fixed positions, but they are not free to move throughout the crystal. Molten (melted) NaCl, however, is an excellent conductor because its ions are freely mobile. Consider a cell in which a source of direct current is connected by wires to two inert graphite electrodes. They are immersed in a container of molten sodium chloride. When the current flows, we observe the following.
 - A pale green gas, which is chlorine, Cl₂, is liberated at one electrode.
 - Molten, silvery white metallic sodium, Na, forms at the other electrode and floats on top of the molten sodium chloride.



(THE DOWNS CELL)

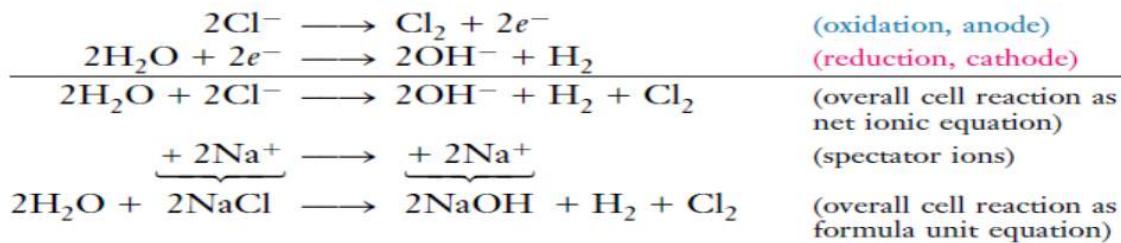


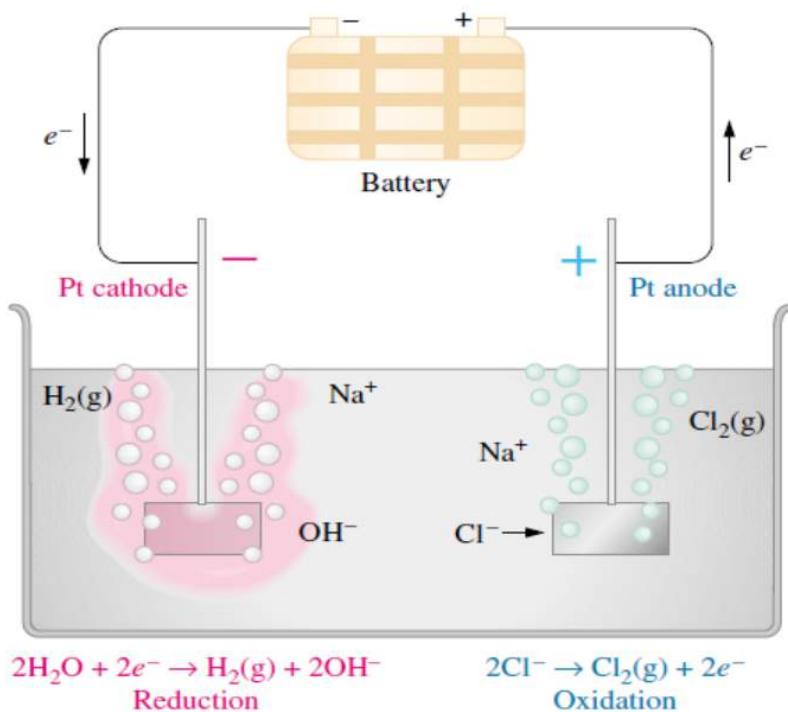


- The formation of metallic Na and gaseous Cl₂ from NaCl is *nonspontaneous except at temperatures very much higher than 801°C*. The direct current (dc) source must supply electrical energy to force this reaction to occur.
- Electrons are used in the cathode half reaction (reduction) and produced in the anode half-reaction (oxidation). They therefore travel through the wire from *anode to cathode*. *The dc source forces electrons to flow nonspontaneously from the positive electrode to the negative electrode*.
- The anode is the positive electrode and the cathode the negative electrode *in all electrolytic cells*.
- Sodium and chlorine must not be allowed to come in contact with each other because they react spontaneously, rapidly, and explosively to form sodium chloride.
- Electrolysis of NaCl in the Downs cell is the main commercial method of producing metallic sodium.

THE ELECTROLYSIS OF AQUEOUS SODIUM CHLORIDE

- Consider the electrolysis of a moderately concentrated solution of NaCl in water, using inert electrodes. The following experimental observations are made when a sufficiently high voltage is applied across the electrodes of a suitable cell.
 - H₂ gas is liberated at one electrode. The solution becomes basic in that vicinity.
 - Cl₂ gas is liberated at the other electrode.
- Chloride ions are obviously being oxidized to Cl₂ in this cell, as they were in the electrolysis of molten NaCl.
- But Na ions are not reduced to metallic Na. Instead, gaseous H₂ and aqueous OH ions are produced by reduction of H₂O molecules at the cathode.
- Water is more easily reduced than Na ions. This is primarily because the reduction of Na would produce the very active metal Na, whereas the reduction of H₂O produces the more stable products H₂(g) and OH(aq). The active metals Li, K, Ca, and Na displace H₂ from aqueous solutions, so we do not expect these metals to be produced in aqueous solution.





- ❑ The overall cell reaction produces gaseous H₂ and Cl₂ and an aqueous solution of NaOH, called caustic soda. Solid NaOH is then obtained by evaporation of the residual solution. This is the most important commercial preparation of each of these substances.
- ❑ It is much less expensive than the electrolysis of molten NaCl, because it is not necessary to heat the solution.

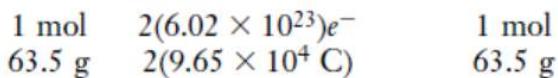
FARADAY'S LAW OF ELECTROLYSIS

- In 1832–1833, Michael Faraday's studies of electrolysis led to this conclusion.
- “The amount of substance that undergoes oxidation or reduction at each electrode during electrolysis is directly proportional to the amount of electricity that passes through the cell.”
- A quantitative unit of electricity is now called **the faraday**.
- **One faraday** is the amount of electricity that corresponds to the gain or loss, and therefore the passage, of 6.022×10^{23} electrons, or *one mole of electrons*.
- A smaller electrical unit commonly used in chemistry, physics, and electronics is **the coulomb (C)**. One coulomb is defined as the amount of charge that passes a given point when 1 ampere (A) of electric current flows for 1 second. One ampere of current equals 1 coulomb per second. One faraday is equal to 96,485 coulombs of charge.

$$1 \text{ ampere} = 1 \frac{\text{coulomb}}{\text{second}} \quad \text{or} \quad 1 \text{ A} = 1 \text{ C/s}$$

$$1 \text{ faraday} = 6.022 \times 10^{23} e^- = 96,485 \text{ C}$$

Calculate the mass of copper metal produced during the passage of 2.50 amperes of current through a solution of copper(II) sulfate for 50.0 minutes.



$$\underline{\quad} \text{ C} = 50.0 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{2.50 \text{ C}}{\text{s}} = 7.50 \times 10^3 \text{ C}$$

$$\underline{\quad} \text{ g Cu} = 7.50 \times 10^3 \text{ C} \times \frac{1 \text{ mol } e^-}{9.65 \times 10^4 \text{ C}} \times \frac{63.5 \text{ g Cu}}{2 \text{ mol } e^-} = \underline{\quad} 2.47 \text{ g Cu}$$

1 MOLE OF ELECTRONS = 96485 C

2 MOLE OF ELECTRONS = $2 * 96485 \text{ C}$

The mass produced of Cu= 63.5 g

1 A = 1 C/S

C = A * S

the amount of electricity = $2.5 * 50 * 60 = 7500 \text{ C}$

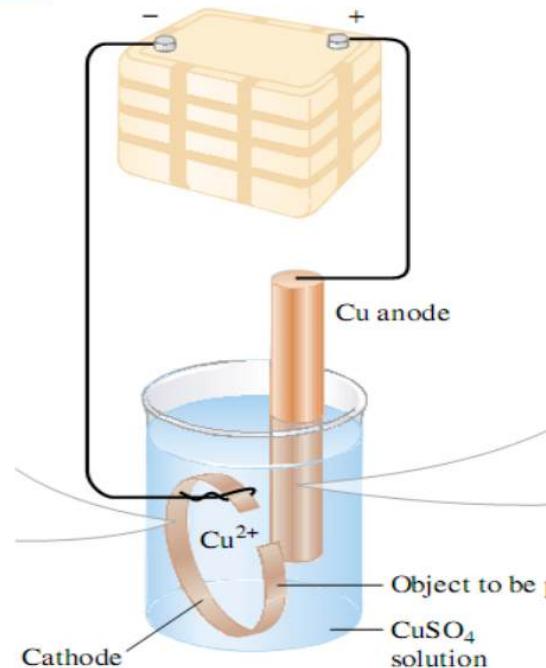
$2 * 96485 \text{ C} \rightarrow 63.5 \text{ g of Cu}$

$7500 \text{ C} \rightarrow X$

$X = 2.468 \text{ g of Cu}$

COMMERCIAL APPLICATIONS OF ELECTROLYTIC CELLS

1. Several elements are produced commercially by electrolysis. Some electrolytic cells produce sodium (the Downs cell), chlorine, hydrogen, and oxygen.
2. Electrolysis of molten compounds is also the common method of obtaining other Group IA metals, IIA metals (except barium), and aluminum.
3. Impure metals can also be refined electrolytically, as copper.
4. Metal-plated articles are common in our society. Jewelry and tableware are often plated with silver. Gold is plated onto jewelry and electrical contacts. Copper is plated onto many objects for decorative purposes. Some automobiles have steel bumpers plated with thin films of chromium.

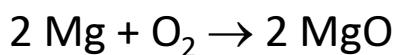




Oxidation and Reduction

Oxidation is...

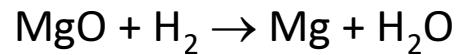
- the **loss** of electrons
- an increase in oxidation state
- the addition of oxygen
- the loss of hydrogen



notice the magnesium is losing electrons

Reduction is...

- the **gain** of electrons
- a decrease in oxidation state
- the loss of oxygen
- the addition of hydrogen



notice the Mg²⁺ in MgO is gaining electrons

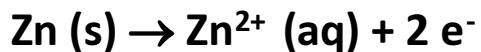
the oxidizing agent always gets reduced in the reaction.

the reducing agent always gets oxidized

The redox reaction is



Oxidation half-reaction:

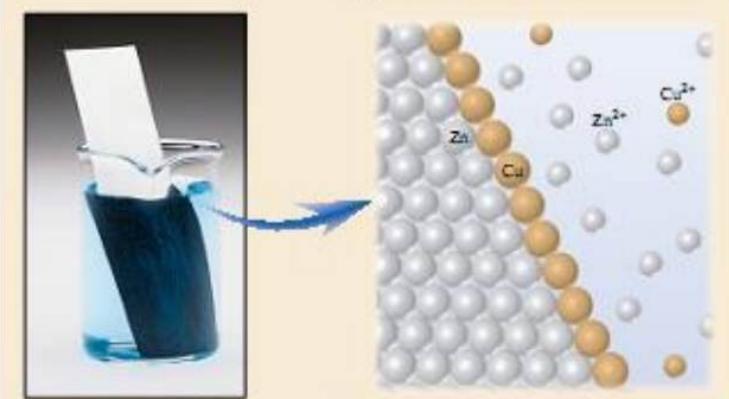
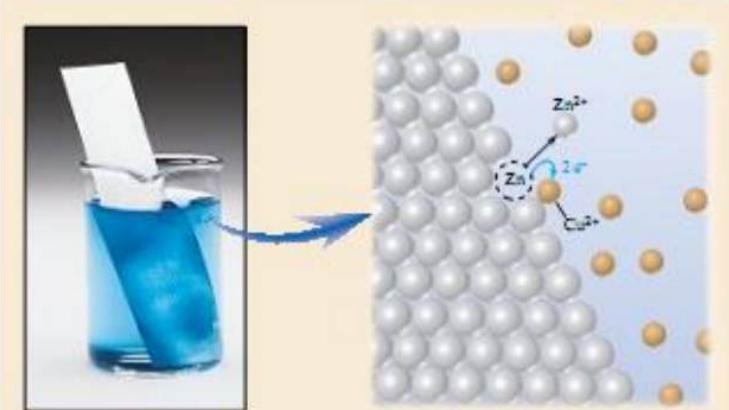


Reduction half-reaction:



Cu²⁺ is the oxidizing agent

Zn is the reducing agent



Electrochemical series.

TABLE 21-2 Standard Aqueous Reduction Potentials in Aqueous Solution at 25°C

Element	Reduction Half-Reaction	Standard Reduction Potential E° , volts
Li	$\text{Li}^+ + e^- \longrightarrow \text{Li}$	-3.045
K	$\text{K}^+ + e^- \longrightarrow \text{K}$	-2.925
Ca	$\text{Ca}^{2+} + 2e^- \longrightarrow \text{Ca}$	-2.87
Na	$\text{Na}^+ + e^- \longrightarrow \text{Na}$	-2.714
Mg	$\text{Mg}^{2+} + 2e^- \longrightarrow \text{Mg}$	-2.37
Al	$\text{Al}^{3+} + 3e^- \longrightarrow \text{Al}$	-1.66
Zn	$\text{Zn}^{2+} + 2e^- \longrightarrow \text{Zn}$	-0.763
Cr	$\text{Cr}^{3+} + 3e^- \longrightarrow \text{Cr}$	-0.74
Fe	$\text{Fe}^{2+} + 2e^- \longrightarrow \text{Fe}$	-0.44
Cd	$\text{Cd}^{2+} + 2e^- \longrightarrow \text{Cd}$	-0.403
Ni	$\text{Ni}^{2+} + 2e^- \longrightarrow \text{Ni}$	-0.25
Sn	$\text{Sn}^{2+} + 2e^- \longrightarrow \text{Sn}$	-0.14
Pb	$\text{Pb}^{2+} + 2e^- \longrightarrow \text{Pb}$	-0.126
H ₂	$2\text{H}^+ + 2e^- \longrightarrow \text{H}_2$	0.000 (reference electrode)
Cu	$\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}$	+0.337
I ₂	$\text{I}_2 + 2e^- \longrightarrow 2\text{I}^-$	+0.535
Hg	$\text{Hg}^{2+} + 2e^- \longrightarrow \text{Hg}$	+0.789
Ag	$\text{Ag}^+ + e^- \longrightarrow \text{Ag}$	+0.799
Br ₂	$\text{Br}_2 + 2e^- \longrightarrow 2\text{Br}^-$	+1.08
Cl ₂	$\text{Cl}_2 + 2e^- \longrightarrow 2\text{Cl}^-$	+1.360
Au	$\text{Au}^{3+} + 3e^- \longrightarrow \text{Au}$	+1.50
F ₂	$\text{F}_2 + 2e^- \longrightarrow 2\text{F}^-$	+2.87

Increasing strength as oxidizing agent;
increasing ease of reduction

Increasing strength as reducing agent;
increasing ease of oxidation

Voltaic cells

Galvanic cells

Anode

the electrode where oxidation occurs

Cathode

the electrode where reduction occurs

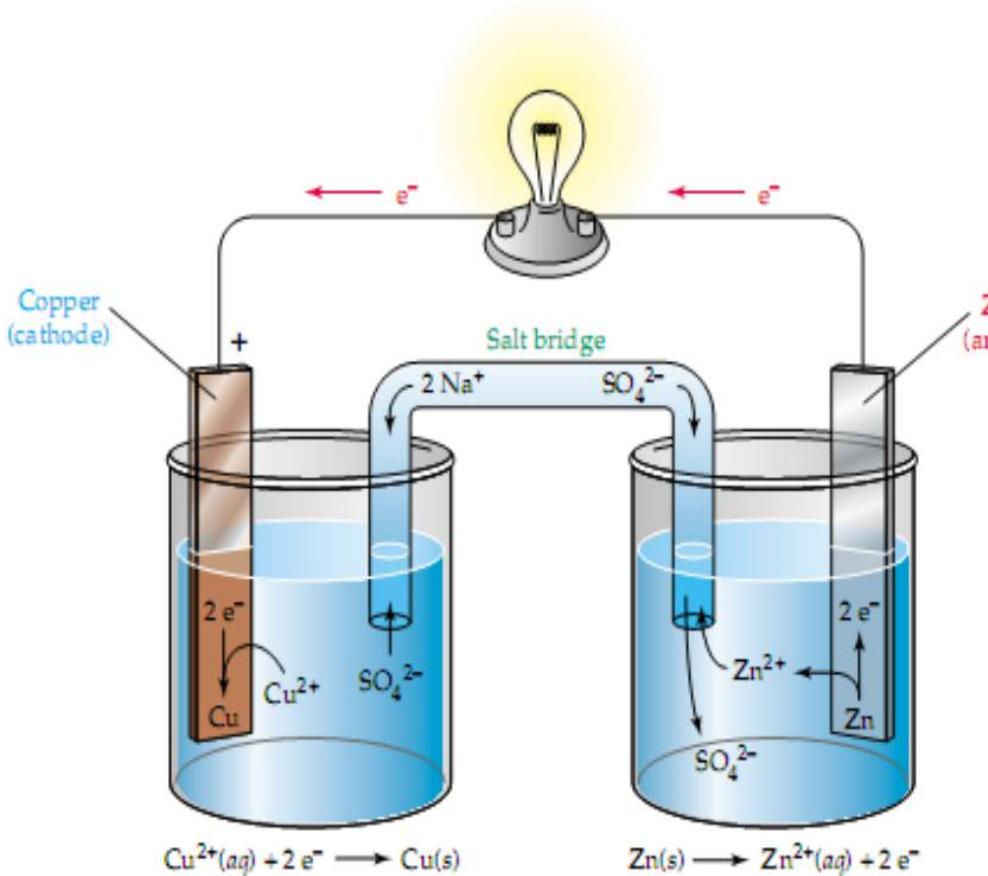
Salt Bridge

connects two “half-cells” to complete the electric circuit.

for example, a U-tube filled with salt solution

Electrolyte

Daniell cell



Describe a galvanic cell that uses the reaction



Identify the anode and cathode half-reactions, and sketch the experimental setup. Label the anode and cathode, indicate the direction of electron and ion flow, and identify the sign of each electrode.

Cell Potential

- The potential difference between the two electrodes of an electrochemical cell provides the driving force that pushes electrons through the external circuit.
- We call this potential difference, denoted E_{cell} , the cell potential.
- Because E_{cell} is measured in volts, we often refer to it as the cell voltage.
- A cell potential is measured with an electronic instrument called a **voltmeter**
- For any cell reaction that proceeds spontaneously, such as that in a voltaic cell, the cell voltage will be positive.

- Calculating Cell Potential

Because we tabulate reduction potentials, the cell potential is calculated (from those tabulated numbers) as

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

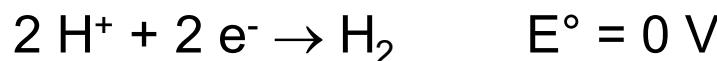
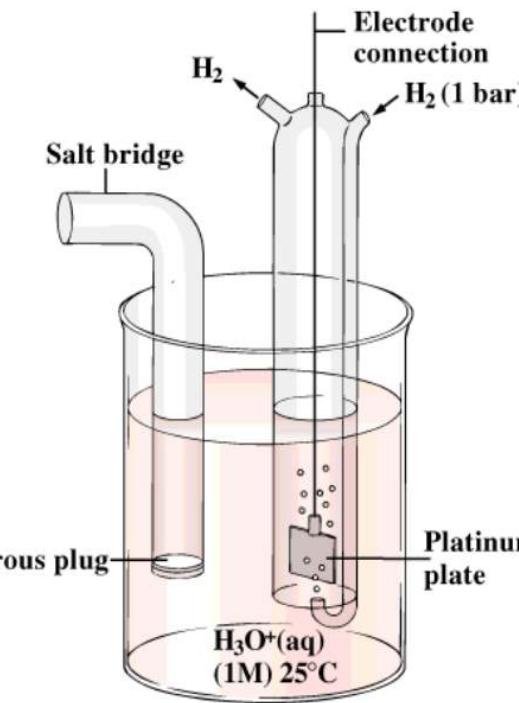
The minus sign is present only because we are using reduction potential tables and, by definition, an anode is where oxidation occurs.

- The standard cell potential E° is the cell potential when both reactants and products are in their standard states—solutes at 1 M concentrations, gases at a partial pressure of 1 atm, solids and liquids in pure form, with all at a specified temperature, usually 25°C.
- $E^\circ_{\text{ox}} = -E^\circ_{\text{red}}$

Standard Hydrogen Electrode (SHE)

- It is impossible to measure the potential of a single electrode.
- Using a voltmeter, we can measure the difference in potential between two electrodes.
- Chemists arbitrarily assigned a potential of 0 V for the SHE.
- By measuring the difference in potential between the SHE and other electrodes, potentials can then be assigned to other electrodes.

Standard hydrogen electrode



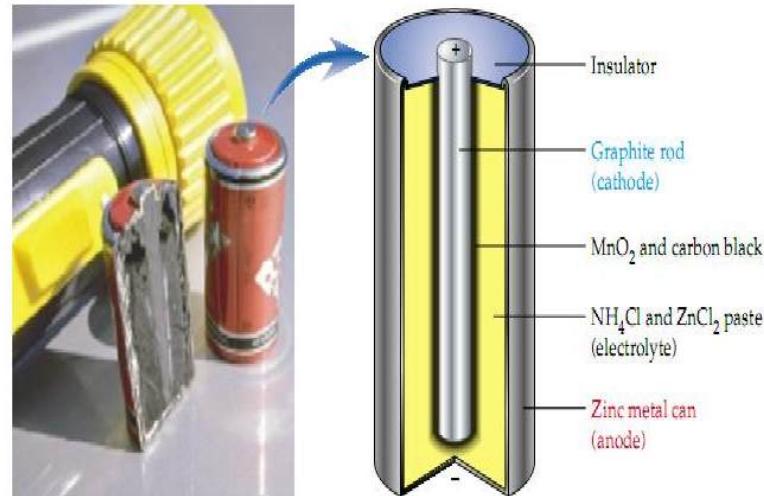
Application of Electrochemistry

PRIMARY VOLTAIC CELLS

- As any voltaic cell produces current (discharges), chemicals are consumed. Primary voltaic cells cannot be “recharged.” Once the chemicals have been consumed, further chemical action is not possible. The electrolytes or electrodes (or both) cannot be regenerated by reversing the current flow through the cell using an external direct current source.

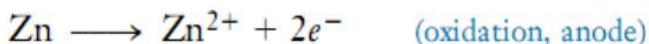
► DRY CELLS

► The first dry cell was patented by Georges Leclanché (1839–1882) in 1866. The container of this dry cell, made of zinc, also serves as one of the electrodes. The other electrode is a carbon rod in the center of the cell. The zinc container is lined with porous paper to separate it from the other materials of the cell. The rest of the cell is filled with a moist mixture (the cell is not really dry) of ammonium chloride (NH_4Cl), manganese(IV) oxide (MnO_2), zinc chloride (ZnCl_2), and a porous, inert filler. Dry cells are sealed to keep the moisture from evaporating.

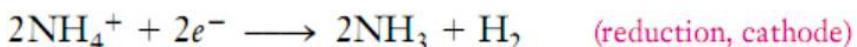


Leclanché Cell

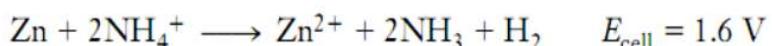
As the cell operates (the electrodes must be connected externally), the metallic Zn is oxidized to Zn²⁺, and the liberated electrons flow along the container to the external circuit. Thus, the zinc electrode is the anode(negative electrode).



The carbon rod is the cathode, at which ammonium ions are reduced.



Addition of the half-reactions gives the overall cell reaction



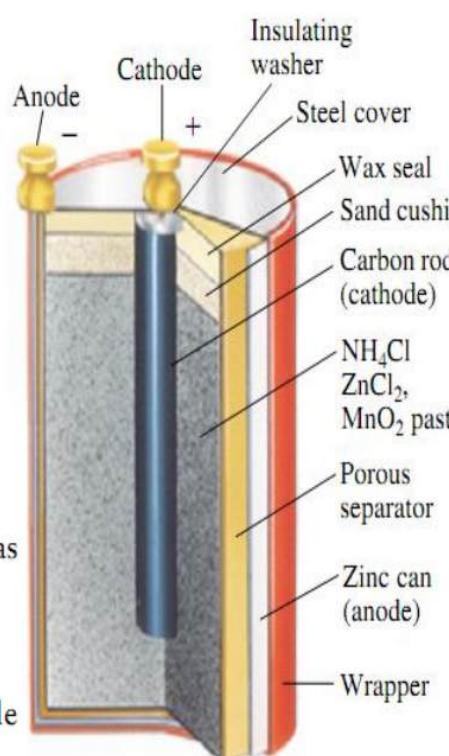
As H₂ is formed, it is oxidized by MnO₂ in the cell. This prevents collection of H₂ gas on the cathode, which would stop the reaction.



The ammonia produced at the cathode combines with zinc ions and forms a soluble compound containing the complex ions, [Zn(NH₃)₄]²⁺.



This reaction prevents polarization due to the buildup of ammonia, and it prevents the concentration of Zn²⁺ from increasing substantially, which would decrease the cell potential.



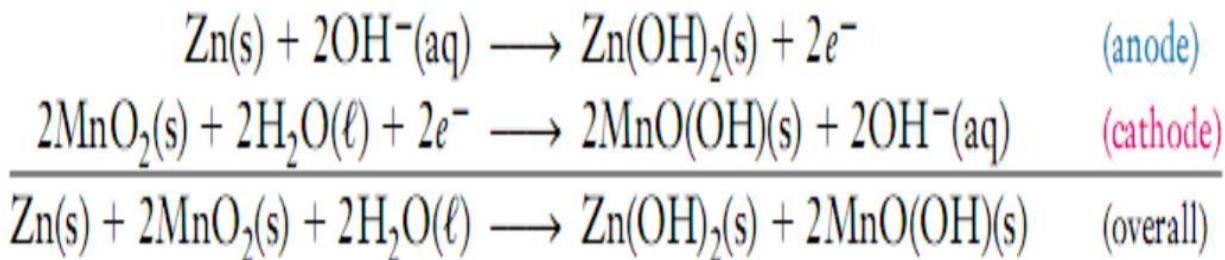
Alkaline dry cells

□ Alkaline dry cells are similar to Leclanché dry cells except that

- (1) the electrolyte is basic (alkaline) because it contains KOH, and
- (2) the interior surface of the Zn container is rough; this gives a larger surface area.

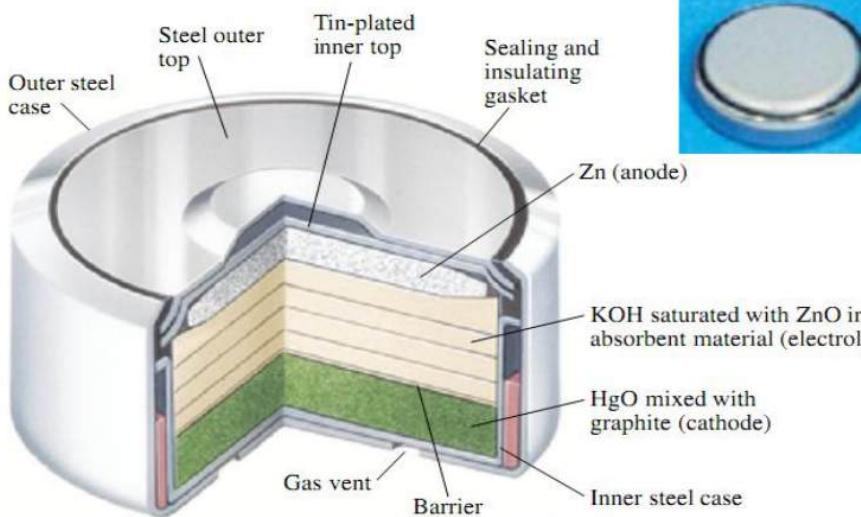
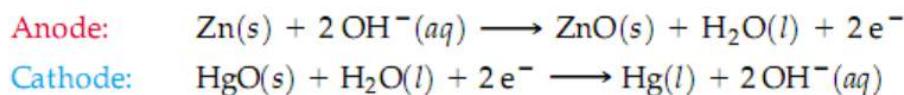
□ Alkaline cells have a longer shelf life than ordinary dry cells, and they stand up better under heavy use. The voltage of an alkaline cell is about 1.5 volts.

□ During discharge, the alkaline dry cell reactions are



The mercury battery

❑ Closely related to the alkaline dry cell is the mercury battery, often used in watches, calculators, heart pacemakers, and other devices where a battery of small size is required. The anode of the mercury battery is zinc, as in the alkaline dry cell, but the cathode is steel in contact with mercury(II) oxide (HgO) in an alkaline medium of KOH and Zinc is oxidized at the anode, and HgO is reduced at the cathode:



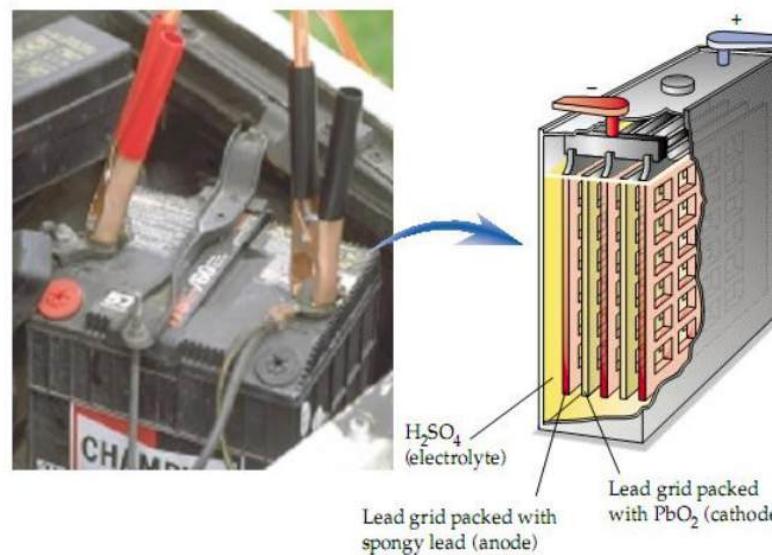
❑ Even though mercury batteries can be made very small, they still produce a stable potential (about 1.3 V) for long periods of time. When possible, used mercury batteries should be recycled to recover the mercury because of its toxicity.

SECONDARY VOLTAIC CELLS

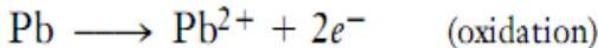
- In secondary voltaic cells, or reversible cells, the original reactants can be regenerated. This is done by passing a direct current through the cell in the direction opposite of the discharge current flow. This process is referred to as charging, or recharging, a cell or battery. The most common example of a secondary voltaic cell is the lead storage battery, used in most automobiles.

THE LEAD STORAGE BATTERY

One group of lead plates contains compressed spongy lead. These alternate with a group of lead plates that contain lead(IV) oxide, PbO_2 . The electrodes are immersed in a solution of about 40% sulfuric acid.



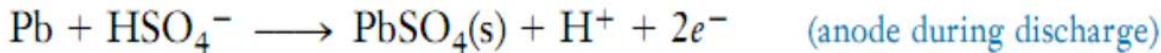
➤ When the cell discharges, the spongy lead is oxidized to lead ions, and the lead plates accumulate a negative charge.



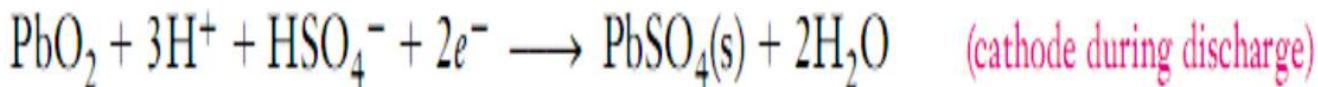
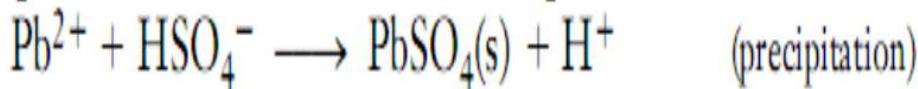
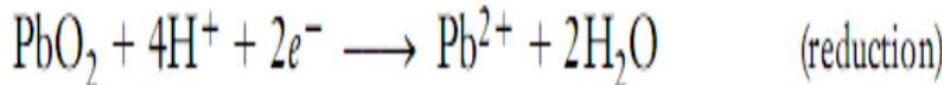
The lead ions then react with hydrogen sulfate ions from the sulfuric acid to form insoluble lead(II) sulfate. This begins to coat the lead electrode.



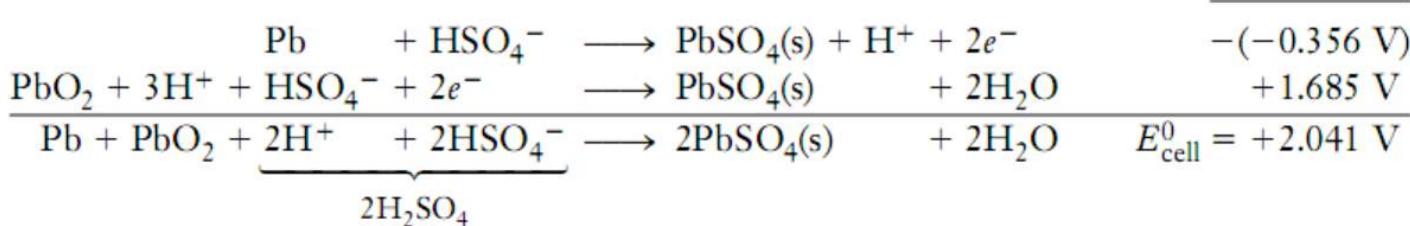
Thus, the net process at the anode *during discharge* is



➤ The electrons travel through the external circuit and re-enter the cell at the PbO_2 electrode, which is the cathode during discharge. Here, in the presence of hydrogen ions, the lead(IV) oxide is reduced to lead(II) ions. These ions also react with HSO_4^- ions from the H_2SO_4 to form an insoluble PbSO_4 coating on the lead(IV) oxide electrode.



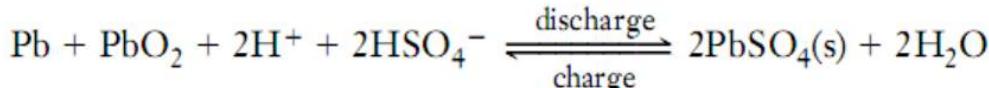
The net cell reaction



One cell creates a potential of about 2 volts. Automobile 12-volt batteries have six cells connected in series. The potential declines only slightly during use, because solid reagents are being consumed. As the cell is used, some H₂SO₄ is consumed, lowering its concentration.

When a potential slightly greater than the potential the battery can generate is imposed across the electrodes, the current flow can be reversed. The battery can then be recharged by reversal of all reactions. The reactions that occur in a lead storage battery are summarized as follows.

The decrease in the concentration of sulfuric acid provides an easy method for measuring the degree of discharge, because the density of the solution decreases accordingly. We simply measure the density of the solution with a hydrometer.



During many repeated charge–discharge cycles, some of the PbSO₄ falls to the bottom of the container and the H₂SO₄ concentration becomes correspondingly low. Eventually the battery cannot be recharged fully. It can be traded in for a new one, and the lead can be recovered and reused to make new batteries.

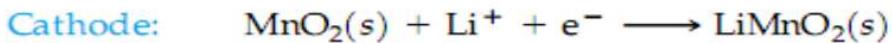
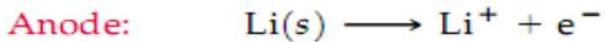
THE NICKEL–CADMIUM (NICAD) CELL

- ❑ it can be recharged.
- ❑ It thus has a much longer useful life than ordinary (Leclanché) dry cells.
- ❑ Nicad batteries are used in electronic wristwatches, calculators, and photographic equipment.
- ❑ The anode is cadmium, and the cathode is nickel(IV) oxide. The electrolytic solution is basic.



Lithium Batteries

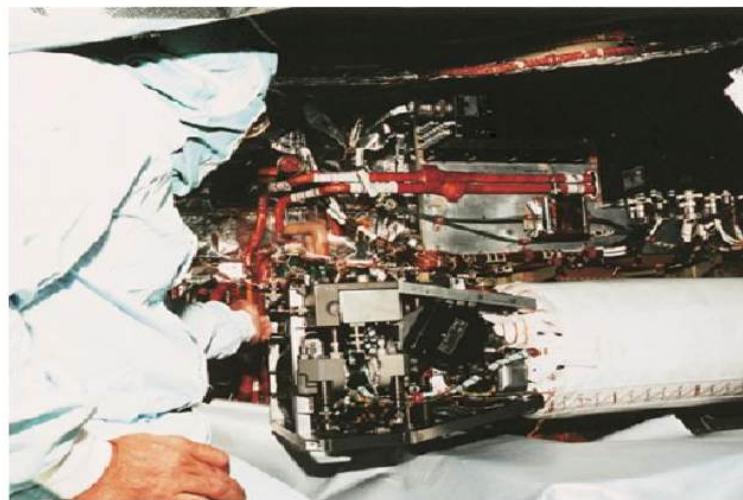
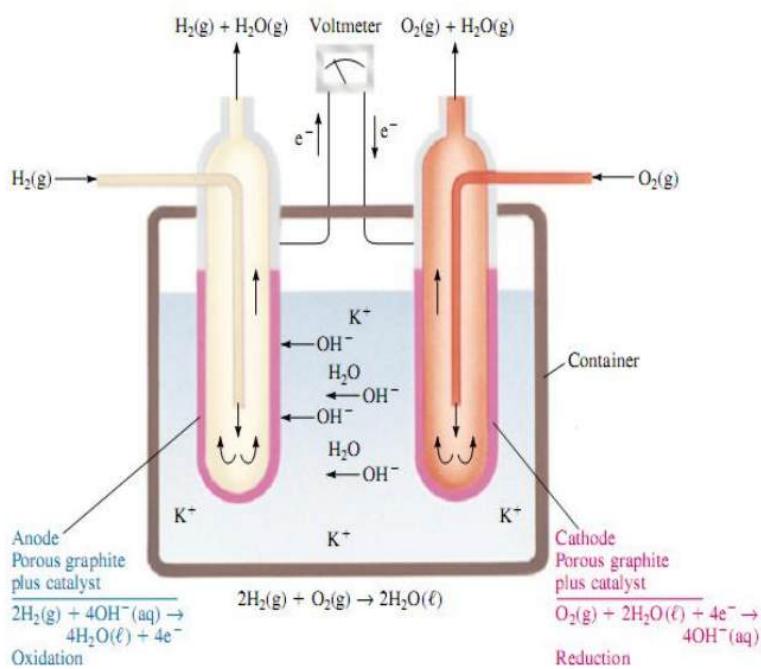
Rechargeable lithium batteries may prove to be the batteries of the future because of their light weight and high voltage (about 3.0 V). More than 900 million were sold in 2001, with production doubling annually. Lithium has a higher E° value for oxidation than any other metal, and only 6.94 g of lithium is needed to provide 1 mol of electrons. Lithium batteries consist of a lithium anode—either lithium metal itself or lithium atoms inserted into a graphite electrode—a metal oxide or metal sulfide cathode that can incorporate Li^+ ions, and an electrolyte that contains a lithium salt, such as LiClO_4 , in an organic solvent. Solid-state polymer electrolytes that can transport Li^+ ions have also been used. When the cathode material is MnO_2 , for example, the electrode reactions are



Lithium batteries are now used in cell phones, laptop computers, and cameras.

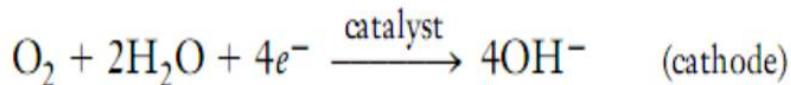
THE HYDROGEN–OXYGEN FUEL CELL

- ❑ Fuel cells are voltaic cells in which the reactants are continuously supplied to the cell and the products are continuously removed.
- ❑ Hydrogen–oxygen fuel cell: A fuel cell in which hydrogen is the fuel (reducing agent) and oxygen is the oxidizing agent.
- ❑ The hydrogen–oxygen fuel cell already has many applications. It is used in spacecraft to supplement the energy obtained from solar cells. Liquid H₂ is carried on board as a propellant. The boiled-off H₂ vapor is used in a fuel cell to generate electrical power.

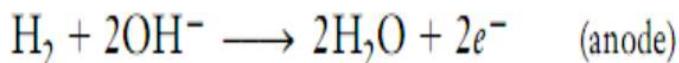


A hydrogen–oxygen fuel cell that is used in spacecraft.

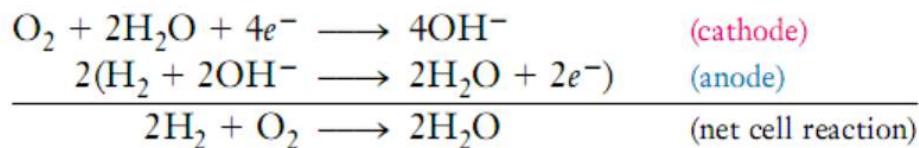
- ❑ Hydrogen (the fuel) is supplied to the anode compartment.
- ❑ Oxygen is fed into the cathode compartment. The diffusion rates of the gases into the cell are carefully regulated for maximum efficiency.
- ❑ Oxygen is reduced at the cathode, which consists of porous carbon impregnated with a finely divided Pt or Pd catalyst.



- ❑ the OH ions migrate through the electrolyte to the anode, an aqueous solution of a base. The anode is also porous carbon containing a small amount of catalyst (Pt, Ag, or CoO). Here H₂ is oxidized to H₂O.



- ❑ The net reaction is obtained from the two half-reactions.



➤ The H₂/O₂ cell is nonpolluting; the only substance released is H₂O. Catalysts have been developed to allow sunlight to decompose water into hydrogen and oxygen, which might be used to operate fuel cells, permitting the utilization of solar energy.

➤ Fuel cells have also been constructed using fuels other than hydrogen, such as methane or methanol.

Corrosion

- Corrosion may be defined as the destruction of a metal or an alloy because of chemical or electrochemical reaction with its surrounding environment or medium
- typically a transfer of electrons from one metal to another through an Oxidation-Reduction Reaction.



Types of corrosion

Type 1 - Dry

- Direct chemical combination – Metals combine directly with gases such as oxygen, chlorine, sulphur gases & carbon dioxide
- In an environment containing oxygen – covalent bonds are formed between metals & oxygen at the surface
- Once exposed to air oxidation starts – slow process at normal temperatures – rate of corrosion increases with increased temperature

Type 2 – Wet

- Electrochemical corrosion – oxygen may assist the process – results mainly from a tendency of metals to ionise (dissolve) when placed in water or an aqueous environment

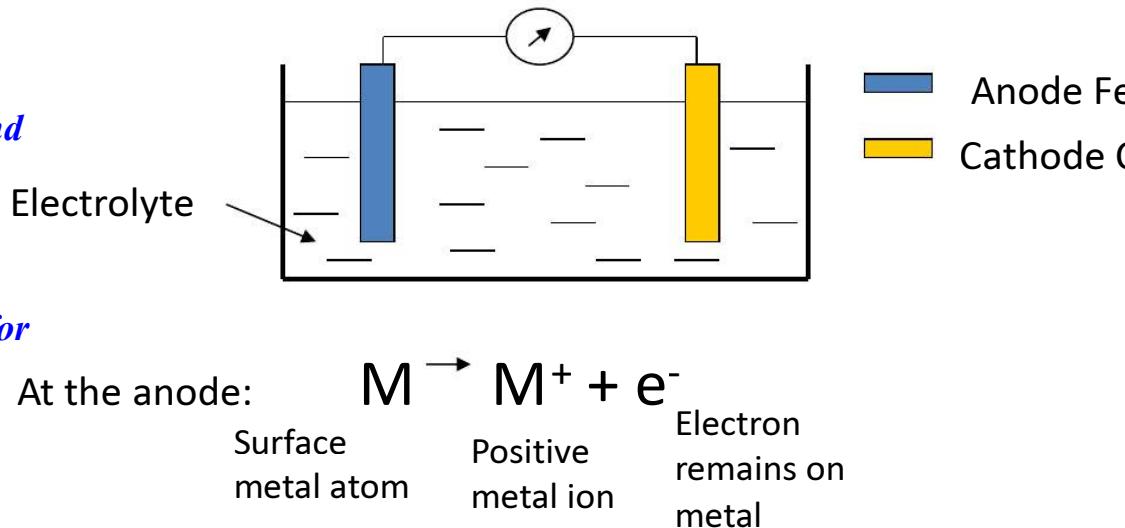
Corrosion Mechanism

*electrochemical corrosion
requires*

*2 dissimilar metals (anode and
cathode)*

*electrolyte (solution that can
support the flow of electrons)*

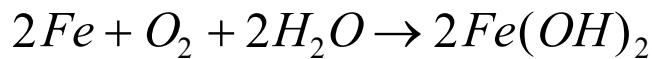
*conductor (metallic pathway for
electrons to flow between
metals)*



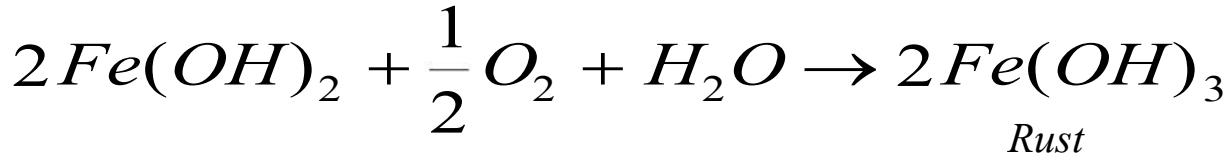
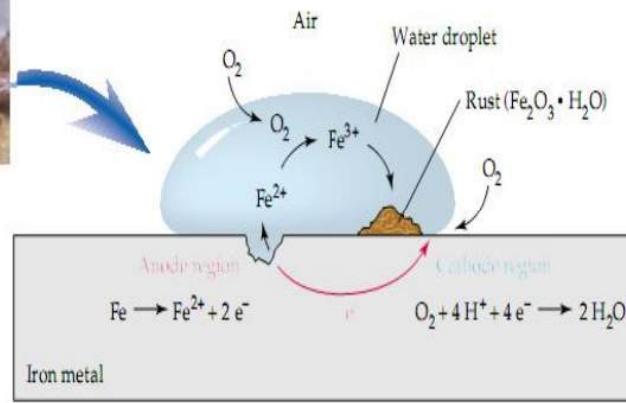
- Corrosion occurs due to differences in electrode potential
- Electrons flow from iron to copper (current in reverse direction) – negative charge on the iron is partly reduced allowing corrosion and the iron is termed the anode – the copper does not corrode and is termed cathode

Steel Corrosion

Initial Oxidation Reaction



Secondary Oxidation Reaction



Forms of Corrosion

- | | |
|---------------------------------|----------------------------|
| 1- Uniform corrosion | 2- Galvanic corrosion |
| 3- Concentration cell corrosion | 4- Pitting corrosion |
| 5- Crevice corrosion | 6- Intergranular corrosion |
| 7-Stress Corrosion Cracking | 8- Reinforcement Corrosion |
| 9- Microbial corrosion | |

1- Uniform corrosion of a single metal

- occurs over the majority of the surface of a metal at a steady and often predictable rate.
- usually an electrochemical reaction
- relatively slow
- rusting of exposed steel, tarnished silver
- Steel corrosion is accelerated by the presence of salts – increases the conductivity of the electrolyte - aids the flow of ions in solution

2- Galvanic Corrosion

- ❑ **A galvanic cell:** is an electrochemical cell that produces electricity as result of the spontaneous chemical reaction occurring inside it.
- ❑ 2 dissimilar metals, electrolyte, electrical connection and oxygen
- ❑ Results from a difference in oxidation potentials of metallic ions between two or more metals. The greater the difference in oxidation potential, the greater the galvanic corrosion.
- ❑ The less noble metal will corrode (i.e. will act as the anode) and the more noble metal will not corrode (acts as cathode).
- ❑ Perhaps the best known of all corrosion types is galvanic corrosion, which occurs at the contact point of two metals or alloys with different electrode potentials.

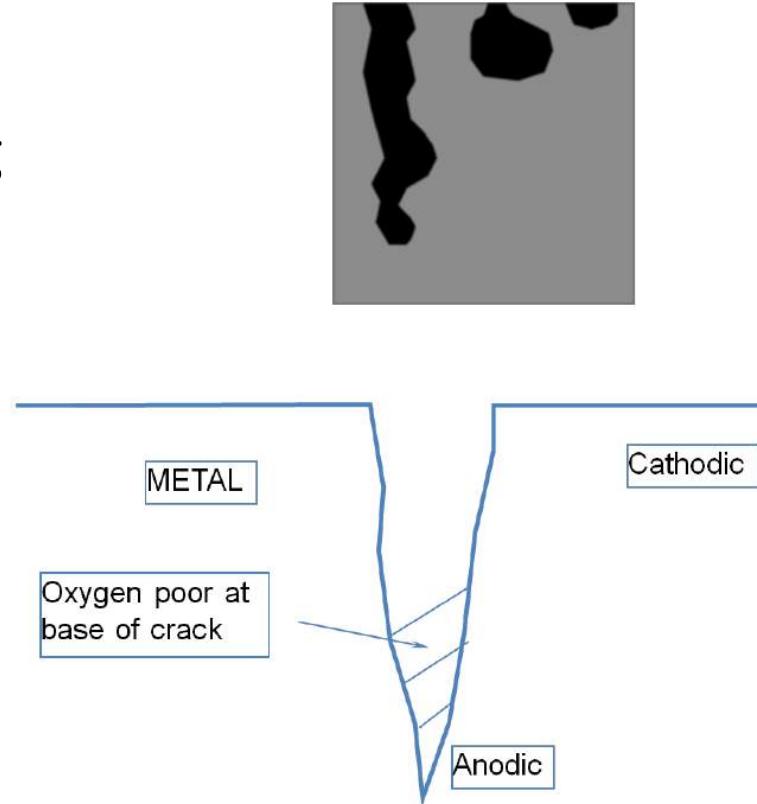


3- Concentration cell corrosion

Preferential corrosion of metal surface due to variations in the electrolyte concentration

4- Pitting Corrosion

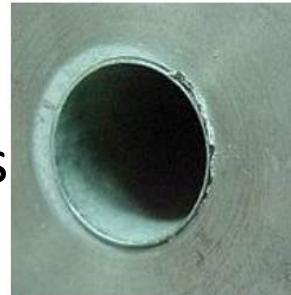
- Localized corrosion forming holes or indentations
- Difficult to initially detect
- pitting where the oxygen poor region at the bottom of the pit is anodic – pit tends to deepen leading to premature failure due to fatigue or brittle fracture



5- Crevice Corrosion

Also known as contact corrosion

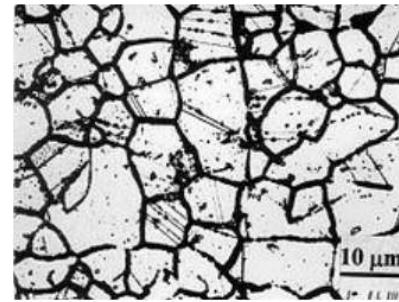
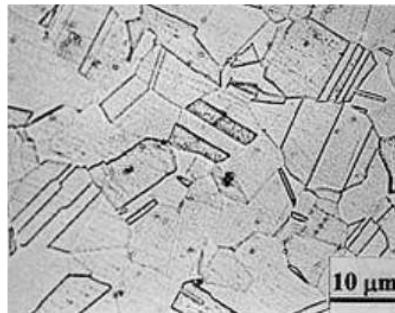
- Produced at the regions of contact of metals with metals or non-metals



6- Intergranular Corrosion

– corrosion along grain boundaries at microscopic level

- Why at grain boundaries?
 - Higher energy areas which may be more anodic than the grains.
 - The alloy chemistry might make the grain boundaries dissimilar to the grains. The grain can act as the cathode and material surrounding it the anode.



7- Stress Corrosion Cracking

- Spontaneous corrosion induced cracking of a material under static (or residual) *tensile* stress.
- tensile stress and corrosive environments
- cracks are initiated at corrosion areas
- tensile stresses propagate the crack
- corrosion further deteriorate crack



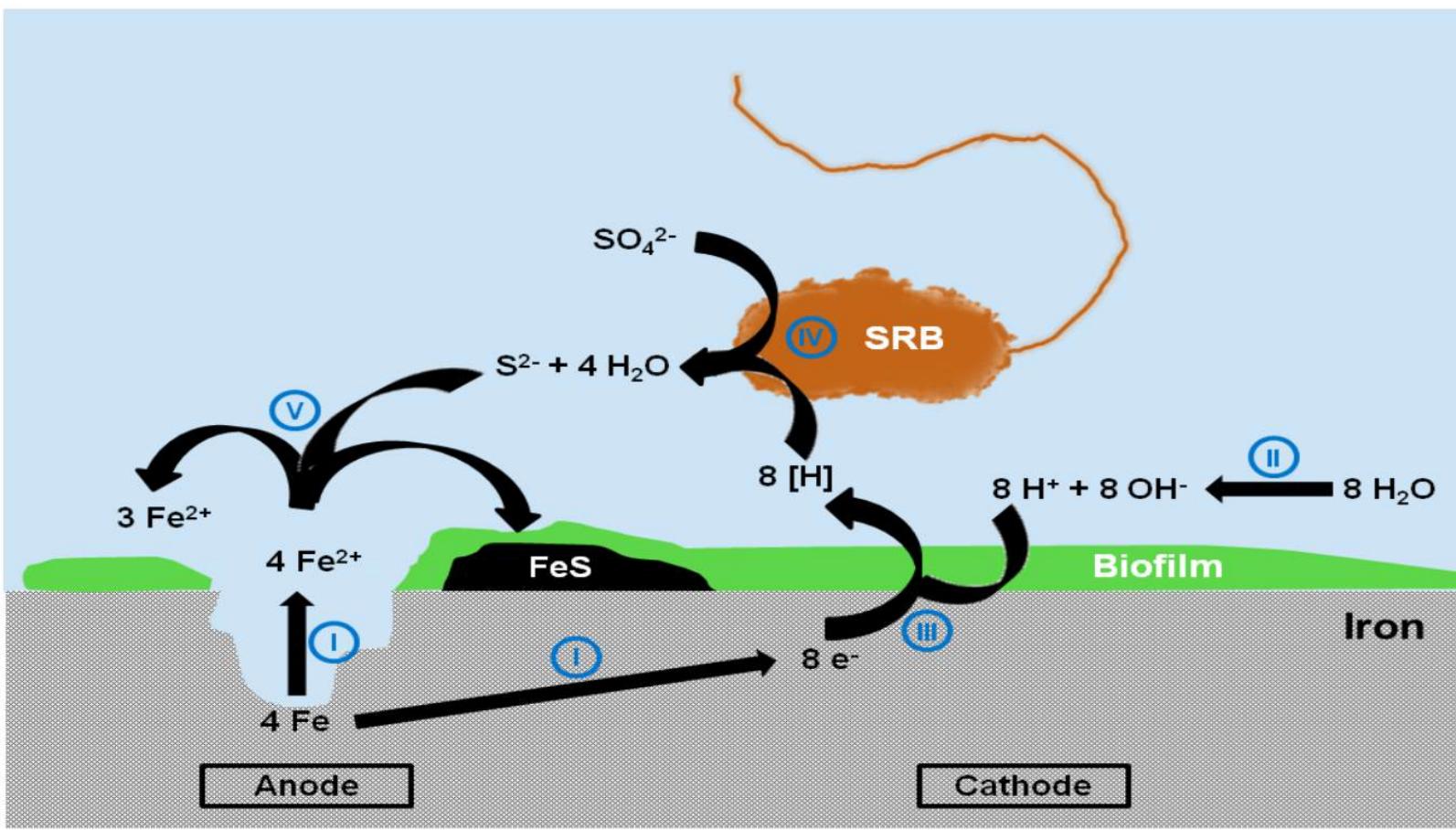
8- Reinforcement Corrosion

- Corrosion of steel reinforcement leads to expansion as corrosion products develop.
- Expansion leads to tension between the reinforcement & the concrete cover.
- Spalling of concrete cover.



Microbial corrosion

- also called **bacterial corrosion**, **bio-corrosion**, **microbiologically influenced corrosion**, or **microbially induced corrosion (MIC)**, is corrosion caused or promoted by microorganisms, usually chemoautotrophs. It can apply to both metals and non-metallic materials.
- Some sulfate-reducing bacteria produce **hydrogen sulfide**, which can cause sulfide stress cracking.
- *Acidithiobacillus* bacteria produce **sulfuric acid**; *Acidothiobacillus thiooxidans* frequently damages sewer pipes.
- *Ferrobacillus ferrooxidans* directly **oxidizes iron to iron oxides** and iron hydroxides; the rusticles forming on the RMS *Titanic* wreck are caused by bacterial activity.
- Other bacteria produce various acids, both organic and mineral, or ammonia.



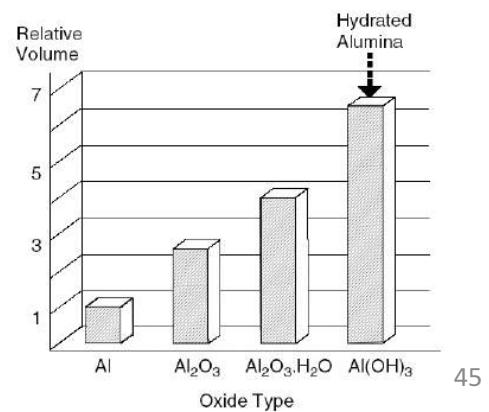
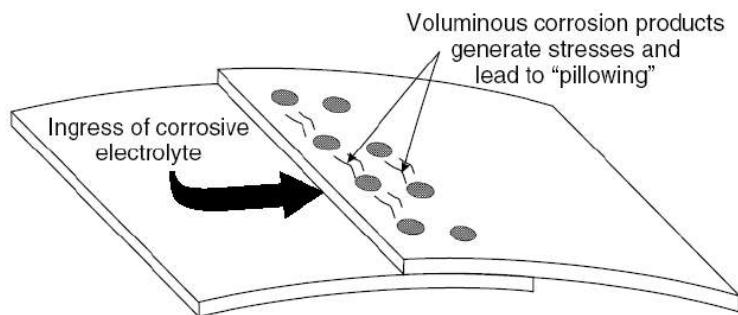
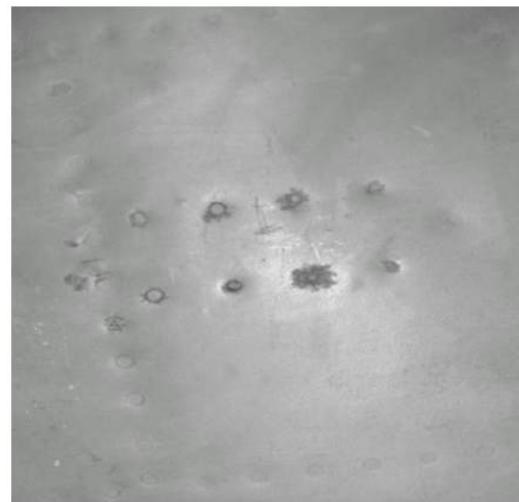
Scheme of iron corrosion by SRB based on reactions as suggested by the cathodic depolarization theory. I, iron dissolution; II, water dissociation; III, proton reduction; IV, bacterial sulfate reduction and V, sulfide precipitation.

Source: Mechanisms of Microbiologically Influenced Corrosion: A Review
 World Applied Sciences Journal 17 (4): 524-531, 2012



Some Corrosion Failure Examples

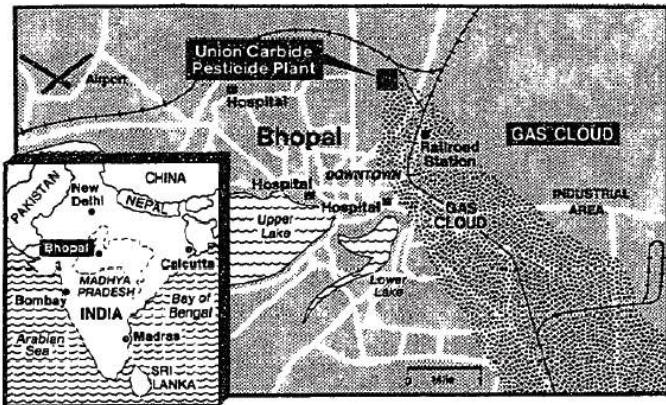
Aloha Incident





Bhopal disaster

The **Bhopal disaster**, also referred to as the **Bhopal gas tragedy**, was a gas leak incident in India, considered the world's worst industrial disaster.

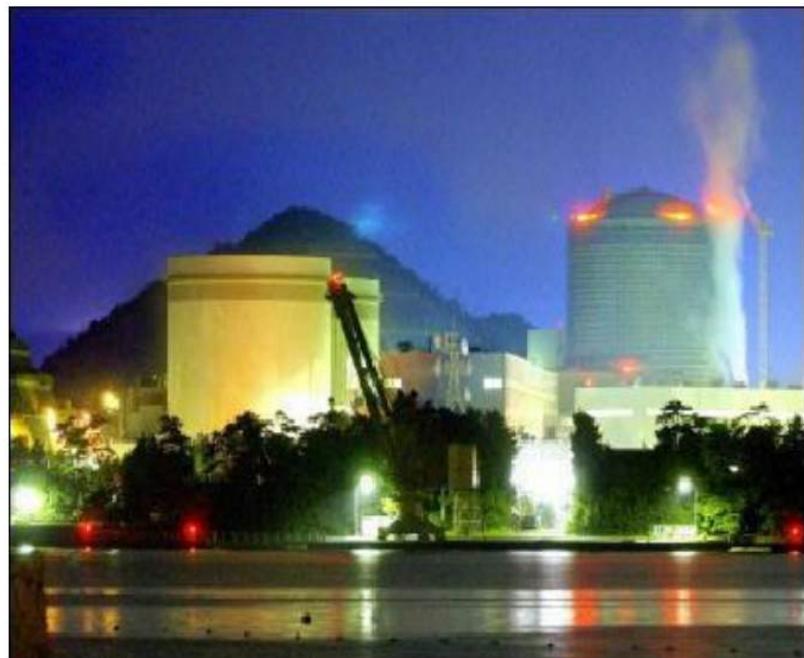


This victim of the Bhopal disaster became a symbol of the destructive power of MIC

Carlsbad Pipeline Explosion



Flow Accelerated Corrosion



Underground corrosion



Buried gas or water supply pipes can suffer severe corrosion which is not detected until an actual leakage occurs, by which time considerable damage may be done.

Electronic components



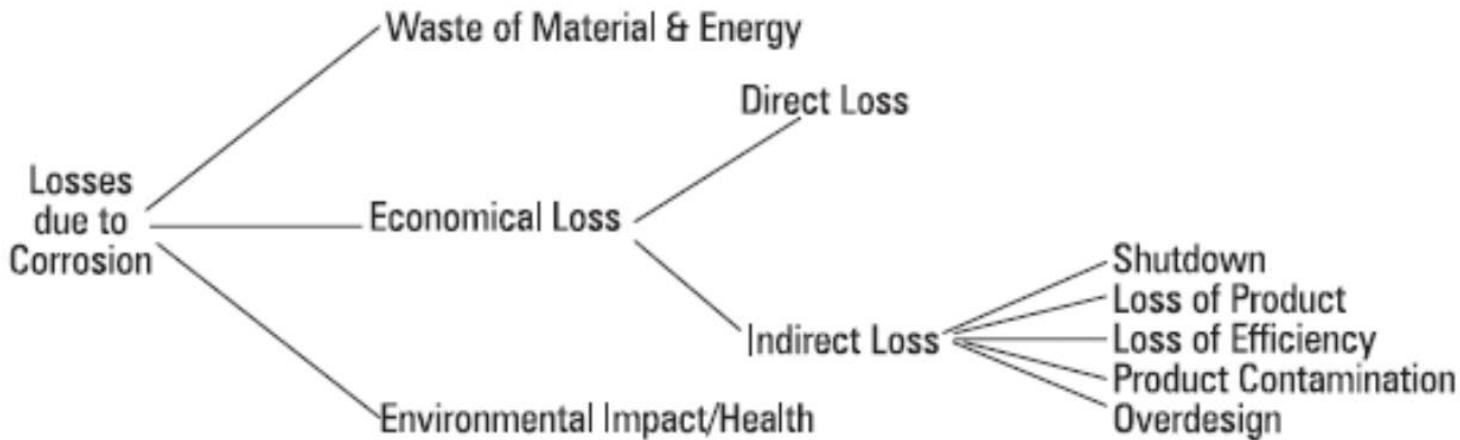
In electronic equipment it is very important that there should be no raised resistance at low current connections. Corrosion products can cause such damage and can also have sufficient conductance to cause short circuits. These resistors form part of a radar installation.

Corrosion at sea



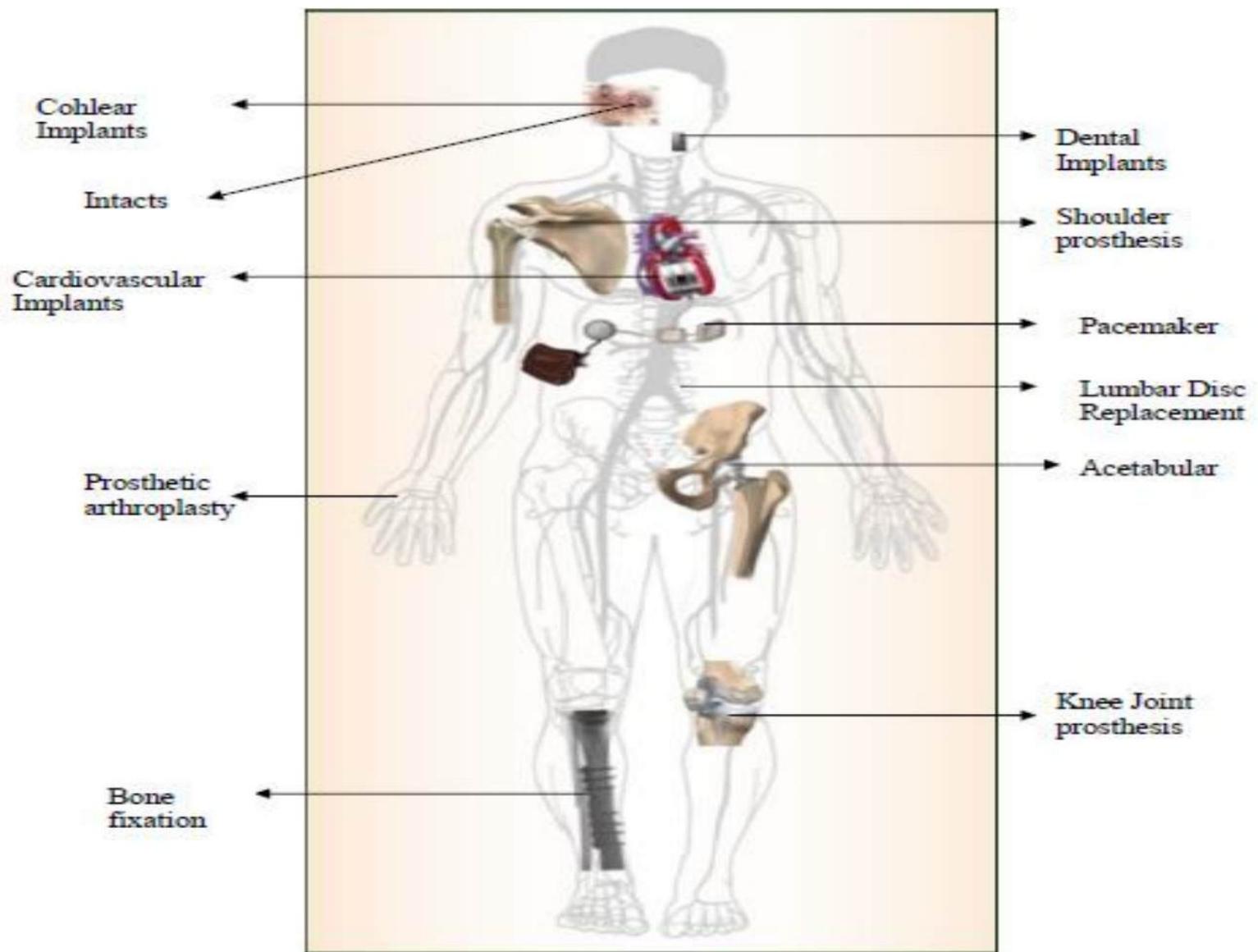
Sea water is a highly corrosive electrolyte towards mild steel. This ship has suffered severe damage in the areas which are most buffeted by waves, where the protective coating of paint has been largely removed by mechanical action.

Losses due to Corrosion



So.....Why Study Corrosion?

- Materials are precious resources
- Engineering design is incomplete without knowledge of corrosion
- Applying knowledge of corrosion protection can minimize disasters
- Corrosion – contaminate products such as pharmaceutical, food and dairy products or luxury items like soap
- Corrosion products – threat to the environment
- Artificial implants for the human body!!!



Protection against Corrosion

1. Organic paints

- cover the surface with some impermeable layer, such as paint, which prevent access of damp air. Unfortunately, this protection fails disastrously if the paint becomes porous. The oxygen then has access to the exposed metal and corrosion continues beneath the paintwork.

2. Chromating and phosphating:

- The Process - chromating and phosphating are surface-coating processes that enhance corrosion resistance of metals. Both involve soaking the component in a heated bath based chromic or phosphoric acids. The acid reacts with the surface, dissolving some of the surface metal and depositing a thin protective layer of complex chromium or phosphorous compound

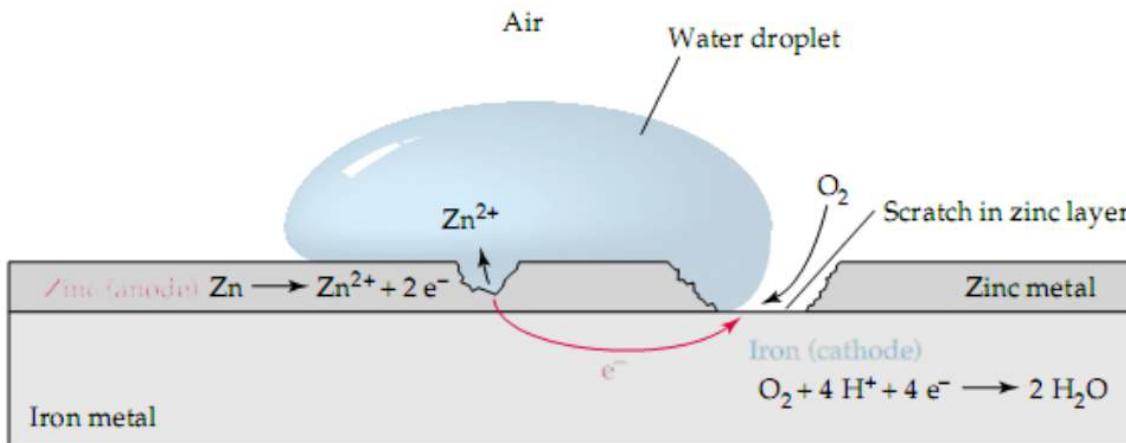
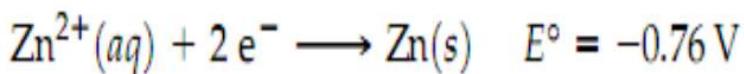
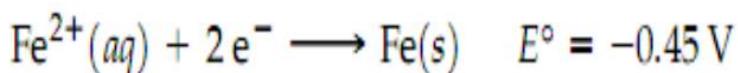
3. Passivation

- A protective film in oxidizing atmospheres
 - By treating metals with strong oxidizing agent as HNO_3
 - ex: chromium, nickel, titanium, aluminum
- Metal oxide layer adheres to parent metal
 - barrier against further damage
 - self-healing if scratched



4. Galvanizing

The steel used in making automobiles, for example, is coated by dipping into a bath of molten zinc, a process known as galvanizing. As the potentials indicate, zinc is oxidized more easily than iron, and therefore, when the metal is oxidized, zinc is oxidized instead of iron. As long as the zinc and iron are in contact, the zinc protects the iron from oxidation even if the zinc layer becomes scratched.



5- Cathodic Protection (CP)

- is a technique to control the corrosion of a metal surface by making it work as a cathode of an electrochemical cell. This is achieved by placing in contact with the metal to be protected another more easily corroded metal to act as the anode of the electrochemical cell. It's unnecessary to cover the entire surface of the metal with a second metal, as in galvanizing iron.
- Cathodic protection systems are most commonly used to protect steel, water or fuel pipelines and storage tanks, steel pier piles, ships, offshore oil platforms and onshore oil well casings.
- **Types of CP:**

1. Galvanic or sacrificial anodes

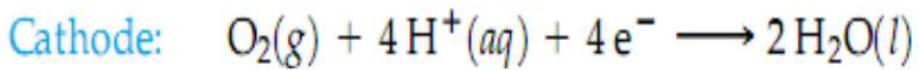
zinc, magnesium or aluminum. The sacrificial anodes are more active (more negative potential) than the metal of the structure they're designed to protect. The anode pushes the potential of the steel structure more negative and therefore the driving force for corrosion halts. The anode continues to corrode until it requires replacement.

2. Impressed current (ICCP)

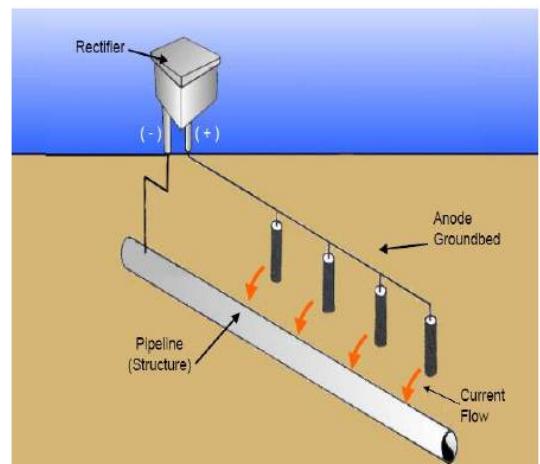
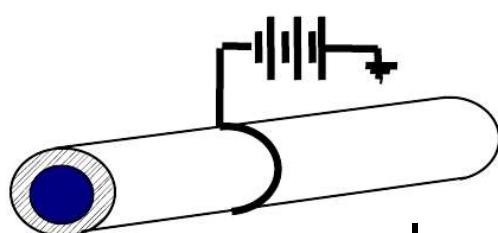
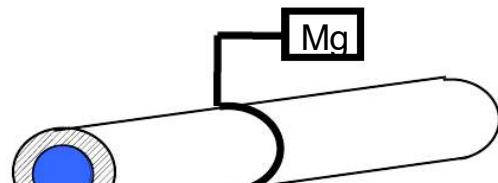
an external cell supplies the electrons and eliminates the need for iron to transfer its own.



$$E^\circ = 2.37 \text{ V}$$



$$E^\circ = 1.23 \text{ V}$$





6 Zinks



**New Zinc
(for 1" diameter shaft)**



**Old Zinc after 8 months
(for 1" diameter shaft)**



Aluminium anodes mounted on a steel jacket structure – (sacrificial anode)

Chapter 5

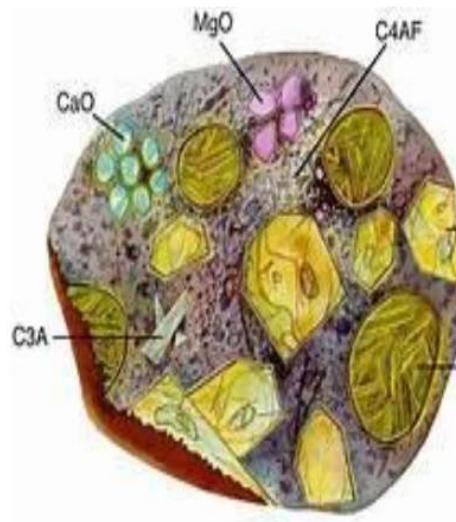
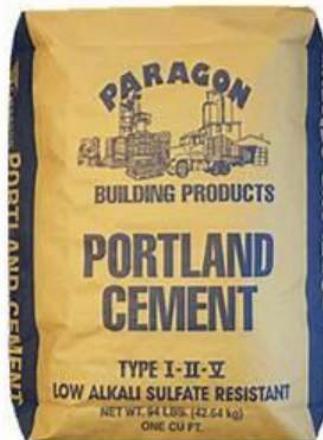
Chemical Industry

Chemistry of cement

Prepared by Dr. Shaimaa Khalaf

1

Chemistry of cement



Portland cement

Concrete

- **Composition of concrete:** It consists of a rationally chosen mixture of binding material such as lime or cement, well graded fine and coarse aggregates, water and admixtures (to produce concrete with special properties).
- In a concrete mix, cement and water form a paste or matrix which in addition to filling the voids of the fine aggregate, coats the surface of fine and coarse aggregates and binds them together. The matrix is usually 22-34% of the total volume.
- Freshly mixed concrete before set is known as wet or green concrete whereas after setting and hardening it is known as set or hardened concrete.
- The moulded concrete mix after sufficient curing becomes hard like stone due to chemical reaction between the water and binding material (hydration).



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Cements

- Cements in a general sense are adhesive and cohesive materials which are capable of bonding together particles of solid matter into a compact durable mass.
- its primary function being to bind the fine (sand) and coarse (grits) aggregate particles together.
- **Cements used in construction industry may be classified as hydraulic and non hydraulic.**
 - **The hydraulic cement** set and harden in water and give a product which is stable. e.g. Portland cement.
 - **The non hydraulic cement** does not set and harden in water or which are unstable in water.
- Cement can be manufactured either from natural cement stones or artificially by using calcareous and argillaceous materials. The examples of natural cements are Roman cement, Puzzolana cement and Medina cement and those of artificial cement are Portland cement and special cements.

Portland cement

- Portland cement is the name given to a cement obtained by intimately mixing together calcareous and argillaceous, or other silica, alumina, and iron oxide bearing materials, burning them at a clinkering temperature, and grinding the resulting clinker.
- It was invented in 1824 in Britain by Joseph Aspdin.
- It was named Portland cement because it looked like the stone quarried on the Isle of Portland.



The manufacture of Portland cement

- **RAW MATERIALS OF P.C.**
- Calcareous and argillaceous raw materials are used in the manufacture of Portland cement.
- The calcareous materials ($\text{CaCO}_3 > 75\%$) used are cement rock, limestone, marl, chalk and marine shell.
- The argillaceous materials ($\text{CaCO}_3 < 40\%$) consist of silicates of alumina in the form of clay, shale, slate and blast furnace slag (SiO_2 , Al_2O_3 , Fe_2O_3).
- From the above materials, others like lime, silica, alumina, iron oxide and small quantities of other chemicals are obtained.

Chemical Composition of Raw Materials

- The three constituents of hydraulic cements are lime (CaO), silica and alumina. In addition, most cements contain small proportions of iron oxide, magnesia, sulfur trioxide and alkalis.
- An increase in lime content beyond a certain value makes it difficult to combine completely with other compounds. Consequently, free lime will exist in the clinker and will result in an unsound cement.
- An increase in silica content at the expense of alumina and ferric oxide makes the cement difficult to fuse and form clinker. The approximate limits of chemical composition in cement are given in the following Table.

Oxide	Function	Composition (%)
CaO	Controls strength and soundness. Its deficiency reduces strength and setting time	60-65
SiO ₂	Gives strength. Excess of it causes slow setting.	17-25
Al ₂ O ₃	Responsible for quick setting, if in excess, it lowers the strength.	3-8
Fe ₂ O ₃	Gives colour and helps in fusion of different ingredients	0.5-6
MgO	Imparts colour and hardness. If in excess, it causes cracks in mortar and concrete and unsoundness	0.5-4
Na ₂ O + K ₂ O TiO ₂ P ₂ O ₅ SO ₃	These are residues, and if in excess cause efflorescence and cracking Makes cement sound	0.5-1.3 0.1-0.4 0.1-0.2 1-2

PRODUCTION STEPS

- 1) Raw materials are crushed& stockpiled.
- 2) Raw materials are mixed with definite proportions to obtain “raw mix” or “raw meal”. They are mixed either dry (dry mixing) or by water (wet mixing).
- 3) Prepared raw mix is fed into the rotary kiln.
- 4) As the materials pass through the kiln their temperature is rised upto 1300-1600 °C. The process of heating is named as “burning” or calcination. The output is known as “clinker” which is 0.15-5 cm in diameter.

5) Clinker is cooled (150°C) & stored.

Rapid cooling produces a better quality clinker

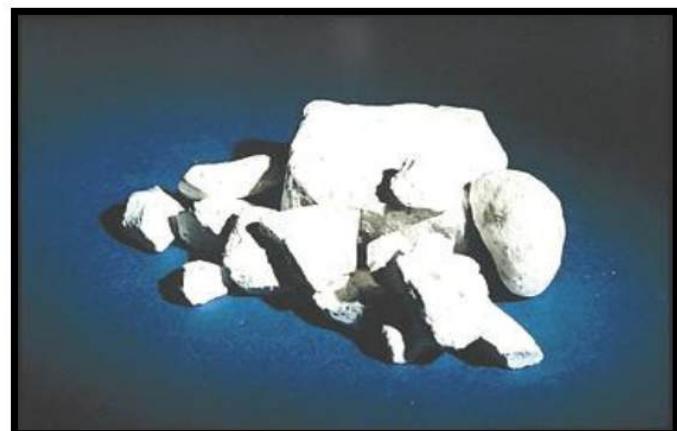
6) Clinker is ground with (3-6%) gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) to adjust setting time.

7) Packing & marketing.

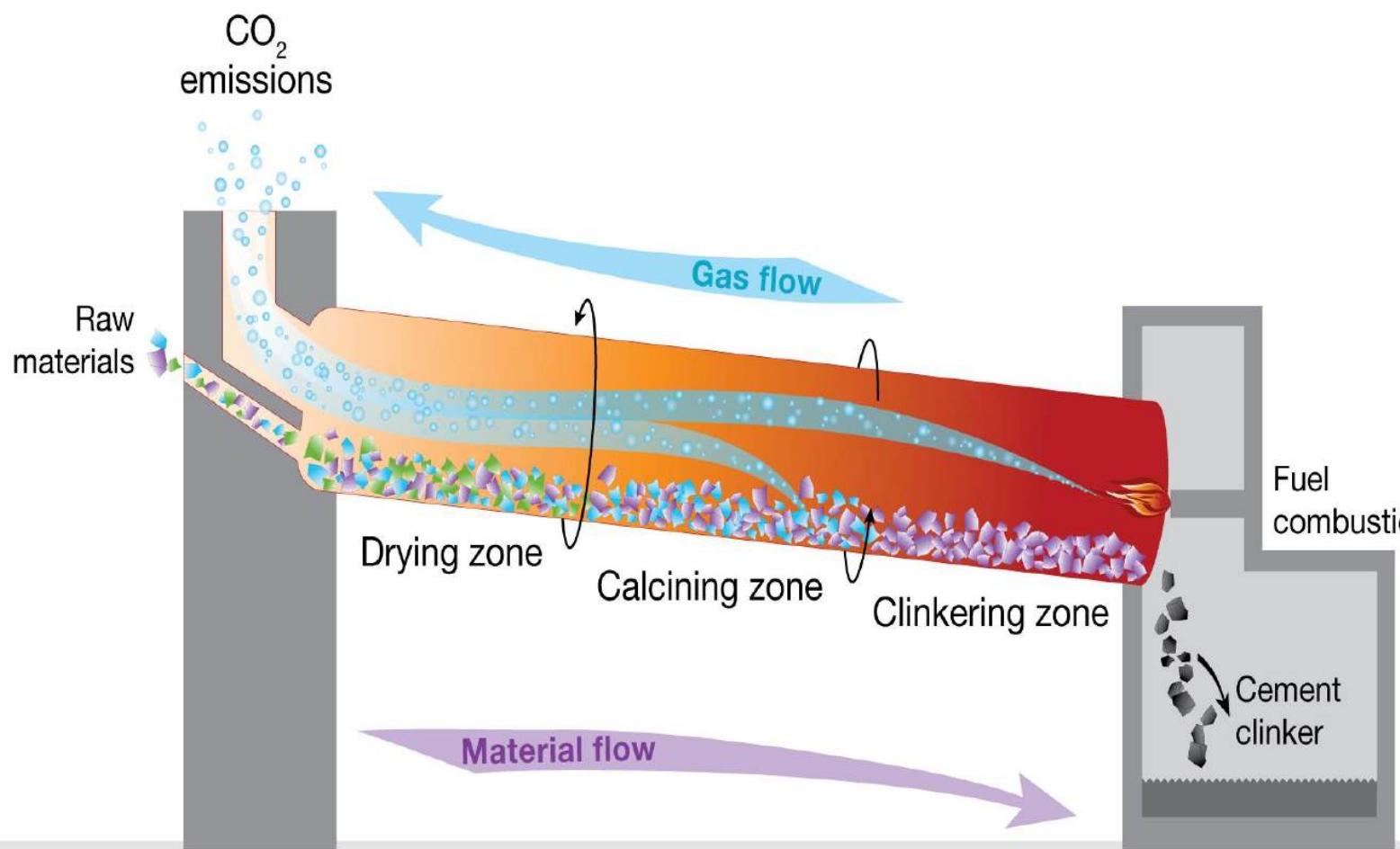


CLINKER

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GYPSUM



CC

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11

Summary of the reactions in the kiln

- $\sim 100^\circ\text{C} \rightarrow$ free water evaporates.
- $\sim 150\text{-}350^\circ\text{C} \rightarrow$ loosely bound water is lost from clay.
- $\sim 350\text{-}650^\circ\text{C} \rightarrow$ decomposition of clay minerals,
 $\rightarrow \text{SiO}_2 + \text{Al}_2\text{O}_3$
- $\sim 600^\circ\text{C} \rightarrow$ decomposition of $\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2$
- $\sim 900^\circ\text{C} \rightarrow$ decomposition of calcium carbonate
 $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$

- $\sim 1250\text{-}1280^\circ\text{C}$ \rightarrow liquid formation & start of compound formation.
- $\sim 1280^\circ\text{C}$ \rightarrow clinkering begins.
- $\sim 1400\text{-}1500^\circ\text{C}$ \rightarrow clinkering
- $100\text{-}150^\circ\text{C}$ \rightarrow clinker leaves the kiln and falls into a cooler. (The liquid crystallizes, giving mainly aluminate and ferrite. Polymorphic transitions of the alite and belite occur.)

Cement chemical nomenclature and abbreviations

Oxide	Common Name	Abbreviation
CaO	Lime	C
SiO ₂	Silica	S
Al ₂ O ₃	Alumina	A
Fe ₂ O ₃	Iron-oxide	F
MgO	Magnesia	M
Na ₂ O	Soda	N
K ₂ O	Potassa	K
SO ₃	Sulfuric Anhydride	S

- CaO→limestone
- SiO₂-Al₂O₃→Clay
- Fe₂O₃→Impurity in Clays
- SO₃→from gypsum→not from the clinker

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Enthalpy changes in clinker formation

- The following Table illustrate the enthalpy of formation of 1 kg of a Portland cement clinker

Component of reaction	ΔH (kJ)
$\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$	+2138
AS_4H (pyrophyllite) $\rightarrow \alpha\text{-Al}_2\text{O}_3 + 4\text{SiO}_2$ (quartz) + $\text{H}_2\text{O(g)}$	+34
AS_2H_2 (kaolinite) $\rightarrow \alpha\text{-Al}_2\text{O}_3 + 2\text{SiO}_2$ (quartz) + $2\text{H}_2\text{O(g)}$	+21
$2\text{FeO}\cdot\text{OH}$ (goethite) $\rightarrow \alpha\text{-Fe}_2\text{O}_3 + \text{H}_2\text{O(g)}$	+9
$3\text{CaO} + \text{SiO}_2$ (quartz) $\rightarrow \text{C}_3\text{S}$	-333
$2\text{CaO} + \text{SiO}_2$ (quartz) $\rightarrow \text{C}_2\text{S}$	-98
$3\text{CaO} + \alpha\text{-Al}_2\text{O}_3 \rightarrow \text{C}_3\text{A}$	-3
$6\text{CaO} + 2\alpha\text{-Al}_2\text{O}_3 + \alpha\text{-Fe}_2\text{O}_3 \rightarrow \text{C}_6\text{A}_2\text{F}$	-7
Total	+1761

Composition of Cement Clinker

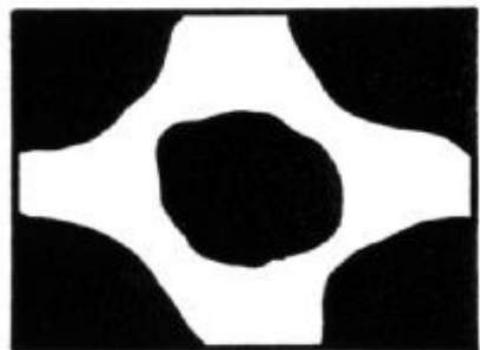
- The various constituents combine in burning and form cement clinker.
- The compounds formed in the burning process have the properties of setting and hardening in the presence of water.
- They are known as Bogue compounds after the name of Bogue who identified them.
- Le-Chatelier and Tornebohm have referred these compounds as Alite (C_3S), Belite (C_2S), Celite (C_3A) and Felite (C_4AF). The following Bogue compounds are formed during clinkering process.

The principal mineral compounds	Formula	Name	Symbol
Tricalcium silicate 25-50% of cement	(Ca ₃ SiO ₅)	Alite	C ₃ S
Dicalcium silicate 25-40% of cement	(Ca ₂ SiO ₄)	Belite	C ₂ S
Tricalcium aluminate 5-11% of cement	(Ca ₃ Al ₃ O ₆)	Celite The aluminate phase	C ₃ A
Tetracalcium aluminoferrite 8-14% of cement	(Ca ₂ AlFeO ₅)	Felite The ferrite phase	C ₄ AF

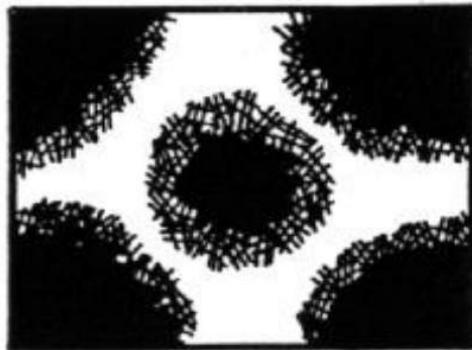
The properties of Portland cement varies markedly with the proportions of the above four compounds, reflecting substantial difference between their individual behavior.

Hydration of P.C.

- The chemical reaction between cement and water is known as hydration of cement.
- The reaction takes place between the active components of cement (C_4AF , C_3A , C_3S and C_2S) and water. process of hydration is a complex one and results in reorganization of the constituents of original compounds to form new hydrated compounds.
- The factors responsible for the physical properties of concrete are the extent of hydration of cement and the resultant microstructure of the hydrated cement.
- As water comes into contact with cement particles, hydration reactions immediately starts at the surface of the particles.
- the hydration products start depositing on the outer periphery of the nucleus of hydrated cement. This reaction proceeds slowly for 2-5 hours and is called induction or dormant period.
- As the hydration proceeds, the deposit of hydration products on the original cement grain makes the diffusion of water to unhydrated nucleus more and more difficult, consequently reducing the rate of hydration with time. as a result hydration may take several years.



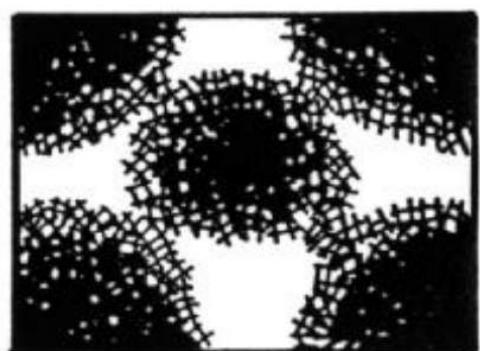
A



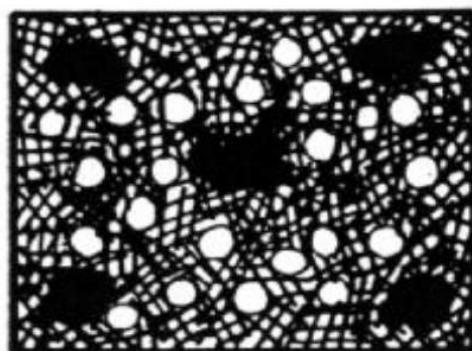
B



unhydrated cement particles



C



D



cement gel



capillary pores and cavities

A) Immediately after mixing

B) Reaction around particles – early stiffening

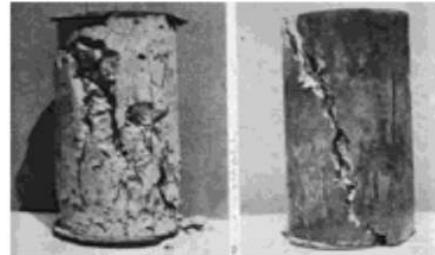
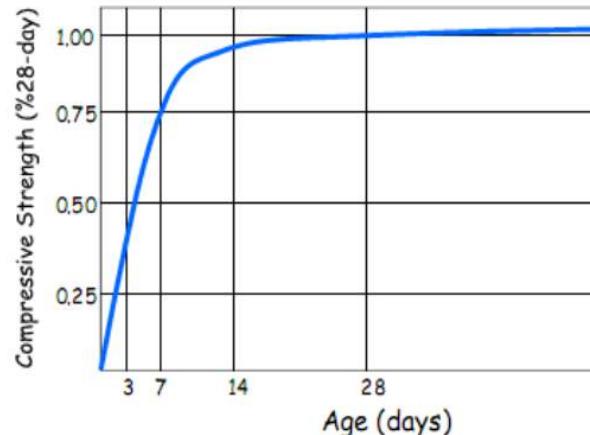
C) Formation of skeletal structure – first hardening

D) Gel infilling – later hardening

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Compressive Strength

- **Compressive Strength** -is defined as the measured maximum resistance of a concrete or mortar specimen to an axial load, usually expressed in psi (pounds per square inch) at an age of 28-days.
- **Concrete compressive strength depends upon many factors:**
 - quality and proportions of the ingredients
 - the curing environment.



Compression testing
of a concrete cylinder



it is important that the concrete not be permitted to freeze or dry out

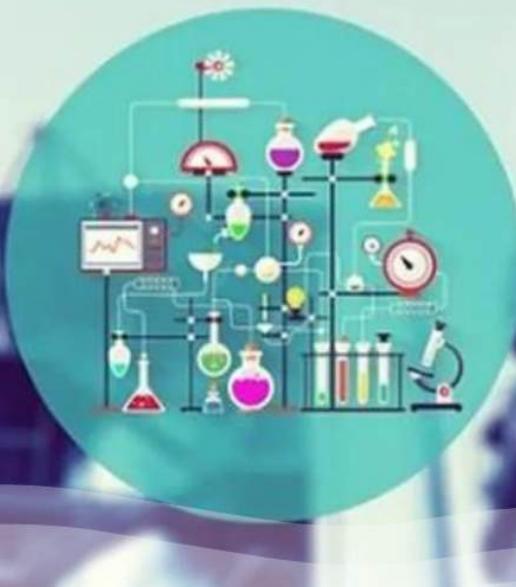
The water-cement ratio (w/c)

- The water-cement ratio (w/c) is one of the major factors (but not the only one) influencing the strength of concrete.
- It is responsible mainly for the porosity of the hardened cement paste.
- Water-cement ratio is the water used to the quantum of cement in the mixture by weight.
- For proper workability the w/c ratio varies **from 0.4–0.6**. However, maximum strength is derived at $w/c = 0.4$ at which minimum capillary cavities are expected to form.
- It may be noted that for complete hydration of cement under controlled conditions the water requirement is about 38 per cent. When it is decreased to less than 0.4 there is improper consistency and workability of cement and honeycombed structure.
- At w/c ratio more than 0.6, the increase in volume of hydrated products will not be able to occupy the space already filled with water. Hence, porosity increases and strength decreases.



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123



Chapter 6

Chemical Thermodynamic

Chemical Thermodynamics

- Thermodynamics can be defined as **the science of energy**.
 - The name *thermodynamics* stems from the Greek words *therme* (heat) and *dynamis* (power), which is most descriptive of the early efforts to convert heat into power. Today the same name is broadly interpreted to include all aspects of energy and energy transformations.
- Thermodynamics**, the study of the transformations of energy and its relationship with work.
- Thermodynamics** is a general macroscopic theory of the behavior of matter.
- examines the means by which a system can exchange energy with its surroundings in terms of the work it may do or the heat that it may produce.
 - how to establish relations between different properties of a system.
 - one very useful aspect of thermodynamics is that a property can be measured indirectly by measuring others and then combining their values.
- Thermodynamics is based on **three** empirical laws.

- Thermodynamics is commonly encountered in many engineering systems and other aspects of life
- Some examples include
 - the electric or gas range,
 - the heating and air-conditioning systems,
 - the refrigerator,
 - the humidifier,
 - the pressure cooker,
 - the water heater,
 - the shower,
 - the iron,
 - and even the computer and the TV.
- On a larger scale, thermodynamics plays a major part in the design and analysis of
 - automotive engines,
 - rockets,
 - jet engines,
 - and conventional or nuclear power plants,
 - solar collectors,
 - and the design of vehicles from ordinary cars to airplanes



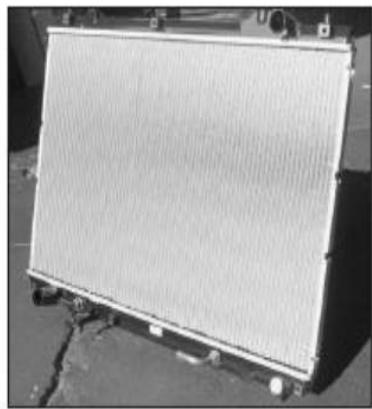
The human body



Air conditioning systems



Airplanes



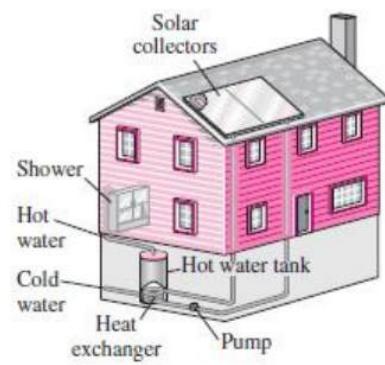
Car radiators



Power plants



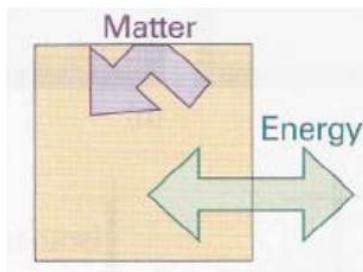
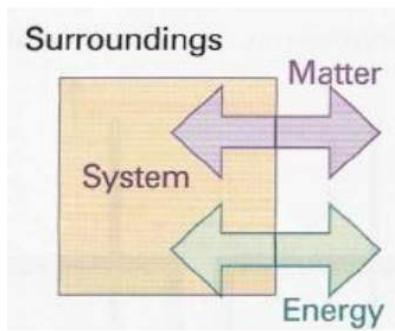
Refrigeration systems



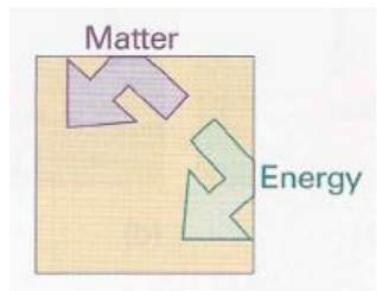
The basic concepts of thermodynamics.

- The universe is divided into two parts, **the system** and its **surroundings**.
- **The system** is the part of the world in which we have a special interest. It may be a reaction vessel, an engine, an electrochemical cell, a biological cell, and so on.
- **The surroundings** comprise the region outside the system and are where we make our measurements.
- The type of system depends on the characteristics of **the boundary** that divides it from the surroundings.
- If matter can be transferred through the boundary between the system and its surroundings the system is classified as **open**. If matter cannot pass through the boundary the system is classified as **closed**. Both open and closed systems can exchange energy with their surroundings.
- An **isolated system** is a closed system that has neither mechanical nor thermal contact with its surroundings.

open



closed



isolated

Boundary

- the space separating the system from the surrounding.
- **Types of boundary**
- A boundary is diathermic (thermally conducting) if a change of state is observed when two objects at different temperatures are brought into contact. A metal container has diathermic walls.
- A boundary is adiabatic (thermally insulating) if no change occurs even though the two objects have different temperatures.

Processes

A process is an occurrence that changes the state of a system.

➤ Isothermal process:

When the temperature of the system is kept constant.

➤ Adiabatic process:

There is no exchange of heat between the system and the surroundings.

➤ Isobaric process:

When the pressure of the system remains constant during the period of change.

➤ Cyclic process:

If a system having undergone a change returns to its initial state.

➤ Reversible and Irreversible Macroscopic Processes

- A reversible process is one that can at any time be reversed in direction by an infinitesimal change in the surroundings.
- a reversible process must occur infinitely slowly, and the system has time to relax to equilibrium at each stage of the process. During a reversible process, the system passes through a sequence of equilibrium states.
- reversible processes are ideal.
- The system is not required to remain in equilibrium states during an irreversible process and the process can occur in a finite time.
- All natural processes are irreversible.

- An extensive property is a property that depends on the amount of substance in the sample. Two examples are mass and volume.
- An intensive property is a property that is independent of the amount of substance in the sample. Examples are temperature, mass density (mass divided by volume), and pressure.
- A molar property, X_m , is the value of an extensive property, X , of the sample divided by the amount of substance present in the sample: $X_m = X/n$.
- A molar property is intensive. An example is the molar volume, V_m , the volume of a sample divided by the amount of substance in the sample (the volume per mole).

State functions:

- These are independent of how the change is accomplished. They depend only upon the initial and the final states of the system.
- Ex: p, V and T

Processes that describe the preparation of the state are called path functions.

- Examples of path functions are the work and heating that are done when preparing a state.

Work

- The fundamental physical property in thermodynamics is work: **work is motion against an opposing force.**
- **w = Force x Distance**
- Doing work is equivalent to raising a weight somewhere in the surroundings. An example of doing work is the expansion of a gas that pushes out a piston and raises a weight. A chemical reaction that drives an electric current through a resistance also does work, because the same current could be driven through a motor and used to raise a weight.

- **Energy** :the capacity to do work.
- **the conservation of energy** : the apparently universal law of nature that *energy is conserved, that is, energy can neither be created nor destroyed*. Although energy can be transferred from one location to another, the total energy is constant.
- **Kinetic and potential energy**
- **The kinetic energy, E_K , of a body is the energy the body possesses as a result of its motion.** For a body of mass m travelling at a speed v .

$$E_k = \frac{1}{2} m v^2$$

The potential energy, E_p , of a body is the energy it possesses as a result of its position. The zero of potential energy is arbitrary. For example, the gravitational potential energy of a body is often set to zero at the surface of the Earth; the electrical potential energy of two charged particles is set to zero when their separation is infinite.

No universal expression for the potential energy can be given because it depends on the type of interaction the body experiences.

The total energy is the sum of the kinetic and potential energies of a particle:

$$E = E_p + E_k$$

- **The energy of a system is its capacity to do work.** When work is done on an otherwise isolated system (for instance, by compressing a gas or winding a spring), the capacity of the system to do work is increased; in other words, the energy of the system is increased. When the system does work (when the piston moves out or the spring unwinds), the energy of the system is reduced and it can do less work than before.
- Experiments have shown that the energy of a system may be changed by means other than work itself. When the energy of a system changes as a result of a temperature difference between the system and its surroundings we say that energy has been transferred as heat. When a heater is immersed in a beaker of water (the system), the capacity of the system to do work increases because hot water can be used to do more work than the same amount of cold water. Not all boundaries permit the transfer of energy even though there is a temperature difference between the system and its surroundings.

➤ ***Heat is one way of transferring energy.***

➤ ***Work is another way of transferring energy.***

The internal energy

- the total energy of a system is called its internal energy, U .
- The internal energy is the total kinetic and potential energy of the molecules in the system.
- The energy is ‘locked up’ within a body or species in three principal ways
 - First, energy is locked within the atomic nuclei. The only way to release it is to split the nucleus, as happens in atomic weapons and nuclear power stations to yield *nuclear energy*. *The changes in energy caused by splitting nuclei are massive*.
 - This second way in which energy is locked away is within chemical bonds. We call this form of energy the *chemical energy*. Chemical energies are smaller than nuclear energies.
 - And third, energy is possessed by virtue of the potential energy, and the translational, vibrational, rotational energy states of the atoms and bonds within the substance, be it atomic, molecular or ionic. These energies are normally much smaller than the energies of chemical bonds.

$$\Delta U = U_f - U_i$$

- The internal energy is a state function in the sense that its value depends only on the current state of the system and is independent of how that state has been prepared.
- In other words, it is a function of the properties that determine the current state of the system. Changing anyone of the state variables, such as the pressure, results in a change in internal energy.
- The internal energy is an extensive property.
- Internal energy, heat, and work are all measured in the same units, the joule (J).
- The joule, which is named after the nineteenth-century scientist J.P. Joule, is defined as

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

- Changes in molar internal energy, ΔU_m , are typically expressed in kilojoules per mole.

the First Law of thermodynamics

- It has been found experimentally that the internal energy of a system may be changed either by doing work on the system or by heating it.
- Whereas we may know how the energy transfer has occurred, the system is blind to the mode employed. *Heat and work are equivalent ways of changing a system's internal energy.*
- It is also found experimentally that, if a system is isolated from its surroundings, then no change in internal energy takes place.
- This summary of observations is now known as the First Law of thermodynamics and expressed as follows:
 - The internal energy of an isolated system is constant.
 - The first law of thermodynamics is a version of the law of conservation of energy.
 - If we write w for the work done on a system, q for the energy transferred as heat to a system, and ΔU for the resulting change in internal energy, then it follows that

$$\Delta U = q + w$$

- the internal energy is constant in an isolated system (for which $q = 0$ and $w = 0$).
- The equation states that the change in internal energy of a closed system is equal to the energy that passes through its boundary as heat or work.
 - $w > 0$ or $q > 0$ if energy is transferred to the system as work or heat
 - $w < 0$ or $q < 0$ if energy is lost from the system as work or heat.
- If an electric motor produced 15 kJ of energy each second as mechanical work and lost 2 kJ as heat to the surroundings, then the change in the internal energy of the motor each second is

$$\Delta U = -2 \text{ kJ} - 15 \text{ kJ} = -17 \text{ kJ}$$

The general expression for work

There are different types of work including:

- **expansion work**, the work arising from a change in volume.

This type of work includes the work done by a gas as it expands and drives back the atmosphere. Many chemical reactions result in the generation or consumption of gases (for instance, the thermal decomposition of calcium carbonate or the combustion of octane), and the thermodynamic characteristics of a reaction depend on the work it can do. The term 'expansion work' also includes work associated with negative changes of volume, that is, compression.

- **electrical work**
- **Surface expansion**

the work required to move an object a distance dz against an opposing force of magnitude F is

$$dw = -F dz$$

The negative sign tells us that, when the system moves an object against an opposing force, the internal energy of the system doing the work will decrease.

- **Work is Not a State Function**

Expansion work

- Now consider the arrangement shown in Fig., in which one wall of a system is a massless, frictionless, rigid, perfectly fitting piston of area A.
- If the external pressure is p_{ex} , the magnitude of the force acting on the outer face of the piston is $F = p_{ex} A$.
- When the system expands through a distance dz against an external pressure p_{ex} it follows that the work done is

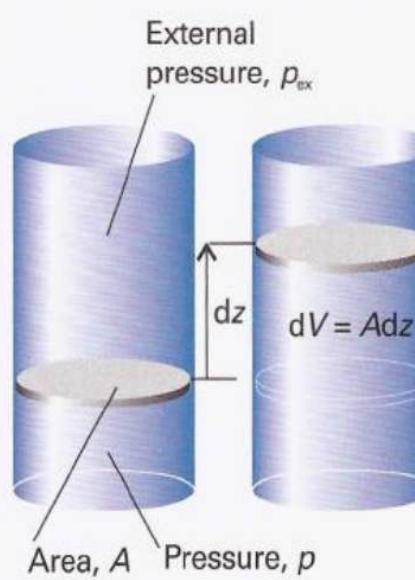
$$dw = -p_{ex} A dz$$

- But $A dz$ is the change in volume, dV , in the course of the expansion.
- Therefore, the work done when the system expands by dV against a pressure p_{ex} is

$$dw = -p_{ex} dV$$

To obtain the total work done when the volume changes from V_i to V_f we integrate this expression between the initial and final volumes:

$$w = - \int_{V_i}^{V_f} p_{ex} dV$$



1- Free expansion

- Expansion of this kind occurs when a system expands into a vacuum.
- expansion against zero opposing force. It occurs when $p_{ex} = 0$.
- $dw = 0$ for each stage of the expansion. Hence, overall:

Free expansion: $w=0$

- That is, no work is done when a system expands freely.

2- Expansion against constant pressure

- the external pressure is constant throughout the expansion.
- A chemical example of this condition is the expansion of a gas formed in a chemical reaction.

$$w = -p_{ex} \int_{V_i}^{V_f} dV = -p_{ex} (V_f - V_i)$$

$$w = -p_{ex} \Delta V$$

- Calculate the work done when 50 g of iron reacts with hydrochloric acid in (a) a closed vessel of fixed volume, (b) an open beaker at 25°C.



- (a) the volume cannot change, so no expansion work is done and $w=0$
- (b) the gas drives back the atmosphere and therefore

$$w = -p_{ex}\Delta V$$

$$\Delta V = V_f - V_i \approx V_f$$

$V_f = nRT/P_{ex}$ where n is the amount of H_2 produced

$$w = -p_{ex} \times \frac{nRT}{P_{ex}} = -nRT$$

1 mol H_2 is generated when 1 mol Fe is consumed, and n can be taken as the amount of Fe atoms that react.

$$w = -\frac{50}{55.85} \times 8.314 \times 298 = -2.2 \text{ kJ}$$