Higher Technological Institute
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Chemical engineering Department

Lecture notes in

Engineering Chemistry

Part (1)

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Gases

Chapter (1) Gaseous State

1.1. Introduction to the Gaseous State

Matter is everywhere: we are made of matter, the pencils you've used are made of matter, the water you drink is made of matter, and the air we breathe is also a form of matter (gas). If the matter didn't exist, nothing would. Without air, how would we breathe? This dependence of humans on air makes the gaseous state of matter, extremely important to us and it is the simplest state of matter.

Figure 1. 1 States of Matter: Solid, Liquid & Gas

The gaseous state is the simplest of all states of matter, but only 11 gases in the periodic table behave as gases under standard temperature and pressure conditions (STP i.e. 1 atm and 273K). These gases are Helium, Neon, Argon, Krypton, Xenon, Radon, Hydrogen, Nitrogen, Oxygen, Fluorine and Chlorine. They are called "pure gases". The difference in the intermolecular distances between the particles of solids, liquids, and gases, as illustrated in Figure (1.1), shows that solids feature very tightly packed particles whereas liquids feature slightly greater intermolecular distances. Of the three states, the gaseous state can be observed to have the largest intermolecular distances.

1.2. General Characteristics of Gases

- **Shape and volume:** Gases have neither definite shape nor definite volume. They take up the shape and volume of the container.
- **Density:** They have very low density because of negligible intermolecular forces.
- **Compressibility:** They are highly compressible and unlimited dispensability.
- **Diffusability:** They diffuse rapidly through each other to form homogenous mixture against the electric, magnetic and gravitational field.
- **Pressure:** They exert pressure on the wall of the container equally in all directions with perfectly elastic collisions.

The above properties are due to the fact that intermolecular forces of attraction among the molecules of a gas are negligible.

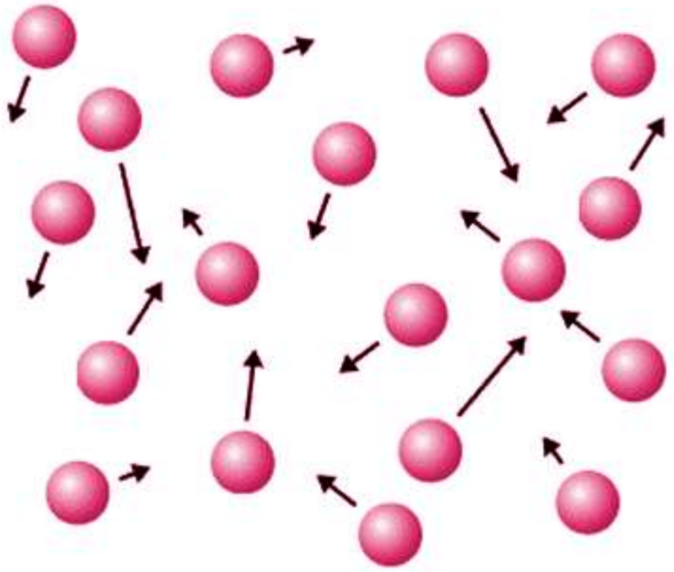


Figure 1. 2 Gas particles can move freely and spread out to fill the available space

1.3. Parameters of Gases

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

a. Pressure (P)　　b. Temperature (T)

c. Volume (V)　　d. Number of moles (n)

The Specific relationships among these four variables are called the **Gas Laws** and gas whose behavior follows the laws exactly is called **Ideal Gas**

1.4. Gas Laws

➢ Charles' Law:

For a fixed amount of gas, the volume of the gas measured at constant pressure is found to be directly proportional to its absolute temperature

$$V \propto T$$

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

[at constant amount of gas, n, and constant pressure, P].

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

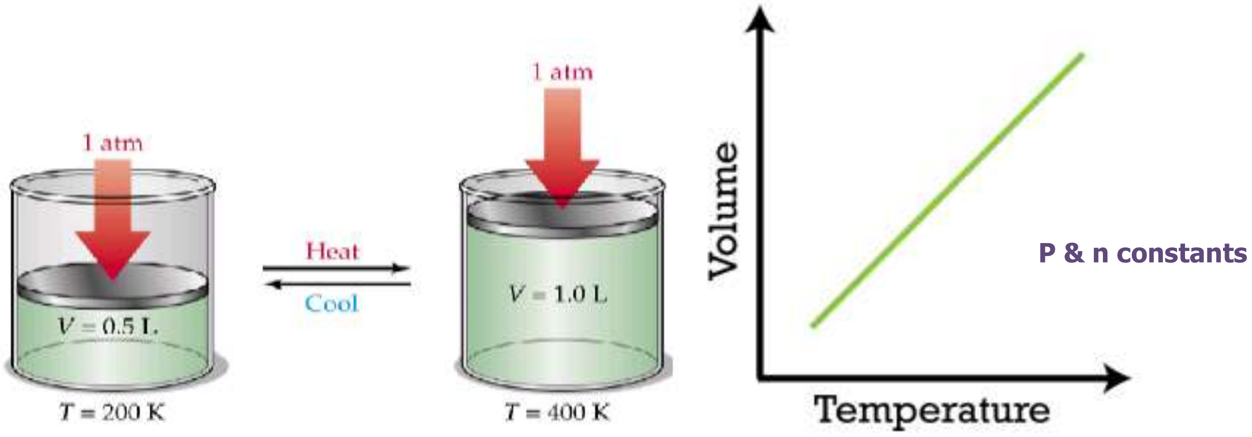


Figure 1. 3 Charles' Law: at constants P & n, V is directly proportional to T

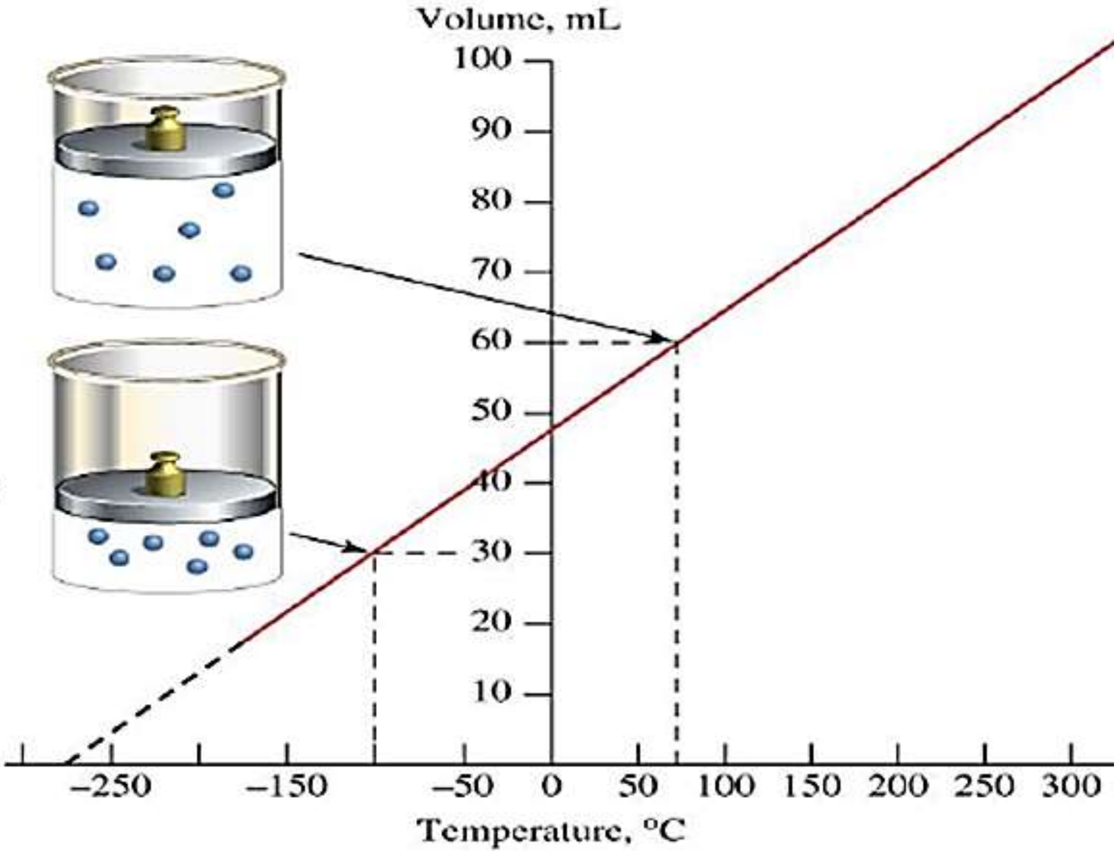


Figure 1. 4 Charles' Law: as T increases, V will increase

➢ Gay-Lussac's Law:

For a fixed number of moles of the gas, the pressure of the gas measured at constant volume is directly proportional to its absolute temperature

$$P \propto T$$

$$P = \text{Constant} \times T$$

[at constant amount of gas, n, and constant volume, V]

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

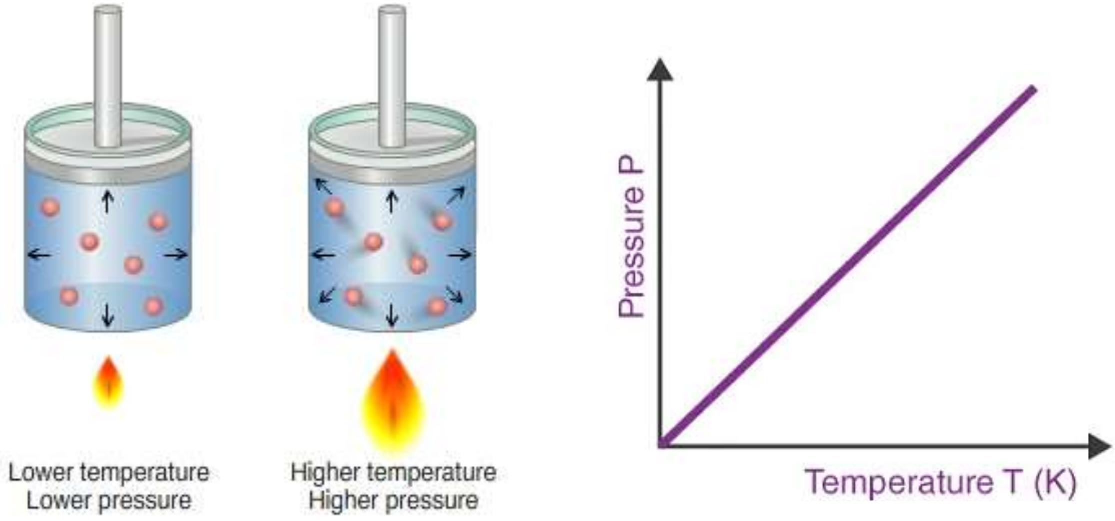


Figure 1. 5 Gay-Lussac's Law: as T increases, P increases

➢ Boyle's Law:

For a fixed amount of gas at constant temperature, the pressure of the gas is found to be <u>inversely proportional</u> to its volume.

$$\mathbf{P \propto 1/V}$$

P V = Constant, as one goes up, the other goes down

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

$$P_1V_1 = P_2V_2$$

[at constant amount of gas, n, and constant temperature, T]

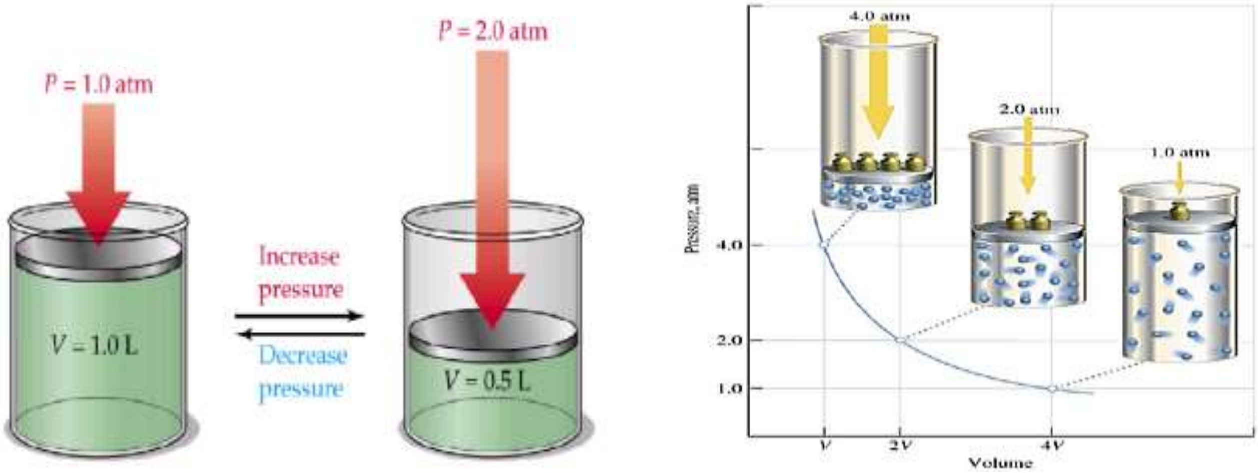


Figure 1. 6 Boyle's Law $P_1V_1 = P_2V_2$

➢ Avogadro's Law:

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

$$V \propto n$$

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

[at constant temperature and pressure of the gas]

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

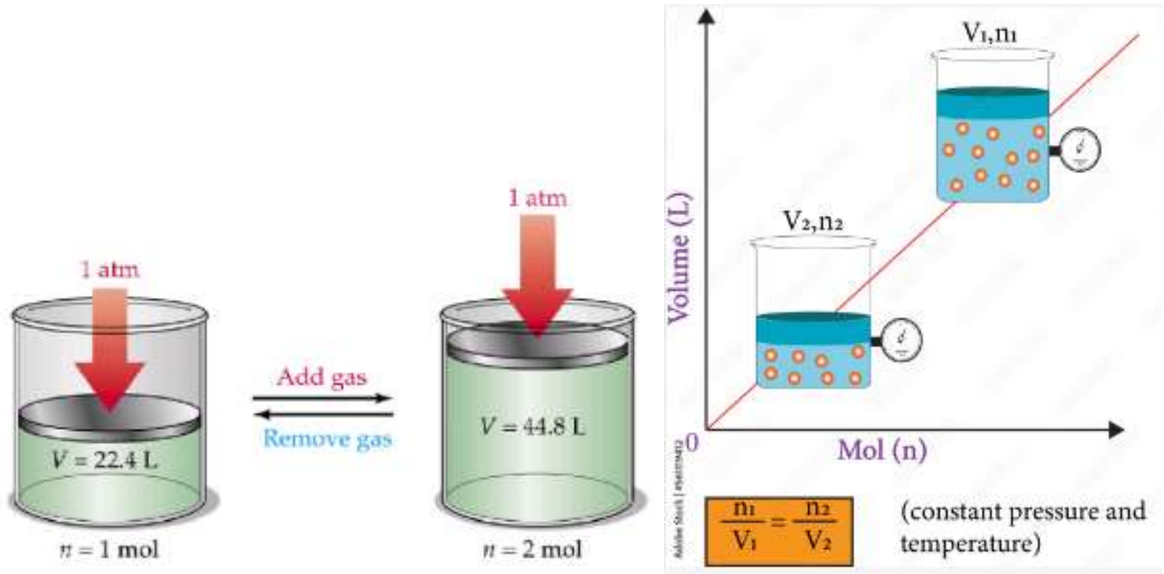


Figure 1. 7 Avogadro's Law

At STP, 1 mole of any gas occupies 22.4 L

STP = 0 °C (273 K) and 1 atm

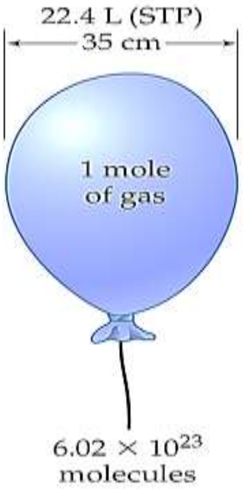
Molar Volume:

One mole of any gas occupies a volume of 22.4 liters (at S.T.P.)

(Standard Temperature & Pressure = 0°Celsius, 1 atmosphere)

Volume:	22.4 L	22.4 L	22.4 L
Pressure:	1 atm	1 atm	1 atm
Temperature	273 K	273 K	273 K
Quantity:	1 mole	1 mole	1 mole
Mass:	20.0 g	32.0 g	28.0 g
Number of gas molecules	6.022×10^{23}	6.022×10^{23}	6.022×10^{23}

Figure 1. 8 Every 1 mole of a gas always occupies a volume of 22.4L at STP



- What will the volume of 5 moles of a gas be at STP?
- A sample of gas occupies 11.2 L at STP, how many moles are present in this sample?
- How many atoms are there in 5 L of a gas at STP?

Example 1.1

Compare the volumes occupied by 16 g of Oxygen and 14 g of Nitrogen present at the same temperature and pressure.

Solution

- Number of moles of O_2 = 16 g/32 g mol^{-1} = 0.5 mole
- Number of moles of N_2 = 14 g/28 g mol^{-1} = 0.5 mole

Since the two gases are at the same temperature and pressure, and they contain equal number of moles, then according to **Avogadro's Law**, they should also occupy the same volume.

Gas Molar Volume (V_m)

It is the volume occupied by one mole of the gas, $V_m=V/n$

This value V_m should be the same for all gases on condition that both T&P are fixed.

Standard Temperature & Pressure (STP) ≈ T= 0 °C, P =1 atm

Standard Ambient Temperature & Pressure (SATP) ≈ T= 25°C, P =1 bar

1.5. Ideal Gas equation of state by combination of the gas laws:

The gases which obey the three laws namely,

1. Charles' law – At constant pressure and number of moles, the volume of a gas is directly proportional to its temperature.

$$V \propto T$$

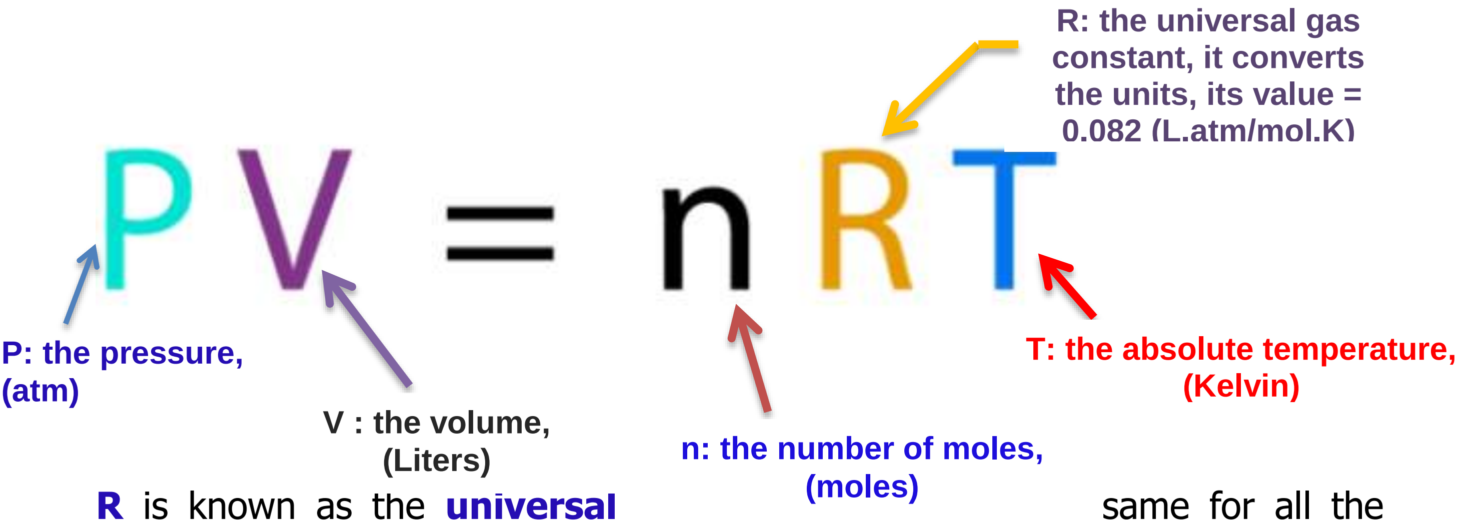
- Boyle's law – At constant temperature and number of moles, the volume of a gas is inversely proportional to its pressure.

$$V \propto 1/P$$

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

$$V \propto n$$

Combining all the three laws we obtain,



R is known as the **universal** same for all the gases. The above equation is called the **ideal gas equation**. So it can be said that at constant temperature and pressure, n moles of any gas will have the same volume.

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

The numerical values of (R) are calculated according the units of P, V & T in the ideal gas equation:

Table 1. 1 Different values of the universal gas constant, R

R = 8.314	L·kPa. K^{-1} · mol^{-1}
R = 8.314	J · K^{-1} · mol^{-1}
R = 1.987	cal · K^{-1} · mol^{-1}
R = 62.36	L · mmHg · K^{-1} · mol^{-1}
R = 62.36	L · Torr · K^{-1} · mol^{-1}

Combined Gas Law:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Example 1.2

Calculate the number of molecules remaining in an electronic vacuum tube of capacity 180 Cm^3, which has been evacuated and sealed off at 25 °C to pressure of 1.0×10^{-7} mmHg.

Solution

$V=180\ Cm^3 = 180\times10^{-6}\ m^3$

$$P = \frac{1.0\times10^{-7}\times1.013\times10^{5}}{760} = 1.33\times10^{-5}\ N/m^2$$

$T = 298\ K$

$$n = \frac{PV}{RT} = \frac{1.33\times10^{5}\times180\times10^{-6}}{8.314\times298} = 9.7\times10^{-13}\text{moles}$$

N.B. Number of molecules = $9.7\times10^{-13}\times 6.022\times10^{23} = 5.8\times10^{11}$ molecules

Avogadro's number:

Number of molecules in one mole of a substance = 6.022×10^{23} molecules.

1.6. Density of Gases (d):

The molar mass and density of a gas can be determined from the ideal gas law:

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

If m= mass and M = molar mass, $\therefore\ n = \frac{m}{M}$

Substituting for n, we get

$$P\,V = \frac{m\,R\,T}{M}$$

$$M = \frac{m\,R\,T}{P\,V} \qquad d = \frac{m}{V}$$

$$M = \frac{d\,R\,T}{P} \qquad\qquad d = \frac{M\,P}{R\,T}$$

$$\boxed{P\,M = d\,R\,T}$$

Example 1.3

What is the density of CCl_4 vapor at 714 torr and 125 °C?

Solution

The absolute temperature is 125 + 273 = 398 K

The pressure is 714/760 = 0.939 atm

The molar mass of CCl_4 is 12.0 + (4) ×35.45 = 153.8 $g.mol^{-1}$. Therefore,

$$d = \frac{(0.939\ \text{atm})\ (153.8\ \frac{g}{mol})}{(0.082\ \frac{L.atm}{mol.K})\ (398\ k)} = 4.42\ g/L$$

Example 1.4

A 2.10-L vessel contains 4.65 g of a gas at 1.00 atm and 27 °C. What is the molar mass of the gas?

Solution

$$d = \frac{m}{V} = \frac{4.65\ g}{2.10\ L} = 2.21\ g/L$$

$$M = \frac{d\,R\,T}{P} = \frac{2.21\ g/L \times 0.0821\ L.atm/mol.K \times 300.15\ K}{1\ atm}$$

M = 54.6 g/mol

1.7. Gas mixtures

Consider now a mixture of gases A and B for which the measured pressure is **P** (which means the total pressure of the gas mixture, **P_T**). If now we imagine that gas B is removed, the pressure within the container will be that due to gas **A** alone, (which means the partial pressure of A, **P_A**).

From the ideal-gas equation

$$\mathbf{P_A = \frac{n_A\, R\, T}{V}}$$

Where; P_A = partial pressure of A and n_A = no. of moles of A.

Similarly, the pressure within the container upon the imaginary removal of gas A is the partial pressure of B,

$$\mathbf{P_B = \frac{n_B\, R\, T}{V}}$$

Where; P_B = partial pressure of B, n_B = no. of moles of B.

For the gas mixture; the total pressure P_T is:

$$\mathbf{P_T = P_A + P_B = \frac{(n_A + n_B)\, R\, T}{V}}$$

$$\mathbf{P_T = \frac{n_T\, R\, T}{V}}$$

Where; n_T = total moles present = n_A+ n_B;

Therefore, the partial pressures of the components can be calculated as:

$$\mathbf{P_A = \frac{n_A\, R\, T}{V}} \quad \text{and} \quad \mathbf{P_B = \frac{n_B\, R\, T}{V}}$$

Mole Fraction (x) & Pressure (P)

The ratio of the number of moles of a gas ($\mathbf{n_1}$) to the total number of moles of the gas mixture ($\mathbf{n_T}$) is called the mole fraction ($\boldsymbol{x_1}$)

$$x_1 = \frac{\text{Moles of compound 1}}{\text{Total moles}} = \frac{n_1}{n_T}$$

$$P_1 = \left(\frac{n_1}{n_T}\right) P_T = x_1 P_T$$

The fractions n_A / n_T and n_B / n_T are described as being the mole fractions of A and B respectively. The symbol " x " is the one most commonly used to represent a mole fraction. Thus

$$x_A = \frac{n_A}{n_T} \quad \& \quad x_B = \frac{n_B}{n_T}$$

$$P_A = x_A P_T \quad \& \quad P_B = x_B P_T$$

1.8. Dalton's Law

In a mixture of gases, each gas contributes to the total pressure of the mixture. This contribution is the partial pressure.

The partial pressure is the pressure that each gas would exert if it alone occupied the volume of the mixture at the same temperature

It is now possible to see that the contribution made by each gas in a mixture to the total pressure is determined by the relative amount of the gas present. Thus, if the gases A and B are present in the mole ratio of 1 : 3 respectively, then $P_A = \frac{1}{4} P_T$ & $P_B = \frac{3}{4} P_T$

The relationship between the measured total pressure and the respective partial pressure can also be rapidly deduced, for

$$P_A = \frac{n_A P_T}{n_T}, \qquad P_B = \frac{n_A P_T}{n_T}$$

$$P_A + P_B = \left(\frac{n_A}{n_T} + \frac{n_B}{n_T}\right) P_T = P_T$$

Thus, the total pressure of a mixture of gases is the sum of the individual partial pressures of the gases in the mixture. This statement is **Dalton's law** of partial pressures.

$$\boxed{\mathbf{P_{Total} = P_1 + P_1 + P_1 + \cdots \text{at constant V and T}}}$$

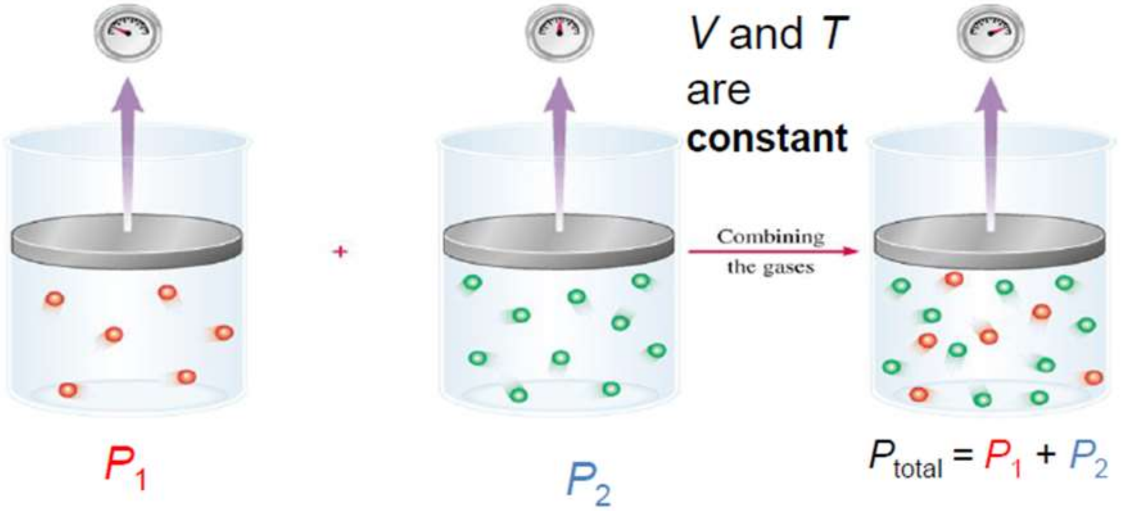


Figure 1. 9 The total pressure of a mixture of gases is the sum of the partial pressure of each individual gas

Example 1.5

A volume of 0.54 L of Argon measured at 72 mmHg and 15°C together with 2.32 g of Neon (at. wt. 20) are placed in a 2L flask. What will be the partial pressures of the two gases when the gas mixture is brought to a temperature of 100°C?

Solution

Solution of this problem could be performed by two different, correct methods as shown below in the answers

◎ First Method

No. of moles of Argon

$$= \frac{P\,V}{R\,T} = \frac{72 \times 1.013 \times 10^5 \times 0.5 \times 10^{-3}}{76 \times 8.314 \times 288} = 0.0216 \text{ mol}$$

No. of moles of Neon

$$= \frac{\text{mass of Neon}}{\text{molar mass of Neon}} = \frac{2.32 \text{ g}}{20.0 \text{ g/mol}} = 0.116 \text{ moles}$$

$$\text{as } n_T = n_{Neon} + n_{Argon}$$

$$\therefore \text{ Total no. of moles, } n_T = 0.1373 \text{ moles}$$

$$P_T = \frac{n_T\,R\,T}{V} = \frac{0.1376 \times 8.314 \times 373}{2 \times 10^{-3}} = 2.134 \times 10^5 \text{ N/m}^2$$

$$P_{Argon} = x_{Argon}\,P_T = \frac{0.0216}{0.1376} \times 2.134 \times 10^5 = 0.3350 \times 10^5 \text{ Pa}$$

$$P_{Neon} = x_{Neon}\,P_T = \frac{0.116}{0.1376} \times 2.134 \times 10^5 = 1.799 \times 10^5 \text{ Pa}$$

◎ Second Method

In this alternative method, Partial pressures are calculated first, then, apply Dalton's law to obtain the total pressure as follows:

$$P_{Argon} = \frac{n_{Argon}\,R\,T}{V} \qquad \& \qquad P_{Neon} = \frac{n_{Argon}\,R\,T}{V}$$

$$= \frac{0.0216 \times 8.314 \times 373}{2 \times 10^{-3}} \qquad = \frac{0.116 \times 8.314 \times 373}{2 \times 10^{-3}}$$

$$P_{Argon} = 0.335 \times 10^5 \text{Pa} \qquad P_{Neon} = 1.799 \times 10^5 \text{Pa}$$

Example 1.6

A mixture of 6.00 g of O_2 (g) and 9.00 g of CH_4 (g) is placed in a 15-L vessel at 0 °C. What is the <u>partial pressure</u> of each gas, and what is the <u>total pressure</u> in the vessel?

Solution:

We need to calculate the pressure of two gases in the same volume and at the same temperature. We first convert the mass of each gas to moles to calculate the pressure each gas would exert if the other were not present

$$\mathbf{n_{O_2} = \frac{mass\ of\ O_2}{molar\ mass\ of\ O_2} = \frac{6.00\ g}{32.0\ g/mol} = 0.188\ moles\ O_2}$$

$$\mathbf{n_{CH_4} = \frac{mass\ of\ CH_4}{molar\ mass\ of\ CH_4} = \frac{9.00\ g}{16.0\ g/mol} = 0.563\ moles\ CH_4}$$

We use the ideal gas equation to calculate the partial pressure of each gas

$$\mathbf{P_{O_2} = \frac{n_{O_2}\ R\ T}{V} = \frac{(0.188\ mol)\times\left(0.082\ \frac{L.atm}{mol.K}\right)\times(273\ K)}{15\ L} = 0.281\ atm}$$

$$\mathbf{P_{CH_4} = \frac{n_{CH_4}\ R\ T}{V} = \frac{(0.563\ mol)\times\left(0.082\ \frac{L.atm}{mol.K}\right)\times(273\ K)}{15\ L} = 0.841\ atm}$$

According to Dalton's law of partial pressures, the total pressure in the vessel is the sum of the partial pressures

$$\mathbf{P_T = P_{O_2} + P_{CH_4} = 0.281 + 0.841 = 1.122\ atm}$$

1.9. The Kinetic Molecular Theory of Gases

A theory describing the quantitative behavior of gases is based on the following assumptions:

1. Gases consist of a large number of tiny particles (molecules) that are in constant, random, straight- line motion, colliding with one another and with the walls of container.

2. The gas molecules are so small and so far apart that the total volume of the molecules of the gas themselves is a negligible fraction when compared with the total volume occupied by the gas.

3. Attractive and repulsive forces between gas molecules are negligible

4. The average kinetic energy of the molecules is directly proportional to the absolute temperature of the gas.

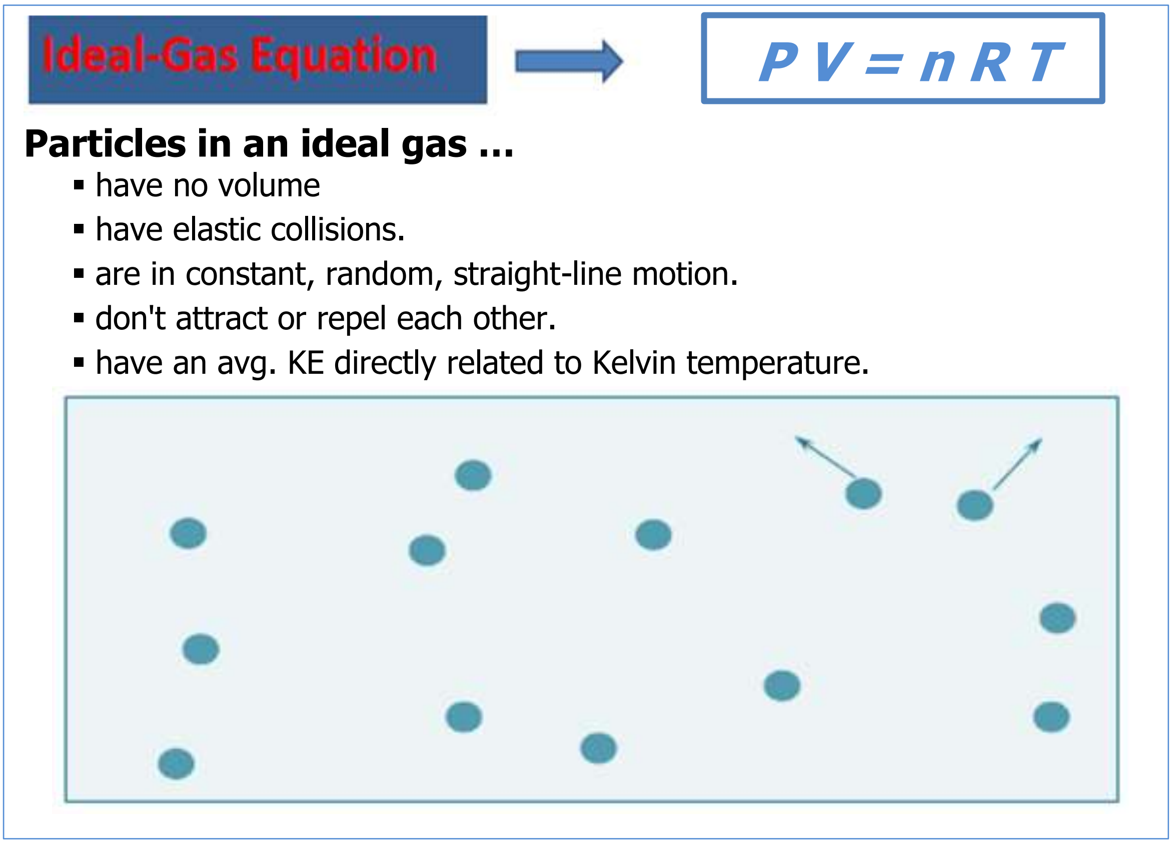
5. Energy can be transferred between molecules during collisions. As collisions of the gas particles, either with other particles or with the walls of a container, are elastic therefore, the total kinetic energy of the gas particles remains constant as long as the temperature of the gas remains constant.

Recall

Ideal Gas: imaginary gas that conforms perfectly to all assumptions of the Kinetic Molecular Theory:

$$\frac{\boldsymbol{P\,V}}{\boldsymbol{R\,T}} = \boldsymbol{n}$$

⬅ This form of the equation tells us that for 1 mole of ideal gas, the quantity PV/RT equals 1 at all pressures



Ideal-Gas Equation → $PV = nRT$

Particles in an ideal gas …

- have no volume
- have elastic collisions.
- are in constant, random, straight-line motion.
- don't attract or repel each other.
- have an avg. KE directly related to Kelvin temperature.

Figure 1. 10 Ideal-gas equation obeying kinetic Molecular theory

In the real world

- **The behavior of gases only conforms to the Ideal-gas equation at relatively high temperature and low pressure.**
- **Even the same gas will show wildly different behavior under high pressure at different low temperatures.**
- **At high pressures, the deviation from ideal behavior ($PV/RT = 1$) is large and different for each gas.**

Real gases, in other words, do not behave ideally at high pressures and low temperatures.

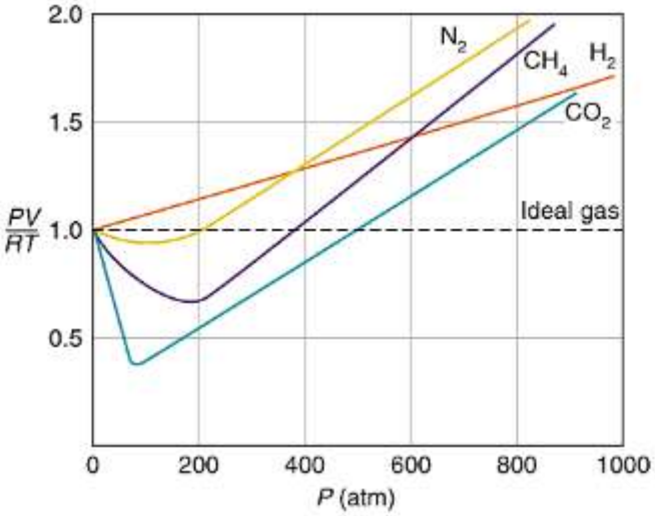


Figure 1. 11 Deviation from ideal gas behavior

- At **lower pressures**, the deviation from ideal behavior is small, and we can use the ideal-gas equation without generating serious error.
- Deviation from ideal behavior also depends on temperature. As **temperature increases**, the behavior of a real gas more nearly approaches that of the ideal gas.

A Real Gas is a gas that does not completely obey all the assumptions of the Kinetic Molecular Theory (KMT)

Real gases deviate from ideal gases because…

- Particles of real gases occupy space (a non-negligible volume)
- Particles of real gases exert significant attractive forces on each other.

1.10. The behavior of Real Gases

Real gases are imperfect because they do not obey the ideal (perfect) gas law exactly. The deviations from the law are particularly important at high pressures and low temperatures

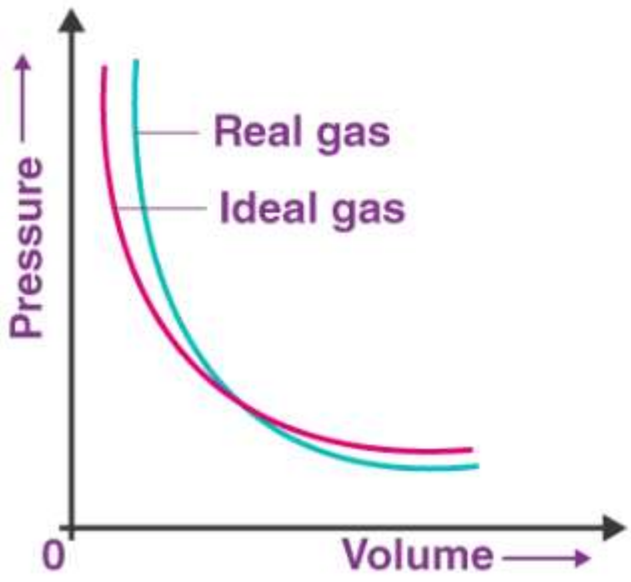


Figure 1. 12 Plot of P vs V showing the difference at high pressures from the behavior of both real gas and ideal gas

The deviation of real gas from ideal gas behavior is also seen when the pressure versus volume graph is plotted. The graph of pressure versus volume should coincide with the experimental data that is the real gas, and the theoretical data that is calculated according to Boyle's law.

It has been observed, that at high pressure, the measured volume of the gas is more than the calculated volume. But at low pressure, the calculated and the measured volumes approach each other. So, it can be stated that the real gases do not follow Charles's law, Boyle's law, Avogadro's law perfectly under all conditions of temperature and pressure.

1.10.1. Compressibility factor

The deviation from ideal behavior is expressed by introducing a factor **Z** known as **compressibility factor** in the ideal gas equation. Z may be expressed by: $\boxed{Z = PV / nRT}$

- **In case of ideal gas, PV = nRT $\therefore Z = 1$**
- **In case of real gas, PV $\neq$ nRT $\therefore$ Z$\neq$ 1**

It may be thought of as the ratio of the actual volume of a real gas to the volume predicted by the ideal gas at the same temperature and pressure as the actual volume. For an ideal gas, Z always has a value of 1. For real gases, the value may deviate positively or negatively, depending on the effect of the intermolecular forces of the gas. The closer a real gas is to its critical point, the larger are the deviations of the gas from ideal behavior

The compressibility factor may also be expressed as:

$$\mathbf{Z = \frac{V_{actual}}{V_{ideal}}}$$

Thus in case of real gases Z can be $<$ 1 or $>$ 1

- When **$Z < 1$**, it is a negative deviation. It shows that the gas is more compressible than expected from ideal behavior. This happens at intermediate pressures because the **intermolecular forces of attraction** cause the actual volumes to be less than the ideal values
- When **$Z > 1$**, and ultimately tends toward infinity, it is a positive deviation. It shows that the gas is less compressible than expected from ideal behavior. This occurs at high pressures because the **intermolecular repulsive forces** cause the actual volumes to be greater than the ideal values

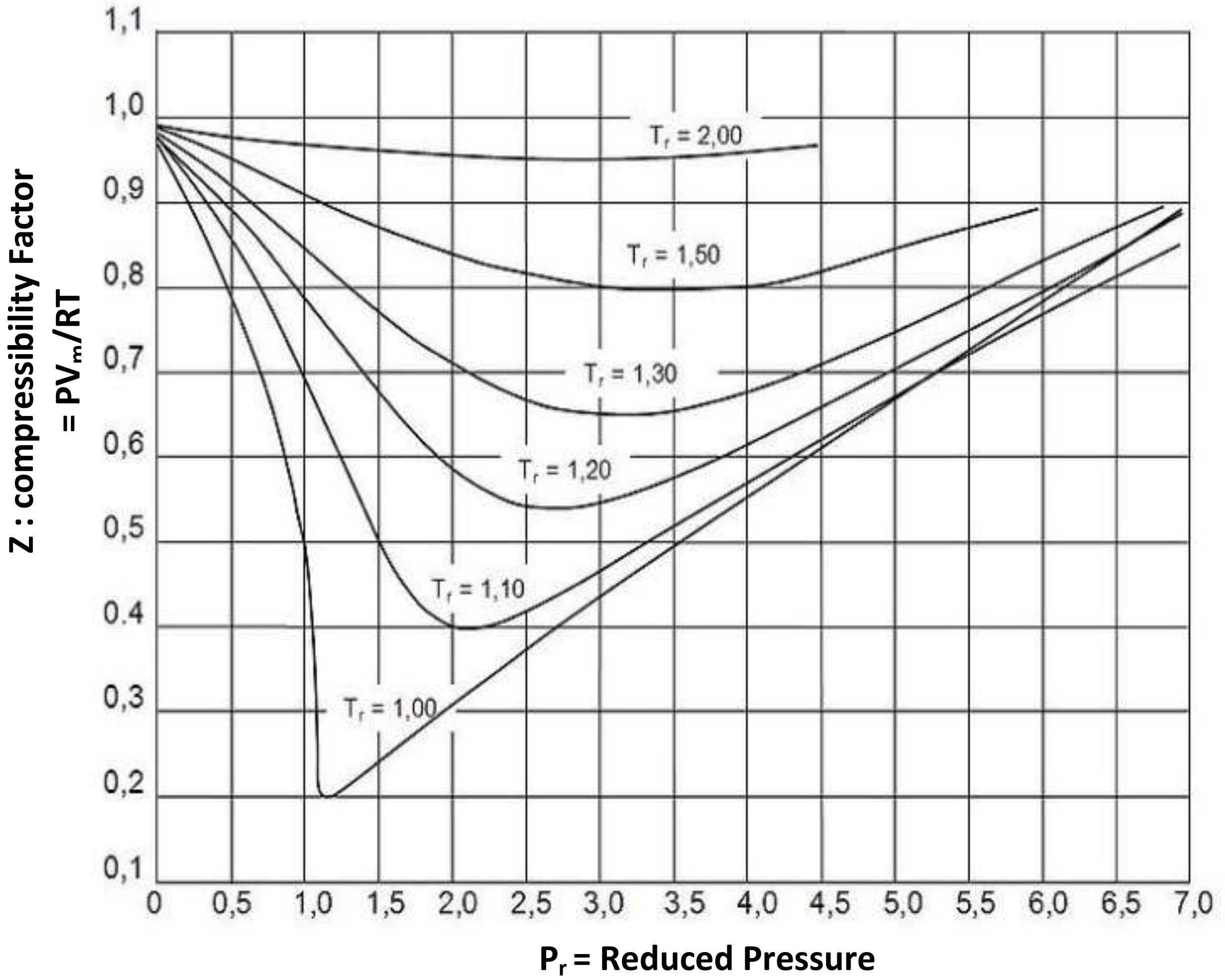


Figure 1. 13 Generalized compressibility factor diagram

Where; Pr: reduced pressure **(Pr = P/Pc)**, **Vr**: reduced volume (**Vr = Vm/Vc**), and **Tr**: reduced Temperature **(Tr = T/Tc)**

Reminder: Vm = V/n
Z = P Vm / RT

1.10.2. The Critical states of the gas

Gases can be converted to liquids by compressing the gas at a suitable temperature. Gases become more difficult to liquefy as the temperature increases because the kinetic energies of the particles that make up the gas also increase.

Critical Temperature, (Tc), is the temperature above which vapor of the substance cannot be liquefied, no matter how much pressure is applied.

Critical Pressure, (Pc), is the pressure required to liquefy a gas at its critical temperature.

Critical Volume, (Vc), is the volume of a unit mass (usually one mole) of a substance measured when it is at its critical temperature and pressure.

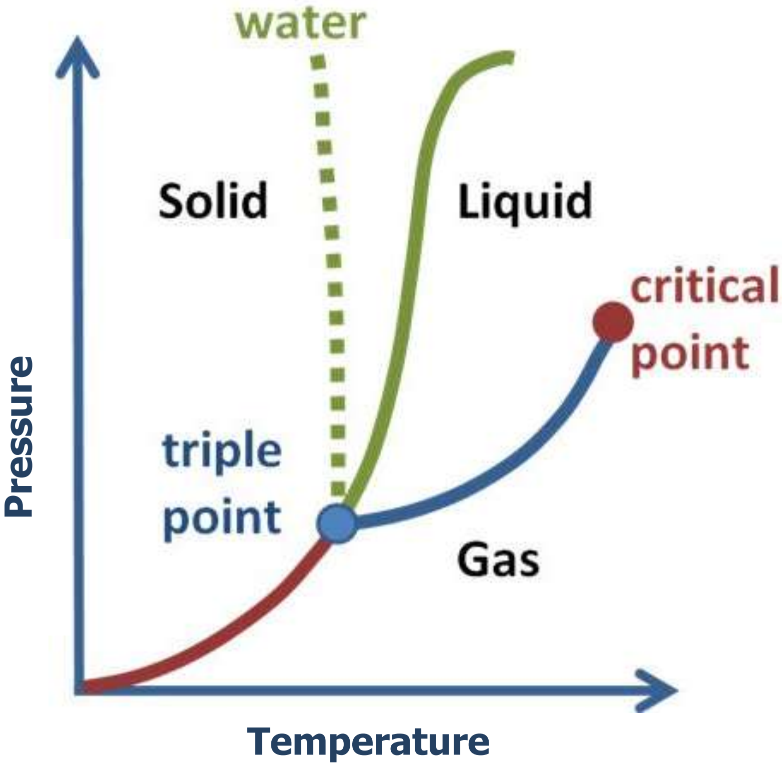


Figure 1. 14 Phase Diagram for a Substance highlighting the critical point

Example 1.7

The critical temperature Tc of Nitrous Oxide (N_2O) is 36.5 °C, and its critical pressure, Pc is 71.7 atm. Suppose that 1 mole of N_2O is compressed to 54.0 atm at 356 K. Calculate the reduced temperature and reduced pressure, and then use compressibility factor to estimate the volume occupied by 1 mole of the gas at those conditions.

Solution

$T_C = 36.5 + 273 = 309.5$ k $\quad T = 356$ K $\quad T_r = 356/309.5 = 1.15$

$P_c = 71.7$ atm $\quad P = 54$ atm $\quad P_r = 54/71.7 = 0.75$

From graph plotted in figure (1.13), we obtain the value of the compressibility factor as follows:

$$Z = 0.83 = (54\times V_m) / (0.082 \times 356)$$

$$V_m = 0.45 \text{ L}/ 1 \text{ mol}$$

RECAP

An ideal gas is one in which

(a) The **molecules are regarded as point masses**, and

(b) **Attraction between the molecules is ignored**.

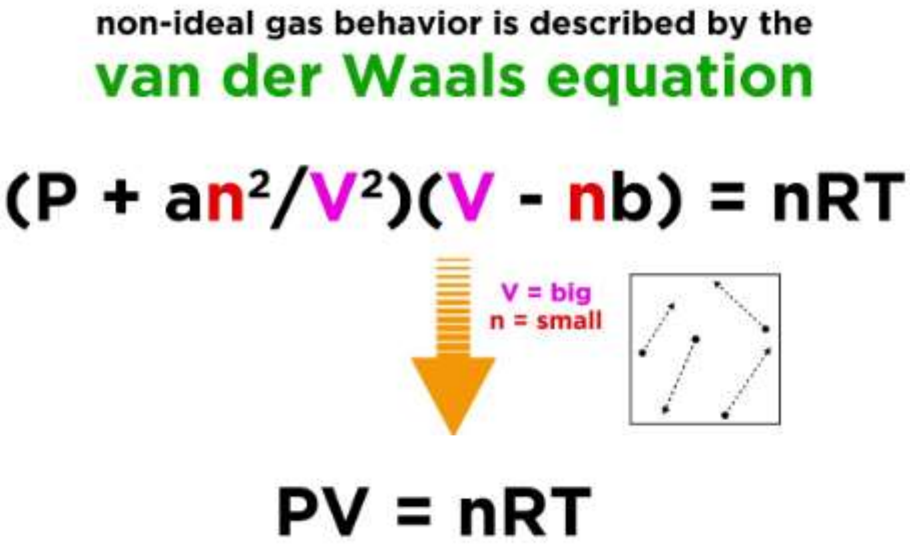
In reality, the molecules of a gas do experience a mutual attraction and do occupy. For Gases which does not follow this assumption we have to use other equations of state.

The behavior of a real gas is often a bit different from that of an ideal gas. For instance, kinetic–molecular theory assumes that the volume of the gas particles themselves is negligible compared with the total gas volume. This assumption is valid at STP, where the volume taken up by molecules of a typical gas is only about 0.05% of the total volume, but this assumption is not valid at 500 atm and 0°C, where the volume of the molecules is about 20% of the total volume. A second issue arising with real gases is the assumption that there are no attractive forces between particles. At lower pressure, this assumption is reasonable because the gas particles are so far apart. At higher pressure, however, the particles are much closer together and the attractive forces between them become more important.

1.10.3. Van der Waals Equation

Correction of the non-ideal behavior of the real gas

The behavior of real gases deviates from the ideal gas law; therefore, the ideal gas equation is adjusted to take the non-ideal behavior of the real gas into consideration. The mathematical modification of the ideal gas law is called **Van der Waals Equation**



The two factors that could be adapted to be suitable for real gases are P and V, by introducing additional terms (are determined by empirical methods) in order to correct,

1. The effect of attraction forces between molecules
2. The effect of the volume occupied by the gas molecules themselves

- By **adding** a term to the pressure in the ideal gas law : $\frac{n^2\,a}{V^2}$, the pressure term will be : $\left(P+\frac{n^2\,a}{V^2}\right)$ where ; a : constant & V : volume of gas
- By subtracting a term from the volume in the ideal gas law : $\mathbf{n\ b}$
  The volume will be: $(\mathbf{V-n\,b})$ Where: b: constant

Van Der Waals equation

$$\boxed{\left(P+\frac{an^2}{V^2}\right)(V-nb)=nRT}$$

Where:

a	**L^2 atm / mol^2**
b	**L /mol**

a is Van Der Waals constant that measures the attractive forces between the gas molecules

b is the volume correction factor

$$\underbrace{\left(P+\frac{a\,n^2}{V^2}\right)}_{\textbf{Corrected Pressure}}\;(\underbrace{V-n\,b}_{\textbf{Corrected Volume}})=n\,R\,T$$

Where; P: pressure exerted by the gas

V: volume occupied by the gas

T: Absolute temperature K

R: universal gas constant

n: no. of gas moles

a, b: constants (different for each gas)

For 1 mole of the gas, we can use Vm (the molar volume of the gas)

Vm = V/n

<u>Van Der Waals Equation becomes</u>:

$$\boxed{P=\frac{R\,T}{(V_m-\;b)}-\frac{a}{{V_m}^2}}$$

Example 1.8

Carbon dioxide (CO_2) gas (1.0 mole) at 373 K occupies 536 mL (Actual Pressure = 50.0 atmosphere). What is the calculated value of the pressure using?

a. Ideal-gas equation

b. Van der Waals equation

[Data - Van der Waals' constants for carbon dioxide: a = 3.61 L^2 atm mol^{-2}; b = 0.0428 L mol^{-1}]

Solution

Using the Ideal Gas Equation

V = 0.536 L

n = 1.00 mol

T = 373 K

$$\mathbf{P = \frac{n\,R\,T}{V} = \frac{1\ \times\ 0.082\ \times\ 373.15}{0.536} = 57.1\ atm}$$

Remember that the actual pressure = 50.0 atm

Using Van der Waals equation:

$$\mathbf{P = \frac{n\,R\,T}{(V\ -\ n\,b)} - \frac{a\,n^2}{V^2}}$$

$$\mathbf{P} = \frac{1.00 \times 0.082 \times 373.15}{(0.536\ -\ 1 \times 0.0428)} - \frac{3.61\ \times 1^2}{0.536^2} = \mathbf{49.6\ atm}$$

1.11. Liquefaction of Gases

1.11.1. General Principle of Liquefaction

A gas can be liquefied by **lowering the temperature** and **increasing the pressure**. At **lower temperatures**, the gas, the only available source of energy is that due to the thermal motion of the molecules. Thus the kinetic energy of the molecules will decrease and this must result in a fall in temperature. At ordinary temperatures, this cooling effect is, for most gases, extremely small. And as the temperature is raised, it becomes even smaller until at on particular temperature characteristic of the gas there is no change in temperature at all. The molecules lose kinetic energy. The slow moving molecules then aggregate due to attraction 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.

1.11.2. Methods of Liquefaction of Gases

There are two main principles:

1. Joule-Thompson Effect
2. Performance of External Work

➢ Joule-Thomson Effect

The general principle employed to liquefy gases on an industrial scale is the **"Joule -Thomson Effect"**.

Joule-Thomson cooling effect occurs when a compressed gas is allowed to pass through a valve or throttle (or a nozzle) into a region of lower pressure by a sudden expansion, a cooling effect is observed. This change in temperature, known as the Joule-Thomson effect is a result that the gas in not being ideal, and arises from the energy required to overcome the intermolecular attraction forces between molecules.

Since the energy required to overcome the intermolecular forces is obtained from the system itself, therefore cooling takes place. The effect can be amplified by using the cooled gas to pre-cool the incoming gas in a heat exchanger.

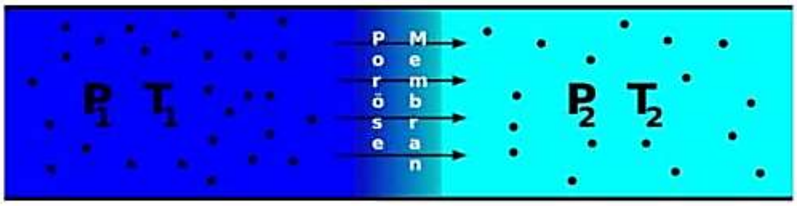


Figure 1. 15 Joule-Thomson effect

➢ Performance of external work

The second of the two principles involves cooling by the performance of **external work**. Consider a gas under pressure enclosed in a cylinder fitted with a piston, when the pressure exerted on the piston is reduced to a value below that of the gas, the latter will expand and cause the piston to move up the cylinder. This performance of work by the gas requires the expenditure of energy. If the expansion is carried out under adiabatic conditions, this can only be achieved at the expense of the kinetic energy of the molecules, and the temperature of the gas drops.

1.11.3. Examples of industrial Liquefaction cycles

Linde process

Carl von Linde in 1895 successfully developed a technique for the liquefaction of air. In this process (Figure 1.16), air, previously freed of carbon dioxide by passage over caustic soda, is compressed to about 200 atm, and passed through cooling coils in order that the heat generated during the compression is removed. The gas stream then passes through the heat exchanger from which it is expanded to about 1 atm through the expansion valve where it is cooled by the **Joule-Thomson effect**. The gas is then returned to the compressor via the heat exchanger, thus causing the temperature of the incoming compressed gas to be lowered prior to its expansion. The repetition of this cycle results in the temperature of the expanding gas dropping sufficiently to cause partial liquefaction.

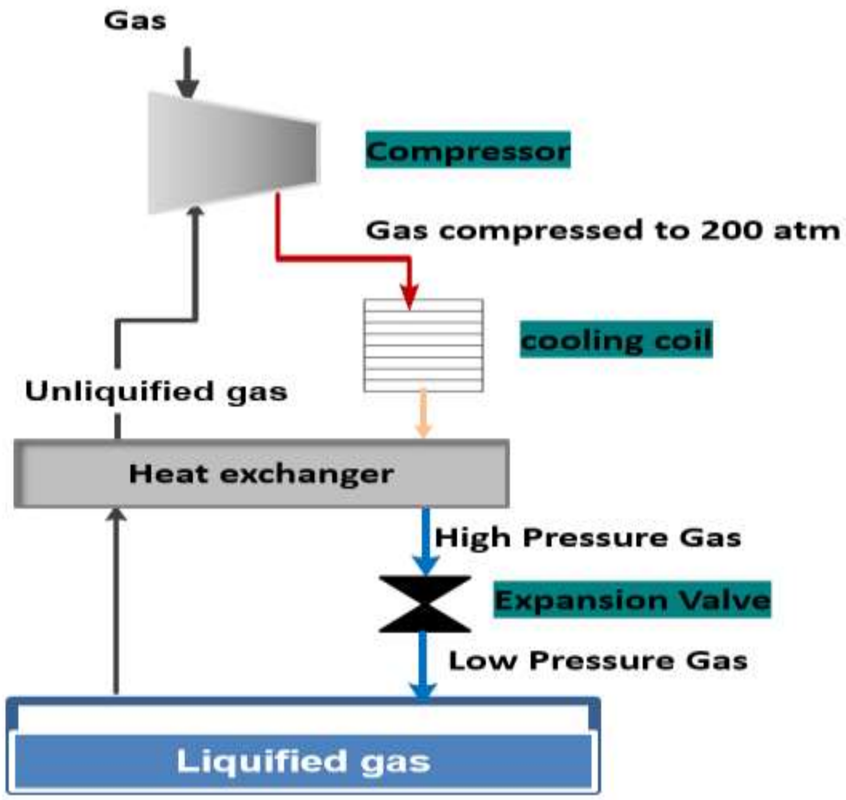


Figure 1. 16 Linde process for liquefaction of air

Claude process

The Claude process for the liquefaction of air employs a combination of the two principles discussed earlier.

The first principle claims that when a gas expands **adiabatically** (no energy is transferred in or out from the system) against an external pressure (as a piston in an engine), it does some external work. This work is done by the molecules at the cost of their kinetic energy, resulting in a fall in the temperature of the gas causing cooling.

In Claude cycle, as shown in Figure (1.17), compressed air is allowed to do mechanical work of expansion through an **expansion engine**, the work is done at the expenses of the kinetic energy of the gas and hence a fall of temperature is noted. This principle is enhanced when combined with the **Joule -Thomson effect**.

Referring to Figure (1.17), the purified air is compressed to about 200 atm in the compressor. However, compression is accompanied with temperature elevation and some of the heat generated is removed from the exiting stream by passing through a set of heat exchangers. The moderately cooled air stream, leaving the first heat exchanger, is divided into two streams; **one** goes to the **expansion engine** (turbine or turbo-expander) where it is re-cooled, expanded and exerted some mechanical work and then returned back to the compressor via heat exchanger (2) after it pre-cools the other stream of air. The **other stream**, leaving heat exchanger (1), continues to the next heat exchanger and is highly pre-cooled by the returning cold streams. The temperature of which is further reduced by its passage through the **expansion (JT) valve** at which point **partial liquefaction** results.

If this cycle was repeated several times, liquefaction of the air would result.

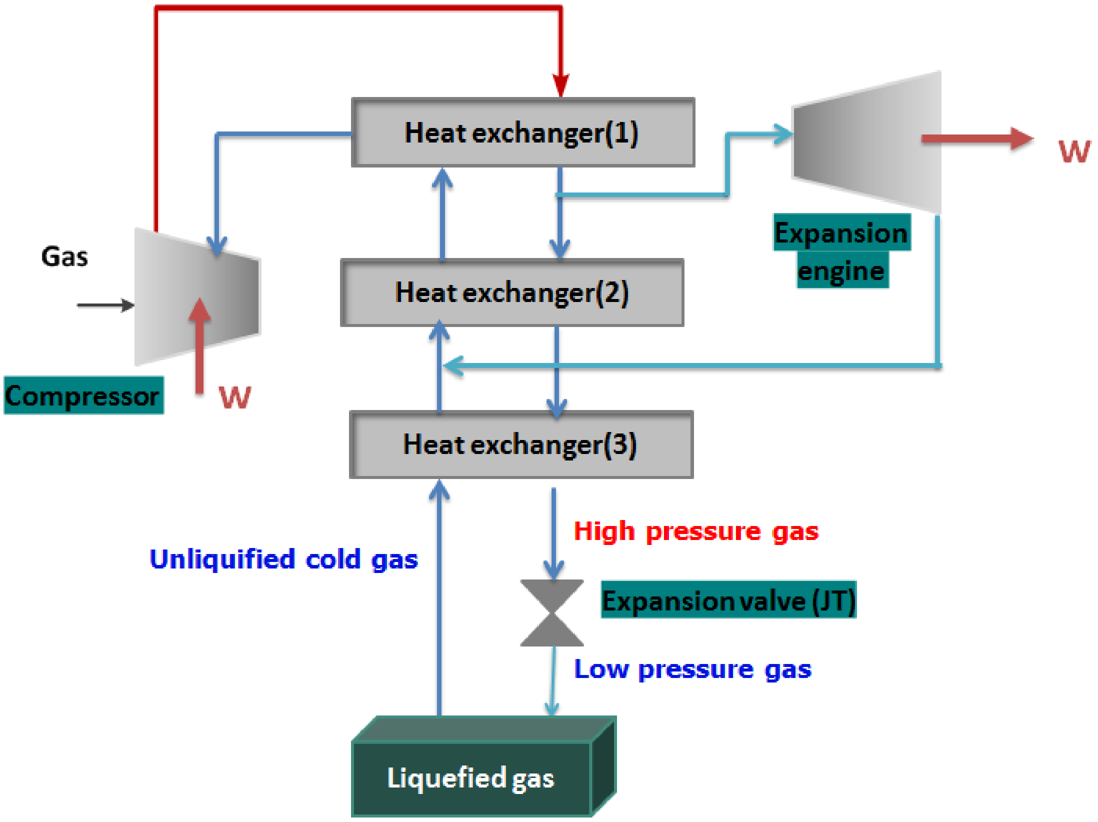


Figure 1. 17 Claude process for gas liquefaction

Some remarks

1. Sometimes, the process occurring in the expansion engine itself would be inefficient because of the formation of some liquids, during expansion, that may ruin the engine if this amount exceeds certain limit (as well known that much liquid cannot be tolerated in the expander). Therefore, practically, the applying of external work using a turbo-expander cannot be used individually in the liquefaction cycle, it is only used to produce a sufficiently low temperature but the gas liquefaction process itself mainly occurs by the Joule-Thomson effect.

2. In Claude cycle, energy is removed from the gas stream by allowing it to do some work in an expansion engine or expander but the expansion valve (J – T valve) is still necessary in the Claude system because of the reason

mentioned above but as advantage in the actual system, the energy resulting from the expander is used to help compressing the gas in the compressor which is economically profitable.

Sheet no. (1)

1. Convert the following

- Pressure of 1150 mmHg to atm , Pascal, cmHg ,bar and mmHg
- Sulfur dioxide, volume of 500 cm^3 to, L,ml and m^3
- Temperature of 25 ^oC to K and Fahrenheit

2. Calculate the number of moles of 500 mg of Hydrogen gas, 64 gr of ammonia gas (N = 14, H = 1).

3. Calculate the pressure exerted by 1.0 mole C_2H_6 behaving as

(a) a perfect gas,
(b) A real gas obeying Van der Waals gas-equation

When confined under the following conditions:

- at T = 273.15 K in 22.414 L
- at t = 800^o C in 100 cm^3.

(a=5.489 L^2atm mol^{-2} and b=0.0638 L mol^{-1})

4. A gaseous mixture composed of 8 gm He, 20 gm Ne and 80 gm of Ar is confined in 22.4-liter container at 0^{o}C. **Calculate** the total pressure of the mixture. (He =4, Ne=20, Ar=40)

5. Calculate the value of the general gas constant R in L.atm/mole.K at S.T.P.

6. Calculate the molar mass of a gas of a density 1.2 g/L at 27 ^oC under one atmospheric pressure.

7. Calculate the pressure exerted by 88 gm of CO_2 gas at 27 ^oC in a 5.0 - L container.

- Suppose Ideal gas state. (C=12, O=16)
- Suppose Real gas state (a = 3.5 L^2.atm.mol^{-2}, b = 0.04 L.mol^{-1})

8. A student collected a sample of a gas in a 0.220 L gas bulb until its pressure reached 0.757 atm at a temperature of 25 ^oC. The sample weighed 0.299 grams. **What** is the molecular mass of the gas?

9. A sample of Oxygen at 24 ^{o}C and 745 Torr (mmHg) was found to have a volume of 455 ml. **how** many grams of O_2 were in the sample? (O = 16)

10. **Compare** the pressures predicted for 0.8 dm^3 (L) of Cl_2 weighting 17.5 g at 273.15 K using:
a) Ideal gas equation
b) Van der Waals equation (a = 3.5 L^2.atm/mol^2, b = 0.04 L/mol)

11. Ethylene (C_2H_4) has a critical pressure of P_c = 61.659 atm and a critical temperature of T_c = 308.6 K. **Calculate** the molar volume of the gas at 97.2 ^{o}C and 90.0 atm using Fig. 1.13. **Compare** the value so found with that calculated from the ideal gas equation.

12. **<u>Choose the correct answer</u>:**

i. For ideal gas conditions, the incorrect statement is:

a. Molecules do not occupy any space
b. No attractive forces exist between the molecules
c. The gas molecules move in random, straight-line motion
d. None of the mentioned

ii. The Correct statement is:

a. Gases at low pressure or high temperature behave as an ideal gas
b. Gases at high pressure or low temperature behave as an ideal gas
c. Gases at high density behave as an ideal gas
d. None of the mentioned

iii. What is the density of Carbon dioxide (CO_2) in kg/m^3 at 27 °C and 100 KPa?

a. 1.76
b. 2.76
c. 3.76
d. 4.76

iv. 1 atmospheric pressure and 0°C conditions are known as:

a. Room temperature and pressure

b. Standard temperature and pressure

c. Atmospheric temperature and pressure

d. None of the mentioned

v. At gases standard conditions, what is the volume occupied by 1 kmole of ideal gas?

a. $22.4m^3$

b. $2240\ m^3$

c. $224000\ m^3$

d. None of the mentioned

vi. For Oxygen gas (assume ideal conditions), 5 moles of the gas at 200 K temperature and 5 atm pressure. What is the volume of the gas?

a. 16.4 L

b. 38.4 L

c. 44.5 L

d. 85.6 L

vii. For ideal gas, which pair of variables is inversely proportional to each other (if all other conditions remain constant)?

a. P, T

b. P, V

c. V, T

d. n, V

viii. The compressor function in the Linde's liquefaction cycle is

a. Decreasing air pressure
b. Increasing air pressure
c. Decreasing air temperature
d. Increasing air temperature

Chapter (2)

Solutions and their Properties

Chapter (2) Solutions and their Properties

2.1. What a Solution is?

Solution is a homogeneous mixture of two or more pure substances which are completely miscible in each other (they don't separate on standing). A solution has two components (substances) known as the **solute** and the **solvent**.

- **Solute** is the substance that dissolved in solvent (small amount)
- **Solvent** is the substance that dissolves the solute (large amount).

Solutes and solvents may be of any form of matter: solid, liquid or gas.

The solutions are of two forms, depending on whether the solvent is water or not.

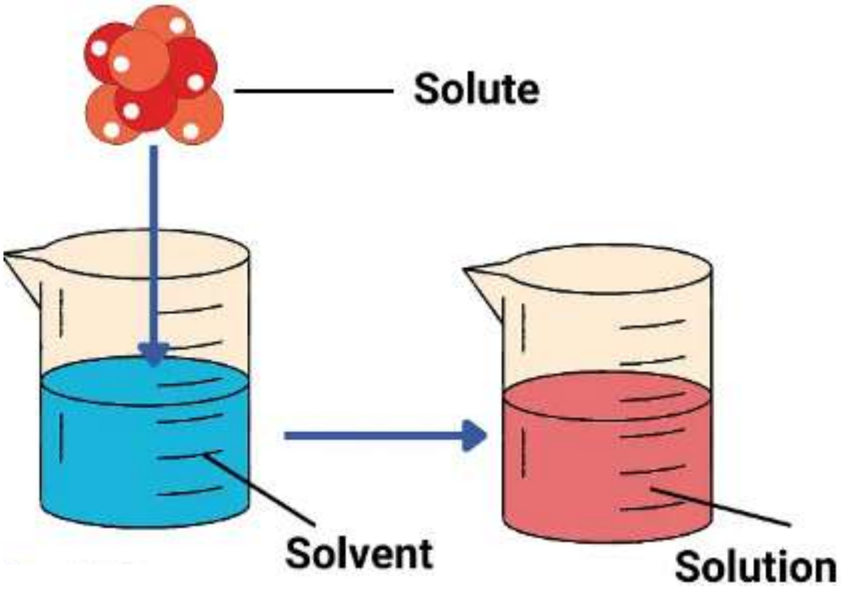


Figure 2. 1 Solutions

Homogeneous means having the same properties throughout it

Mass of solution = mass of solute + mass of solvent

- **Aqueous solution** – When a solute is dissolved in water the solution is called an aqueous solution. e.g: salt in water, sugar in water and Copper Sulfate in water.
- **Non-aqueous solution** – When a solute is dissolved in a solvent other than water, it is called a non-aqueous solution. e.g: Iodine in Carbon Tetrachloride, Sulphur in Carbon disulfide, Phosphorus in Ethyl alcohol.

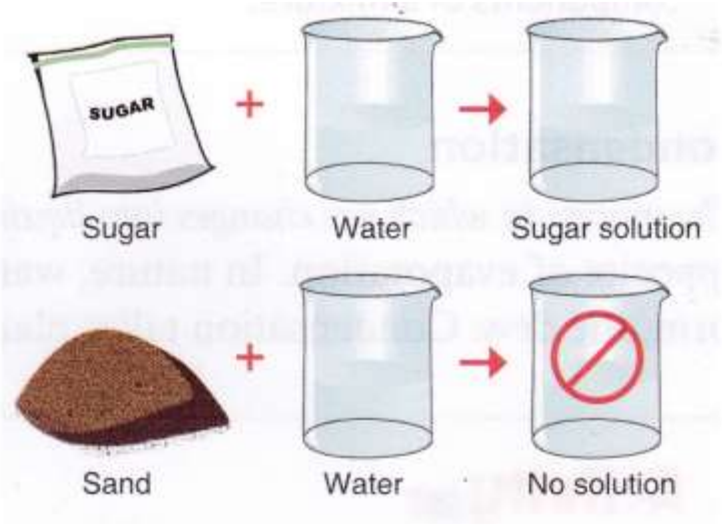


Figure 2. 2 Soluble and insoluble substances

Not all substances dissolve in water. Only some substances like salt and sugar dissolve in water and are known as **soluble substances**. Substances like chalk, sand and oil do not dissolve in water and are known as **insoluble substances.**

2.2. Types of Solutions

We usually think of a solution as a solid dissolved in a liquid or as a mixture of liquids, but there are many other kinds of solutions. In fact, Solutions can be any combination of solids, liquids, and gases. Nine different kinds of solutions are possible (Table 2.1). All solutions are described or characterized by the state of matter of their solvent, not their solutes.

Table 2. 1 Some Different Kinds of Solutions

Kinds of Solutions	Different Examples
Gas in gas (G/G)	- **Air** (Oxygen and other gases dissolved in Nitrogen) - **Natural gas,** a homogeneous mixture of Methane (CH_4) as solvent and other components, including Ethane (C_2H_6), Propane (C_3H_8) and Butane (C_4H_{10}), as solutes
Gas in liquid (G/L)	- **Soda water** (Carbon dioxide, CO_2, dissolved in water)
Gas in solid (G/S)	**H_2 in palladium metal**
Liquid in gas (L/G)	**Humid Air** (Water vapor in air)
Liquid in liquid (L/L)	- **Gasoline** (mixture of hydrocarbons) - **Vinegar** (Acetic acid in water)
Liquid in solid (L/S)	**Dental amalgam** (mercury in silver)
Solid in liquid (S/L)	- **Sugar Water** (Sugar in water) - **Sea water** (Sodium Chloride, NaCl, in water)
Solid in gas (S/G)	- **Moth balls** (Naphthalene in air)
Solid in solid (S/S)	Metal **alloys,** such as - **Steel** (Carbon in iron, C content should not exceed 0.2%) - **Stainless steel** when it contains 12 – 30 % by weight chromium - **Sterling Silver** (92.5% Silver, Ag, 7.5% other metals usually Copper, Cu) - **Brass** (Zinc, Zn in Copper, Cu)

2.3. Electrolytes and Electrolytic Solutions

Electrolytic solutions are those that are capable of conducting an electric current. A substance that, when added to water, gives ions and conducts electricity through the movement of those ions (not electrons). It renders the solution conductive, and is known as an **electrolyte**.

Most soluble salts, acids, and bases dissolved in a polar solvent, such as water, fall into this category. When a substance dissolves, it splits into cations and anions, which are evenly dispersed throughout the solvent.

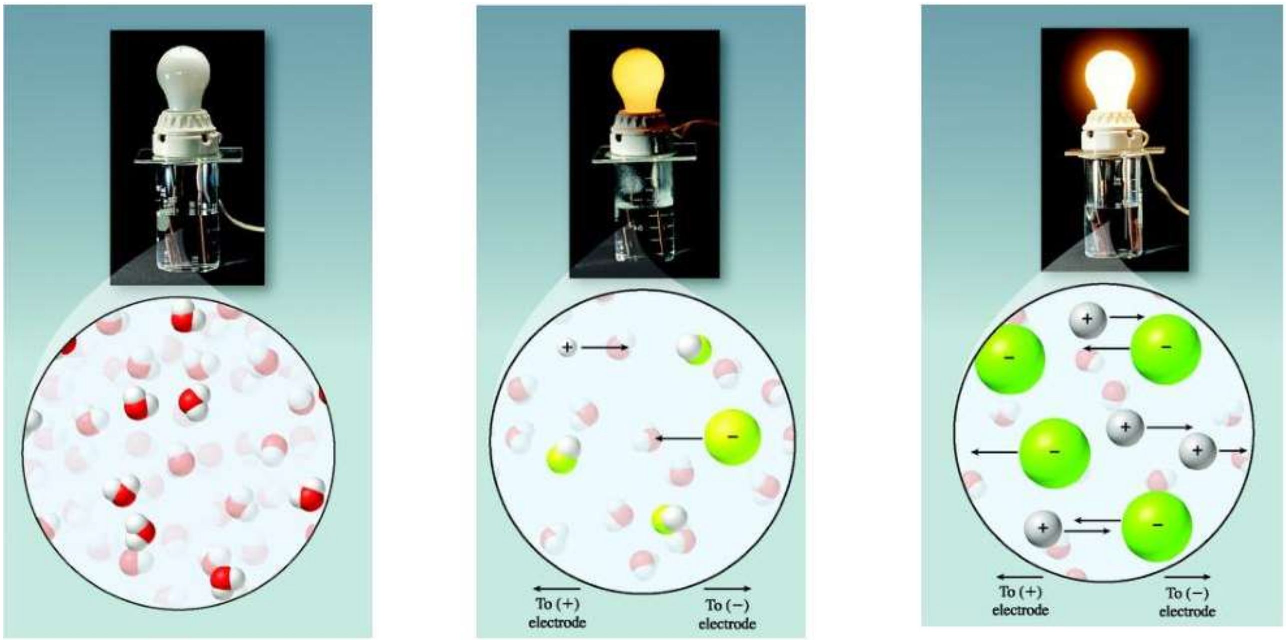
A common example of an electrolyte is ordinary salt, sodium chloride. Solid NaCl and pure water are both non-conductive, but a solution of salt in water is readily conductive. A solution of sugar in water, by contrast, is incapable of conducting a current; sugar is therefore a **non-electrolyte**.

Types of Electrolytes:

- **Strong electrolytes** dissociate completely and are present in solutions almost exclusively as **ions**. They are good conductors. Examples : KCl, NaCl, NaOH, KOH, HCl, H_2SO_4, …etc

- **Weak electrolytes** dissociate partially in aqueous solutions and are present in the form of **ions** and **molecules**. They are poor conductors as partially ionized in water. Examples: HF, NH_3, CH_3COOH, H_2CO_3, $H_2C_2O_4$, …etc

- **Nonelectrolytes** don't dissociate and are present in solutions only as **molecules**. They don't conduct electricity. Examples: (non-polar gases and non-polar organic compounds) sugar, Benzene, Chloroform …etc.



nonelectrolyte weak electrolyte strong electrolyte

Figure 2. 3 Types of Electrolytes

2.4. Solubility

It is the ability of a substance, the solute, to form a solution with another substance, the solvent. It is defined as the maximum amount of solute that can dissolve in a given amount of solvent at a specified temperature and pressure. It is also the measure of how much a solid substance (solute) remains dissolved in a given amount of a specified liquid (solvent) at a specified temperature and pressure.

Solubility is often expressed as the mass of solute per volume (g/L) or mass of solute per mass of solvent (g/g), or as the moles of solute per volume of solution (mol/L).

- **Different Types of Solutions**

Saturation is the State that occurs when no more of something can be absorbed, combined, or added so depending upon the extent of dissolution of the solute in the solvent, solutions can be categorized into supersaturated, unsaturated and saturated solutions as shown in Figure 2.4.

The **unsaturated solution** contains less solute amount than the solvent has the capacity to dissolve at a specific temperature

A **saturated solution** contains the maximum amount of a solute that could be dissolved in a given solvent at a specific temperaure.

supersaturated solution contains more solute than is present in a saturated solution at a specific temperature and is unstable.
A supersaturated solution contains more dissolved solute than required for preparing a saturated solution and can be prepared by heating a saturated solution, adding more solute, and then cooling it gently. Excess dissolved solute crystallizes by seeding supersaturated solution with a few crystals of the solute.

Figure 2. 4 Types of solutions

- **Dissolution and Precipitation**

(a) When a solid is added to a solvent in which it is soluble, solute particles leave the surface of the solid and become solvated by the solvent, initially forming an unsaturated solution. (b) When the maximum possible amount of solute has dissolved, the solution becomes saturated. If excess solute is present, the rate at which solute particles leave the surface of the solid equals the rate at which they return to the surface of the solid. (c) A supersaturated solution can usually be formed from a saturated solution by filtering off the excess solute and lowering the temperature. (d) When a seed crystal of the solute is added to a supersaturated solution, solute particles leave the solution and form a crystalline precipitate.

Although the terms ***precipitation*** and ***crystallization*** are both used to describe the separation of solid solute from a solution, **crystallization** refers to the formation of a solid with a well-defined crystalline structure, whereas **precipitation** refers to the formation of any solid phase, often one with very small particles.

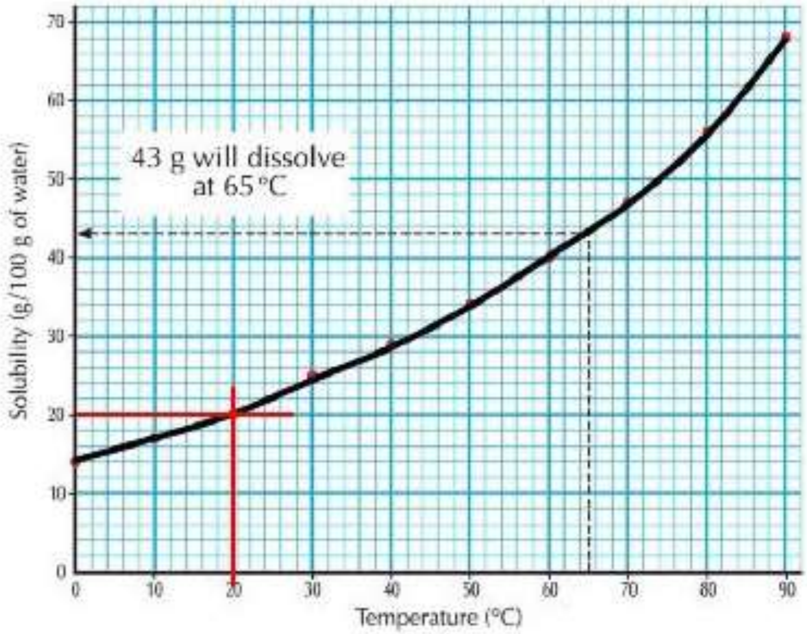


Figure 2. 5 Solubility curve of $CuSO_4$ in Water

As shown in Figure 2.5, solubility is usually expressed by the amount of solute present in 100 g solvent or per one liter of solution

Example 2.1

Will a solution made by adding 2.5 g of $CuSO_4$ to 10 g of H_2O be saturated for unsaturated at 20^oC?

Solution:

We first need to know the solution of $CuSO_4$ at 20^oC. From Figure 2.5 we see that the solubility of $CuSO_4$ at 20^oC is about 21 g per 100 g of H_2O. This amount is equivalent to 2.1 g of $CuSO_4$ per 10 g of H_2O.

Since 2.5 g per 10 g of H_2O is greater than 2.1 g per 10 g of H_2O, the solution will be saturated and 0.4 g of $CuSO_4$ will be maintained.

2.5. Types of interactions in the solution process

There are three types of interactions among particles that are relevant to the dissolution process and have to be taken into account: ***solute-solute***, ***solvent-solvent***, and ***solute-solvent***.

As illustrated in Figure 2.6 , the formation of a solution may be viewed as a stepwise process in which energy is consumed to overcome solute-solute and solvent-solvent attractions (endothermic processes) and released when solute-solvent attractions are established (an exothermic process referred to as **solvation**). The relative magnitudes of the energy changes associated with these stepwise processes determine whether the dissolution process overall will release or absorb energy. In some cases, solutions do not form because the energy required for separating solute and solvent species is so much greater than the energy released by solvation.

Heat of Solution is the amount of heat energy absorbed (endothermic) or released (exothermic) when a specific amount of solute dissolves in a solvent. The enthalpy of solution can be either negative (exothermic) or positive (endothermic)

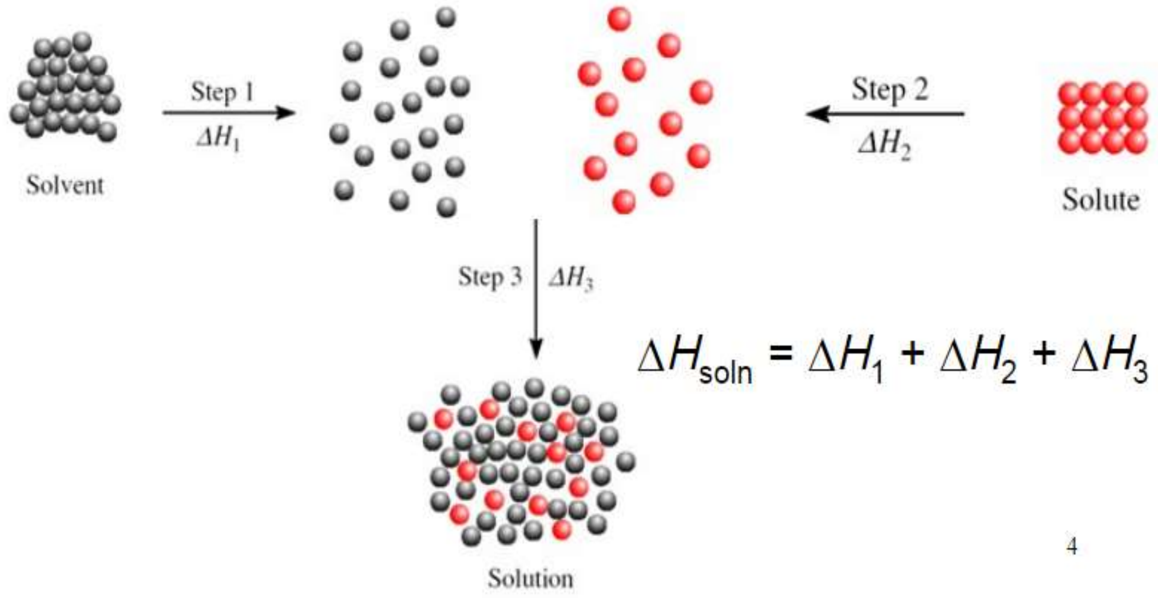
Molar heat of solution is the amount of energy absorbed or released per one mole of the solute.

- When solute-solvent attraction is stronger than solvent-solvent attraction and Solute-solute attraction, the solution process is **Exothermic** ($\Delta H_{soln.} < 0$).
- When solute-solvent attraction is weaker than solvent-solvent attraction and solute-solute attraction, the solution process is **Endothermic** ($\Delta H_{soln.} > 0$).

Three types of interactions in the solution process:

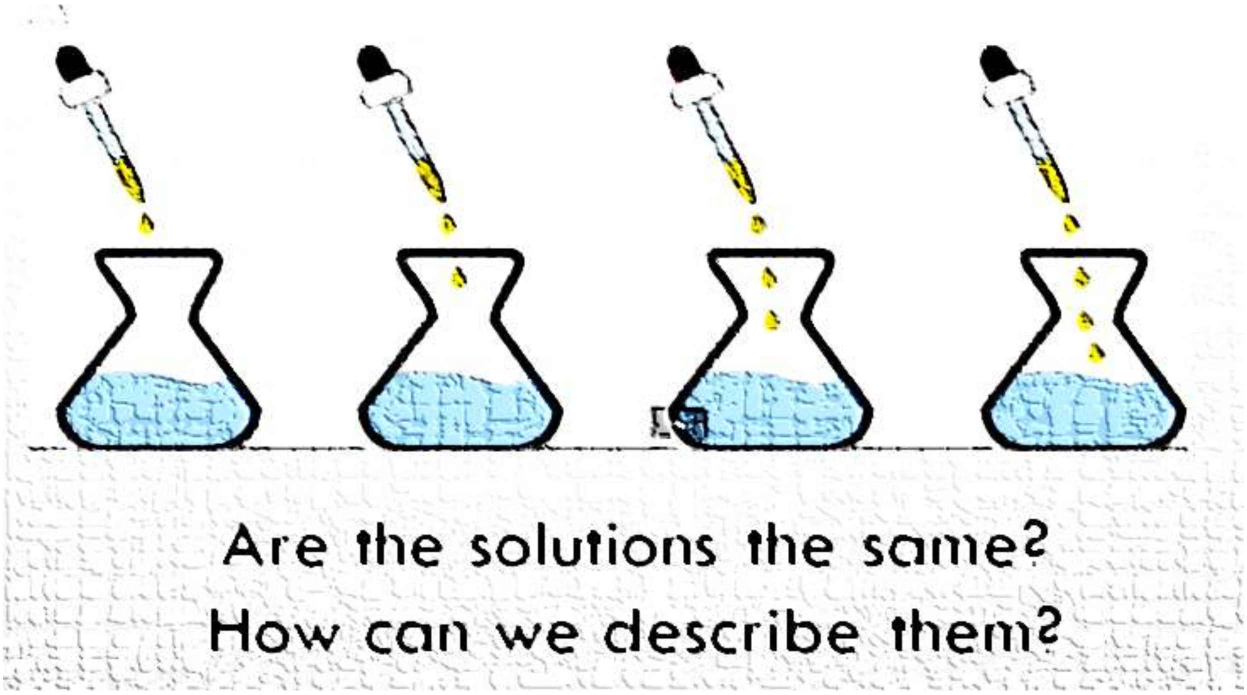
- **Solvent – Solvent** interaction
- **Solute – Solute** interaction
- **Solvent – Solute interaction**

Molecular View of the formation of Solution



- **When energy is released, the reaction is exothermic; ΔH is negative (–).**
- **When energy is absorbed, the reaction is endothermic; ΔH is positive (+).**

Figure 2. 6 This schematic representation of dissolution process



2.6. Concentration Definitions

The concentration of a solution is the amount of solute present in a given quantity of solvent or solution. There are many ways of expressing concentration; we'll look briefly at some of the most common methods

- **Common units of concentration are:**

- Percent by mass
- Mole fraction
- Molarity
- molality
- Normality

Percent by Mass or by Weight (%)

$$\text{mass } \% = \frac{\text{mass of Solute}}{\text{mass of Solution}} \times 100$$

$$= \frac{\text{mass of Solute } (g)}{\text{mass of Solute } (g) + \text{mass of solvent } (g)}$$

Mole fraction **(dimensionless)**

$$\text{mole fraction} = \frac{\text{number of mole of Solute}}{\text{Sum of moles of all components in a mixture}}$$

Where; $\text{number of moles} = \dfrac{\text{mass}}{\text{molecular weight}}$

Molarity (M) **(mol/L)**

The number of moles of solute that are present in one litter of solution

$$\mathrm{M} = \frac{\text{moles of solute } (mol)}{\text{Volume of solution } (L)}$$

$$\mathrm{M} = \frac{\text{mass of solute } (g)}{\text{M.Wt of solute} \times \text{Volume of solution } (L)}$$

molality (m) **(moles/Kg)**

The number of moles of solute present in one kilogram of solvent

$$\mathrm{m} = \frac{\text{mole of Solute}}{\text{mass of Solvent(Kg)}}$$

$$\mathrm{m} = \frac{\text{mole of Solute}}{\text{mass of Solvent(g)}} \times 10^3$$

$$\mathrm{m} = \frac{\text{mole of Solute}}{\text{M.WT of solute} \times \text{mass of Solvent(g)}} \times 10^3$$

Normality (N) **(no. of gram-equivalent)**

$$\mathrm{N} = \frac{\text{No.of gram}-\text{equivalents of solute}}{\text{Volume of solution (L)}}$$

$$\mathrm{N} = \frac{\text{mass of solute}}{\text{Eq.Wt of solute} \times \text{Volume of solution (mL)}} \times 10^3$$

Where; $\text{number of gram} - \text{equivalents} = \dfrac{\text{mass}}{\text{Equivalent weight}}$

$$\text{Equivalent weight} = \frac{\text{Molecular weight}}{\text{valency}}$$

Solutions are classified according to the amount of solute added to the solvent as:

- **Dilute solution** contains a small amount of solute in a large amount of solvent.
- **Concentrated solution** contains a large amount of solute dissolved in a small amount of solvent.

2.7. Dilution

Dilution is the procedure for preparing a less concentrated solution from a more concentrated one

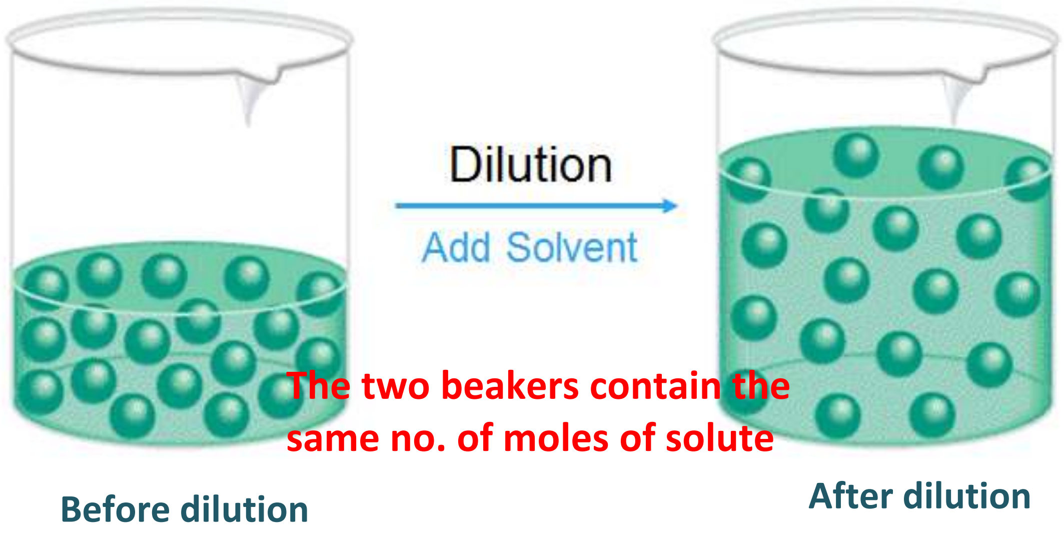
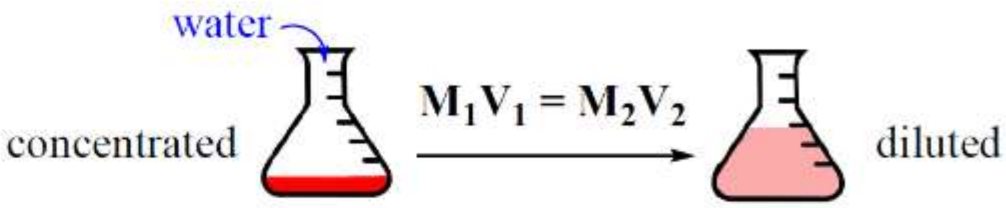


Figure 2. 7 Dilution: Concentrated solution + Solvent → Dilute solution



M_1 and V_1 are the concentration and the volume of the stock solution, while M_2, V_2 are the concentration and the volume of the final solution that we prepare.

Where; $(\mathbf{M} \times \mathbf{V})_{\textbf{concentrated solution}} = (\mathbf{M} \times \mathbf{V})_{\textbf{dilute solution}}$

And; $(N \times V)_{concentrated\ solution} = (N \times V)_{dilute\ solution}$

2.8. Factors Affecting Solubility

2.8.1 Temperature

Solubility is a temperature dependent

2.8.1.1 Effect of temperature on solid solubility

For solids: as temperature increases, solubility of the solids will increase too. The temperature increases the kinetic energy of solvent particles therefore, more solute can be dissolved.

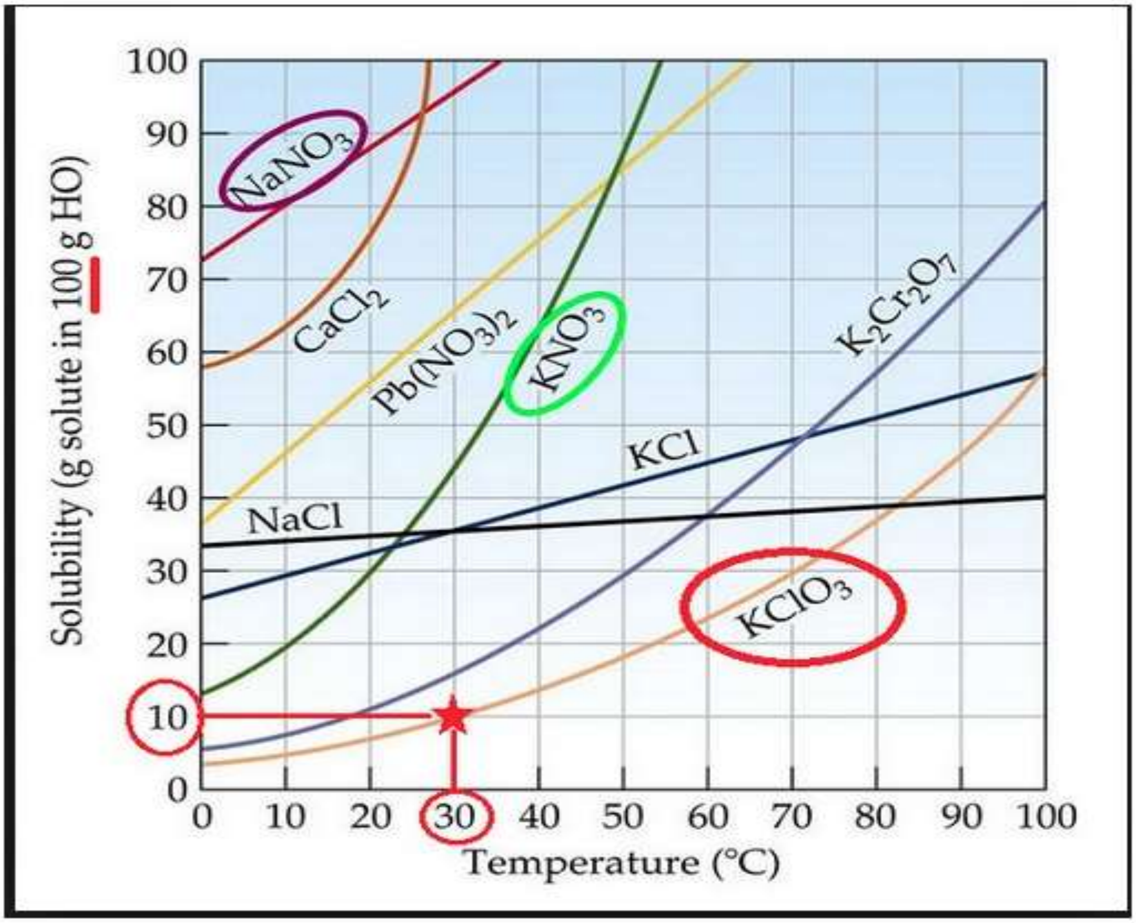


Figure 2. 8 Effect of temperature on the Solubility of solid in liquid

- The solute giving a straight line graph means that its solubility is directly proportional to some temperature ranges.
- Direct proportionality are observed in $NaNO_3$, $Pb(NO_3)_2$ NaCl and KCl. Please note their temperature ranges

2.8.1.2 Effect of temperature on gas solubility

The gas solubility in liquids is highly affected by temperature and pressure as well as the nature of the solute and the solvent.

For gases: on the other hand, as temperature increases, the kinetic energy of the solute gas particles increases and more particles **escape** from solution, therefore, solubility of the gas will decrease.

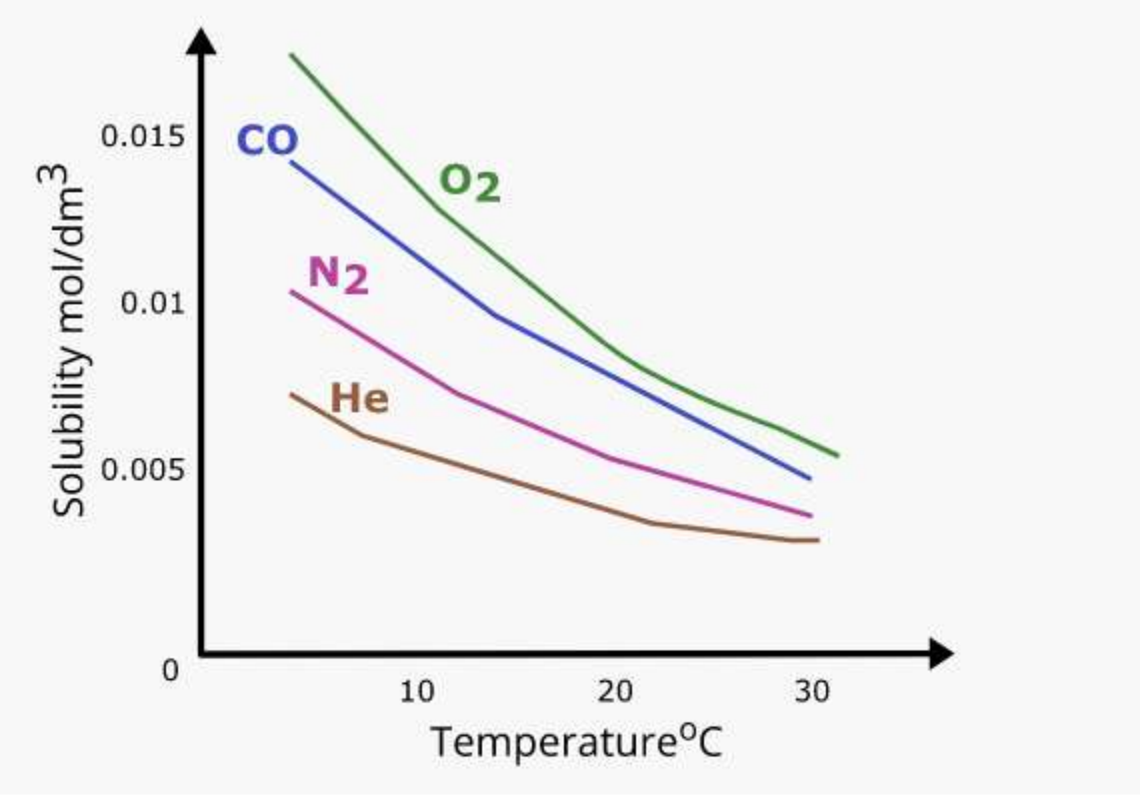


Figure 2. 9 Effect of Temperature on Solubility of Gases

Solubility of gases usually decreases upon increasing temperature. This happens due to two main reasons:

1. The average kinetic energy of gas molecules is already very high.
2. The gas dissolution process is generally an exothermic reaction.

WHY SOFT DRINKS NEED TO BE COLD?

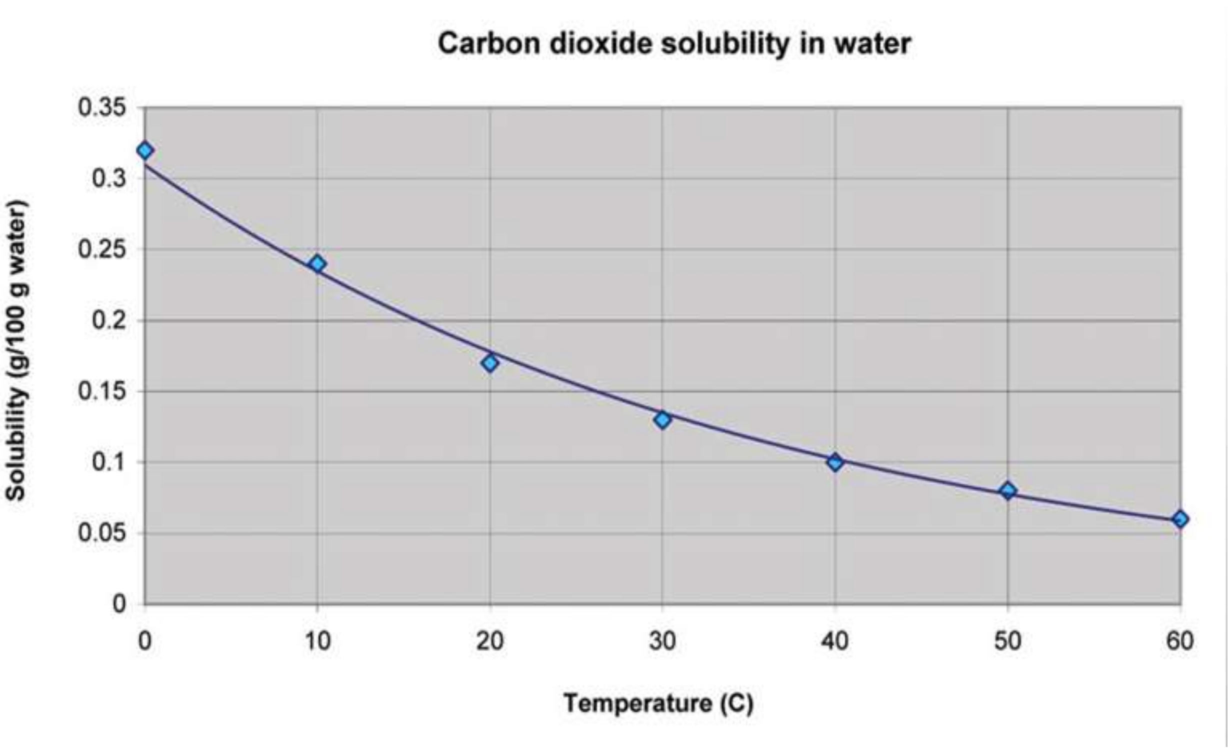


Figure 2. 10 Solubility of CO_2 gas in water at different temperatures

2.8.2. Pressure (Gasses Only)

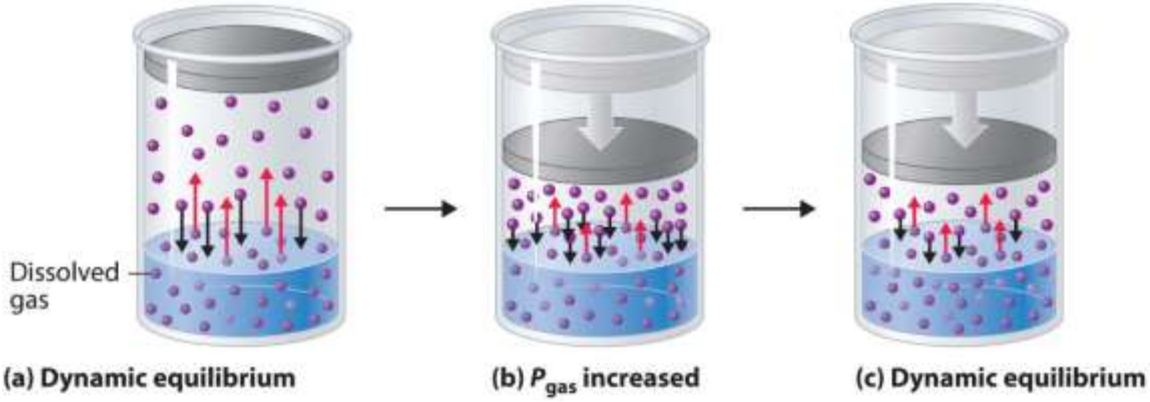


Figure 2. 11 The solubility of a gas can be understood as a dynamic process where gaseous particles are transitioning across the boundary between the two phases.

There are many gases that readily dissolve in water, while there are gases that do not dissolve in water under normal conditions, the required to maintain the pressure to dissolve.

1. Oxygen is only sparingly soluble in water
2. Ammonia readily dissolves in water.
3. Carbon dioxide is only water-soluble, when pressure is maintained. After pressure drops the CO_2 gas will try to escape to air. It is characterized by the bubbles formation of CO_2 into water.

Typically, a gas will increase in solubility with an increase in pressure.

The higher the pressure above the liquid, the more gas that can be dissolved in that liquid, till a limit is reached. Also, a decrease in pressure decreases gas solubility.

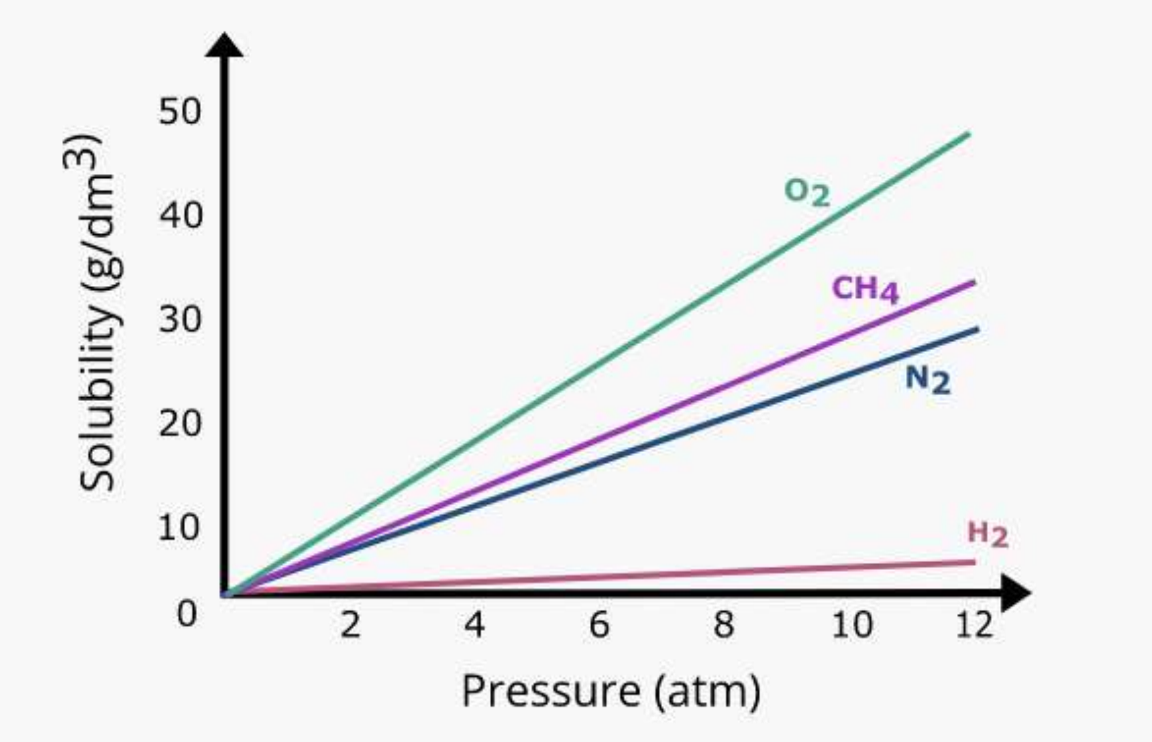


Figure 2. 12 Effect of Pressure on Solubility of Gases

Henry's Law

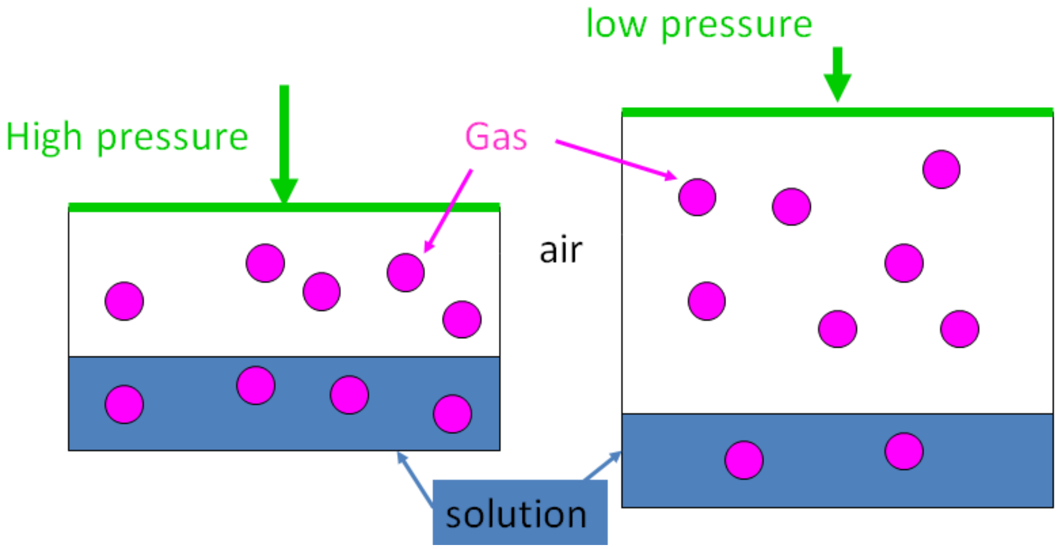


Figure 2. 13 Effect of Pressure on Solubility of Gases

This law is named after English chemist William Henry, who published his findings in 1803.

Henry’s law states that the solubility of a gas in a liquid is directly related to the absolute pressure of the gas over the liquid. That is, the amount of gas that can dissolve in a liquid increases as the pressure of the gas in the space above the liquid increases.

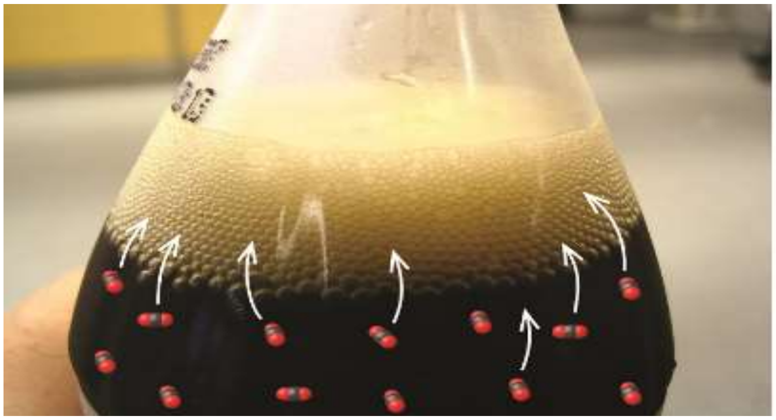


Figure 2. 14 Low Pressure = Low solubility, High Pressure = High Solubility

Carbonated beverages provide a nice illustration of this relationship. The carbonation process involves exposing the beverage to a relatively high pressure of carbon dioxide gas and then sealing the beverage container, thus saturating the beverage with CO_2 at this pressure. When the beverage container is opened, a familiar hiss is heard as the carbon dioxide gas pressure is released, and some of the dissolved carbon dioxide is typically seen leaving solution in the form of small bubbles Figure 2.14. At this point, the beverage is **supersaturated** with carbon dioxide and, with time, the dissolved carbon dioxide concentration will decrease to its **equilibrium** value and the beverage will become "flat".

Henry's Equation

$$\mathbf{C = K \times P}$$

C: The concentration (M) of the dissolved gas, $mol.L^{-1}$

P: The pressure of the gas over the solution, atm

K: Henry's constant (different for each gas and depends on temperature), $mol.L^{-1}.atm^{-1}$

Example 2.2

The Henry's law constant (K) of CO_2 in water at a temperature of 293 K is 3.1×10^{-2} atm.L^{-1}.mol^{-1}. At what partial pressure would the gas has solubility in water of 2×10^{-3} M?

Solution

By applying Henry's equation

$$\mathbf{C = K \times P}$$

$$\mathbf{P = \frac{C}{K} = \frac{2\times10^{-3}}{3.1\times10^{-2}} = 0.0645\,atm}$$

Example 2.3

At 20 °C, the concentration of dissolved Oxygen in water exposed to gaseous Oxygen at a partial pressure of 101.3 kPa (760 torr) is 1.38×10^{-3} mol.L^{-1}. Using Henry's law, determine the solubility of Oxygen when its partial pressure is 20.7 kPa (155.3 torr), the approximate pressure of Oxygen in earth's atmosphere.

Solution:

According to Henry's law, for an ideal solution the solubility, ***C***, of a gas (1.38×10^{-3} mol.L^{-1}, in this case) is directly proportional to the pressure, ***P***, of the undissolved gas above the solution (101.3 kPa, or 760 torr, in this case). Because we know both *C* and *P*, we can rearrange this expression to solve for *k*.

$$\mathbf{C = K \times P}$$

$$\mathbf{k = \frac{C}{P} = \frac{1.38\times10^{-3}mol.\,L^{-1}}{101.3\,kPa} = 1.36\times10^{-5}mol.\,L^{-1}.\,kPa^{-1}}$$

$$\mathbf{K = 1.82 \times 10^{-6}\ mol.L^{-1}.torr^{-1}}$$

Now we can use **k** to find the solubility at the lower pressure.

$$\mathbf{C = K \times P}$$

$$\mathbf{C = 1.36 \times 10^{-5} mol.L^{-1}.kPa^{-1} \times 20.7\ kPa}$$

$$\mathbf{(\,or = 1.82 \times 10^{-6} mol.L^{-1}.torr^{-1} \times 155\ torr)}$$

$$\mathbf{C = 2.82 \times 10^{-4} mol.L^{-1}}$$

2.9. Colligative Properties

Colligative properties are physical properties of solutions depend only on the **number** of solute particles in solution. Their **natures** (chemical structures) are not factors in determining these properties!

- ☐ **Vapor pressure lowering**
- ☐ **Boiling point elevation**
- ☐ **Freezing point depression**
- ☐ **Osmotic pressure**

2.9.1. Colligative properties of non-electrolytes

2.9.1.1. Vapor-Pressure Lowering

The pressure at which vapor is formed above a solid or liquid at a particular temperature is called the vapor pressure. Vapor and solid or liquid are in dynamic equilibrium at this temperature. In 1980s, Raoult discovered when a non-volatile solute is dissolved in a solvent the vapor pressure decreases.

According to Raoult's law, the vapor pressure of a solution containing a non-volatile solute is equal to the vapor pressure of pure solvent times the mole fraction of solvent.

$$\mathbf{P_{soln} = x_{solv}\, P^{\circ}_{solv}}$$

Where, $\mathbf{P^o_{solv}}$ **=** vapor pressure of the pure solvent

$\mathbf{X_{solv}}$ **=** mole fraction of the solvent

$\mathbf{P_{soln}}$ **=** Vapor pressure of the solution

For example, when a non-volatile solute is added to a pure solvent, molecules of solute block the surface of the solvent. This affects the evaporation of the solvent which results in decreased vapor pressure. Let's say P^o_{solv} is the vapor pressure of the solvent and P_{soln} is the vapor pressure of the solution. The lowering of vapor pressure (ΔP) will be ($P^o_{solv} - P_{soln}$).

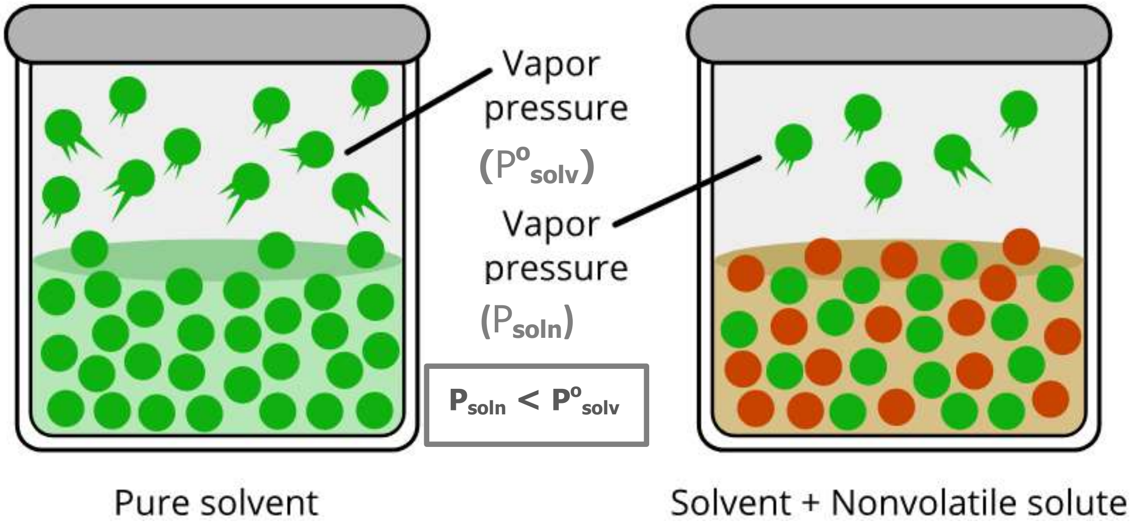


Figure 2. 15 Relative lowering of vapor pressure due to solute addition

$\Delta P = P^{o}_{\mathbf{solv}} - P_{\mathbf{soln}}$

$\Delta P = P^{o}_{\mathbf{solv}} - X_{\mathbf{solv}} \cdot P^{o}_{\mathbf{solv}}$

$\Delta P = P^{o}_{\mathbf{solvent}} (1- X_{\mathbf{solvent}}) = P^{o}_{\mathbf{solvent}} \cdot X_{\mathbf{solute}}$

If an ionic substance (electrolyte) such as NaCl is the solute, we have to calculate mole fraction based in the total concentration of solute particles

The mole fraction of water in a solution composed of 1.00 mole sugar (non-electrolyte) in 15.0 moles of water is

$$\mathbf{X}_{\text{water in a sugar soln.}} = \frac{\mathbf{15.0\ mole\ H_2O}}{(\mathbf{1.00\ mole\ sugar + 15.0\ moles\ H_2O})}$$

$$= \mathbf{0.938}$$

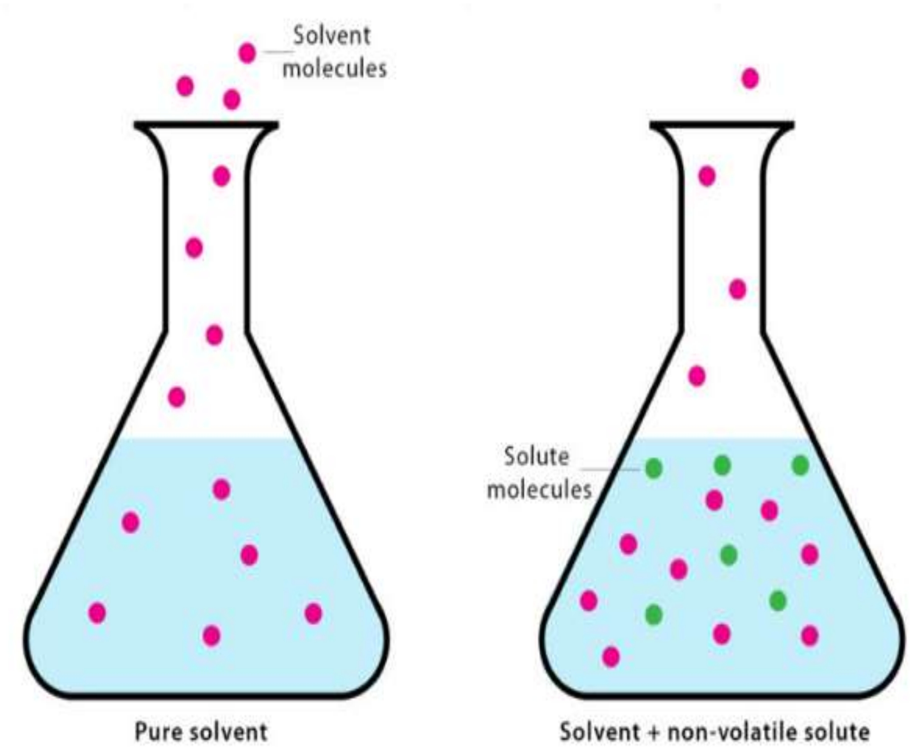
While the mole fraction of water in a solution composed of 1.00 moles NaCl (electrolyte) in 15.0 moles water is

$$\mathbf{X}_{\text{water in NaCl soln.}} = \frac{\mathbf{15.0\ mole\ H_2O}}{(\mathbf{1.00\ mole\ Na^{+} + 1.00\ mole\ Cl^{-} + 15.0\ moles\ H_2O})}$$

$$= \mathbf{0.883}$$

Raoult's Law

Vapor pressure of an ideal solution of a non-volatile solute is equal to the vapor pressure of the pure solvent at that temperature multiplied by its mole fraction



$$P_{soln} = x_{solv} P^{\circ}_{solv}$$

P^{o}_{solv} = vapor pressure of the pure solvent
X_{solv} = mole fraction of the solvent
P_{soln} = Vapor pressure of the solution

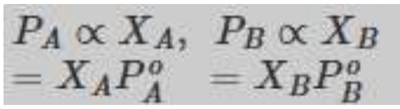
Figure 2. 16 Relative lowering of vapor pressure due to solute addition

Further, we will understand the principle behind the law by looking at the example below.

Consider a solution of volatile liquids A and B in a container. Because A and B are both volatile, there would be both particles of A and B in the vapor phase.

Hence, the vapor particles of both A and B exert partial pressure, which contributes to the total pressure above the solution.

Raoult's law further states that at equilibrium



$$P_A \propto X_A, \quad P_B \propto X_B$$
$$= X_A P_A^o \quad = X_B P_B^o$$

$\mathbf{P_A = P_A^\circ . x_A}$, $\mathbf{P_B = P_B^\circ . x_B}$

Where: P_A is the partial pressure of A.

$P°_A$ is the vapor pressure of pure A at that temperature.

x_A is the mole fraction of A in the liquid phase.

Similarly, P_B, $P°_B$, x_B

This new pressure (partial pressure) of each (A and B) is given by Raoult's law and depends on the concentration of each component in the liquid phase.

Hence,

$$\mathbf{P_T = P_A + P_B} \quad \textit{(Dalton's law)}$$
$$= \mathbf{P_A^\circ . x_A + P_B^\circ . x_B}$$

What Is the Importance of Raoult's Law?

From Raoult's law, it is evident that as the mole fraction of a component reduces, its partial pressure also reduces in the vapor phase.

Raoult's law is also quite similar to the ideal gas law. The only exception of Raoult's law is that it applies to solutions. The ideal gas assumes the ideal behavior of gases in which the intermolecular forces that are present between dissimilar molecules are zero or non-existent. On the other hand, Raoult's law assumes that the intermolecular forces that exist between different molecules and similar molecules are equal.

Example 2.4

Using Raoult's Law, find the vapor pressure lowering

Calculate the vapor pressure lowering, Δ*P*, when 10.0 mL of Glycerol ($C_3H_8O_3$) is added to 500 mL of water at 50°C. At this temperature, the vapor pressure of pure water is 92.5 torr and its density is 0.988 g/mL. The density of Glycerol is 1.26 g/mL.

Solution:

Number of moles of Glycerol is :

$$= \mathbf{10\ mL\ C_3H_8O_3} \times \frac{\mathbf{1.26\ g\ C_3H_8O_3}}{\mathbf{mL\ C_3H_8O_3}} \times \frac{\mathbf{mol\ C_3H_8O_3}}{\mathbf{92.09\ g\ C_3H_8O_3}}$$

$$= \mathbf{0.137\ mol\ C_3H_8O_3}$$

Number of moles of Water is :

$$= 500.0\ \text{mL H}_2\text{O} \times \frac{0.988\ \text{g H}_2\text{O}}{\text{mL H}_2\text{O}} \times \frac{\text{mol H}_2\text{O}}{18.02\ \text{g H}_2\text{O}}$$

$$= 27.4\ \text{mol H}_2\text{O}$$

The vapor pressure lowering is:

$$\boxed{\Delta P = x_{\text{solute}} \times P^{o}_{\text{solvent}}}$$

$$x_{\text{Solute}} = x_{H_2O} = \frac{0.137}{(0.137 + 27.4)} = 0.00498$$

$$\Delta P = \frac{0.137\ \text{mol C}_3\text{H}_8\text{O}_3}{0.137\ \text{mol C}_3\text{H}_8\text{O}_3 + 27.4\ \text{mol H}_2\text{O}} \times 92.5\ \text{torr}$$

$$\Delta P = 0.461\ \text{torr}$$

Example 2.5

When 8.05 g of unknown compound x was dissolve in 100 g of Benzene (C_6H_6), the vapor pressure of Benzene decreased from 100.0 torr to 94.8 torr at 26 °C. What is the mole fraction of solute? What is the molar mass of x?

Solution:

$$P_{\text{soln}} = x_{\text{solv}}\, P^{\circ}_{\text{solv}}$$

$$x_{\text{solv}} = \frac{P_{\text{soln}}}{P^{\circ}_{\text{solv}}}$$

$$x_{solute} = 0.052 = \frac{\mathbf{n}_{\text{Solute}}}{\mathbf{n}_{\text{Solute}} + \mathbf{n}_{\text{Solvent}}}$$

$$\mathbf{n}_{\text{Solvent}} = \frac{100.0\ \text{g}}{78\ \text{g/mol}} = 1.28\ \text{mol}$$

$$x_{solute} = 0.052 = \frac{\mathbf{n}_{\text{Solute}}}{\mathbf{n}_{\text{Solute}} + 1.28}$$

$$\mathbf{n}_{\text{Solute}} = 0.0702\ \text{mol}$$

The solute molar mass is:

$$\text{M.Wt} = \frac{\text{mass}_{(\text{Solute})}}{\text{number of moles}_{(\text{solute})}} = \frac{100\ \text{g}}{0.0708\ \text{mol}}$$

$$\text{M.Wt} = 115.9\ \text{g/mol}$$

2.9.1.2. Boiling point elevation (ΔT_B)

The **boiling point of the solution** is the temperature at which its vapor pressure equals the external atmospheric pressure.

As the addition of a non-volatile solute **lowers** the vapor pressure of solution, it was found that this **decrease** in the vapor pressure leads to an **increase in the boiling Point of the solution**.

Ex: Dissolve sugar in the water

The magnitude of the effect is proportional to solute concentration

$$\mathbf{T}_{bp} - \mathbf{T}_{bp}^{0} = \Delta T_b = \mathbf{K}_\mathbf{b} \times \mathbf{m}$$

m is the **molality** of the solution (mol/Kg)

K_b is the **molal boiling-point elevation constant** (°C/m)

T^0_{bp} is the **pure solvent boiling point**

T_{bp} is the **solution boiling point**

ΔT_b is the **boiling point elevation** or the change in the boiling point of the solution (+) $T_{bp} > T^0_{bp}$ & $\Delta T_b > 0$

Example 2.6

Calculate the boiling point of 2.47 m solution containing Naphthalene dissolved in Benzene. If the boiling point of pure Benzene is 80.1°C, K_b = 2.45 °C/m

Solution:

$$T_{bp} - T^0_{bp} = \Delta T_b = K_b \times m$$

$$\Delta T_b = K_b \times m = 2.45 \times 2.47 = 6.05°C$$

$$T_{bp} = T^0_{bp} + K_b \times m = 80.1 + 2.45 \times 2.47 = 86.15°C$$

2.9.1.3. Freezing point depression

Adding **solute** to **solvent lowers the freezing point** and **raises the boiling point** of the solvent.

- Solute particles disrupt crystallization and evaporation.
- The **change** in **freezing point** or **boiling point** is directly proportional to the **molality** of solute particles.
- A solute that produces more **ions** in solution has the greatest effect.

The magnitude of the depression in the freezing point is proportional to solute concentration

$$\Delta T_f = T_{fp}^0 - T_{fp} = K_f \times m$$

m : The **molality** of the solution (mol/Kg)

K_f : The **molal freezing-point depression constant** (°C/m)

T_{fp}^0: The **pure solvent freezing point**

T_{fp}: The **solution freezing point**

ΔT_f: The **freezing point depression** or the change in the freezing point of the solution (-) $T_{fp} < T_{fp}^0$ & $\Delta T_f < 0$

Example 2.7

When 1.0 g of a non-electrolyte solute dissolves in a given 50 g of benzene, it lowers its freezing point by 0.40 K. The freezing depression constant of benzene is given as 5.12 K/kgmol. Calculate the molar mass of the solute.

Solution:

Given wt. of solute (m_2) = 1g,

Wt. of solvent (m_1) =50g,

ΔT_f =0.40 K,

k_f = 5.12 K. kg mol^{-1}

Putting these values in the formula

$$\Delta T_f = k_f \times \text{molality}$$

$$\Delta T_f = k_f \times (\text{mol of solute/ wt. of solvent in kg})$$

$\Delta T_f = k_f \times (\text{wt. of solute} / (\text{Molecular wt. of solute} \times \text{wt. of solvent (kg)}))$

$\Delta T_f = k_f \times (1000 \times m_2 / M_2 \times m_1)$

$M_2 = k_f \times (1000 \times m_2 / \Delta T_f \times m_1)$

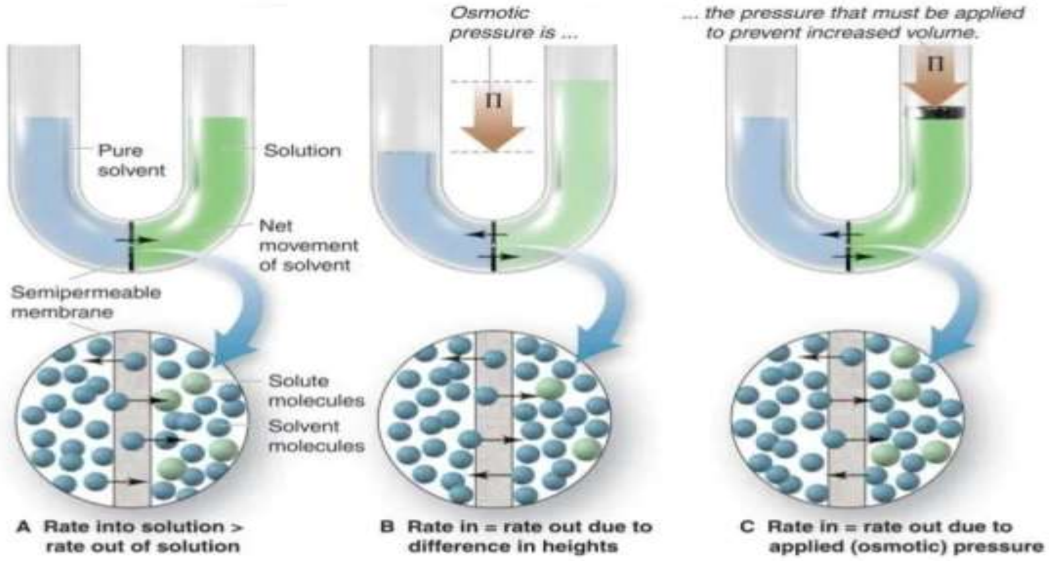
$M_2 = 5.12 \times (1000 \times 1 / 0.40 \times 50) = 256\ \text{gmol}^{-1}$.

2.9.1.4. Osmotic pressure (π)

Osmosis is the selective passage of **solvent** molecules through a **porous membrane** from a **dilute** solution to a **more concentrated** one.

A semipermeable membrane allows the passage of solvent molecules but blocks the passage of solute molecules.

Osmotic pressure (**π**) is the pressure required to stop osmosis



A Rate into solution > rate out of solution

B Rate in = rate out due to difference in heights

C Rate in = rate out due to applied (osmotic) pressure

Figure 2. 17 The development of Osmotic Pressure

For non-electrolyte solution:

$$\pi = \mathbf{M\,R\,T}$$

$\mathbf{M}$..... is the molarity of the solution.

$\mathbf{R}$ ......is the gas constant (0.0821 L.atm/mol.K)

T ......is the temperature (in K)

Example 2.8

300 cm^3 of an aqueous solution contains 1.56 g of a polymer. The osmotic pressure of such solution at 270 ^{o}C is found to be 2.57 × 10^{-3} bar. Calculate the molar mass of the polymer.

Solution:

Mass of polymer (m_1) = 1.56 g

Osmotic pressure (π) = 2.57 × 10^{-3} bar = 2.537× 10^{-3} atm

Volume (V) = 300 cm^3 = 0.3 L

Temperature = 270 °C + 273 = 543 K

$$\pi = \mathbf{M\,R\,T}$$

$$\mathbf{M} = \frac{\pi}{\mathbf{R\,T}} = \frac{2.537 \times 10^{-3}}{0.082 \times 543} = 5.698 \times 10^{-5}$$

To calculate the molar mass of the Polymer

$$\mathbf{M} = \frac{\mathbf{mass_{polymer}}}{\mathbf{M.Wt_{polymer}} \times \mathbf{Volume_{solution\,(L)}}}$$

$$5.698 \times 10^{-5} = \frac{m_1}{\mathbf{M_1} \times \mathbf{V}} = \frac{1.56\ \mathbf{g}}{\mathbf{M_1} \times 0.3\ \mathbf{L}}$$

$$\mathbf{M_1 = 91.26 \times 10^3\ g/mol}$$

2.7. Colligative Properties of Electrolyte Solutions

The Van’t Hoff factor offers insight on the effect of solutes on the colligative properties of solutions. It is denoted by the symbol ‘i’.The Van’t Hoff factor can be defined as the ratio of the concentration of particles formed when a substance is dissolved to the concentration of the substance by mass.

Vant hoff factor (i)

$$i = \frac{\textbf{Actual number of particles in solution after dissociation}}{\textbf{Number of formula units initially dissolved in Solution}}$$

The extent to which a substance associates or dissociates in a solution is described by the Van’t Hoff factor. For example, when a non-electrolytic substance is dissolved in water, the value of i is generally 1. However, when an ionic compound forms a solution in water, the value of i is equal to the total number of ions present in one formula unit of the substance.

For non-electrolyte i=1

For NaCl i=2 $NaCl \longrightarrow Na^+ + Cl^+$

For $CaCl_2$ i=3 $CaCl_2 \longrightarrow Ca^{++} + 2Cl^-$

- ❑ **Boiling point elevation of electrolyte solution = $i\, K_b\, m$**
- ❑ **Freezing point depression of electrolyte solution = $i\, K_f\, m$**
- ❑ **Osmotic pressure of electrolyte solution= $i\, MRT$**

Table 2. 2The Va n’t Hoff Factor of 0.05 M Electrolyte Solution at 25° C

Electrolyte	i (Measured)	i (Calculated)
Sucrose	1.0	1.0
HCl	1.9	2.0
NaCl	1.9	2.0
$MgSO_4$	1.3	2.0
$MgCl_2$	2.7	3.0
$FeCl_3$	3.4	4.0

Example 2.9

Calculate the osmotic pressure of 0.05 M $MgSO_4$ solution at 25 °C if you know that van't Hoff factor is 1.3

Solution:

R = 0.0821 L.atm/mol.K

T = 25 + 273 = 298 k

M = 0.05 mol/L

i = 1.3

$$\pi = \text{i M R T} = 1.3 \times 0.05 \times 0.082 \times 298$$

$$\pi = 1.59 \text{ atm}$$

Sheet no. (2)

1. Define the following:

Solution – Solute – Solvent – electrolyte – non electrolyte – saturated solution – solubility – unsaturated solution – supersaturated solution – mass percent – mole fraction – molality – Molarity – Osmotic pressure – Henry's law – colligative properties – Raoult's law.

2. Why are some solution processes exothermic others are endothermic?

3. What are the types of interactions in the solution process?

4. Calculate the molarity of 117 gm NaCl in 1/2 liter solution?

5. What are the effects of temperature on solid and gas solubilities?

6. When can we apply Henry's law?

7. The average osmotic pressure of seawater is 30 atm at 25^oC. **Calculate** the molar concentration of this aqueous solution.

8. Calculate the mole fraction of 128 gm HNO_3 in 720 gm water (H=1,N=14,O=16)

9. Calculate the boiling point of 3m sucrose in water solution if boiling point of water is 100 ^{o} C , where Kb=2.5 ^{o} C/m

10. The osmotic pressure of a 0.010 M potassium iodide (KI) solution at 25 ^{o}C is 0.465 atm. **Calculate** the Van't Hoff factor for KI at this concentration.

11. The osmotic pressure of 0.05 M **Magnesium sulfate ($MgSO_4$)** solution at 25 °C is 1.6 atm. **Calculate** the Van't Hoff coefficient of **$MgSO_4$** at this temperature.

12. Calculate the freezing point of a solution when adding 651 g of Ethylene glycol, EG, (**$C_2H_6O_2$**), to 2505 g of water. The molar mass of EG is 62.01 g, K_f = 1.86 °C/m and the pure water freezes at 0°C?

13. How would you prepare 100.0 mL of 0.2 M **H_2SO_4** from a stock solution of 2.00 M H_2SO_4?

14. Choose the correct answer:

- **5 cm^3 of a non-volatile solute is added to 100 cm^3 of water, the vapor pressure of water over the solution will be…**
  a. Equal to the vapor pressure of pure water.
  b. Less than the vapor pressure of pure water.
  c. Greater than the vapor pressure of pure water.
  d. Very large.

- **Which of the following aqueous solutions will be the best conductor of electricity?**
  a. NH_3
  b. CH_3COOH
  c. HCl
  d. $C_6H_{12}O_6$

- **People add Sodium Chloride to water while boiling eggs. This is to…**
  a. Decrease the boiling point.
  b. Increase the boiling point.
  c. Prevent the breaking of eggs.
  d. Make eggs tasty.

- **The law which indicates the relation between solubility of a gas in liquid and partial pressure is:**
  a. Raoult’s law
  b. Henry’s law
  c. Dalton's law
  d. Van’t Hoff law

- **The osmotic pressure of a solution can be increased by:**
  a. Increasing the volume
  b. Increasing the number of solute molecules
  c. Decreasing the temperature
  d. Removing semipermeable membrane

- **Which of the following units is useful in relating concentration of solution with its vapor pressure?**
  a. Mole fraction
  b. Parts per million
  c. Mass percentage
  d. Molality

- **How much Oxygen is dissolved in 100 mL water at 298 K if partial pressure of Oxygen is 0.5 atm and K = 1.4×10^{-3} M/atm?**
  a. 22.4 mg
  b. 22.4 g
  c. 2.24 g
  d. 2.24 mg

- **A solution that can hold more solute is called**
  a. saturated
  b. supersaturated
  c. unsaturated

d. Insoluble

Chapter (3)

Chemical Equilibrium

Chapter (3) Chemical Equilibrium

3.1. Static and Dynamic Equilibrium

The state equilibrium can be observed in physical and chemical systems. Also, equilibrium can be static or dynamic in nature. The forces of action and reaction cancel each other and no change takes place. Thus it is a case of static equilibrium.

On the other hand, when an escalator is coming down and a passenger is going up at the same speed it is a case of dynamic equilibrium. Here, because both are moving in opposite directions and at the same speed, no net change takes place. The equilibrium established in the above example occurs in physical systems.

Equilibrium is the state where the concentrations of all reactants and products remain constant with time.

Chemical equilibrium is achieved when:

- The rates of the **forward** and **reverse** reactions are equal and
- The concentrations of the **reactants** and **products** remain constant

A common example of reversible reactions of the type A + B ⇋ C+ D

$$\mathbf{CH_3COOH + C_2H_5OH \leftrightharpoons CH_3COOC_2H_5 + H_2O}$$

The following graph shows the equilibrium state in a reversible reaction.

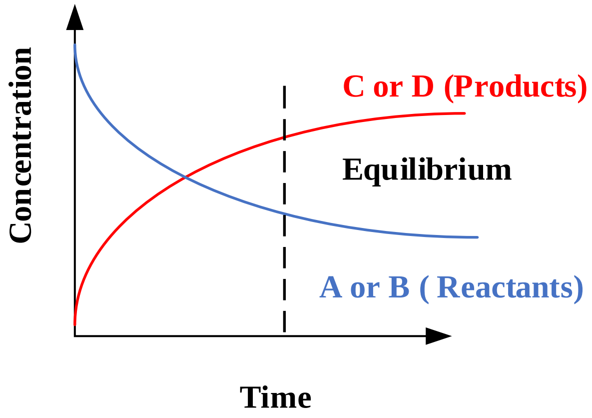


Figure 3. 1 Equilibrium state in a reversible reaction

$$A + B \leftrightharpoons C+D$$

The graph depicts that the rate of forward reactions gradually decreases while the rate of backward reaction gradually increases till they become constant and equal to each other.

3.2. Equilibrium Constant and Chemical Equation (Kc)

The expression of equilibrium constant depends upon the manner in which the chemical equation representing it is written.

$$a\,A + b\,B \rightleftarrows c\,C + d\,D$$

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

For the reaction

$$H_{2(g)} + I_{2(g)} \leftrightharpoons 2HI_{(g)}$$

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

For the reaction

$$N_2O_{4\,(g)} \leftrightharpoons 2\,NO_{2\,(g)}$$

$$k_C = \frac{[NO_2]^2}{[N_2O_4]}$$

3.3. Homogenous equilibrium

A homogeneous equilibrium is defined as a homogeneous mixture (reactants and products in a single solution) in one phase. The usual examples include reactions where everything is a gas, or everything is present in the same solution.

$$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$$

$$K_C = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

$[H_2O]$ = constant

➢ Pressure Equilibrium Constant (K_p)

In case of gases their partial pressures can also be used in place of the molar concentrations (since the two are directly proportional to each other) in the equilibrium law. The new equilibrium constant **(K_p)** is called the pressure equilibrium constant.

$$K_P = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^B}$$

$$N_2O_4\,_{(g)} \leftrightharpoons 2\,NO_2\,_{(g)}$$

$$K_P = \frac{P^2_{NO_2}}{P_{N_2O_4}} \qquad K_c = \frac{[NO_2]^2}{[N_2O_2]}$$

In most cases

$$K_c \neq K_P$$

$$aA_{(g)} + bB_{(g)} \rightleftarrows cC_{(g)} + dD_{(g)}$$

$$\boxed{K_p = K_c\,(RT)^{\Delta n}}$$

Δn = moles of gaseous products – moles of gaseous reactants

$\Delta n = (c + d) - (a + b)$

Example 3.1

The equilibrium concentrations for the reaction between Carbon monoxide and molecular Chlorine to form $COCl_2\,_{(g)}$ at 74° C are $[CO] = 0.012$ M, $[Cl_2] = 0.054$ M, and $[COCl_2] = 0.14$ M. Calculate the equilibrium constants K_c and K_p.

$$CO_{(g)} + Cl_2\,_{(g)} \rightleftarrows COCl_2\,_{(g)}$$

Solution:

$$T = 273 + 74 = 347\ K$$

$$K_c = \frac{[COCl_2]}{[CO][Cl_2]} = \frac{0.14}{0.012 \times 0.054} = 220$$

$$K_p = K_c\,(R\,T)^{\Delta n}$$

$$\Delta n = 1 - 2 = -1$$

$$K_p = 220 \times (0.0821 \times 347)^{-1} = 7.582$$

Example 3.2

The equilibrium constant (K_p) for the reaction;

$$2NO_{2\,(g)} \rightleftarrows 2NO_{(g)} + O_{2\,(g)}$$

is 158 at 1000 K. What is the equilibrium pressure of O_2 if P_{NO2} = 0.40 atm and P_{NO} = 0.270 atm

Solution:

$$K_P = \frac{P_{NO}^2 P_{O_2}}{P_{NO_2}^2}$$

$$P_{O_2} = K_P \frac{P_{NO_2}^2}{P_{NO}^2}$$

$$P_{O_2} = 347\ atm$$

3.4. Heterogeneous equilibrium

Consider the following equilibrium

$CaCO_3$ (s) ⇋ CaO (s) + CO_2 (g)

Here $CaCO_3$ and CaO are pure solids. The concentration of any solid is constant at a fixed temperature, therefore these are not written in expression for equilibrium constant for heterogeneous reactions. Equilibrium constants for the reaction can be written as

$K_c = [CO_2]$ and **$K_p = P_{CO2}$**

The concentration of solids and pure liquids are not included in the expression for the equilibrium constant.

Example 3.3

Consider the following equilibrium at 295 K:

$$NH_4HS\,(s) \rightleftharpoons NH_3\,(g) + H_2S\,(g)$$

The partial pressure of each gas is 0.265 atm. Calculate K_p and K_c for the reaction?

Solution:

$$K_p = P_{NH3} \times P_{H2S} = 0.265 \times 0.265 = 0.0702$$

$$K_p = K_c (R\,T)^{\Delta n} \qquad K_c = K_p (R\,T)^{-\Delta n}$$

$$\Delta n = 2 - 0 = 2$$

$$T = 295\ K$$

$$K_c = 0.0702 \times (0.0821 \times 295)^{-2} = 1.20 \times 10^{-4}$$

Example 3.4

Calculate the equilibrium constant for the reaction

$$A_{(g)} + B_{(g)} \leftrightharpoons C_{(g)} + D_{(g)}$$

If at equilibrium 1 mol of A, 0.5 mole of B, 3.0 mole of C and 10.0 mol of D are present in 1.0-L vessel.

Solution:

From the equilibrium law

$$K_c = \frac{[C][D]}{[A][B]}$$

$$K_c = \frac{3 \times 10}{1 \times 0.5} = 60$$

Example 3.5

In an experiment carried out at 298 K, 4.0 mol of NOCl were placed in a 2-L flask. After equilibrium was reached, 1.32 mol of NO were formed. Calculate K_c at 298 K for the reaction

$$2NOCl\ (g) \leftrightharpoons 2\ NO\ (g) + Cl_2\ (g)$$

Solution:

	2 NOCl (g)	⇋	2 NO (g)	+	Cl_2 (g)
Initial	4		0		0
Change	X		X		0.5 X
Equilibrium	(4 - X)		X		0.5 X

From given data,

X= 1.32

At equilibrium:

$$K_c = \frac{[NO]^2[Cl_2]}{[NOCl]^2}$$

$$[NOCl] = \frac{4-1.32}{2} = 1.34\ \text{mol/L}$$

$$[NO] = \frac{1.32}{2} = 0.66\ \text{mol/L}$$

$$[Cl_2] = \frac{(1.32/2)}{2} = 0.33\ \text{mol/L}$$

$$K_c = \frac{0.33 \times (0.66)^2}{1.34^2} = 0.08$$

Note no. (1)

For the reaction: N_2O_4 (g) $\leftrightharpoons$ $2NO_2$ (g)

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

So for the reverse reaction: $2NO_2$ (g) $\leftrightharpoons$ N_2O_4 (g)

$$K' = \frac{[N_2O_4]}{[NO_2]^2} = \frac{1}{K}$$

When the equation for a reversible reaction is written in the opposite direction, the equilibrium constant becomes the reciprocal of the original equilibrium constant

Note no. (2)

For the reaction $A \leftrightharpoons B$ Rate constant = K1

So for the reaction n × ($A \leftrightharpoons B$) Rate constant $K_2 = (K1)^n$

Example 3.6

If K_c = 1.5 x 10^2 at 100°C for the reaction;

$$2\,SO_{2\,(g)} + O_{2\,(g)} \leftrightharpoons 2\,SO_{3\,(g)}$$

What will be the value of K_c for the reaction;

$$SO_{2\,(g)} + \tfrac{1}{2}\,O_{2\,(g)} \leftrightharpoons SO_{3\,(g)}?$$

Solution:

- K_c for first reaction $= (\mathbf{Kc\ for\ second\ reaction})^2$
- K_c for second reaction $= \sqrt[2]{1.5 \times 10^2} = 12.25$

Example 3.7

If Kc = 8 at 100°C for the reaction, $2A_{(g)} + B_{(g)} \leftrightharpoons 2C_{(g)}$, then what is the value of Kc for the reaction, $2C_{(g)} \leftrightharpoons 2A_{(g)} + B_{(g)}$?

Solution:

$$K_c = \frac{1}{8} = 0.125$$

3.5. Factors Affecting Equilibrium State

Supposing a reaction has reached the equilibrium state and then some conditions like concentrations, temperature, pressure etc. are changed, would it be affecting the equilibrium state. If yes how? In this section, we shall discuss these questions.

The state of equilibrium is in a dynamic balance between forward and backward reaction. This balance can be disturbed by changing concentration, temperature or pressure. If done so a certain net change occurs in the system. The direction of change can be predicted with the help of **Le Châtelier Principle.** The principle can be applied to various situations.

3.5.1. Change in Concentration

Consider the state of equilibrium for the formation of ammonia from nitrogen and hydrogen

$$2N_2\,(g) + 3H_2\,(g) \quad \leftrightharpoons \quad 2NH_3\,(g), \;\; \Delta H = -92.4 \text{ kJ/mol}$$

The concentration of Nitrogen, Hydrogen and Ammonia become constant at the point of equilibrium. Now if any amount of reactants or Ammonia is added or removed their concentration will change and the equilibrium will get disturbed.

- **Increase concentration of reactant:** When the concentration of either Nitrogen or Hydrogen is increased; a net forward reaction will take place which consumes the added reactant.

- **Increase in the concentration of any product:** If the concentration of product Ammonia is increased, a net backward reaction would take place to utilize the added Ammonia.

3.5.2. Change in Pressure

Change in pressure affects equilibrium involving gaseous phase either in a homogeneous or heterogeneous system.

Le Chatelier principle for systems involving gases can be studied as follows:

- **When the pressure increased** the equilibrium shift to side of fewest moles of gas

- **When the pressure decreased** the equilibrium shift to side of largest moles of gas

- **When there is no change** in the total number of moles of reactant and product as in the following state of equilibrium.

$$H_2\ (g) + I_2\ (g) \leftrightharpoons 2HI$$

There is no net change in equilibrium state when pressure is changed.

3.5.3. Change of Temperature

- **Effect of Changing Temperature on the Equilibrium state**

According to Le Chatelier principle, when the temperature is changed (increased or decreased) the equilibrium system reacts to nullify the change in heat content. However, the net change in equilibrium is directed by the exothermic or endothermic nature of reaction.

- **Exothermic Equilibrium:** For the following system of equilibrium of exothermic nature:

$$N_2\ (g) + 3H_2\ (g) \leftrightharpoons 2NH_3\ (g) \qquad \Delta H = -\ 92.4\ \text{kJ/mole}$$

According to Le Chatelier principle **increase in temperature** brings a net change in the equilibrium state in that direction where this extra heat is consumed. The net change is in the **backward** direction and some Ammonia will decompose producing Nitrogen and Hydrogen.

Similarly, if the temperature is **decreased** the equilibrium shifts to the **forward** direction.

- **Endothermic Equilibrium**

$N_2\ (g) + O_2\ (g) \leftrightharpoons 2NO(g) \qquad \Delta H = 180.7\ kJ/mole$

If the temperature is **increased** the added heat will be absorbed by the reactant and the net change takes place to the equilibrium in the **forward direction**. If the temperature in **decreased** it will bring a 'net' change to equilibrium in the **backward** direction.

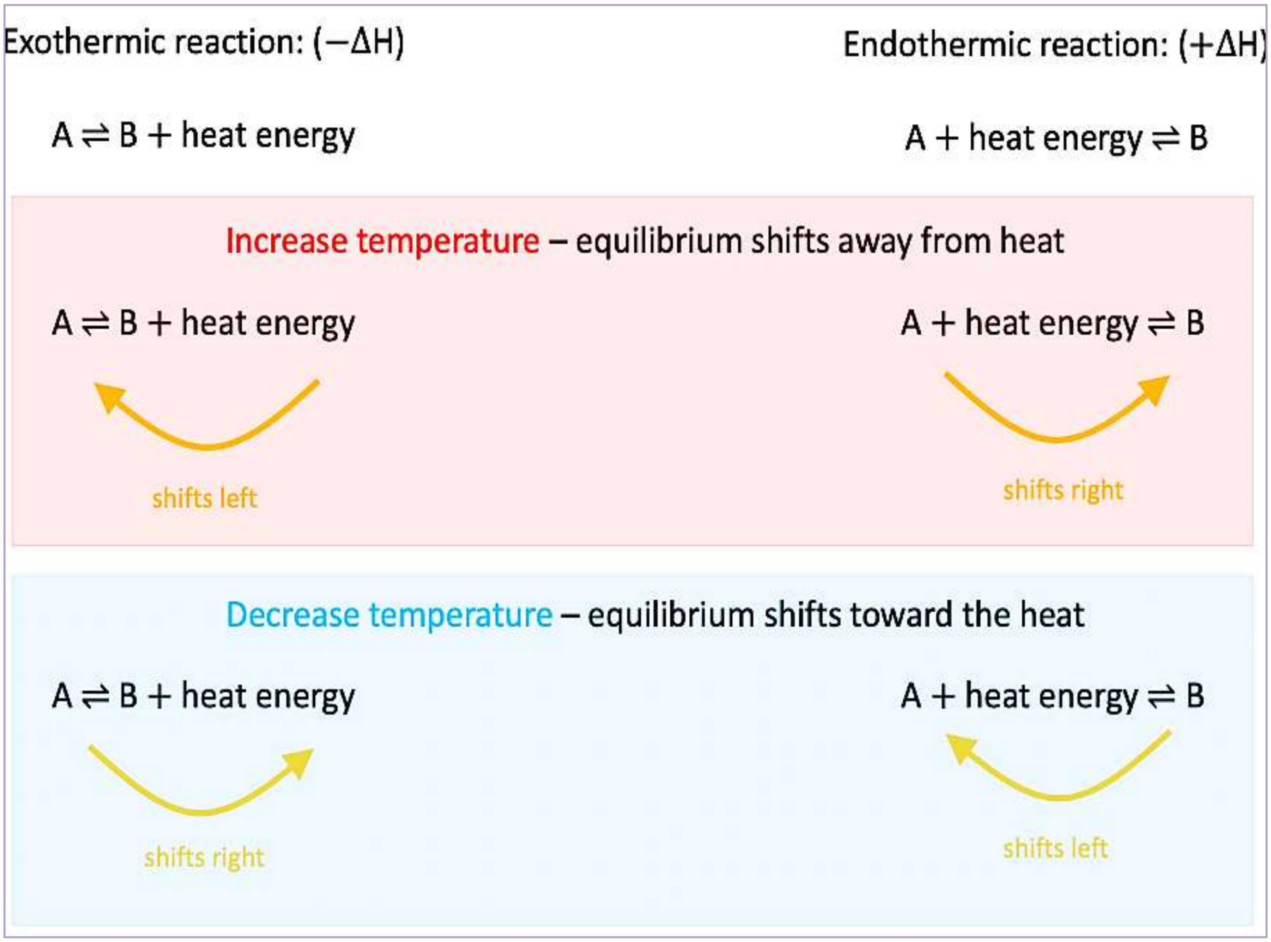


Figure 3. 2 Effect of temperature on equilibrium

- **Effect of Changing Temperature on the Value of the Equilibrium Constant:**

❑ Equilibrium constants are changed if you change the temperature of the system. Kc or Kp are constant at constant temperature, but they vary as the temperature changes.

❑ The value of the equilibrium constant K falls as the temperature increases with any equilibrium where the forward reaction is exothermic.

- ☐ Where the forward reaction is endothermic, increasing the temperature will increase the value of the equilibrium constant.

- **Temperature Dependence of Equilibrium Constants measured using Van't Hoff Equation:**

  The effect of changing temperature on the equilibrium constant can be calculated by using Van't Hoff equation

$$\frac{d\ \ln K}{d\ T} = \frac{\Delta\ H_r^{\circ}}{R\ T^2}$$

R is the Ideal Gas Constant

T is the absolute temperature

ΔH_r^{o} = Standard reaction enthalpy

If we integrate the above equation from T_1 to T_2, we get

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta\ H^{\circ}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

We can also integrate the above equation, to obtain,

$$\ln K = -\frac{\Delta\ H_r^{\circ}}{R\ T} + C$$

According to the above equation, lnK varies with temperature **linearly.** However, the slope is equal to – $\Delta Hr^{o}/R$

For Exothermic Reactions

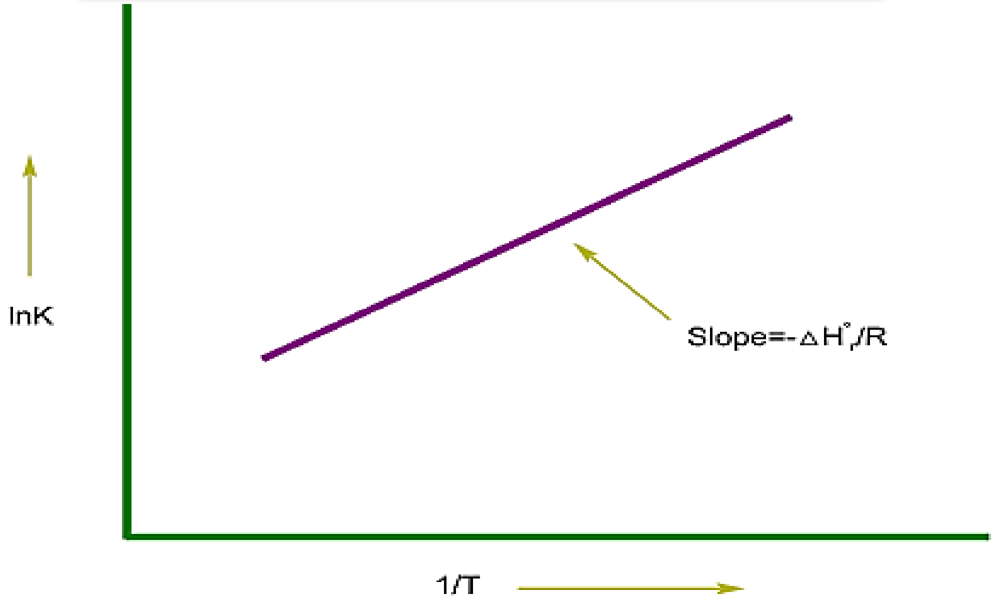


Figure 3. 3 The plot of (lnK) versus (1/T) when ΔH_r° is negative

For Endothermic Reaction

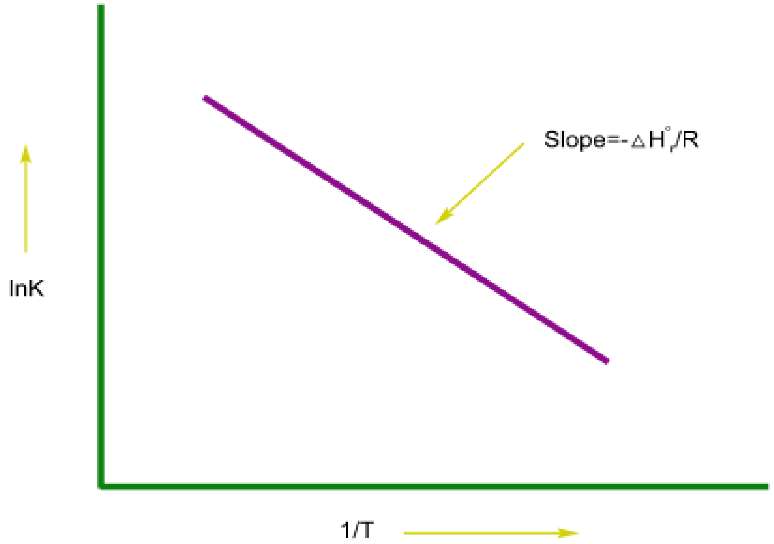


Figure 3. 4 The plot of (lnK) versus (1/T) when ΔH_r° is positive

Example 3.7

A certain reaction has a value of the equilibrium pressure constant (K_p) = 0.0260 at 25°C, Where ΔH^o_r = 32.4 kJ/mol. Calculate the value of K_p at 37 °C.

Solution:

This is a job for the van 't Hoff equation!

- $T_1 = 298$ K
- $T_2 = 310$ K
- $\Delta H^o_r = 32.4$ kJ/mol
- $K_1 = 0.0260$
- $K_2 = ?$

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H^\circ_r}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{K_2}{0.026}\right) = -\frac{32400\ \mathrm{J/mol}}{8.314\mathrm{J/(mo\ K)}}\left(\frac{1}{310} - \frac{1}{298}\right)$$

K_2= 0.0431

Note: the value of K_2 **increased** with **increasing** temperature, which is what is expected for an **endothermic** reaction. An increase in temperature should result in an increase of product formation in the equilibrium mixture. But unlike a change in pressure, a change in temperature actually leads to a change in the value of the equilibrium constant.

3.5.4. Addition of a Catalyst

It does not affect the equilibrium. However, it helps to achieve the equilibrium faster.

So adding a Catalyst

- Does not change **K**
- Does not shift the position of an equilibrium system
- System will reach equilibrium sooner

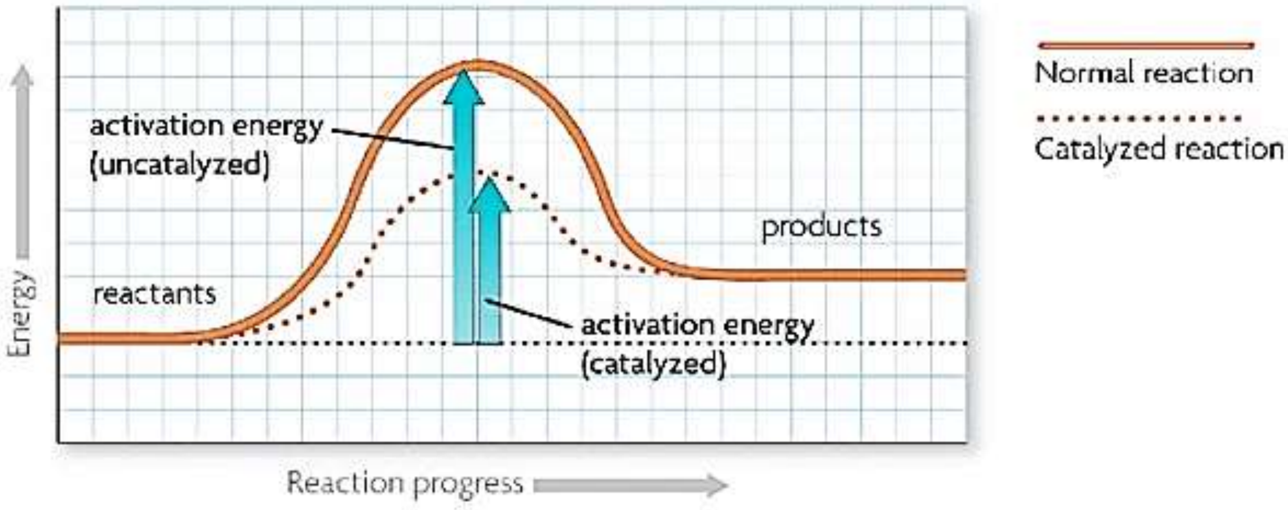


Figure 3. 5 Catalyst lowers E_a (activation energy) for both forward and reverse reactions.

Catalyst does not change equilibrium constant or shift equilibrium

Example 3.8

What will be the effect of the following factors on the following systems at equilibrium?

$$2\,X\,(g) \leftrightharpoons 2Y\,(s) + Z\,(g); \qquad \Delta H = +\,ve$$

(i) Addition of X,
(ii) removal of Z
(iii) addition of a catalyst
(iv) increasing the pressure
(v) Increasing the temperature.

Solution:

i. Addition of X makes net change takes place to the equilibrium in the **forward direction**.

ii. Removal of Z, will shift equilibrium to the forward direction

iii. Addition of a catalyst, system will reach equilibrium sooner and a change in the equilibrium direction will never occur

iv. Increasing the pressure will shift the system to the side of fewer numbers of moles. As the product side contains only one mole of Z, while the reactant side contains 2 moles of X, therefore, the equilibrium will shift to the forward direction and more Z will be produced.

v. As the reaction is endothermic reaction (ΔH is positive), therefore, by increasing the temperature, the added heat will be absorbed by the reactant and the net change takes place to the equilibrium in the **forward direction**.

Sheet no. (3)

1. Define:

Equilibrium – chemical equilibrium

2. What is the effect of a catalyst on equilibrium state?

3. Write the equilibrium constant Kc expression for the following reactions

a. $3\ Fe_{(s)} + 4H_2O_{(g)} \leftrightharpoons Fe_3O_{4(s)} + 4H_{2(g)}$

b. $CH_{4(g)} + 2\ H_2O_{(g)} \leftrightharpoons CO_{2\ (g)} + 4H_{2(g)}$

c. $CaCO_{3(s)} \leftrightharpoons CaO_{(s)} + CO_{2(g)}$

d. $H_{2(g)} + I_2\ (g) \leftrightharpoons 2HI_{(g)}$

4. If Kc = 2 at 100°C for the reaction, $2\ A_{(g)} + B_{(g)} \leftrightharpoons 2\ C_{(g)}$, then **what** is the value of **Kc** for the reaction, $4\ C_{(g)} \leftrightharpoons 4\ A_{(g)} + 2\ B_{(g)}$?

5. What is the value of Kp for the reaction $2\ NOCl_{(g)} \leftrightharpoons 2\ NO_{(g)} + Cl_{2\ (g)}$ at 400 °C if Kc for this reaction is $2.1\text{x}10^{-2}$ mol/L?

6. What is the effect of decreasing pressure on the following reactions?

$$C_{(s)} + CO_{(g)} \leftrightharpoons 2CO_{(g)}$$

$$2HI_{(g)} \leftrightharpoons H_{2\ (g)} + I_{2\ (g)}$$

7. The equilibrium constant K_p for the decomposition of

$$PCl_{5\,(g)} \leftrightharpoons PCl_{3\,(g)} + \grave{}\,Cl_{2(g)}$$

is 1.05 at 250 ^oC . If the equilibrium partial pressures of PCl_5, and PCl_3 are 0.875 atm and 0.463 atm, respectively. **What** is the equilibrium partial pressure of Cl_2 at 250 ^oC.

8. Consider the following system at equilibrium:

$$CH_{4\,(g)} + 2H_2O_{\,(g)} \leftrightharpoons CO_{2\,(g)} + 4H_{2\,(g)}$$

What changes will cause the equilibrium to shift to form more CO_2?

9. What is the value of K_p for the reaction $2\ COCl_{\,(g)} \leftrightharpoons 2\ CO_{\,(g)} + Cl_{2\,(g)}$ at 900 °C if Kc for this reaction is 0.083 mol/L?

10. At 300^OC, the equilibrium constant (Kc = 0.016) for the reaction

$$N_{2(g)} + O_{2\,(g)} \leftrightharpoons 2NO_{\,(g)}$$

At equilibrium the molar concentration of N_2 and O_2 are 0.04 and 0.06 M, respectively. **Calculate** the concentration of NO g at equilibrium.

11. Write the expression relates K_p to K_c for the following reactions:

$$2\ A_{\,(g)} + B_{\,(g)} \leftrightharpoons C_{\,(g)}$$

$$3\ A_{\,(g)} + 2\ B_{\,(g)} \leftrightharpoons 5C_{\,(g)}$$

12. Which procedure will shift the equilibrium reaction from right to left?

$$A_{(g)} + 2B_{\,(g)} \leftrightharpoons C_{(g)} + D_{\,(g)}$$

13. What happened if the temperature increased for the following reaction?

$$2SO_{3(g)} + \Delta H \leftrightharpoons 2SO_{2(g)} + O_{2(g)}$$

14. Choose the correct answer:

i. When this system A + B $\rightleftharpoons$ C + D is at equilibrium………

a. The sum of the concentrations of A and B must equal the sum of the concentrations of C and D.

b. The forward reaction has stopped.

c. The reverse reaction has stopped.

d. Neither the forward nor the reverse reaction has stopped.

ii. Consider the equilibrium system: $2ICl(s) \rightleftharpoons I_2(s) + Cl_2(g)$, which of the following changes will increase the total amount of Cl_2 that can be produced?

a. Removing some of the $I_2(s)$

b. Adding more ICl(s)

c. Removing the Cl_2 as it is formed

d. Decreasing the volume of the container

iii. What will be the effect of decreasing pressure on the following systems at equilibrium

$$A(g) + B(g) \rightleftharpoons C(g)$$

a. The equilibrium shifts to the left

b. The equilibrium shifts to the right

c. There is no change in the system

iv. Which one of the following statements regarding a dynamic equilibrium is false?

a. At equilibrium, there is no net change in the system.

b. At equilibrium, the concentration of reactants and products stays the same.

c. At equilibrium, the forward and back reactions stop .

d. At equilibrium, the rates of the forward and back reactions are identical.

v. **For the following equilibrium reaction $A_{(g)} + B_{(g)} \rightleftharpoons 4C_{(g)}$ $\Delta H = +58$ kJ, Under which set of the following conditions would the highest concentration of $C_{(g)}$ be obtained?**

a. Temperature = 50°C, Pressure = 200 kPa

b. Temperature = 300°C, Pressure = 200 kPa

c. Temperature = 50°C, Pressure = 100 kPa

d. Temperature = 300°C, Pressure = 100 kPa

vi. **Which one of the following equilibrium reactions is not affected by pressure change?**

a. $N_{2(g)} + 3H_{2(g)} \leftrightharpoons 2NH_{3(g)}$

b. $H_{2(g)} + I_{2(g)} \leftrightharpoons 2HI_{(g)}$

c. $PCl_{3(g)} + Cl_{2(g)} \leftrightharpoons PCI_{5(g)}$

d. $2NO_{2(g)} \leftrightharpoons N_2O_{4(g)}$

vii. **On increasing the concentration of reactants in a reversible reaction, then equilibrium constant value will …..**

a. Depend on the concentration

b. Increase

c. Remain unchanged

d. Decrease

viii. **If the equilibrium constant for the reaction $A+2B \leftrightharpoons C + 2.5\ D$ has a value of 4.0, what is the value of the equilibrium constant for the reaction $2C + 5D \leftrightharpoons 2A + 4B$?**

a. 0.25

b. 0.063

c. 2.0
d. 8.0

Chapter (4)

Mass and Energy Balance

Chapter (4) Mass and Energy Balance

4.1. Introduction

Material balance involves calculating the quantities of all materials that enter and leave any system or process as well as what goes on internally. Without accurate material balances, it is impossible to design or operate a chemical plant safely and economically. They are almost always prerequisite to all other calculations in the solution of process engineering problems. Material balances are nothing more than the application of the law of conservation of mass, which states that mass can neither be created nor destroyed. In industry, they are used to calculate mass flow rates of different streams entering or leaving chemical or physical processes.

The importance of material balances for a Chemical engineer

- They are the basis of process design
- They allow the design of process' units themselves by determining the quantities of raw materials required for a certain required productivity.
- They represent a real useful tool for studying plant; operations, troubleshooting, checking actual plant performance versus the design performance and can help locate sources of material loss.
- When we learned material balances, we were able to track the movement of chemical species throughout a system or process.

The first material balances are determined in the exploratory stages of a new process, improved during pilot plant experiments when the process is being planned and tested, checked out when the plant is commissioned and then refined and maintained as a control instrument as production continues.

Similar to mass balances, a balance on energy is crucial to solving many problems. The concept of energy conservation as expressed by an **energy balance** is central to chemical engineering calculations, **why?**

- ♣ The increasing cost of energy has caused the industries to examine means of reducing energy consumption in processing.
- ♣ Energy balances are used in the examination of the various stages of a process, over the whole process and even extending over the total production system from the raw material to the finished product.
- ♣ Another important aspect of process analysis is the determination of the energy requirements and temperatures around systems.

4.2. Material balance

Material balances also called mass balances, is an application of the law of conversation of mass, which states matters is neither created nor destroyed.

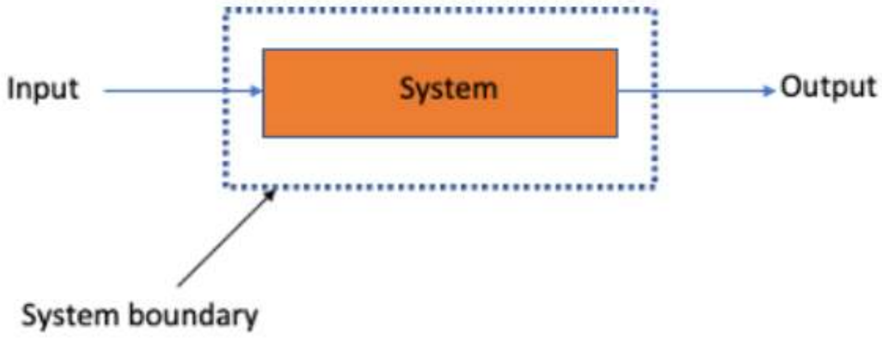


Figure 4. 1 Overall material balance approach

The material balance can be seen as the accounting for materials that enter and leave a process and accounts for all materials even if they undergo chemical reactions, separation, heating, cooling, mixing, drying or any other operation that occurs in the system.

4.2.1. Material Balance without Chemical Reactions

The balance results simply from the application of the principle of conservation of matter to a particular unit operation or group of processing units. It is readily understood that for a physical process such as a **mixing** or **distillation**: Under **steady state** conditions.

Steady-state operation

Under steady-state conditions, the values of all variables associated with the process do not change with time. That is, at any given location in the process, the values of temperature, pressure, composition, flowrates, etc. are independent of time. Even though a process may be steady state, it is important to realize that temperature, flow rates, or other variables may, and typically do, change from one location to another (e.g. from one process stream to another).

Steady state material balance without chemical reaction:

$$\sum \text{Mass In} = \sum \text{Mass Out}$$

$$\sum \text{Moles In} = \sum \text{Moles Out}$$

Overall Material Balance (OMB) :

Total amount of matter in = Total amount of matter out

Component Material Balance (CMB):

Amount of component (i) in = amount of component (i) out

4.2.1.1. Solving Material Balance Problems for Single Units without Chemical Reactions

1. Mixing unit (Mixer):

Mixer combines **two or more inputs** (usually of different compositions) into a **single output** (no reaction)

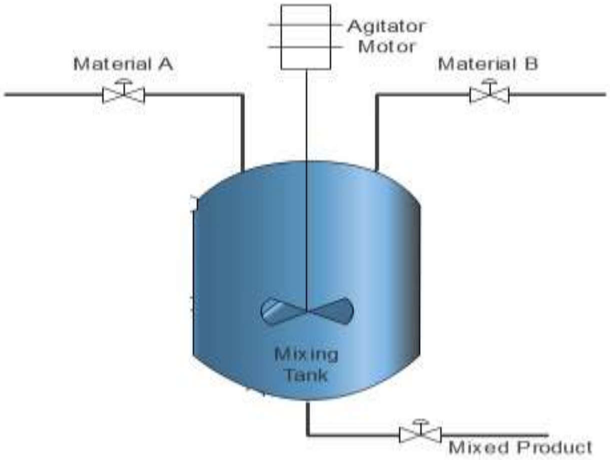


Figure 4. 2 Mixing Tank

Example 4.1

A mixing unit is fed with three streams; the first stream is 20 Kg of mixture A and B. The second stream is 60Kg of A, B (20% A) and the third stream is 30 Kg of A and B (50% A). If the final product contains 40% A. Find the composition of each stream.

Solution:

- **Over all mass balance**

$$M_1 + M_2 + M_3 = M_4$$

$$60 + 20 + 30 = M_4$$

$$M_4 = 110 \text{ Kg}$$

- **Component Material Balance on component (A)**

$$20 \times (\text{mass \% A})_{M1} + 60 \times 0.8 + 30 \times 0.5 = 110 \times 0.6$$

$$(\text{mass \% A})_{M1} = 15 \ \%$$

- **Component Material Balance on component B**

$$20 \times (\text{mass \% B})_{M1} + 60 \times 0.8 + 30 \times 0.5 = 110 \times 0.6$$

$$(\text{mass \% B})_{M1} = 15\ \%$$

2. Separating Unit (Separator):

Ex: Distillation Unit

Separators separate a single input into two or more outputs of different composition (no reaction)

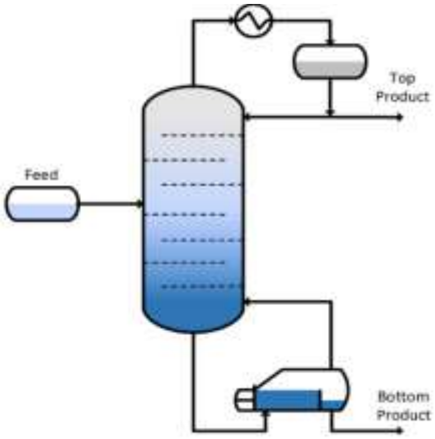


Figure 4. 3 Distillation Unit

Example 4.2

A distillation unit is feed with 30 Kg/sec with 30 % (by mass) Ethanol. If the concentration of Ethanol in the distillate stream is 95 % (by mass) and that in the bottom product is 2%. Calculate the total amount (mass) of distillate & bottom products.

Solution:

- **Over all mass balance**

$$F = D + B$$

$$30 = D + B \qquad \therefore D = 30 - B$$

- **Component mass balance with respect to ethanol**

F × (mass % Ethanol) $_F$ = D × (mass % Ethanol) $_D$ + B × (mass % Ethanol) $_B$

Let x = mass % and Ethanol = A, then the mass balance equation can be written in the following form:

$$F \times (x_A)_F = D \times (x_A)_D + B \times (x_A)_B$$

$$30 \times 0.3 = D \times 0.95 + B \times 0.02$$

9 = 0. 95 D + 0.02 B

9 = 0. 95 D + 0.02 (30 - D)

9 = 0.95 D + 0.6 + 0.02 D

8.4 = 0.93 D

D = 9.03 Kg/sec

B = 30 - 9.03 = 20.97 Kg/sec

4.2.2. Material balance with Chemical reaction

Reactor – carries out a chemical reaction that converts atomic or molecular species in the input to different atomic or molecular species in the output

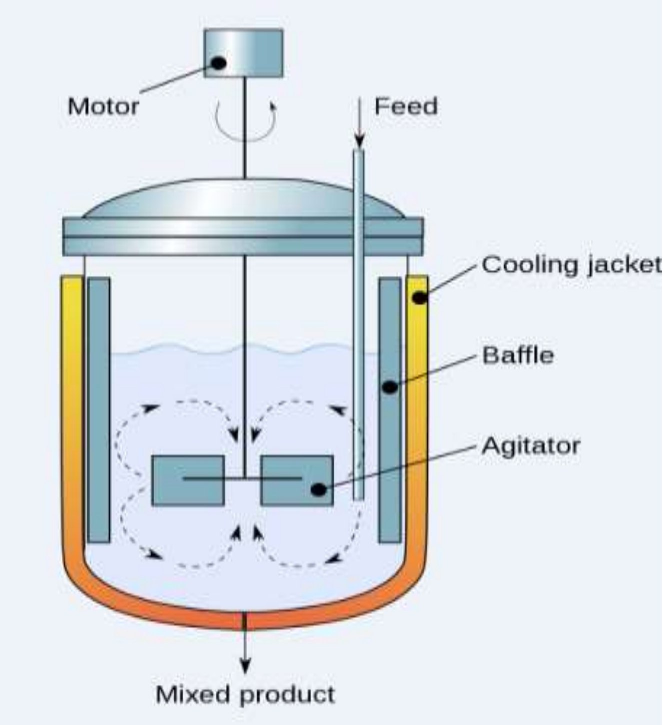


Figure 4. 4 A Chemical Reactor Unit

Material Balance for Reacting system:

The Chemical Reaction Equation and Stoichiometry

$$\sum \text{Mass of Reactant} = \sum \text{Mass of Product}$$

$$\sum \text{Mole of Reactant} \neq \sum \text{Mole of Product}$$

The overall mass balance will remain the same as in the previous case

Material Balances Involving Combustion

Combustion, or burning, is a high-temperature exothermic chemical reaction between a **fuel** (Hydrocarbon) and an oxidant, usually atmospheric **Oxygen,** producing gaseous products. For **complete**

combustion process, only Carbon dioxide (CO_2) and water vapor (H_2O) are produced. Combustion reactions are widely encountered in the production of electricity and heat. They are used for waste burning.

Combustion of carbon based fuels, involves mostly C, H, and S atoms. When the fuel is reacted with Oxygen, the carbon is converted to CO_2 or CO, the hydrogen to H_2O, and the sulfur is primarily oxidized to SO_2. Formation of **CO** (carbon monoxide) indicates **partial combustion**. Complete combustion would realize the fully oxidized species CO_2 (carbon dioxide).

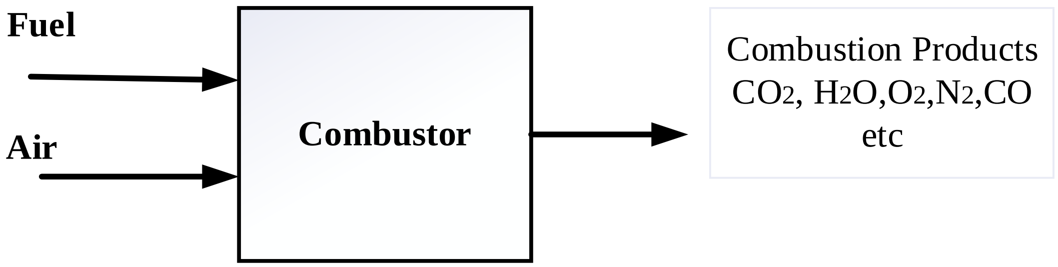


Figure 4. 5 Combustion Unit Diagram

Fossil fuels are mainly compounds of carbon and hydrogen (hydrocarbons - C_m H_n). The reaction of its oxidation can by written by the equation of stoichiometry:

$$C_m H_n + \left(m + \frac{n}{4}\right) O_2 \rightarrow m\, CO_2 + \frac{n}{2} H_2O$$

This is an equation of stoichiometry of combustion

Tips for balancing Order:

1. Balance all Carbon atoms
2. Balance all Hydrogen atoms
3. Balance all Oxygen atoms (don't hesitate to use fractions in moles)

Example: Combustion reaction for **Ethane**

$$C_2H_6 \;+\; ?\; O_{2(g)} \longrightarrow \;?\; CO_{2(g)} \;+\; ?\; H_2O$$

1. Balance C: $C_2H_6 + O_{2(g)} \longrightarrow 2\, CO_{2(g)} + H_2O$

2. Balance H: $C_2H_6 + O_{2(g)} \longrightarrow 2\, CO_{2(g)} + 3\, H_2O$

3. Balance O: $C_2H_6 + 3.5\, O_{2(g)} \longrightarrow 2\, CO_{2(g)} + 3\, H_2O$

To get the balanced equation:

$$C_2H_6 \;+\; 3.5\; O_{2(g)} \rightarrow 2\; CO_{2(g)} \;+\; 3\; H_2O$$

Combustion reactions are usually run with an excess of Oxygen, it is necessary to use more than the stoichiometric amount of air, to ensure complete combustion. This additional air is referred to as **excess air**, and is denoted as a percentage or fraction over the stoichiometric amount

Concept of excess air

For optimum combustion, the real amount of combustion air must be greater than that required theoretically. This additional amount of air is called "excess air". A certain amount of excess air is needed for complete combustion. The amount of excess air required depend on both the type and the amount of fuel used

Express the excess as %

$$\%\ \text{of excess}\ O_2 = \frac{(O_2)_{\text{Feed}} - (O_2)_{\text{Theoretical}}}{(O_2)_{\text{Theoretical}}} \times 100$$

So for a **20%** Oxygen excess for CH_4 combustion would be:

$$CH_4 + 2\, O_2 \longrightarrow O_2 + 2\, H_2O$$

If we use **20 % excess of oxygen**, the reaction will be:

$$CH_4 + (2 + 2\times 0.2)\, O_2 \longrightarrow CO_2 + 2\, H_2O + 0.4\, O_2$$

Propane (C_3H_8) burns in this reaction: $C_3H_8+5O_2 \rightarrow 4H_2O+3CO_2$

With 50% excess O_2, If 200 g of Propane are burned, how many grams of H_2O are produced?

Solution:

$$C_3H_8 + (5+2.5)\,O_2 \longrightarrow 4\,H_2O + 3\,CO_2 + 2.5\,O_2$$

$$C_3H_8 + 7.5\,O_2 \rightarrow 4\,H_2O + 3\,CO_2 + 2.5\,O_2$$

Theoretical weight:	**44×1**	**7.5×32**	**4×18**	**3×44**	**2.5×32**
Actual weight:	200	**?**	**?**	**?**	**?**

Actual wt. of O_2 in feed = (200 ×7.5×32) / 44 = 1090.9 gm

Actual wt. of H_2O = (200×4×18) / 44 = 327.27 gm

Actual wt. of CO_2 = (200×3×44) / 44 = 600 gm

Actual wt. of O_2 in product = (200 ×2.5×32) / 44 = 363.63 gm

4.3. Energy Balance

Energy balances are essential both for process design and in process analysis; i.e. where we make analysis for the performance of the process.

4.3.1. Energy balance in case of physical process (Without chemical reaction)

1. Without any phase change

Ex: Heat exchanger

The energy lost or gained is given by:

$$E = \int_{T_1}^{T_2} m\,Cp\,dT$$

E … Sensible Energy

m … mass of the fluid (kg)

Cp … Specific heat capacity of the fluid (kJ/kg K)

Sensible Energy
Energy causing a change in system temperature

If the specific heat doesn't vary with temperature

$$E = m\ cp\ \Delta t$$

2. Case of physical process with phase change

The energy lost or gained is given by:

$$E = m\ cp\ \Delta t + m' \times \text{latent heat}$$

m ... total mass of the fluid.

m'... mass of the fluid changing its phase.

Latent energy

Energy causing change in phase without change in temperature

Example 4.4

Saturated steam is produced from a boiler at 5 bar and 145 °C. if water is pumped regularly at a rate of 0.1 kg/sec and temperature 20 °C. determine the energy required per unit time; given that the latent heat of vaporization of water at 5 bar is 2857 kJ/kg; Cp = 4.2 KJ/kg °c

Solution:

Since water is pumped regularly, then the rate of production of steam is also 0.1 kg/s.

$$\mathbf{E = mCp\ \Delta t + m' \times latent\ heat}$$

$$\mathbf{= 0.1 \times 4.2\ (145 - 20) + 0.1 \times 2857 = 338.2\ KJ.}$$

Heat Exchanger

A heat exchanger is a device used to transfer heat from one medium to another (no reaction)

The energy balance is calculated according to:

$$\text{Heat lost} = \text{Heat gained}$$

$$(\mathbf{mCp\Delta T})_{\text{hot fluid}} = (\mathbf{mCp\Delta T})_{\text{Cold fluid}}$$

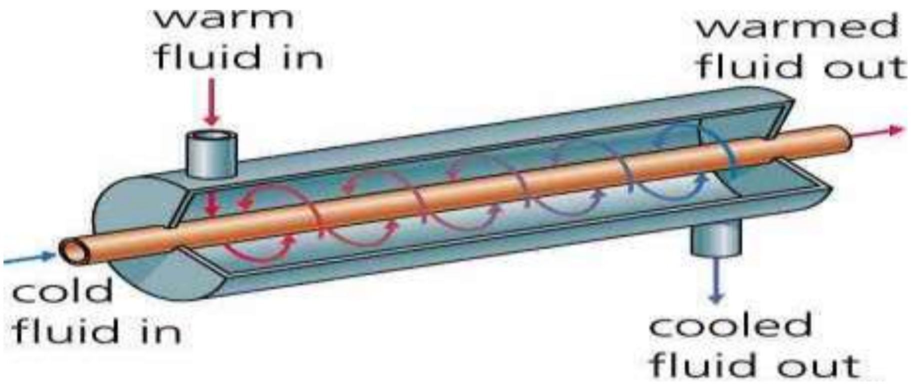


Figure 4. 6 Heat Exchanger Unit

Example 4.5

Calculate the mass of hot oil required to raise the temperature of 200 kg water from 20 ^{o}c to 70 ^{o}c; given that:

- **Cp for water =4.18 kg /kg ^{o}c**
- **Cp for oil = 2.1**
- **Initial temperature of oil = 120 ^{o}c**
- **Final temperature of oil = 90 ^{o}c**

Solution:

According to the energy balance

Heat lost = Heat gained

Since no phase change occurs, the equation will be:

$$\mathbf{m_{water}} \times \mathbf{Cp_{water}} \times (\mathbf{70} - \mathbf{20}) = \mathbf{m_{Oil}} \times \mathbf{Cp_{Oil}} \times (\mathbf{120} - \mathbf{90})$$

$$\mathbf{200} \times \mathbf{4.18} \times \mathbf{50} = \mathbf{m_{Oil}} \times \mathbf{2.1} \times \mathbf{30}$$

$$\mathbf{m_{Oil}} = \mathbf{663.5\ kg}.$$

4.3.2. Energy balance in case of reacting system (with Chemical Reactions)

The heat of reaction is **produced** or **absorbed** during chemical reactions. The value of the enthalpy change reported for a reaction is the amount of heat released or absorbed when reactants are converted to products.

Enthalpies of Chemical Change

Enthalpy

- is a state function whose value depends only on the current state of the system, not on the path taken to arrive at that state

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

- The physical states of reactants and products must be specified as solid (*s*), liquid (*l*), gaseous (*g*), or aqueous (*aq*) when enthalpy changes are reported

When the heat of reaction is measured under
Standard Thermodynamic Conditions
❑ 1 atm pressure
❑ specified temperature usually 25 °C,
❑ 1 M concentration for all substance in solution
is called a **Standard heat of reaction** and is indicated by the symbol ΔH^0r.

The heat of reaction could be calculated by different methods, as follows:

1. By the knowledge of heat of formation of both reactants and products.
2. Using Hess's law
3. Using the bond dissociation energy.

1. Standard Heat of Reaction by the knowledge of the heat of formations of both reactants and products

The standard heat of formation is the amount of heat produced or absorbed during the formation of one-gram mole of a substance in its standard state from its constituent elements

N.B….. The heat of formation of all elements is equal zero

The standard heat of reaction (ΔH^{o}_{r}) is calculated according to the equation.

$$\Delta H^{\circ}_{r} = \sum \text{Heat of formation of products} - \sum \text{Heat of formation of reactants}$$

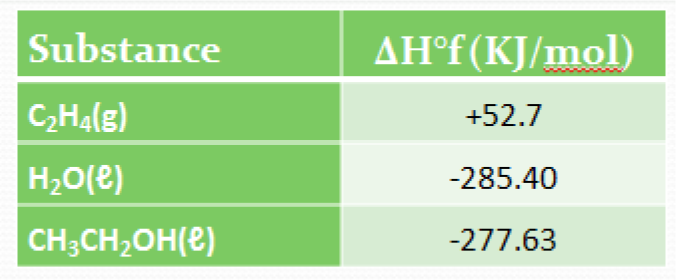
$$2\,A + 3\,B \rightarrow 2\,C + D$$

$$\Delta H^{o}_{reaction} = [2\times(H_{f\,(C)})+1\times(H_{f\,(D)})] - [\,2\times(\,H_{f\,(A)}\,) + 3\times(H_{f\,(B)})]$$

Example 4.6

Calculate ΔH for this reaction:

$$H_2C{=}CH_2(g) + H_2O(\ell) \text{ ---> } CH_3\text{-}CH_2\text{-}OH(\ell)$$



Substance	ΔH°f (KJ/mol)
$C_2H_4(g)$	+52.7
$H_2O(\ell)$	-285.40
$CH_3CH_2OH(\ell)$	-277.63

Solution:

ΔH^0_r = heat of formation of products – heat of formation of reactants

$$\Delta H^0_r = H_{f(CH3CH2OH)} - H_{f(H2O)} - H_{f(C2H4)}$$

$$\Delta H^0_r = 1 \times (-277.63) - [1 \times (-285.4) + 1 \times (52.7)] = -44.93 \text{ kJ}$$

2. Heat of reaction using Hess′s law

Hess′s law states that the overall energy change of a chemical reaction is equal to the sum of energy changes for the individual steps in the reaction.

Example 4.7

Methane gas burns in Oxygen to yield Carbon dioxide and water

$CH_4 + O_2 \rightarrow CH_2O + H_2O$ $\quad \Delta H_1 = -275.6$ KJ

$CH_2O + O_2 \rightarrow CO_2 + H_2O$ $\quad \Delta H_2 = -526.6$ KJ

Solution:

$CH_4 + O_2 \rightarrow CH_2O + H_2O$ $\quad \Delta H_1 = -275.6$ KJ --------- ①

$CH_2O + O_2 \rightarrow CO_2 + H_2O$ $\quad \Delta H_2 = -526.6$ KJ --------- ②

By adding 1 & 2, we obtain equation 3:

$CH_4 + 2\,O_2 \rightarrow CO_2 + 2H_2O$ ---------- ③

$\mathbf{\Delta H^0_r} = \Delta H_3 = \Delta H_1 + \Delta H_2 = (-\,275.6) + (-\,526.6) = -\,802.2$ KJ.

Example 4.8

Calculate ΔH^o for the following reaction.

$$\mathbf{C + H_2O \rightarrow CO + H_2}$$

given that

$C + O_2 \rightarrow CO_2$ $\Delta H_1 = -393.8$ KJ
$2\,CO + O_2 \rightarrow 2\,CO_2$ $\Delta H_2 = -566.6$ KJ
$2\,H_2 + O_2 \rightarrow 2\,H_2O$ $\Delta H_3 = -483.6$ KJ

Solution:

Multiplying equations (2) & (3) by 0.5, then adding the three equations, we obtain the required one as follows:

1) $C + O_2 \rightarrow CO_2$ $\Delta H_1 = -393.8$ KJ

2) $0.5 \times [2\,CO_2 \rightarrow 2\,CO + O_2]$ $\Delta H_2 = 0.5 \times (+566.6)$ KJ

3) $0.5 \times [2\,H_2O \rightarrow 2\,H_2 + O_2]$ $\Delta H_3 = 0.5 \times (+483.6)$ KJ

$C + H_2O \rightarrow CO + H_2$ $\Delta H = -393.5 + 283 + 241.8 = 131.3$ KJ.

N.B. the same is done with the reactions enthalpies.

3.Calculating the Standard Heat of Reaction using the Bond Dissociation Energy

It's often possible to estimate $\mathbf{\Delta H^0_r}$ Reaction by using the average bond dissociation energy (D), where the bond dissociation energy is really just a standard enthalpy change for the corresponding bond-breaking reaction.

When we say, for example, that the bond dissociation of Cl_2 is 243 kJ/mol, this means that the **standard enthalpy change (ΔH^0_r)** for the reaction **$Cl_2(g) \rightarrow 2\,Cl(g)$** = 243 kJ.

Bond dissociation energies are always **positive** because energy must always be put into bonds to break them

$$\Delta H^0_r = D_{\text{(Reactant bonds)}} - D_{\text{(Product bonds)}}$$

Ex: For the reaction **$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$**

According to the dissociation energies, the standard heat of reaction can be calculated as following:-

$$\Delta H^0_r = \sum D\,(\text{Reactant bonds}) - \sum D\,(\text{Product bonds})$$

$$\Delta H^0_r = [D_{(Cl-Cl)} + D_{(H-H)}] - [2 \times D_{(H-Cl)}]$$

$\Delta H^0_r = (1\text{mol} \times 243\ \text{kJ/mol} + 1\ \text{mol} \times 436\ \text{kJ/mol}) - (2\ \text{mol} \times 432\ \text{kJ/mol}) = -185\ \text{kJ}$ **(exothermic reaction)**

Example 4.8

Calculate the standard heat of the following reaction

$$CH_4 + 3\,Cl_2 \longrightarrow CHCl_3 + 3\,HCl$$

Given that:

C – H D = 410 KJ / mole.

C – Cl D = 330 KJ / mole.

Cl – Cl D = 243 KJ / mole.

H – Cl D = 432 KJ / mole.

Solution:

$$\Delta H^0_r = [3\ D_{Cl-Cl} + 4\ D_{C-H}] - [\ D_{C-H} + 3\ D_{H-Cl} + 3\ D_{C-Cl}]$$

$$= [\ 3\times 243 + 4\times 410] - [\ 1\times 410 + 3\times 432 + 3\times 330]$$

$$= -327\ \text{KJ.}$$

Sheet no. (4)

1. In a mixing unit 200 Kg of 98% Sulfuric acid (H_2SO_4) are mixed with pure water to obtain 40% Sulfuric acid. **How** much water is used and **how** much acid is produced?

2. A mixing unit is fed with 80 Kg of mixture A, B and C (20%A, 70%B), and second stream of A, B (50%A) and third stream of 60 Kg of B, C (40%B). If the final product contains 100 Kg of B **Find**:

- Total weight of final product
- Composition of final product by mass percent

3. Mixing unit is fed with 60 Kg of 70% Sulfuric acid and 40 Kg of 50% Sulfuric acid. **Find** the final concentration of the product

4. A 300 Kg mixture of 45% Benzene and 55% Toluene is fed to a distillation column, the top product is composed of 95% Benzene and the bottom product composed of 2% Benzene. **Calculate** the mass of each stream

5. Ethanol is fed to a distillation column; the two streams are discharged. The top product is 200 Kg and it is composed of 95% ethanol, and the bottom product is 100 kg of composition 5% Ethanol. **Calculate** mass and composition of the feed.

6. 1000 Kg 0f 65% Methanol and 35% Ethanol is fed to a distillation column, the top product is 600 Kg and it is composed of 98% Methanol. **Calculate** the mass and composition of bottom product.

7. Calculate the mole fraction of CO_2 produced from complete combustion of C_3H_8

a) No excess Oxygen

b) 50% excess Oxygen

8. Calculate the mole fraction of CO_2 produced from complete combustion of Propanol (C_3H_7OH), if 20% excess Oxygen is used and also calculate the mass of water produced if mass of propanol (C_3H_7OH) is 120 gm

(C=12, H=1, O=16)

9. 1f 10 moles of C_4H_{10} reacts with Oxygen in presence of 60% excess Oxygen, **calculate** the moles of the products and mole fraction of water produced

10. How much heat is given off when an 869 g Iron bar cools from 94 ^oC to 5 ^oC? If $Cp_{(Fe)}$ = 0.444 J/g ^oC.

11. 466 gm of water is heated from 8.5 ^oC to 74.6 ^oC. **Calculate** the amount of heat absorbed by water. If Cp Water =4.18 J/gm. ^oC

12. Copper metal has a specific heat of 0.385 J/g$^\circ$ C. **Calculate** the amount of heat required to raise the temperature of 22.8 g of Cu from 20.0°C to 875°C.

13. Calculate the specific heat of metal if you know that 18.51g of metal absorbed a certain amount of heat 1170 J and increased in temperature from 25^oC to 92.5 ^oC.

14. 12000 J of heat energy raises the temperature of a 2 kg block of a metal from 200°C to 300°C. **What** is the specific heat capacity of the metal?

15. When a heater provides 2000 J of energy to a liquid of mass 0.1kg; the temperature rises by 5 K. **What** is the specific heat capacity of the liquid?

16. Calculate the total amount of heat required to vaporize 360 gm of water at its boiling point. if the latent heat of vaporization of water is 40 KJ /mole

17. Calculate the amount of heat required to raise the temperature of 4 Kg/sec of benzene from 30 to 50 ^{o} C if specific heat of benzene liquid = 1.9 J/gm. ^{o}C

18. Calculate the amount of heat required to vaporize 4 Kg/sec of benzene at 80.1 ^{o}C If the initial oil temperature is 30 ^{o}C, specific heat of benzene liquid = 1.9 J/gm. ^{o}C and latent heat of vaporization 390 J/gm.

19. Calculate the mass of hot oil required to raise the temperature of 100 kg water from 30 ^{O}C to 80 ^{o}C; given that:

- Cp for water =4.18 kJ /kg ^{o}C
- Cp for oil = 2.1kJ /kg ^{o}C
- Initial temperature of oil = 120 ^{o}C
- Final temperature of oil = 90 ^{o}C

20. Calculate ΔH for the reaction:

$$\mathbf{H_2C{=}CH_{2(g)} + H_2O_{(\ell)} \text{ ---> } CH_3\text{-}CH_2\text{-}OH_{(\ell)}}$$

Substance	**ΔH°_f (KJ/mol)**
$C_2H_{4(g)}$	+52.7

$H_2O_{(\ell)}$	-285.40
$CH_3CH_2OH_{(\ell)}$	-277.63

21. Calculate the standard enthalpy of formation of liquid Methanol, $CH_3OH(l)$, using the following information:

$C_{(graph)} + O_2 \rightarrow CO_{2(g)}$	$\Delta H^\circ = -393.5$ kJ/mol
$H_{2(g)} + \frac{1}{2} O_2 \rightarrow H_2O_{(l)}$	$\Delta H^\circ = -285.8$ kJ/mol
$CH_3OH_{(l)} + 1.5\ O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$	$\Delta H^\circ = -726.4$ kJ/mol

22. Determine the enthalpy of reaction for the following:

$$H_2(g) + 1 / 2O_2(g) \text{ ---> } H_2O(g)$$

Using the following bond enthalpies (in kJ/mol): H-H (432); O=O (496); H-O (463)

23. Choose the correct answer:

- **If 80 kg of propanol C_3H_7OH are burnt in 20%excess air, calculate the mole fraction of CO_2 produced.**
  a. 0.38
  b. 0.83
  c. 0.5

- **Solution-1 at the rate F combines with solution-2 at the rate D, their combination gives the product at the rate P, what is the equation of material balance?**
  a. F + D = P
  b. F – P = D

c. D – F = P

- **In a steady-state reactive system, 5 molar CH_4 and 5 molar O_2 are supplied to the system, then what is the amount of CO_2 produced?**
  a. 2.5 molar
  b. 5 molar
  c. 7.5 molar

- **According to the reaction: $C_{(s)} + 2S_{(s)} \leftrightharpoons CS_{2(l)}$, ΔH of the reaction equals to:**
  a. H_f (products) - H_f (reactants)
  b. H_f (reactants) - H_f (products)
  c. Neither (a) nor (b)

- **The Heat of formation of an element (O_2, N_2,..etc.) in its standard state is**
  a. = zero
  b. > zero
  c. < zero

- **Latent energy results in:**
  a. Phase change
  b. Temperature change
  c. Both (a) and (b)

- **If 45.3 kJ of heat is required to vaporize 600 g of Benzene at its boiling point, the latent heat of vaporization per gram of Benzene is …….**
  a. 75.5 J
  b. 755 J
  c. 0.755 J

Chapter (5)

Electrochemistry and metallic corrosion

Chapter (5) Electrochemistry and metallic corrosion

5.1. What is Electrochemistry?

Electrochemistry is the science that unites electricity and chemistry. It is the study of chemical processes that cause electrons to move. This movement of electrons is called **electricity**, which can be generated by movements of electrons from one element to another in a reaction known as an **oxidation-reduction** ("**redox**") reaction.

If a chemical reaction is driven by an external applied voltage, as in electrolysis, or if a voltage is created by a chemical reaction, as in a battery, it is an **electrochemical reaction**. It is enormously important in modern science and technology not only because of batteries but also because it makes possible the manufacture of essential industrial chemicals and materials.

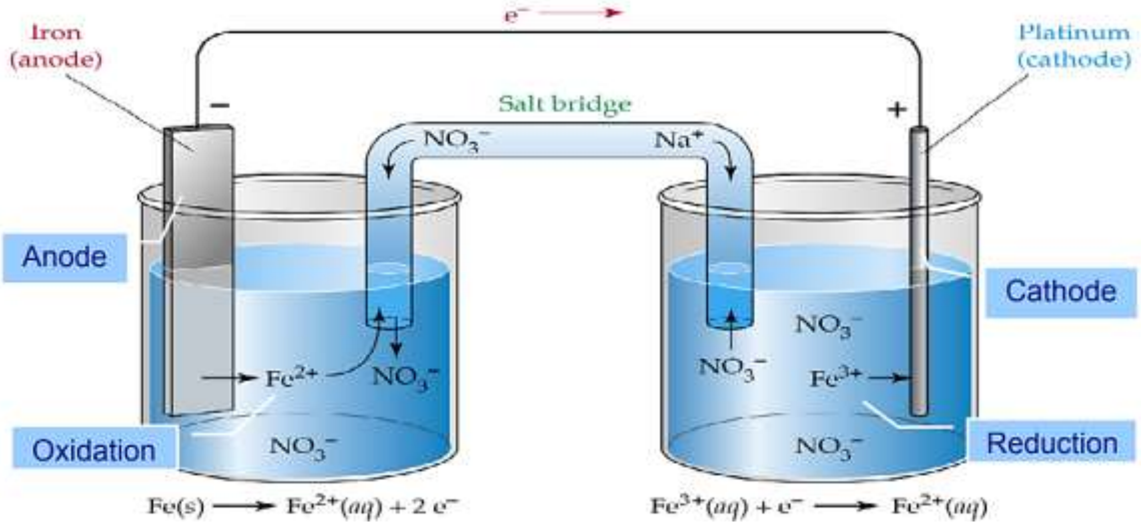


Figure 5. 1 Electro-Chemical Cell

An **electrochemical cell** is any device that converts chemical energy into electrical energy or electrical energy into chemical energy. There are three components that make up an electrochemical reaction. There must be a **solution** where redox reactions can occur. These reactions generally take place in water to facilitate electron and ion movement. A **conductor** must exist for electrons to be transferred. This conductor is usually some kind of wire so that electrons can move from one site to another. Ions also must be able to move through some form of **salt bridge** that facilitates ion migration.

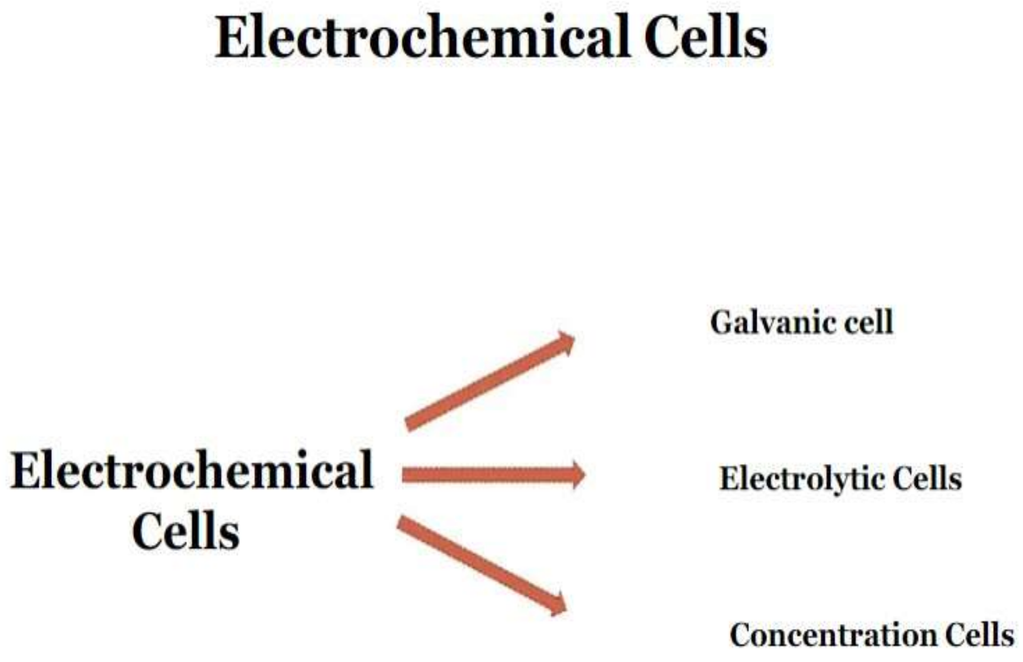


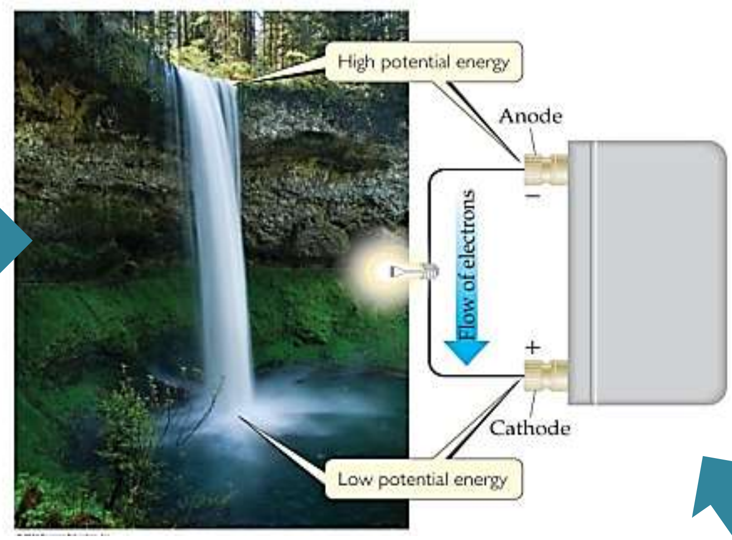
Figure 5. 2 Types of Electro-chemical cells

- **Galvanic cells** which convert chemical energy into electrical energy while electron and current flows exist. The electrochemical reactions are **spontaneous**.

- **Electrolytic cells** for converting electrical energy into chemical energy. The electrochemical reactions are **not spontaneous**.

- **Concentration cells** when the two half-cells are equal, but the concentration of a species j is higher in the anode half-cell than in the cathodic counter part

Water only spontaneously flows one way in a waterfall.



Likewise, electrons only spontaneously flow one way in a redox reaction from higher to lower potential energy

Figure 5. 3 Spontaneous motion of electrons is like in waterfall from higher to lower potential energy

In electrochemical cell, a spontaneous redox reaction is carried out in an indirect manner and the decrease in free energy during chemical reaction appears as electrical energy. An indirect redox reaction is such that reduction and oxidation processes are carried out in two separate vessels called half-cells. It has two conductive electrodes, called the **anode** and the **cathode**.

The **anode** is defined as the electrode where **oxidation** occurs. The **cathode** is the electrode where **reduction** takes place.

5.2. Some important applications of Electrochemistry in our daily life

- **Batteries** (car batteries – calculators - digital watches)
- **Corrosion of iron**
- **Preparation of some industrial materials** eg. Al, Cl_2, NaOH, etc.
- In **analytical chemistry**. Ex: the analysis of chemicals in blood to determine the development of a certain diseases

5.3. Oxidation and Reduction

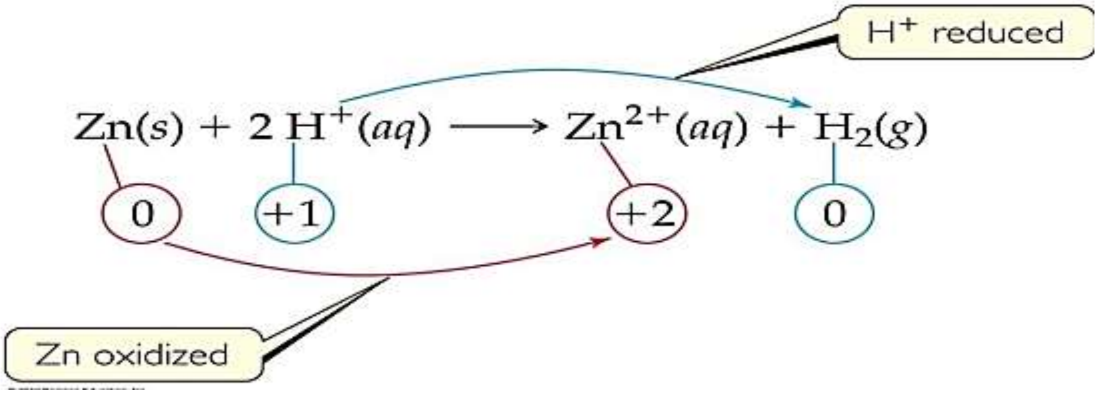


Figure 5. 4 Redox reaction

- A species is **oxidized** when it loses electrons. Here, zinc loses two electrons to go from neutral zinc metal to the Zn $^{2+}$ ion.

- A species is **reduced** when it gains electrons. Here, each of the H^+ gains an electron, and they combine to form H_2.

- What is reduced is the **oxidizing agent**. H^+ oxidizes Zn by taking electrons from it.

- What is oxidized is the **reducing agent**. Zn reduces H^+ by giving it electrons.

All electrochemical processes involve <u>Redox reactions</u>

Review of Terms:

Oxidation is the loss of electrons (Increase in charge).

Reduction is the gain of electrons (Decrease in charge)

An **oxidizing agent**, or oxidant, gains electrons and is reduced in a chemical reaction.

A **reducing agent**, or reductant, loses electrons and is oxidized in a chemical reaction.

$$Mg \rightarrow Mg^{++} + 2e^- \qquad \textbf{(Oxidation Reaction)}$$

$$O_2 + 4e^- \rightarrow 2O^{--} \qquad \textbf{(Reduction Reaction)}$$

When these half equations are paired and electrons balanced

a. $(Mg \rightarrow Mg^{++} + 2e^-) \times 2$ loses electrons, oxidized, reducing agent

b. $O_2 + 4e^- \rightarrow 2O^{--}$ gains electrons, reduced, oxidizing agent

Adding (a) and (b)

$$2Mg + O_2 + 4e^- \rightarrow 2Mg^{++} + 4e + 2O^{--}$$

$$2Mg + O_2 \rightarrow 2\,MgO$$

In (redox) reactions, electrons are transferred and energy is released

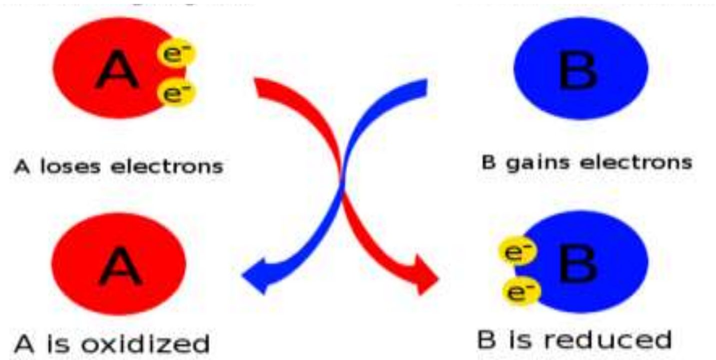


Figure 5. 5 Oxidizing and Reducing agents

5.4. Galvanic Cells

- A device in which chemical energy is converted to electrical energy is simply called **"Galvanic cells"** or **"Voltaic cell"**.

- It uses a spontaneous redox reaction to produce a current that can be used to generate energy or to do work.

In a galvanic cell, if you immerse a strip of zinc metal in an aqueous solution of copper sulfate, you find that a dark colored solid deposits on the surface of the zinc and that the blue color characteristic of the Cu^{+2} ion slowly disappears from the solution

Figure 5. 6 The redox reaction of zinc metal with aqueous

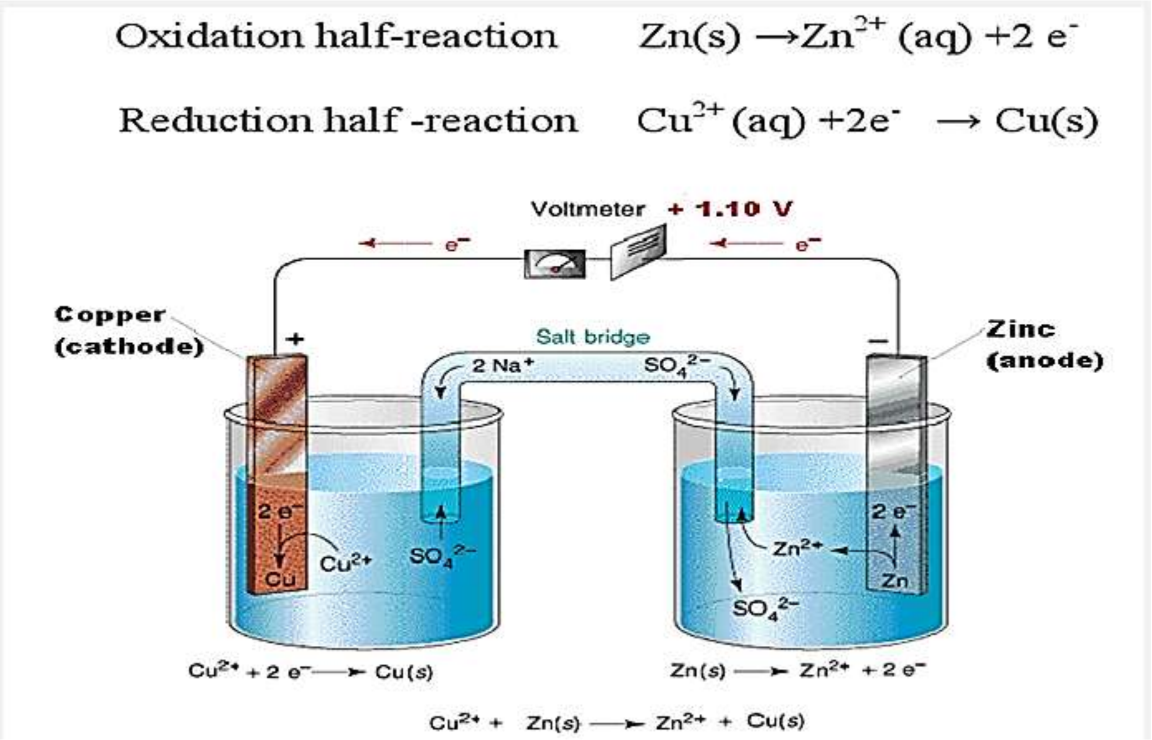


Figure 5. 7 A Daniell cell, an example of a Galvanic cell

- Once even one electron flows from the anode to the cathode, the charges (ions) in each beaker would not be balanced and the flow of electrons would stop.

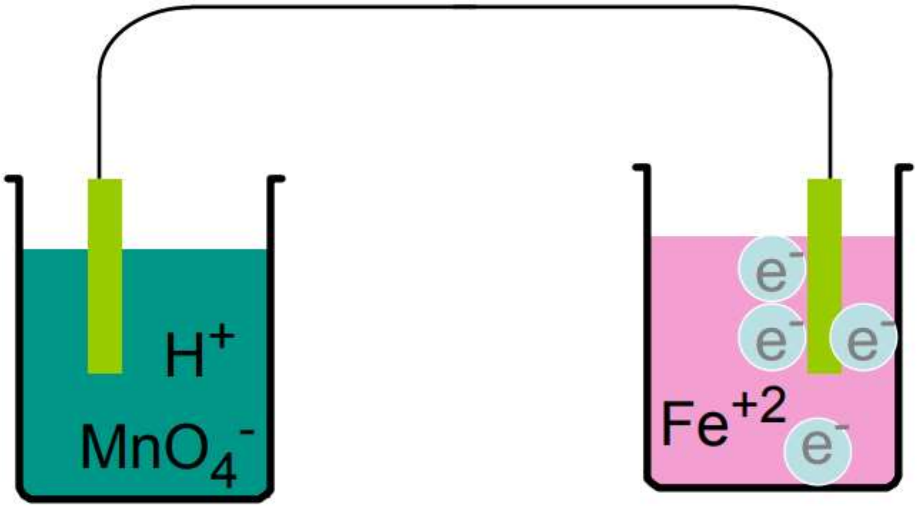


Figure 5. 8 Connected this way the reaction starts Stops immediately because charge builds up

- Therefore, we use a **salt bridge**, usually a U-shaped tube that contains a salt solution, to keep the charges balanced. Only ions flow through the salt bridge!

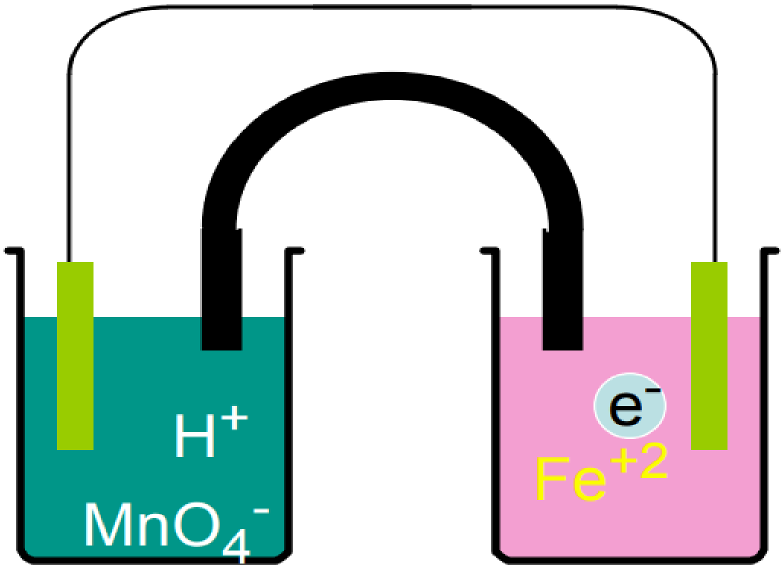


Figure 5. 9 Electricity travels in a complete circuit

Salt bridge or **porous disk** allows ions to flow without extensive mixing of the solutions.

♣**Salt bridge –** contains a strong electrolyte held in a gel–like matrix.

♣**Porous disk –** contains tiny passages that allow hindered flow of ions

- **Cations** move toward the **cathode.**
- **Anions** move toward the **anode**
- In the cell, electrons leave the anode_and flow through the wire to the cathode.
- As the electrons leave the anode, the cations formed dissolve into the solution in the anode compartment.

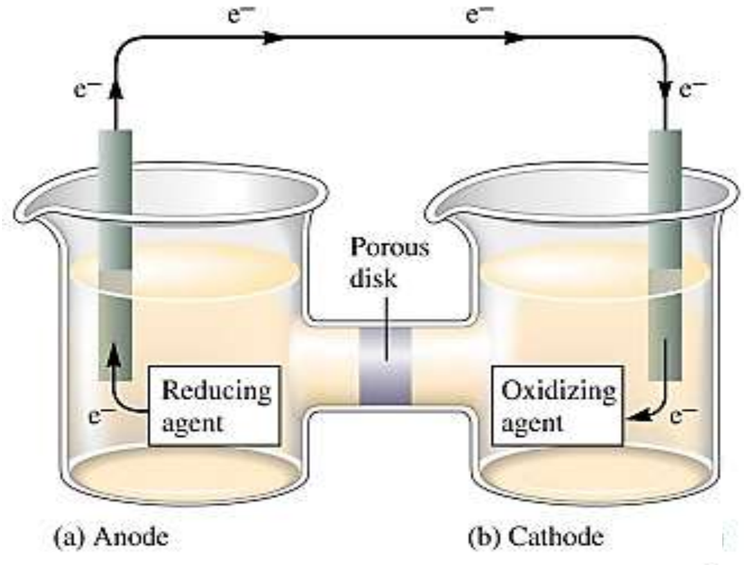
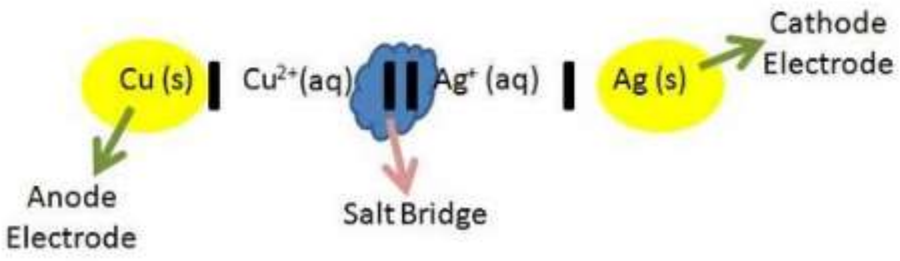


Figure 5. 10 In galvanic cell, Oxidation occurs at the anode. - Reduction occurs at the cathode

- **The Anode will decrease in size**
- As the electrons reach the cathode, cations in the cathode compartment are attracted to the now negative cathode.
- The metal is deposited on the cathode.
- **The Cathode will increase in size.**

Cell Diagram



5.5. Electromotive Force (emf)

It is the "driving force" on the electrons from reducing agent to oxidizing agent (E_{cell}). Electrons flow through a wire from the anode half-cell to the cathode half-cell.

The unit of the electrical potential is the volt (V)

- **1 V = 1 J/C of charge transferred**.

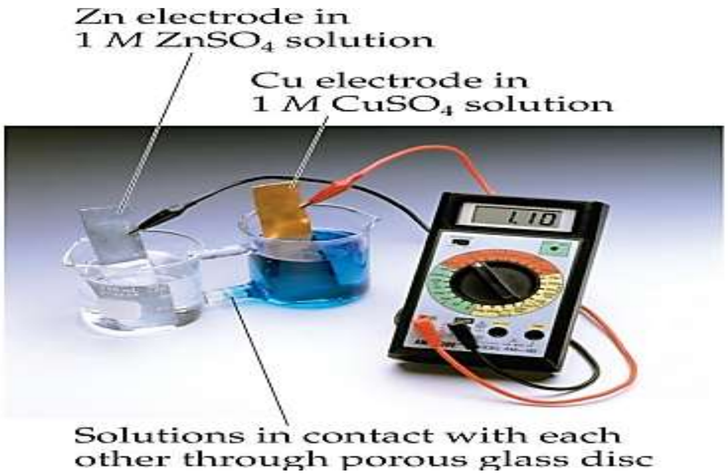


Figure 5. 11 The potential difference between the anode and cathode in a cell is called the electromotive force (emf).

5.6. Electrode Potential

5.6.1. Standard Hydrogen electrode

The chemists have chosen a reference half-cell called **Standard Hydrogen electrode** (SHE), shown in Figure 5.12. It consists of a platinum electrode in contact with H_2 gas and aqueous H^+ ions at standard-state condition [1 atm $H_2(g)$, 1 M $H^+_{(aq)}$, 25 ^oC], is assigned an arbitrary potential of exactly 0 V.

By definition, the reduction potential for hydrogen is 0 V

$$E^o = 0$$

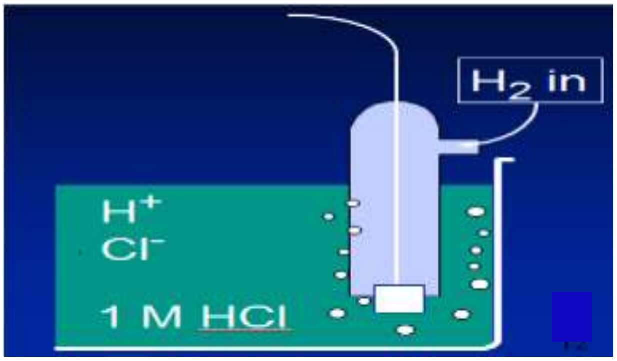


Figure 5. 12 Standard Hydrogen electrode

We can determine standard potentials for other half-cells simply by constructing galvanic cells in which each half-cell of interest is paired up with SHE.

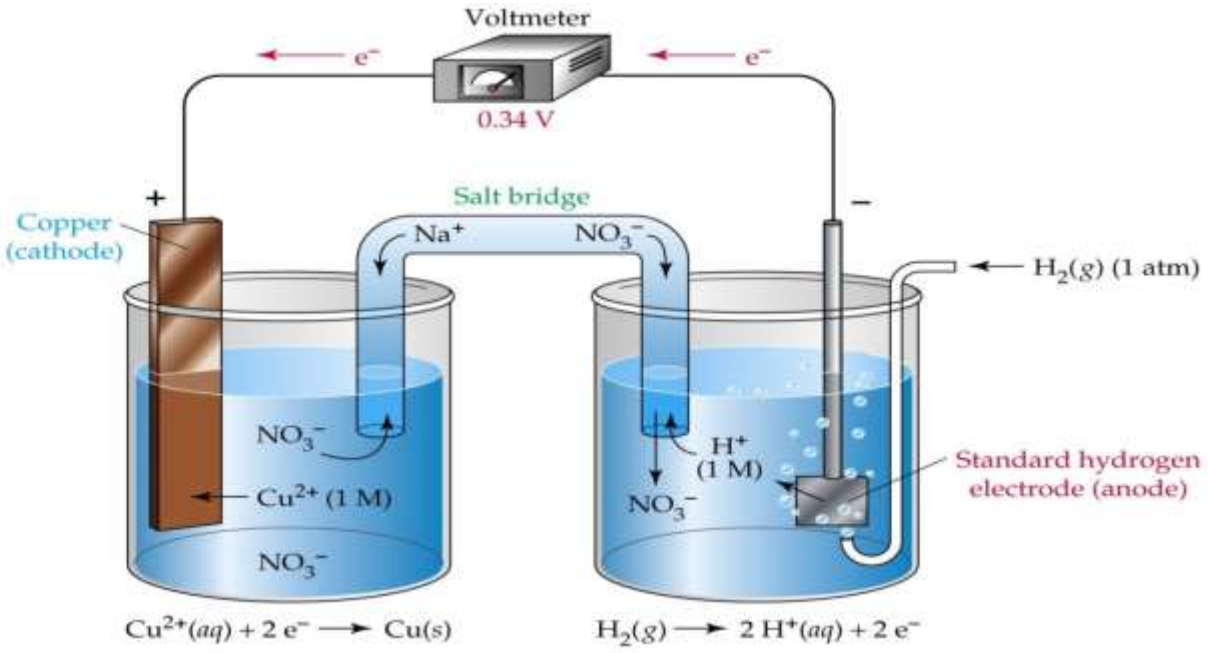


Figure 5. 13 Reduction potentials for many electrodes are compared to the reduction of hydrogen as a standard

5.6.2. Standard Electrode (Reduction) Potentials

From experiments, hundreds of half–cell potentials have been determined. Reduction potentials for many electrodes have been measured and tabulated. A short list is represented in Table (5.1), the list half-cell potentials are standard electrode potentials which means electrode potential at standard conditions.

Table 5.1 Standard reduction potential at 25 °C

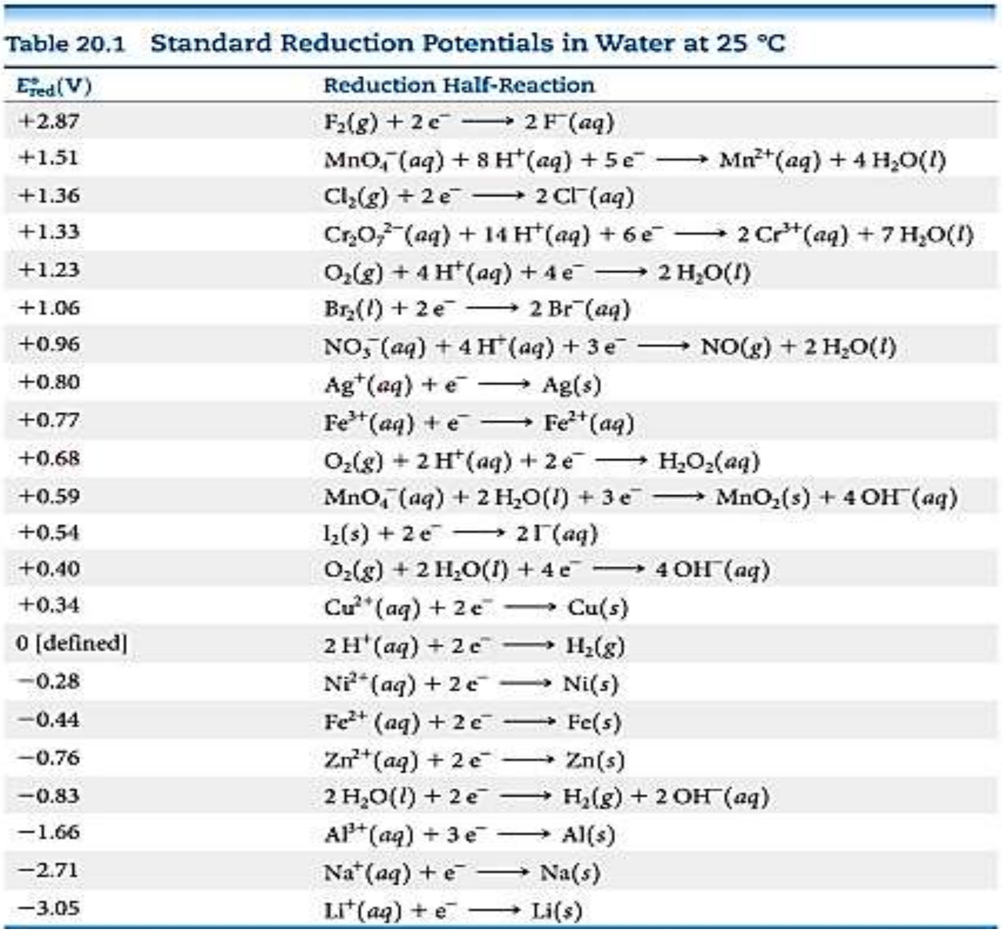


Table 20.1 Standard Reduction Potentials in Water at 25 °C

E°_{red}(V)	Reduction Half-Reaction
+2.87	$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$
+1.51	$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$
+1.36	$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$
+1.33	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
+1.23	$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$
+1.06	$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$
+0.96	$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O(l)$
+0.80	$Ag^+(aq) + e^- \longrightarrow Ag(s)$
+0.77	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$
+0.68	$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$
+0.59	$MnO_4^-(aq) + 2H_2O(l) + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$
+0.54	$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$
+0.40	$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$
+0.34	$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$
0 [defined]	$2H^+(aq) + 2e^- \longrightarrow H_2(g)$
−0.28	$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$
−0.44	$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$
−0.76	$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$
−0.83	$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$
−1.66	$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$
−2.71	$Na^+(aq) + e^- \longrightarrow Na(s)$
−3.05	$Li^+(aq) + e^- \longrightarrow Li(s)$

- The more positive the value of E° red, the greater the tendency for reduction under standard conditions.

- The strongest oxidizers have the most positive reduction potentials

- The strongest reducers have the most negative reduction potentials

5.7. Standard Cell Potential

The E^o values are tabulated with all solutes at 1 M and all gases at 1 atm. These values are called **standard reduction potentials**. Each half-reaction has a different reduction potential; the difference of two reduction potentials gives the voltage of the electrochemical cell.

The cell potential at standard conditions can be found through this equation:

$$E^0_{\text{Cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}}$$

- If E^o_{cell} is **positive** the reaction is spontaneous and it is a **voltaic** cell.
- If the E^o_{cell} is **negative**, the reaction is non-spontaneous and it is referred to as an **electrolytic** cell.

º indicates standard states of 25ºC, 1 atm, 1 M solutions.

- When a half-reaction is reversed, the algebraic sign of E° changes.
- When a half-reaction is multiplied by an integer, the value of E° remains the same.

Consider, for example, a cell in which H_2 gas is oxidized to H^+ ions at the anode and Zn^{2+} ions are reduced to zinc metal at the cathode.

Anode (oxidation)	$H_2(g) \rightarrow 2H^+(aq) + 2e^-$
Cathode (reduction)	$Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn(s)$
Overall cell reaction	$H_2(g) + Zn^{2+}_{(aq)} \rightarrow 2H^+_{(aq)} + Zn(s)$

The standard potential for this cell, 0.76 V at 25° C, measures the sum of the reaction tendencies of the oxidation and reduction half - reactions:

It's not possible to measure the potential of a single electrode; we can measure only a **potential difference** by placing a **voltmeter** between two electrodes.

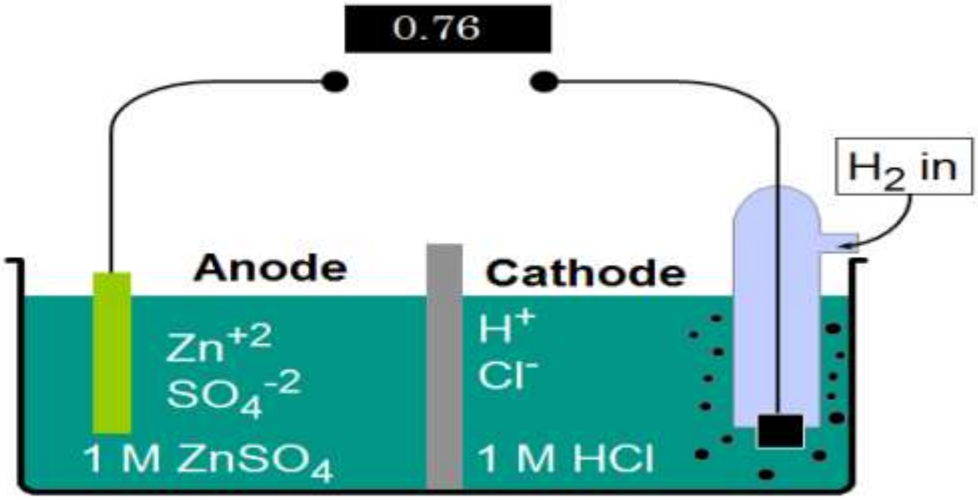


Figure 5. 14 Measuring the potential difference by placing a voltmeter between two electrodes.

Example 5.1

For the Zn//Cu^{2+} voltaic cell shown in the figure above, we have $Zn(s) + Cu^{2+}$ (aq, 1 M) → Zn^{2+} (aq, 1 M) **+ Cu(s), E°cell = 1.10 V Given that E^0 (Zn^{2+}/ Zn) = - 0.76 V, calculate the E°red for the reduction of Cu^{2+} to Cu:**

Cu^{2+} (aq, 1 M) **+ 2 e- → Cu(s)**

Solution:

E° Cell = E° red(cathode) - E° red (anode)

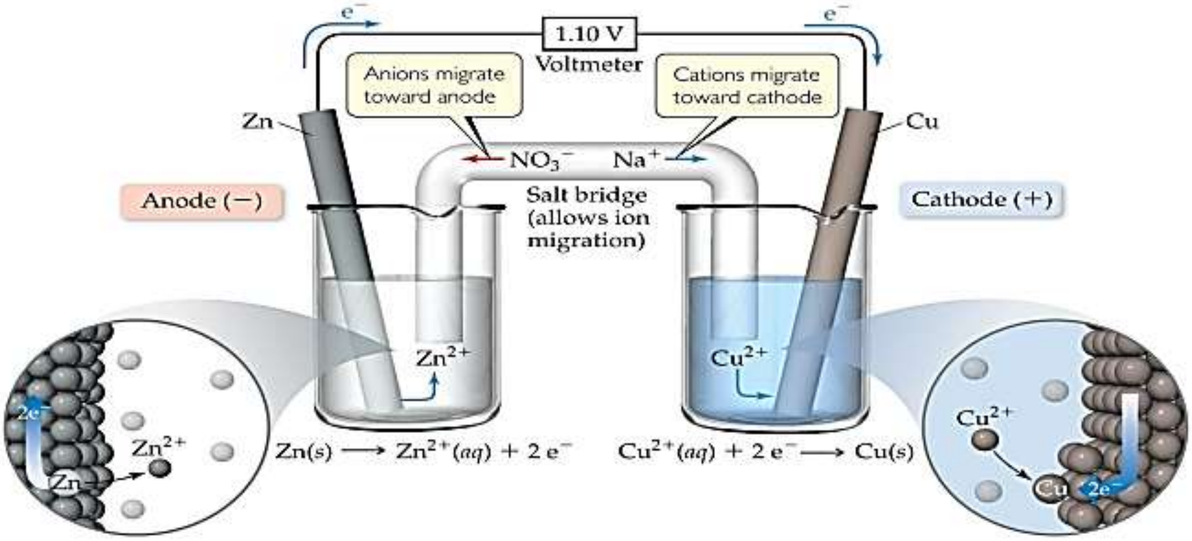
1.10 V = E° red(cathode) - (-0.76V)

E° red(cathode) = 1.10 V – 0.76 V = 0.34 V

Example 5.2 Calculating E^0_{Red} from E^0_{Cell}

Calculate the cell potential

$$Zn(s) + Cu^{2+} (aq) \rightarrow Zn^{2}+ (aq) + Cu(s)$$



$$Zn(s)\ |\ Zn^{2+}(aq)\ ||\ Cu^{2+}(aq)\ |\ Cu(s)$$

Anode material | Anode solution || Cathode solution | Cathode material

Solution:

For the anode in this cell, E° red = – 0.76 V

For the cathode, E° red = +0.34 V

So, for the cell,

E° cell = E° red (cathode) – E° red (anode)

= +0.34 V – (– 0.76 V) = +1.10 V

5.8. Electrode Potential from Nernst Equation

Electrode potentials **"potential difference between the metal and its ions in the solution"**, depend on **temperature** and on the **composition** of the reaction mixture, represented by **Nernst equation**

$$\mathbf{E = E^0 - \frac{R\,T}{n\,F} \times \ln[M^+]}$$

The equation could be written in the form:

$$\mathbf{E = E^0 - \frac{2.303\,R\,T}{n\,F} \times \log[M^+]}$$

At a temperature = 25 °C (T = 298 k)

$$\mathbf{E = E^0 - \frac{0.059}{n} \times \log[M^+]}$$

Where

E … Electrode potential, Volt

E^0… Standard electrode potential, Volt

n … Number of electron gained or lost

R … Universal gas constant, 8.314 volt. Coulomb/ mol.K

T… Temperature, K

F… Faraday's constant = 96500 coulomb

[**Mn^{n+}**] **…** Solution concentration by molar

Example 5.3

If $E°_{cell}$ = 0.48 V for the galvanic cell based on the reaction

$$2Al_{(s)} + 3\,Mn^{++}_{(aq)} \rightarrow 2Al^{+++}_{(aq)} + 3\,Mn_{(s)}$$

What will be the value of the cell potential if $[Mn^{++}]$ = 0.5 M and $[Al^{+++}]$=1.5 M

Solution:

$$E_{cell} = E^0{}_{cell} - \frac{0.059}{n} \times \log\frac{[Al^{+++}]^2}{[Mn^{++}]^3}$$

$$E_{cell} = 0.48 - \frac{0.059}{6} \times \log\frac{[Al^{+++}]^2}{[Mn^{++}]^3}$$

$$E_{cell} = 0.48 - \frac{0.059}{6} \times \log\frac{[Al^{+++}]^2}{[Mn^{++}]^3}$$

$$E_{cell} = 0.48 - \frac{0.059}{6} \times \log\frac{1.5]^2}{[0.5]^3} = 0.47\,V$$

Example 5.4

Calculate the electrode potential and the electromotive force of the following cell; Zn/Zn^{2+} (0.1 M) // Cu^{2+}(0.1M) /Cu, E^0_{Zn}=-0.76 V, E^0_{Cu}=+0.34 V.

Solution:

Oxidation $Zn \rightarrow Zn^{2+} + 2e$ **(Anode)**

Reduction $Cu^{2+} + 2e \rightarrow Cu$ **(Cathode)**

$$\mathrm{E_{Zn\ (anode)}} = -0.76 - \frac{0.059}{2} \times \log[0.1] = -0.7895\ \mathrm{V}$$

$$\mathrm{E_{Cu\ (Cathode)}} = 0.34 - \frac{0.059}{2} \times \log[0.1] = 0.3105\ \mathrm{V}$$

$$\mathrm{e.m.f} = \mathrm{E_{Cathode}} - \mathrm{E_{anode}} = 0.3105 + 0.7895 = 1.1\ \mathrm{V}$$

Example 5.5

Calculate the e.m.f (electro motive force) of the following cell:

$Zn\ /\ Zn^{2+}\ (0.01M)\ //\ Zn^{2+}\ (0.1M)/\ Zn$

where $E^{o}_{zn} = -0.76V$

Solution:

Oxidation: $Zn \longrightarrow Zn^{2+} + 2e$ (Anode)

Reduction: $Zn^{2+} + 2e \longrightarrow Zn$ (Cathode)

$$\mathbf{E = E^{0} - \frac{0.059}{n} \times \log[M^{+}]}$$

$$\mathbf{E_{anode} = -0.76 - \frac{0.059}{2} \times \log[0.01] = -0.701\ V}$$

$$\mathbf{E_{Cathode} = -0.76 - \frac{0.059}{2} \times \log[0.1] = -0.7305\ V}$$

$$\mathbf{e.m.f = E_{Cathode} - E_{anode} = -0.7305 + 0.701}$$

$$\mathbf{= -0.0295\ V}$$

5.9. Corrosion

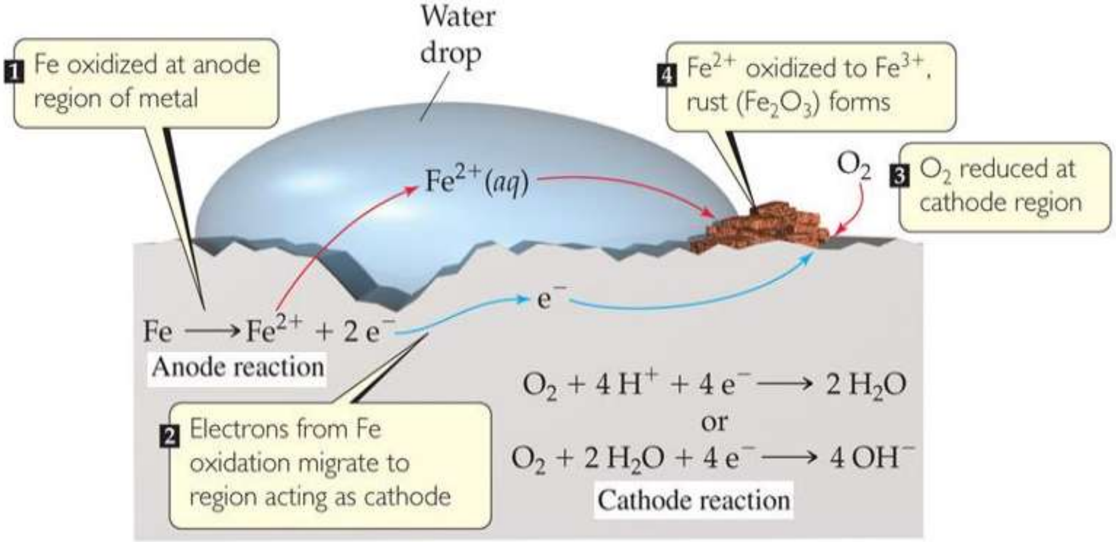


Figure 5. 15 Corrosion

Corrosion is the breaking down or destruction of a material especially a metal, through chemical reactions. The most common form of corrosion is rusting, which occurs when iron combines with oxygen and water. To prevent corrosion, we first have to understand how it occurs and different types of corrosion.

- Corrosion is oxidation.
- The process that returns metals to their oxidized state (Involves oxidation of the metal).
- Its common name is rusting.

5.9.1. Corrosion types

1. **Direct corrosion "Uniform corrosion":** Whenever corrosion takes place by direct chemical attack by gases like' oxygen, nitrogen and

halogens, a solid film of the corrosion product is formed on the surface of the metal which protects the metal from further corrosion.

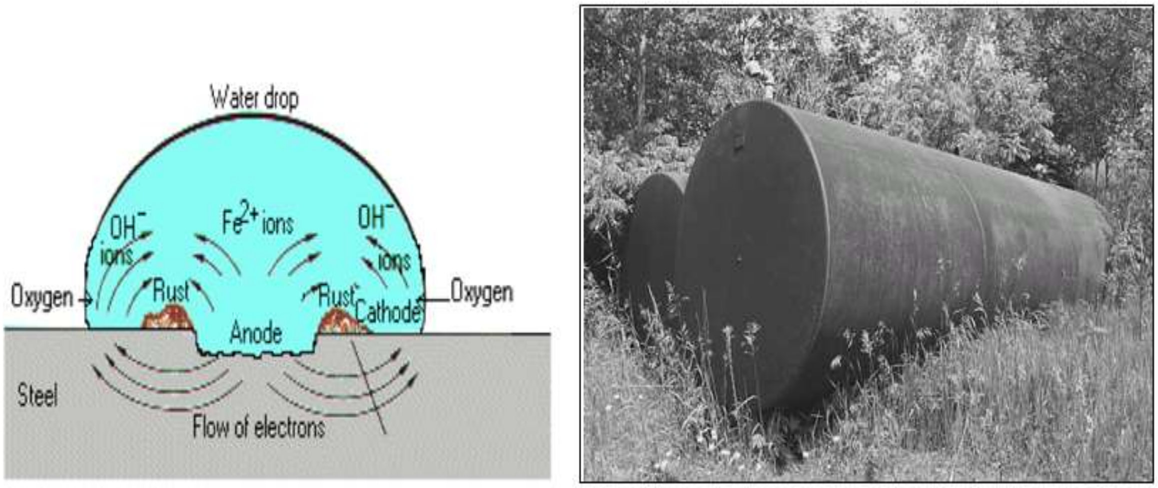


Figure 5. 16 Direct corrosion

2. **Indirect corrosion “Galvanic cell**”: Galvanic corrosion (also called “dissimilar metal corrosion”) refers to corrosion damage induced when two dissimilar materials are coupled in a corrosive electrolyte

Figure 5. 17 Indirect corrosion “Galvanic corrosion”

3. **Stress corrosion cracking:** Corrosion of metals is also influenced by some physical differences like internal stresses in the metals. Such differences result during manufacture, fabrication and heat treatment. Metal components are subjected to unevenly distributed stresses during their manufacturing process. The electrode potential thus varies from one point to another. **Areas under great stress act as the anode while areas not under stress act as the cathode.**

Figure 5. 18 Stress corrosion cracking

4. **Pitting corrosion:** This is a localized type of attack, with the rate of corrosion being greater at some areas than at others. Very dangerous and grows with the gravity.

Figure 5. 19 Pitting corrosion

5.9.2. Corrosion prevention

Corrosion Control Corrosion can be controlled by the following ways:

- **Proper material selection**; materials are selected to have the least corrosion rates in the given medium like stainless steels.
- **Improving the design** of some equipment; like avoiding sharp bends, galvanic couple
- **Apply coating** to protect the outer surface by; metallic coating like chromium, inorganic coating like phosphate, Organic coating like rubber, PVC and polyurethane (such as paint or metal plating)
- Alteration the environment; lowering the temperature, decreasing the velocity, and altering pH
- **Galvanizing**: is the coating of iron with zinc. Zinc is more easily oxidized than iron, which protects and reverses oxidation of the iron.

- **Adding inhibitors**; substances add by small concentration like amines
- **Cathodic protection**: is the protection of a metal from corrosion by connecting it to a metal (a sacrificial anode) that is more easily oxidized.
  - **Sacrificial anode**: Sacrificial Anodes are highly active metals that are used to prevent a less active material surface from corroding.
  - **Impressed current**: These consist of anodes connected to a DC power source.

All that is required is an electrical connection to the sacrificial anode (usually magnesium or zinc).

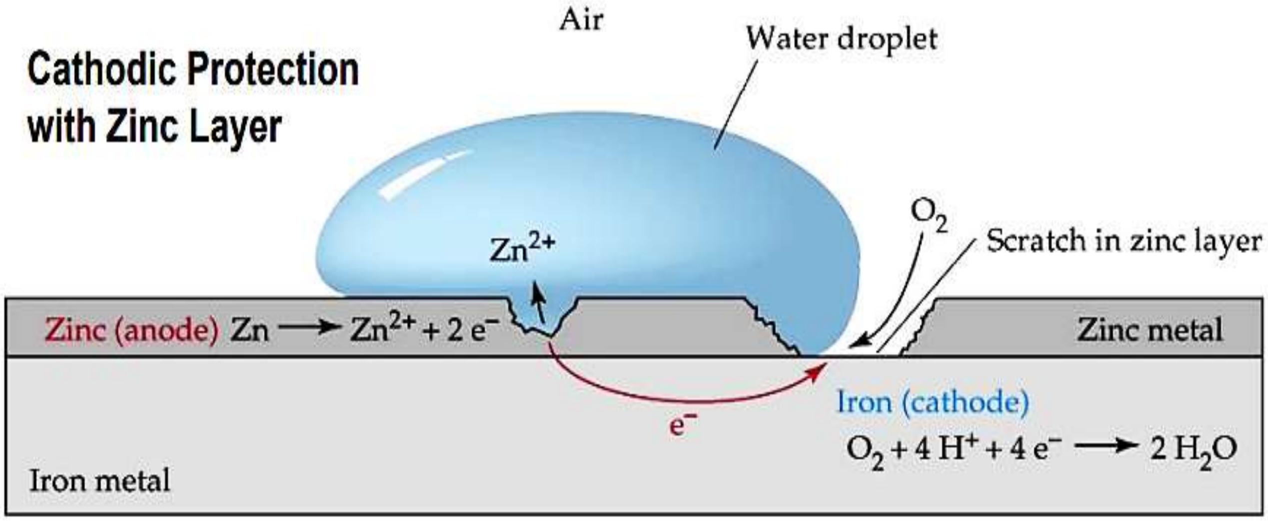


Figure 5. 20 Cathodic Protection

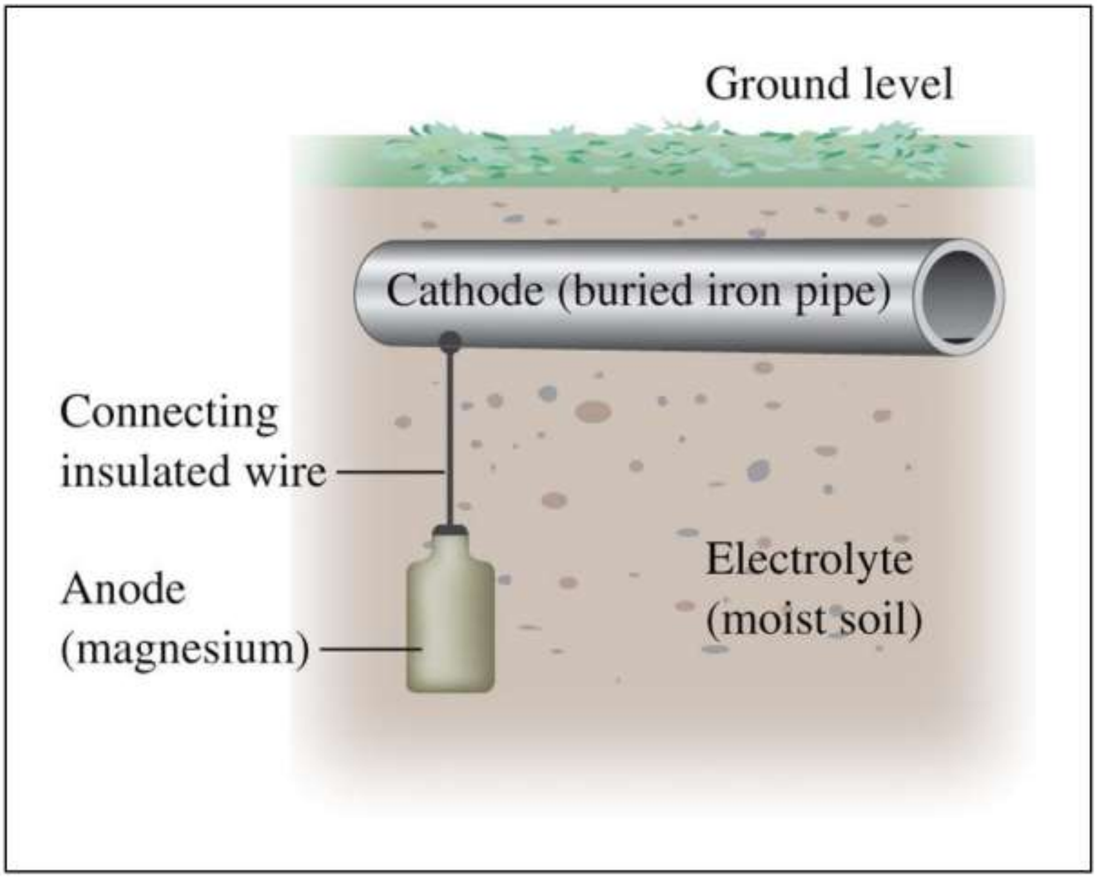


Figure 5. 21 Cathodic Protection with Magnesium Anode

Sheet no. (5)

1. **Define:**

Oxidation – Reduction – Oxidizing agent – Reducing agent – standard electrode potential – Nernst equation

2. **Write** the oxidizing agent and reducing agent in the following reactions

   a. $Zn (s) + Cu^{++} \rightarrow Zn^{++} + Cu (s)$

   b. $Cu (s) + 2Ag^{+} (aq) \rightarrow Cu^{++}(aq) + 2Ag (s)$

   c. $Ni(s) + 2Cr^{3+} (aq) \rightarrow 3Ni^{2+} (aq) + 2Cr(s)$

3. **Find** the cell potential of a cell based on the following reduction half-reactions at 35 °C

   $Cd \rightarrow Cd^{2+} + 2 e^{-}$ $E^{0} = +0.403$ V

   $Pb^{2+} + 2 e^{-} \rightarrow Pb$ $E^{0} = -0.126$ V

   where $[Cd^{2+}] = 0.020$ M and $[Pb^{2+}] = 0.200$ M

4. **Find** the emf of the cell described by the cell diagram

   $Ni \mid Ni^{2+} (0.750 M) \mid\mid Cu^{2+} (0.0500 M) \mid Cu$

   [$E^{O}_{(Ni \mid Ni^{2+})} = 0.25$ V, $E^{O}_{(Cu+2/Cu)} = 0.337$ V]

5. **Define** corrosion

6. **Discuss** corrosion forms

7. **Write** the methods of corrosion prevention

8. **Discuss** the methods of cathodic protection

9. **Write** about different types of coatings

10. **Draw** and **define** standard electrode

11. **Compare** between general corrosion and galvanic corrosion

12. **<u>Choose the correct answer</u>:**

- **In an electrolytic cell the electrode at which the electrons enter the solution is called the __ ; the chemical change that occurs at this electrode is called ___.**
  a. anode, oxidation
  b. anode, reduction
  c. cathode, oxidation
  d. cathode, reduction

- **Which of the following methods is used for the prevention of corrosion?**
  a. greasing
  b. painting
  c. plating
  d. Heating

- **Corrosion between the dissimilar metals is called as ____**
  a. Galvanic corrosion
  b. Dry corrosion
  c. Oxidation corrosion
  d. Concentration cell corrosion

- **The process of deterioration of a metal due to unwanted chemical or electrochemical interaction of the metal with its environment is called _____:**
    a. Electrolysis
    b. Electro-dialysis
    c. Corrosion
    d. Deposition

- **Corrosion due to the formation of cavities around the metal is called as the _____**
  a. Pitting corrosion
  b. Soil corrosion
  c. Water line corrosion
  d. Galvanic corrosion

- **In Redox Reactions, electrons may be**
  a. Gained only
  b. Lost only
  c. Shared
  d. Gained and lost

- **A galvanic cell with a measured standard cell potential of 0.27 V is constructed using two beakers connected by a salt bridge. One beaker contains a strip of gallium metal immersed in a 1 M solution of $GaCl_3$, and the other contains a piece of nickel immersed in a 1 M solution of $NiCl_2$. The half-reactions that occur when the compartments are connected are as follows:**

  Cathode: $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$
  Anode: $Ga(s) \rightarrow Ga^{3+}(aq) + 3e^-$

  If the potential for the oxidation of Ga to Ga^{3+} is 0.55 V under standard conditions, what is the potential for the oxidation of Ni to Ni^{2+}?

a. $E°_{cathode} = -0.28$ V
b. $E°_{cathode} = -0.46$ V
c. $E°_{anode} = -0.28$ V

Chapter (6)

Thermodynamics

Chapter (6) Thermodynamics

6.1 Thermodynamics Definition

Thermodynamics is the science that deals with heat, work and temperature, and their relation to energy, radiation and physical properties of matter.

6.2. Thermodynamics Terms

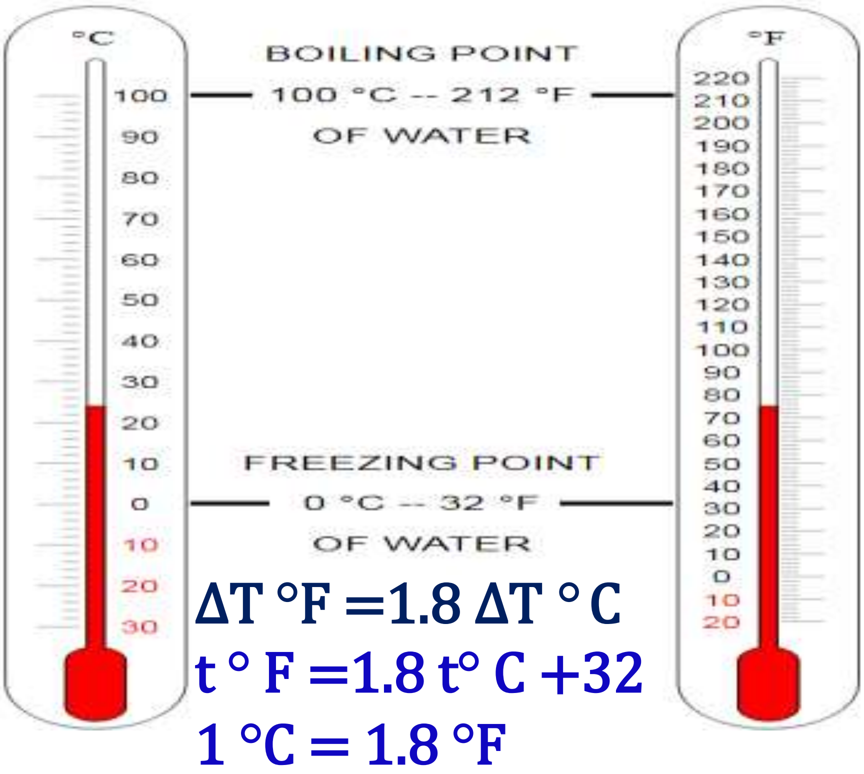
- **Heat (q)**: The form of energy that flows spontaneously from a body at a higher temperature to a body at a lower temperature.
- **Temperature:** Degree of hotness or coldness; that property of matter that determines the direction in which heat flows spontaneously.
- **Energy:** is the ability to do work or to change temperature or to change phase
- **Internal Energy:** The total energy substance possess as a result of the rotational & vibrational motion of the molecules. The symbol U is used for the internal energy and the unit of measurement is the joules (J).
- **Work (w):** it is a type of energy that may cause motion or change in volume

Units of Temperature, Heat, Energy and Work

The most common units of energy used in SI system is Joule

- **1 Joule =1/4.18 calorie**

Temperature scales



$$\Delta T\,^\circ F = 1.8\,\Delta T\,^\circ C$$

$$t\,^\circ F = 1.8\,t^\circ C + 32$$

$$1\,^\circ C = 1.8\,^\circ F$$

Figure 6. 1 Temperature Scale

Examples 6.1

What is a temperature change on the Fahrenheit scale which is equivalent to a 30 degree change on the Celsius scale

Solution:

$$\Delta t\,^\circ F = 1.8\,\Delta t\,^\circ C$$

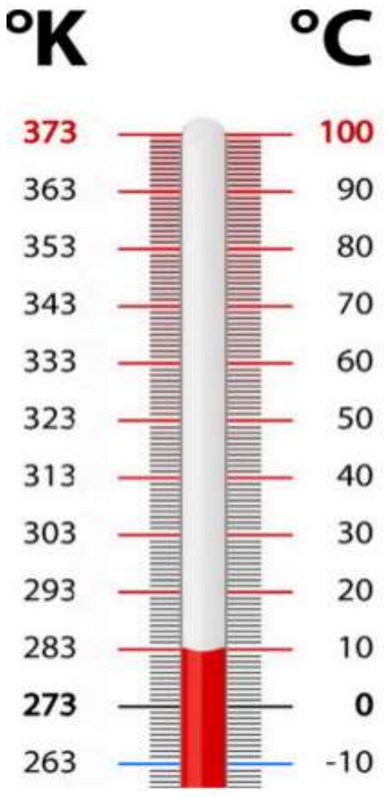
$$\Delta t\,^\circ F = 30 \times 1.8 = 54$$

Examples 6.2

What is a temperature change on the Kelvin scale which is equivalent to a 20 degree change on the Celsius scale

Solution:

$\Delta T\ K = \Delta t\ ^{o}C = 20$



$$T\ K = t\ ^{o}C + 273$$

$$\Delta T\ ^{o}C = \Delta T\ K$$

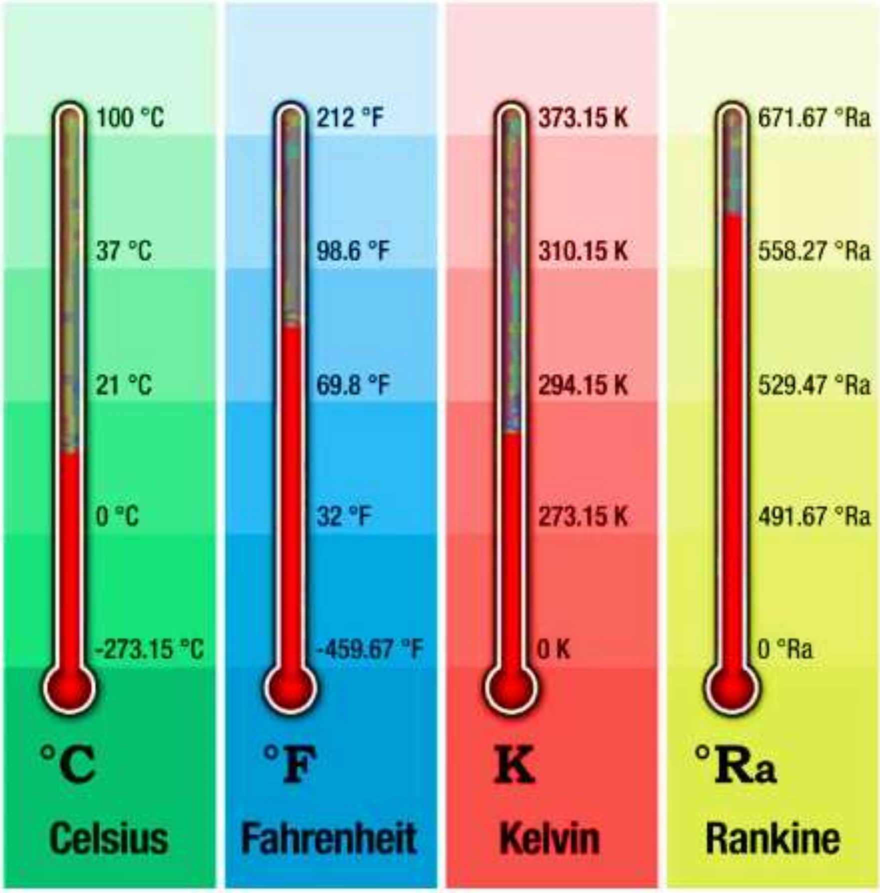
Examples 6.3

What is a temperature on the Kelvin scale which is equivalent to a 20 degree on the Celsius scale?

Solution:

$T\ K = t\ ^{o}C + 273$

$T\ K = 20\ ^{o}C + 273 = 293\ K$



Examples 6.4

Convert:

(a) 300 K to ^{O}F

(b) 85 ^{O}F to k and ^{O}C

Solution:

(a) $t\ ^{o}C = T\ K - 273$

$t\ ^{o}C = 300 - 273 = 27\ ^{\circ}C$

$t\ ^{o}F = 1.8\ t\ ^{o}C + 32$

$t\ ^{o}F = 1.8 \times 27 + 32 = 80.6^{\circ}F$

(b) $t\ ^{\circ}C = (t\ ^{\circ}F - 32) / 1.8$

- $t\ ^{o}F = 1.8\ t\ ^{o}C + 32$
- $T\ K = t\ ^{o}C + 273$
- $T\ R = t\ ^{o}F + 460$
- $\Delta t\ ^{o}C = \Delta T\ K$
- $\Delta t\ ^{o}F = 1.8\ \Delta t\ ^{o}C$
- $\Delta t\ ^{o}F = \Delta T\ R$
- $\Delta T\ R = 1.8\ \Delta T\ K$
- $1\ ^{\circ}C = 1.8\ ^{\circ}F$
- $1\ K = 1.8\ R$
- $1\ ^{\circ}C = 1\ K$
- $1\ ^{\circ}F = 1\ R$

t °C = (85 – 32) / 1.8 = 29.44 °C

T K = t °C + 273

T K = 29.44 + 273 = 302.44 K

$$°F = (°C \times 1.8) + 32 = \\ = (°C \times \frac{9}{5}) + 32$$

6.3. Types of energy

■ Radiant energy (light energy or electromagnetic energy)

It is a type of kinetic energy that travels in waves it comes from the sun and it is a primary energy source of the earth.

Examples: include the energy from the sun, x-rays, and radio waves.

■ Thermal energy or (heat energy)

Thermal energy reflects the temperature difference between two systems. The energy resulted with the random motion of atoms and molecules

Example: A cup of hot coffee has thermal energy. You generate heat and have thermal energy with respect to your environment.

■ Nuclear energy

It is the energy stored within the collection of neutrons and protons in the nucleus

Example: Nuclear fission, nuclear fusion, and nuclear decay are examples of nuclear energy

■ Kinetic Energy

Kinetic energy is the energy of motion, observable as the movement of an object or subatomic particle. Every moving object and particle has kinetic energy.

Example: a moving ball, flowing water etc.

$$\mathbf{Kinetic\ Energy} = \frac{1}{2}\mathbf{m} \times \mathbf{v}^2$$

Where,

m …… Mass of the object

v……... Velocity of the object

■ Potential Energy

It is the energy available as a result of an object's position

Example: pen on a table, water in a lake etc.

$$\mathbf{Potential\ Energy} = \mathbf{m} * \mathbf{g} * \mathbf{h}$$

Where,

m ……. Mass of the object (in kilograms)

g ……. Acceleration due to gravity

h ……. Height in meters

■ Mechanical Energy

It is the sum of potential energy and kinetic energy that is the energy associated with the motion & the position of an object is known as Mechanical energy. Thus, we can derive the formula of mechanical energy as

$$\text{Mechanical Energy} = \text{Kinetic Energy} + \text{Potential Energy}$$

Example: A falling ball. If we hold a ball with our hand it has potential energy and it has no kinetic energy. If we stop holding the ball, it will begin to gain speed and lose altitude. This is similar to increase the kinetic energy and decrease the potential energy.

■ Chemical Energy

Chemical energy is stored in a chemical substance in between the bonds of atoms in compounds. In a same given temperature and environment, energy can be released (or absorbed) because of a reaction between a set of chemical substances is equal to the difference between the energy content of the products and the reactants.

Examples:

- **Coal Combustion reaction** converts chemical energy into light and heat.
- **Wood Combustion reaction** converts chemical energy into light and heat.
- **Petroleum burning**: Can release light and heat or changed into another form of chemical energy, such as gasoline.

- **Chemical batteries**: Store chemical energy to be changed into electricity.
- **Biomass Combustion reaction** converts chemical energy into light and heat.
- **Natural gas Combustion reaction** converts chemical energy into light and heat.
- **Food**: Digested to convert chemical energy into other forms of energy used by cells.
- **Cold packs**: Chemical energy is absorbed in a reaction.

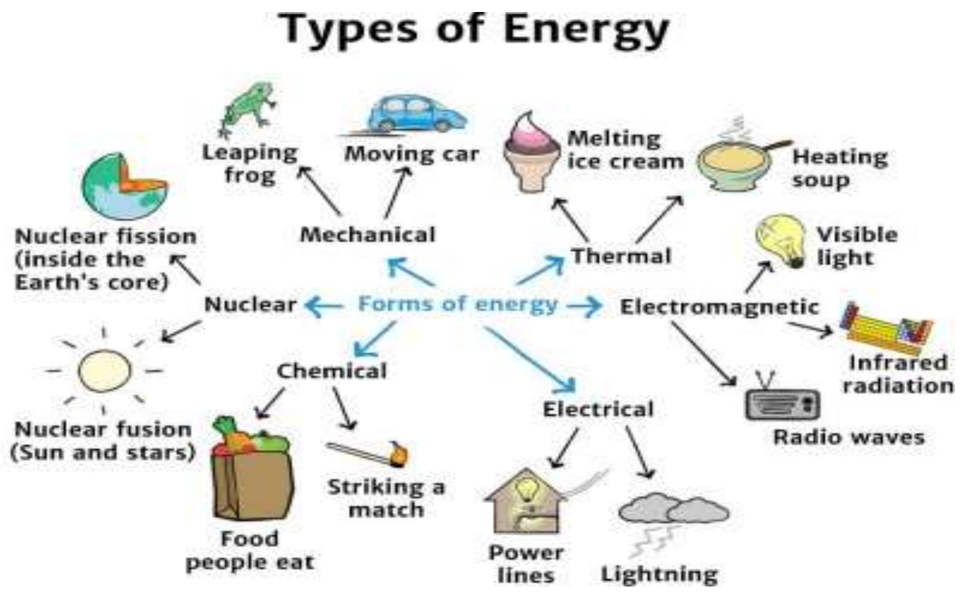


Figure 6. 2 Types of Energy

6.4. System and Surroundings

- **System** is the specific part of the universe that is of interest in the study

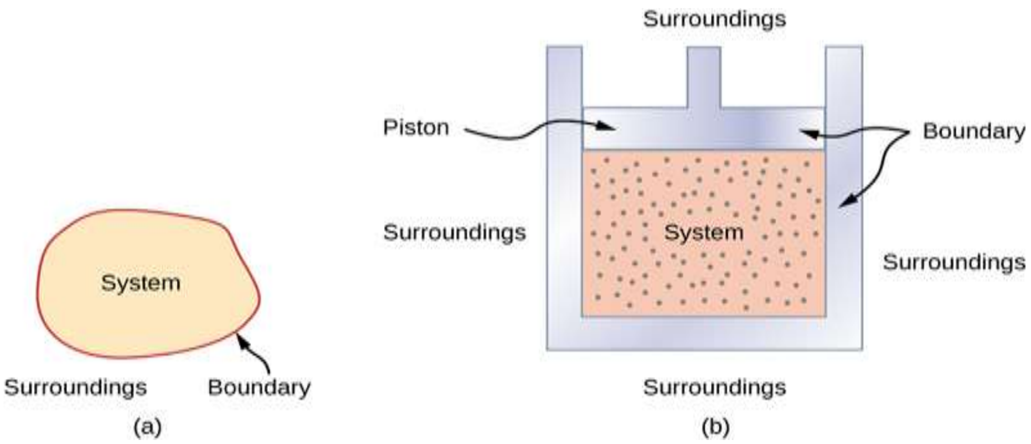


Figure 6. 3 The System and the Surroundings

(a) A system, which can include any relevant process or value, is self-contained in an area. The surroundings may also have relevant information; however, the surroundings are important to study only if the situation is an open system.

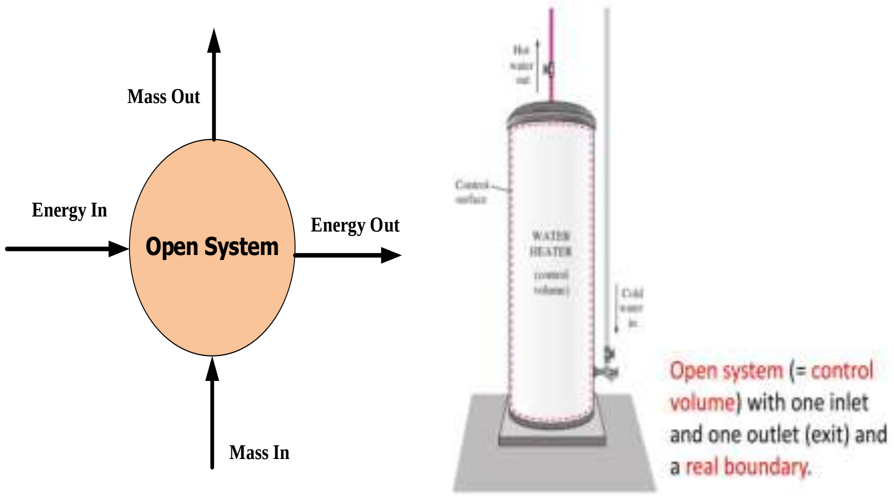
(b) The burning gasoline in the cylinder of a car engine is an example of a thermodynamic system.

- **<u>Surroundings</u>** are the portion of the universe that is outside of the system.[surroundings are everything outside the system]
- The **<u>boundary</u>** between a system and its surroundings is the **system wall.**

Types of Systems

The system is further classified according to the movements of matter and energy in or out of it.

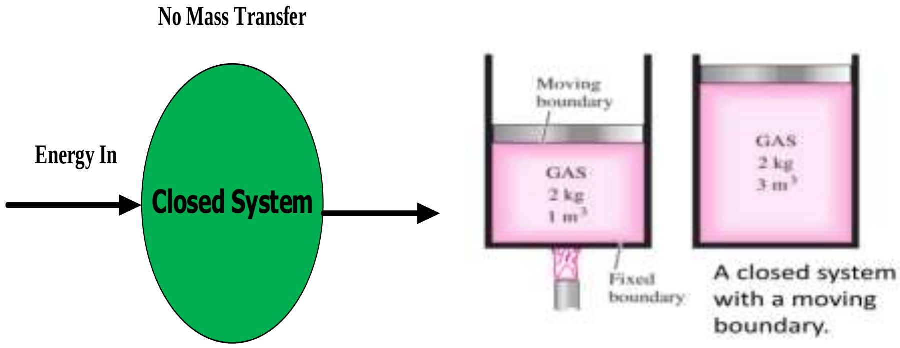
1. **Open System** in an open system, there is exchange of energy and matter between system and surroundings.



Open system (= control volume) with one inlet and one outlet (exit) and a real boundary.

Figure 6. 4 Open System

2. **Closed System** in a closed system, there is no exchange of matter, but exchange of energy is possible between system and the surroundings.



A closed system with a moving boundary.

Figure 6. 5 Closed System

3. **Isolated System** in an isolated system, there is no exchange of energy or matter between the system and the surroundings.

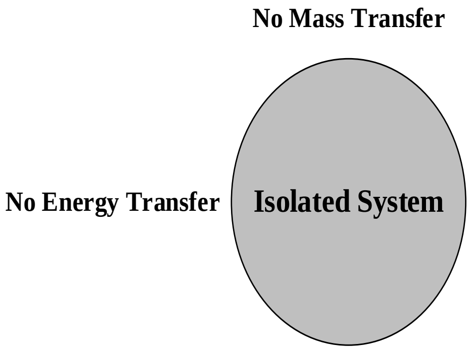


Figure 6. 6 Isolated System

6.5. Thermodynamics processes

The **process** is any change from one equilibrium state to another. (If the end state = initial state, then the process is a cycle)

The **process path** is a series intermediate states through which a system passes during the process

Processes are categorized based on how the properties behave:

- **An isobaric process** (P = constant) it is a process where no change in pressure during the process
- **An isochoric or isometric process** (V = constant) it is a process where no change in volume during the process
- **An isothermal process** (T = constant) it is a process where no change in temperature during the process

- **An adiabatic process** is one in which no heat enters or leaves the system; i.e. $q = 0$ i.e the system is thermally isolated.
- **An isenthalpic Process** (h = constant) is one in which there is no transfer of heat energy to or from the surroundings as if the system were surrounded by a perfect insulator

For a Chemical Reaction Process

- **Exothermic process: it is a** process in which heat is transferred from the system to the surroundings

$$2\,H_2\,(g) + O_2\,(g) \longrightarrow 2\,H_2O\,(l) + \text{energy}$$

$$H_2O\,(g) \longrightarrow H_2O\,(l) + \text{energy}$$

- **Endothermic process: it is a** process that absorbs heat from the surroundings

$$\text{energy} + 2HgO\,(s) \longrightarrow 2Hg\,(l) + O_2\,(g)$$

$$\text{energy} + H_2O\,(s) \longrightarrow H_2O\,(l)$$

In general

If heat of reaction is negative, the reaction is exothermic. If heat of reaction is positive, the reaction is endothermic

6.6. First law of thermodynamics

The first law of thermodynamics deals with the **quantity** of energy and asserts that energy cannot be created or destroyed but it can be converted one from to another form.

The first law of thermodynamics as it applies to a system whose kinetic and potential energies do not change: For a closed system and for any process that begins and ends with equilibrium states

The total energy of the system is equal to the sum of three types of energy

$$\Delta E_{sys} = \Delta U + \Delta P.E + \Delta K.E$$

ΔU ..... change in internal energy

ΔPE ..... Potential energy

ΔK.E ..... Kinetic energy

For a non-mobile body ΔPE=0 & ΔK.E=0

So $\Delta E_{sys} = \Delta U$ For non-mobile body

The only two forms of energy interactions associated with a fixed mass or closed system are **Q** and **W**.

$$\Delta E_{sys} = Q - W$$

Where:

Q ... is the amount of heat transferred to the system

W … is the work done on the system

A rising piston, a rotating shaft, and an electrical wire crossing the system boundaries are all associated with work interactions.

$$W=-\int P\, dV$$

6.7. Second law of thermodynamics

This is the second law of thermodynamics. Namely, the net flow of thermal energy in an isolated system will always be from the warmer to the cooler and never the reverse.

It is applied either in closed cycles as:

- heat engines
- refrigeration
- heat pumps

Heat engines convert heat to work. There are several types of heat engines, but they are characterized by the following:

1- They all receive heat from a high-temperature source (oil furnace, nuclear reactor, etc.)
2- They convert part of this heat to work
3- They reject the remaining waste heat to a low-temperature sink
4- They operate in a cycle.

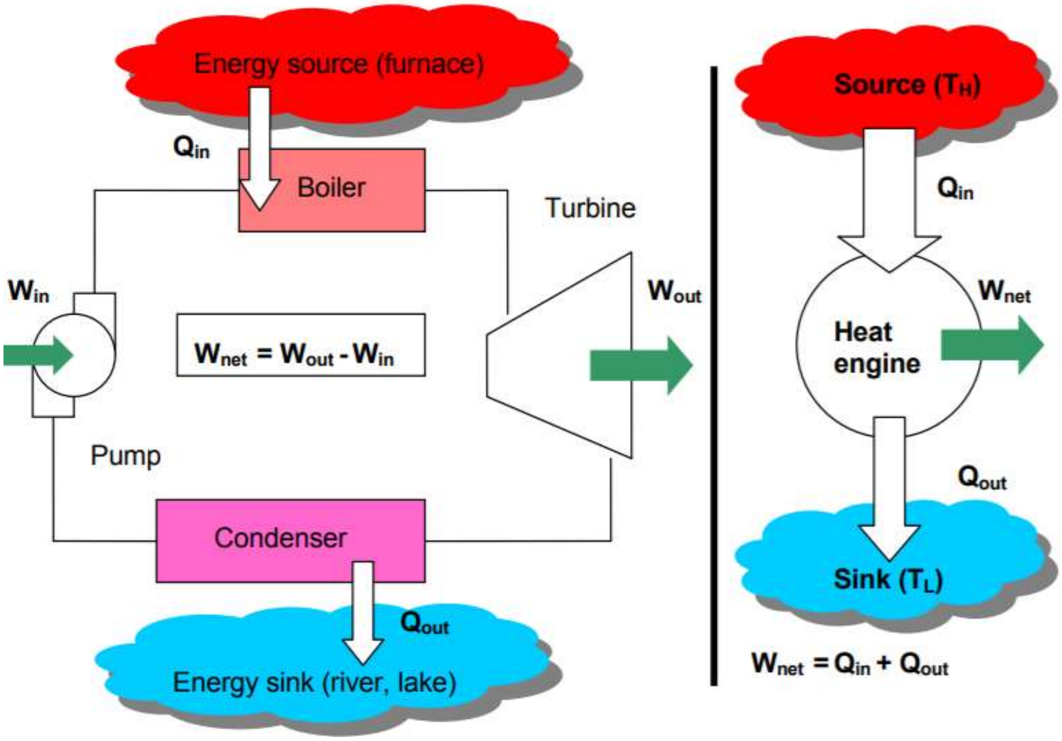


Figure 6. 7 Steam power plant is a heat engine

Thermal efficiency: is the fraction of the heat input that is converted to the network output (efficiency = benefit / cost).

$$\eta_{th} = \frac{W_{net,out}}{Q_{in}} \qquad \text{and} \qquad W_{net,Out} = Q_{in} - Q_{Out}$$

$$\eta_{th} = 1 - \frac{Q_{Out}}{Q_{in}}$$

Examples 6.5

In a heat engine 200 J of heat from hot reservoir does 36 J of useful work, calculate the thermal efficiency of heat engine.

Solution:

$Q_h = W + Q_c$

$$\eta_{th} = \frac{W_{net}}{Q_h} = \frac{36}{200} \times 100 = 18\%$$

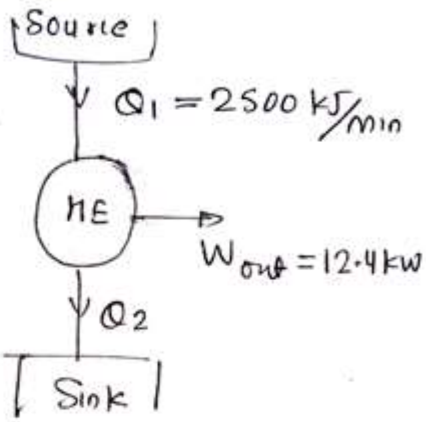
Examples 6.6

A heat engine receives heat at the rate of 2500 KJ/min from source and gives a power output of 12.4 Kw. What will be the % thermal efficiency of the heat engine?

Solution:

Thermal efficiency of a heat engine:

$$\eta_{thermal} = \frac{\text{Power output of the heat engine } (W_{out})}{\text{Power supplied to heat engine } (Q_1)}$$



Q_h = 25000 KJ/min = 25000/60 = 41.67 Kw

W_{net} = 12.4 Kw

$$\eta_{thermal} = \frac{12.4}{41.67} = 0.2976$$

$$\eta_{thermal} = 29.76\ \%$$

Thermodynamics work

In general form **W = -PΔV**

(a) Isochoric process

ΔV = 0

W = - PΔV

W = 0

(b) Isobaric process

P = Constant

$$W = - P\Delta V$$

$$W = - P (V_2 - V_1)$$

(c) Isothermal process

T = Constant $P = n R T / V$

$$W = -\int P dV = - n R T \int dV/V = - n R T \ln(V_f / V_i).$$

Sheet no. (6)

1. Define:

Heat – temperature – work – energy – system – surrounding – isolated system – closed system – open system – isothermal process – isobaric process – adiabatic process – exothermic process – endothermic process – First law of thermodynamics.

2. State different types of energy

3. In a heat engine 300 J of heat from hot reservoir does100 J of useful work, **calculate** amount of heat discharged from heat engine and thermal efficiency of heat engine.

4. What is a temperature change on the Kelvin scale which is equivalent to a 40 degree change on the Celsius scale

5. What is a temperature on the Kelvin scale which is equivalent to a 50 degree on the Celsius scale

6. What is a temperature change on the Fahrenheit scale which is equivalent to a 30 degree change on the Celsius

7. What is a temperature on the Fahrenheit scale which is equivalent to a 20 degree change on the Celsius

8. In a heat engine 300 J of heat from hot reservoir does100 J of useful work, calculate amount of heat discharged from heat engine and thermal efficiency of heat engine

9. Calculate the work done on a closed system consisting of 56 g of nitrogen, assumed ideal, when it expands isothermally and reversibly from a volume of 10 L to a volume of 20 L at a temperature of 298.15 K? (Molar mass of nitrogen is 14 g/mol).

10. 11- How much work is done by a gas that expands from 2 liters to 3 liters against an external pressure of 700 mmHg?

Chapter (7)

Chemical Industries

Chapter (7) Chemical Industries

7.1. Cement industry:

- Cement is a finely ground, non-metallic, inorganic powder when mixed with water forms a paste that **sets and hardens.**
- Cement is the most important building construction material. It has the property of setting into hard mass after mixing with water in required amount.
- It is also known as Portland cement because after setting into hard mass it resembles with the rocks found in Portland in United Kingdom.
- It is fine grey powder which is made from limestone and clay.
- The chemical formula of cement is $CaO.Al_2O_3.Fe_2O_3$
- The most common type of cement is the Ordinary Portland Cement (OPC), which has been defined as the product obtained by pulverizing the sintered mass known as clinker consisting essentially of calcium silicates.
- **Cement** is an important building material and is applied everywhere in the construction of homes, public buildings, roads, industrial plants, dams, tunnels and many other structures

Figure 7. 1 Cement is an important building material

7.1.1. Difference between setting and hardening:

- "**Setting of cement**" refers to changes of cement paste from a fluid to rigid state.
- "**Hardening**" refers to the gain of strength of a set cement paste; although during setting the cement paste acquires some strength.

7.1.2. Cement chemical composition

Constituents	**Percent Content (%)**
Lime (CaO) from limestone or chalk	60-67
Silica (SiO_2) from sand or clay	20-25
Alumina (Al_2O_3) from bauxite or clay	5.0-10
Iron Oxide (Fe_2O_3) from clay or iron ore	0.5-6.0
Magnesium Oxide (MgO)	0.1-4.0

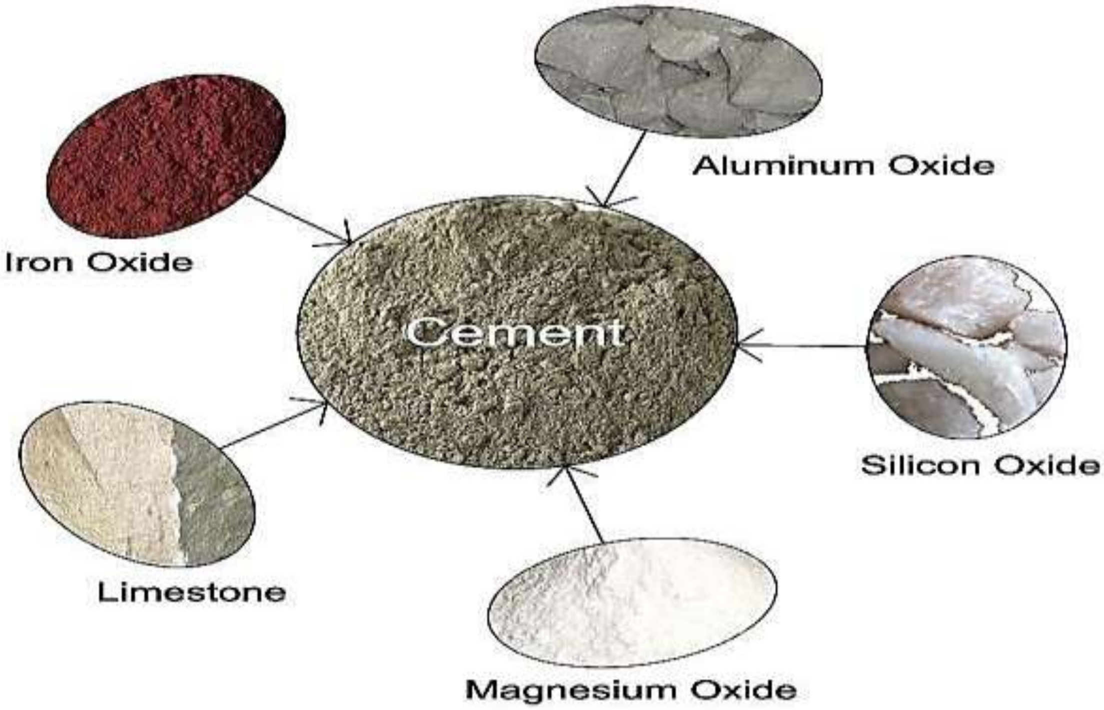


Figure 7. 2 Raw material used in manufacturing of cement

7.1.3. Raw materials for Cement manufacturing

1. Materials rich in **calcium** such as **lime stone** [$CaCO_3$]

2. Materials rich in **silica** such as **clay** [$Al_2O_3.2SiO_2.2H_2O$]

3. **Wastes** of [$MgCO_3+SiO_2+Fe_2O_3$]

The most important raw materials used for cement preparation

1. Limestone

The chemical formula of limestone is $CaCO_3$.

It is used in the manufacture of cement just to provide CaO.

Lime stone

2. Clay

Clay is hydrated aluminum silicate and ferric oxide

Chemical formula: $Al_2O_3SiO_2Fe_2O_3.2H_2O$.

Clay

Thus clay consists of:

Aluminum oxide (Al_2O_3), Silicon dioxide (SiO_2), and Ferric oxide (Fe_2O_3) along with Water molecules

Iron oxide

3. Gypsum

In addition to limestone and clay one more substance is important in cement manufacture which is **gypsum**. It acts as a retarder and it delays the setting action of cement.

The slow setting of cement helps us to work conveniently and it also leads to more hardening of cement

7.1.4. Methods of Cement manufacturing

There are two types of processes that can be used to manufacture Portland cement according as to whether the raw materials are ground in wet or dry state

- **Dry Process**

- **Wet Process**

The selection of suitable process depends upon certain factors

- Overall techno- economic feasibility
- Suitability of raw materials for the particular process
- Availability and cost of utilities

Wet process is used when the percentage of the moisture in the raw materials is high.

Dry process is used When the raw materials is so hard (solid) that they do not disintegrate by water. This process is also used in cold countries, because the water might freeze in the mixture and when there is shortage of the water needed for mixing process.

Manufacture mine and process different kinds of raw materials and put them via a chemical reaction procedure to make cement.

They required an understanding of the chemical composition of all the raw materials so that the reaction in their procedure takes place accurately. As a result, they make good, perfect quality cement that will gradually get utilized to manufacture concrete by contractors and "ready-mix" industries.

7.1.4.1 Basic manufacturing steps

In both wet and dry processes the 3 distinct operations are carried out:

(a) Mixing, Ball mill

(b) Burning, Rotary kiln

(c) Grinding

Step 1: Mining

A cement manufacturing facility is an extension of a **cement mining** process, as cement plants are usually central to the minerals needed to make the cement. This **reduces transportation expenses** and **overcomes the cost of the cement**.

As mentioned above, Cement manufacturing process starts from the cement mining process, where raw materials such as limestone, silica, aluminates, ferric minerals, and other materials are obtained. The ore rocks are quarried and crushed to little parts of about 6 inches.

Figure 7. 3 Mining of raw materials

The limestone is excavated from open cast mines after drilling and blasting. Loaded onto dumpers which transport the materials and unload into hoppers of Limestone crushers.

Figure 7. 4 Extracting raw material from quarry for cement manufacturing

Limestone mining,
Open pit mine

Excavator for the mining of Limestone

Limestone mining and transportation

Figure 7. 5 The limestone is excavated from open cast mines after drilling and blasting

Secondary crushers or hammer mills then mitigate them to an even more mini size of 3". After that, the material will be ready for pyro processing.

The **Clays** are also excavated from open cast mines and loaded onto dumpers which transport the materials and unload it into open yard storage. Then it is transported by trucks and unloaded into the hopper of a clay crusher.

Figure 7. 6 Clays are excavated from open cast mines

Step 2: Crushing of raw materials

The limestone is crushed in the first crusher, called **"Jaw crusher".** It is then fed into the second crusher called **"Impact crusher".** Then, Clay is added and mixed with limestone to reduce the particle size of the raw mixture below 50mm.

The discharged raw mix (limestone 70%, clays 30%) is fed onto a belt convey and then fed into a circular storage unit called a raw mix storage.

Figure 7. 7 Jaw crusher

Step 3: Grinding, Proportioning, and Blending

The crushed raw material is now prepared for the cement-making procedure in the kiln by mixing them with additives and grinding them to provide a fine homogenous combination. The consistency of cement is proportioned here; it depends upon the required properties of the cement.

Usually, limestone is 80 percent, and the remaining 20 percent is clay. The crushed materials are again grinded to get fine particles into ball mill or tube mills.

Figure 7. 8 Ball mill

The raw mix is dried in the cement mining process or cement plant, and heavy wheel rollers and moving tables mix the raw material. And then, the rotating roller crushes the material into a fine powder. Now these powdered materials are mixed in required proportion to get dry raw mix. The raw mix is then stored in silos and kept ready to be sent into rotary kiln.

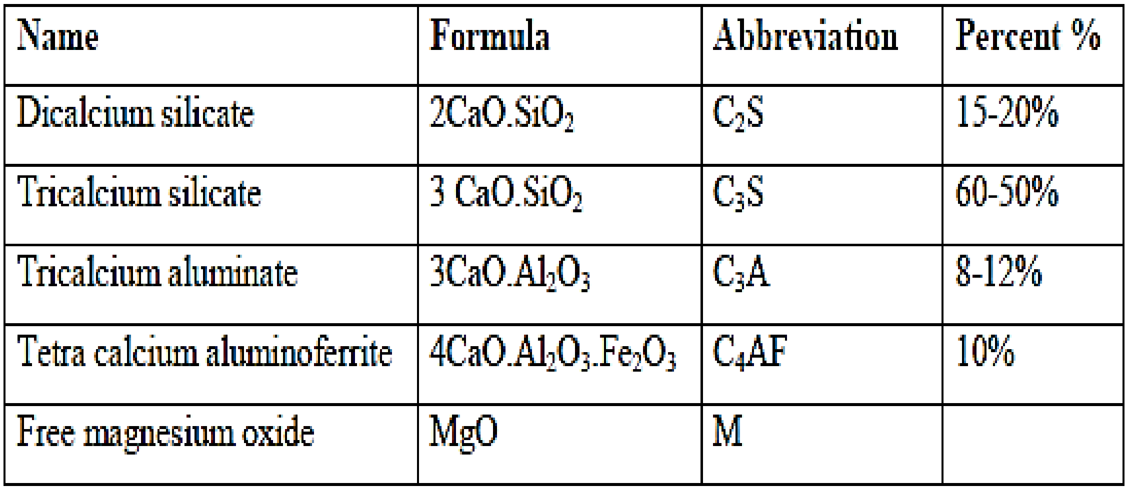
Step 4: Preheating raw materials

A pre-heating chamber has a variety of a series of cyclones. It employs the hot gasses generated from the kiln to overcome energy consumption and make the cement mining process or the procedure more environment-friendly.

Step 5: Clinkerization in the Rotary Kiln

The kiln phase is the primary stage of the cement manufacturing procedure. The raw mix is then burnt in rotary kilns to form hard granular sintered masses called **clinker** which contains the compounds shown in table 7.1.

Table 7. 1 Cement Clincker content and composition



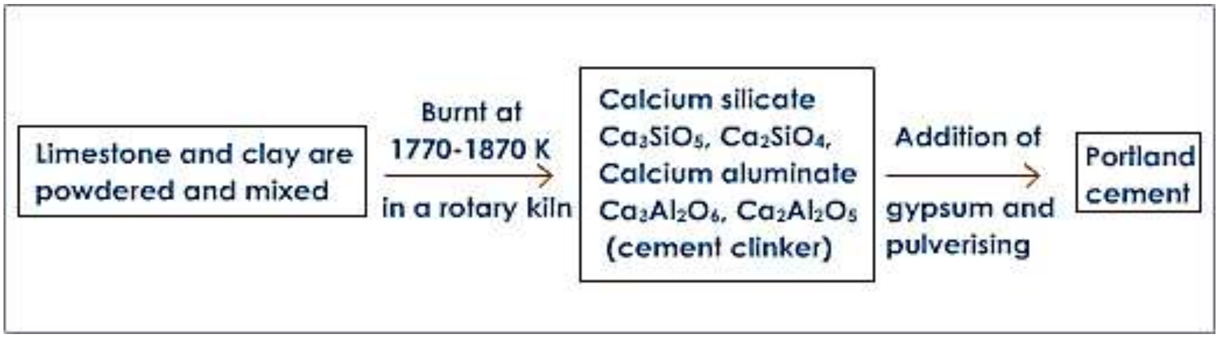
Name	Formula	Abbreviation	Percent %
Dicalcium silicate	$2CaO.SiO_2$	C_2S	15-20%
Tricalcium silicate	$3\ CaO.SiO_2$	C_3S	60-50%
Tricalcium aluminate	$3CaO.Al_2O_3$	C_3A	8-12%
Tetra calcium aluminoferrite	$4CaO.Al_2O_3.Fe_2O_3$	C_4AF	10%
Free magnesium oxide	MgO	M	

Clinker generates from the raw mix via a series of chemical reactions between calcium and silicon dioxide compounds. Though the whole procedure is complex, we have written the events of the clinker manufacturing in the following flow:

1. Evaporation of free water
2. Evolution of mixed water in the argillaceous components
3. Calcination of the Calcium carbonate ($CaCO_3$) to calcium oxide (CaO)
4. Reaction of CaO along with silica to form Dicalcium silicate
5. Reaction of CaO with the aluminum & iron-bearing constituents to shape the liquid phase
6. Formation of the clinker nodules
7. Evaporation of volatile
8. Reaction of excess CaO with Dicalcium silicate to generate Tricalcium silicate

The above events are further divided into four main stages based on the change of temperature inner side of the kiln:

1. 100°C (212°F): Evaporation of free water
2. 100°C (212°F)-430°C (800°F): Dehydration and formation of oxides of silicon, aluminum, and iron
3. 900°C (1650°F)-982°C (1800°F): CO_2 evolves, and CaO produces through calcination
4. 1510°C (2750°F): Cement clinker forms



Rotary Kiln

A cement rotary kiln is a large, refractory-lined cylindrical furnace used for the production of clinker, which is a crucial ingredient in the manufacturing of cement. The kiln is inclined slightly from the horizontal and rotates on its longitudinal axis. The cement rotary kiln is composed of rotary kiln hood cover, rotary kiln shell, rotary kiln riding ring, rotary kiln girth gear, rotary kiln transmission unit and so on.

The cement rotary kiln shell is supported on multiple riding rings usually 2~3, they allow the kiln to rotate smoothly on its axis and help distribute the kiln's weight. The thickness of the plate under the riding ring is increased to facilitate strength of the shell.

The kiln has an angle of 3 degrees in a horizontal shape. It permits the material to pass for 20 – 30 minutes. When the raw material reaches the bottom side of the kiln, the clinker generates and comes out of the kiln in the marble-sized nodules.

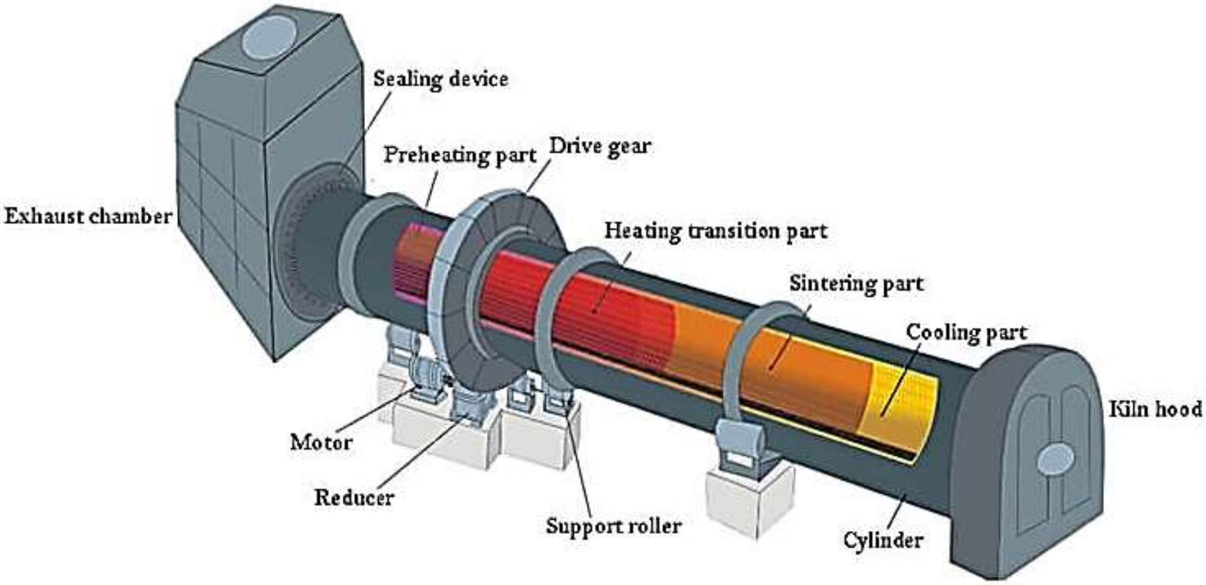


Figure 7. 9 Cement Rotary Kiln diagram

7.1.4.2 The basic chemistry of Cement manufacturing

- **Calcination process** begins with the decomposition of calcium carbonate ($CaCO_3$) at about 900 °C to leave calcium oxide (CaO, lime) and liberate gaseous Carbon dioxide (CO_2)

- **Clinkering process** in which the CaO reacts at high temperature (typically 1400-1500 °C) with silica, alumina, and ferrous oxide to form the silicates, aluminates, and ferrites of calcium which comprise the **Clinker** (C_3A, C_4AF, C_2S, C_3S).

- **Cement production** in which the clinker is ground or milled together with gypsum to produce cement.

7.1.4.3 Wet Process

(a) Mixing

- ☐ The crushed raw materials (Limestone as a source of calcium oxide and Clay) in desired proportions are fed into ball mills.

- ☐ 35-40% water is added to it to form slurry.

- ☐ The two mixtures are now pumped as slurry in predetermined proportions into storage tanks.

- ☐ Their proportioning is finally adjusted to ensure the correct chemical composition.

- ☐ **The slurry** is a liquid of creamy consistency, with water content of between 35 and 50%.

- ☐ The slurry passes into the **rotary kiln** for burning.

Composition of raw mix can be controlled better by the wet process than in dry process.

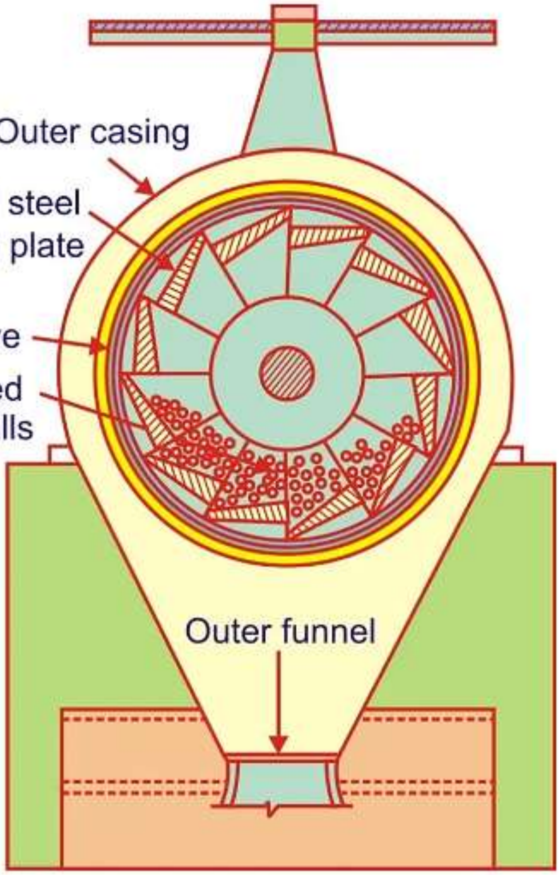


Figure 7. 10 Ball mill is a rotating steel cylinder, while rotating, hardened steel balls pulverize the slurry of the raw materials

(b) Burning

- The slurry is fed at the upper end of the inclined rotary kiln whereas from the lower end of the kiln flame is produced by injecting pulverized coal (oil or natural gas also might be used as a fuel) with a blast of air, where the temperature reaches about 1450°C.

- Slurry on entering the furnace first losses moisture, the water is driven off and CO_2 is liberated, secondly, small lumps or "nodules" are formed.

- The nodules gradually roll down passing through zones of rising temperature until they reach burning zone where they are finally burnt at 1500 to 1650ºC. The dry material undergoes a series of chemical reactions until finally, 20 to 30% of the material becomes liquid, and lime, silica and alumina recombine.

- At the burning zone where the temperature reaches 1500 to 1650ºC, they are finally burnt. At this temperature, the nodules then fuses into balls, 3 to 25 mm in diameter, **known as clinker**.
- Electrostatic precipitator is used to purify the flue gases. It removes fine particles, like dust and smoke using the force of an induced electrostatic charge and recycled it back to the kiln.

(c) Cooling, grinding and packaging

- After the previous step, the hot clicker, discharging from the kiln, drops onto another inclined tube similar to the kiln but of lesser length whereas, it is, fastly, cooled down from 2000°C to 100°C-200°C by passing air over it.
- Grinding of the Clinker to required fineness is done in large tube mills (or ball mills), which are kept cool by spraying water on them from outside.
- At this point, various additives are mixed with the clinker to grind to generate the cement's final product.
- While grinding the clinker, 3-4 % **gypsum** (Calcium Sulphate) is
- added so as to control the setting time of cement.
- The **gypsum** acts as a retarder and it delays the setting action of cement.

- ❑ Finely ground cement is stored in silos from where it is drawn for packing.

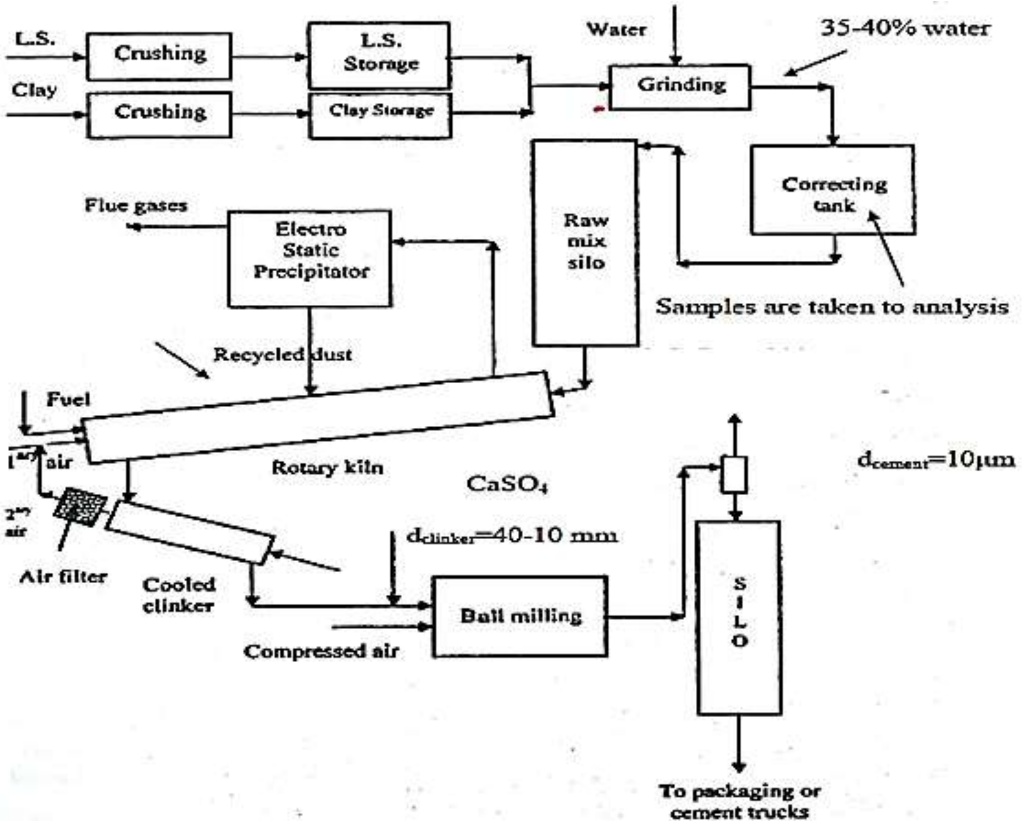


Figure 7. 11 Simple schematic diagram for the production of OPC by Wet Process

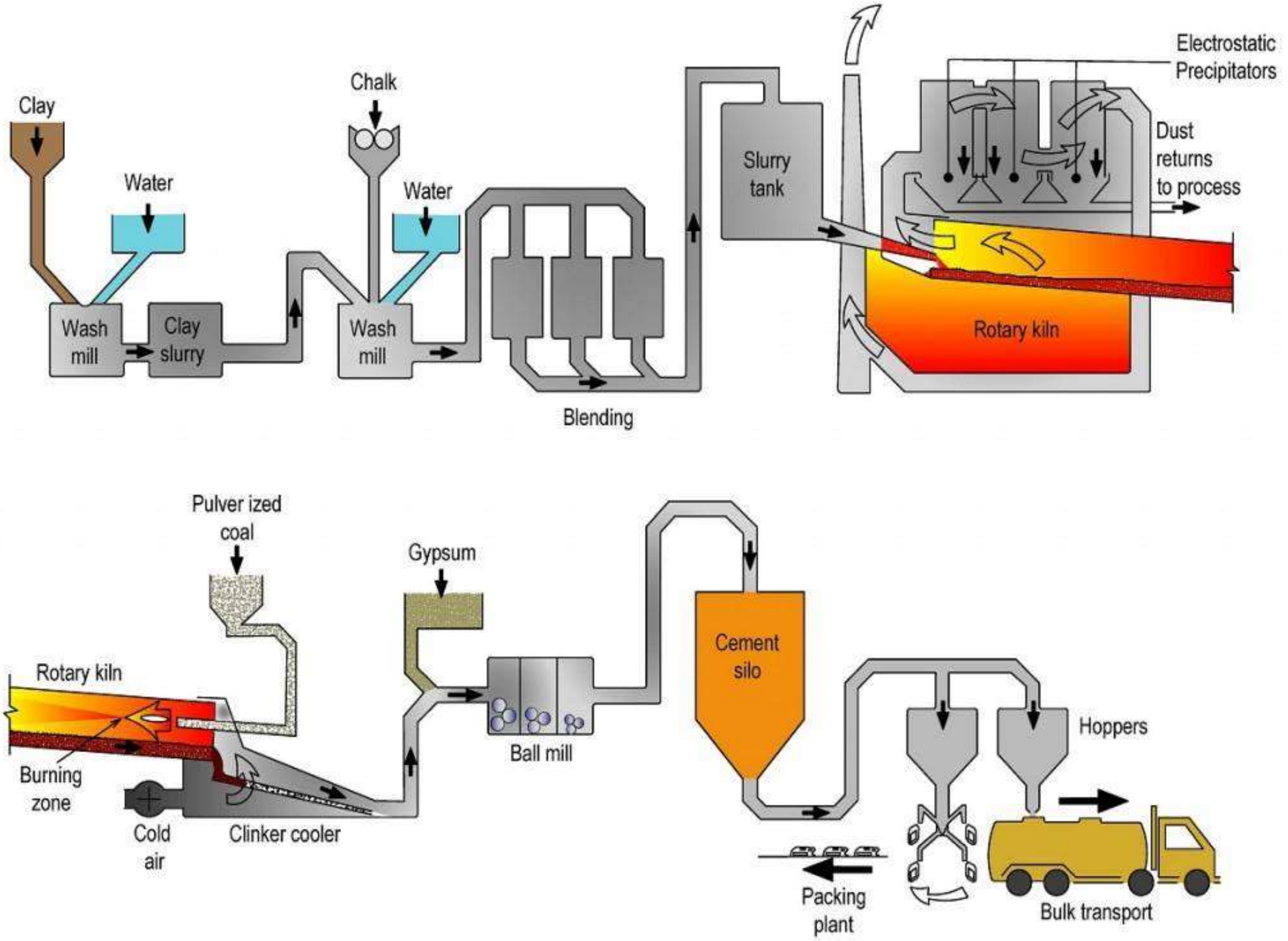


Figure 7. 12 Wet Process for Cement manufacturing

7.1.4.3.1 Advantages and disadvantages of the Wet Process

Advantages:

- It is required for specific types of cement due to high homogeneity in the raw material mixture. The good fluidity of raw materials slurry makes more even mixed materials and produces high-quality clinker.

- Dry process owns the perfect dust removal effect, it decreases the quantity of dust in operation which improves the operational environment and makes environmental protection more convenient and faster.

Disadvantages: very tall kilns, high required energy due to its more heat consumption requirements.

7.1.4.4 Dry Process

- The raw materials (Lime stone and clay) are crushed and fed in the correct proportions into a grinding mill, where they are dried and reduced in size to a fine powder.

- The dry powder is then pumped to a blending silo, and final adjustment is now made in the proportions of the materials required

- Water is then added to it so as to get a thick paste of which cakes are then made, dried and burnt in kilns.

- The pellets then enter the kiln, where temperature is about 1450°C. The total consumption of coal in this method is only about 100 kg when compared to the requirement of about 220 kg for producing a ton of cement in the wet process.

- The dry material undergoes a series of chemical reactions

- The mixture is fed into an electrostatic precipitator that removes fine particles, like dust and smoke using the force of an induced electrostatic charge

- The fused mass turns fuses into balls of diameter 3 to 25 mm known as clinker

- Cooled clinker and 3 to 5 percent of gypsum are ground in ball mill to required fineness and then taken it to storage silos from where the cement is bagged.

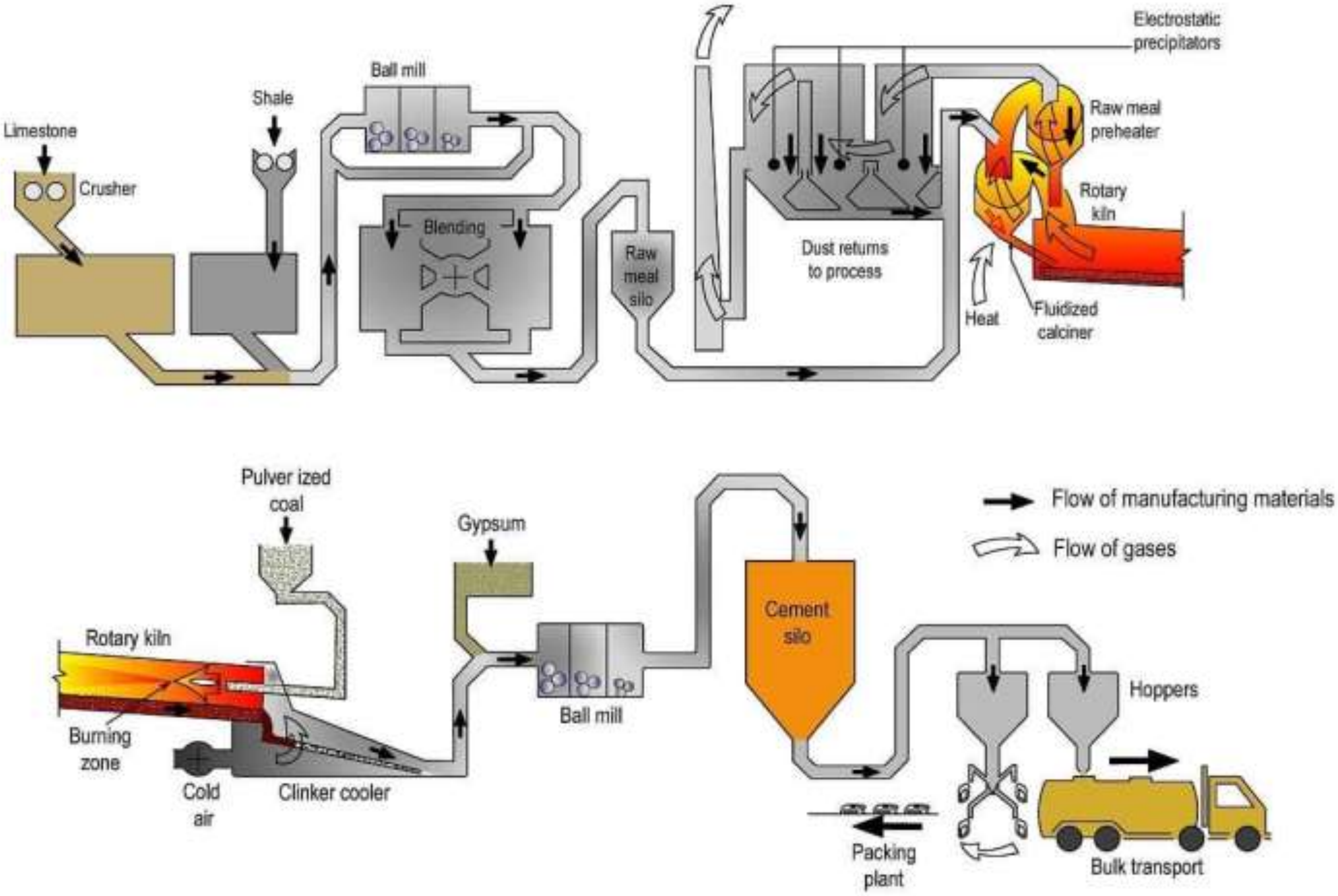


Figure 7. 13 Dry Process for Cement manufacturing

7.1.4.4.1 Advantages and disadvantages of the Dry Process

Advantages: Shorter kilns (45 m), saving heat energy, more than 90% of cement production in Egypt is made through dry process.

Disadvantages: This process is slow and costly. Also it is difficult to have the correct proportion of constituents. The quality of cement is not so good as that manufactured by the Wet process.

Important Remarks

The materials, without the gypsum, are proportioned to produce a mixture with the desired chemical composition and then ground and blended by one of two processes - **dry process or wet process**. The materials are then fed through a kiln at 2,600º F to produce grayish-black pellets known as clinker. The alumina and iron act as fluxing agents which lower the melting point of silica from 3,000 to 2600º F. After this stage, the clinker is cooled, pulverized and gypsum is added to regulate setting time. It is then ground extremely fine to produce cement.

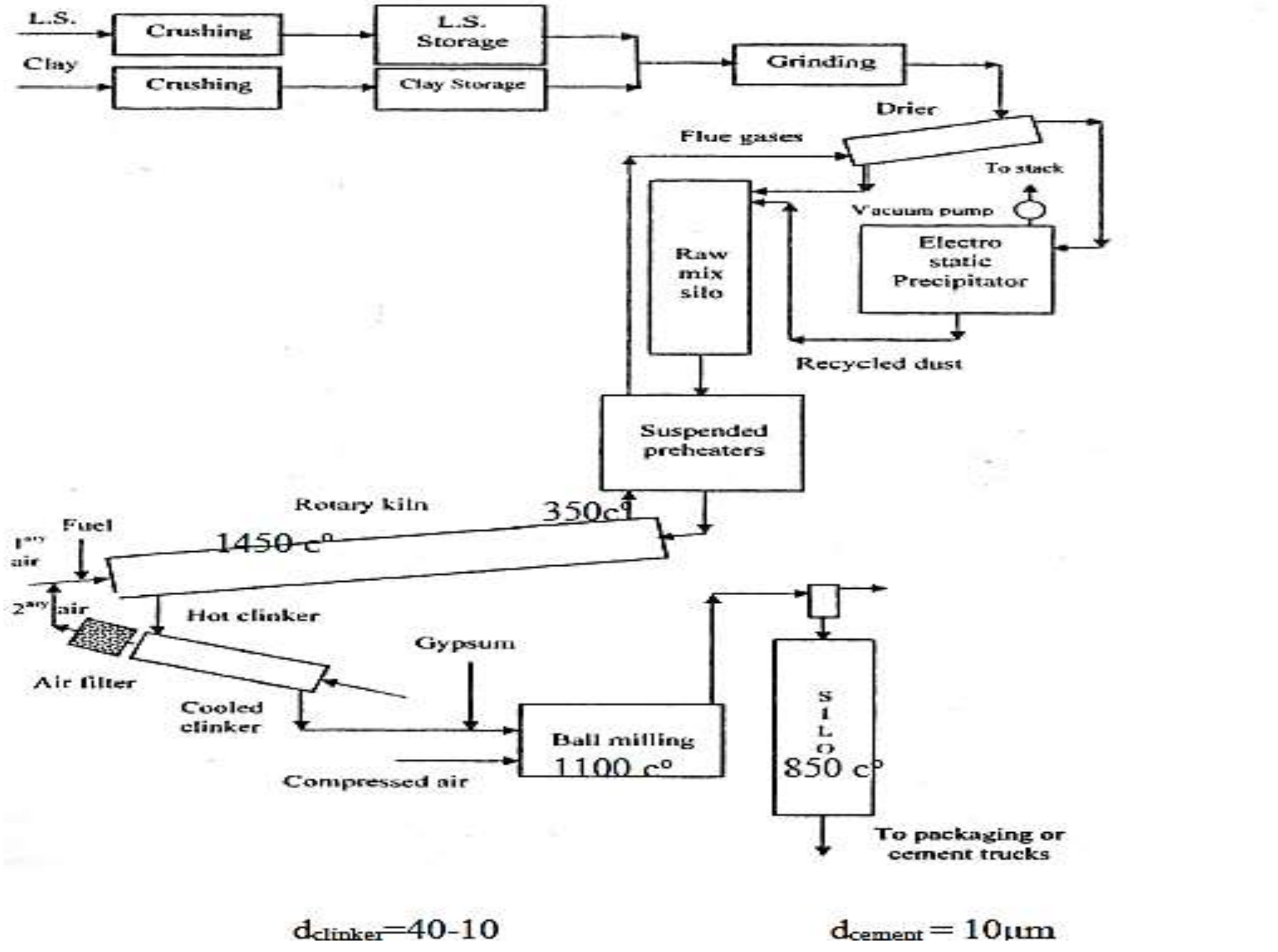


Figure 7. 14 Simple schematic diagram for the production of OPC by Dry Process

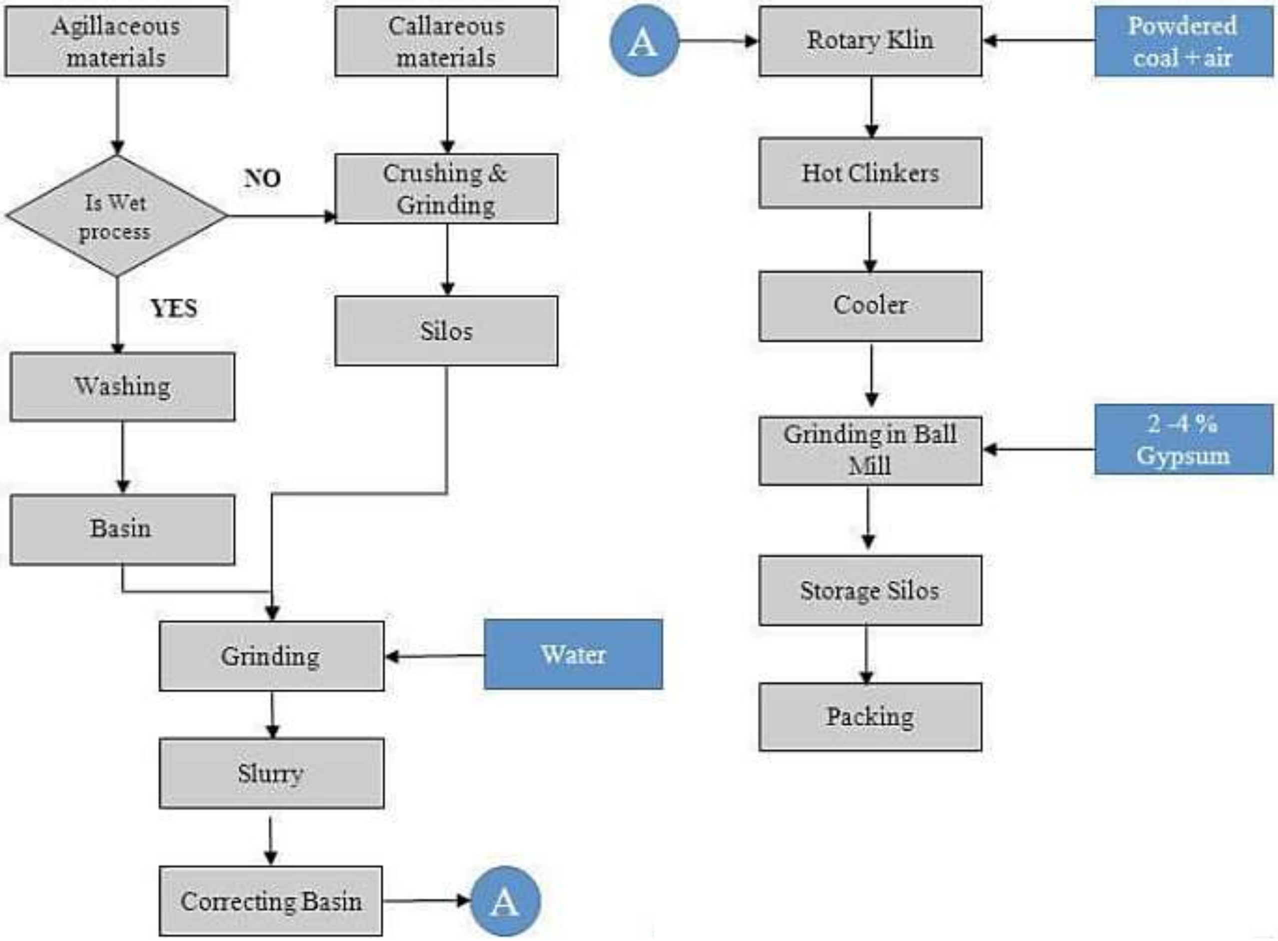


Figure 7. 15 Flowchart of Portland Cement manufacturing process

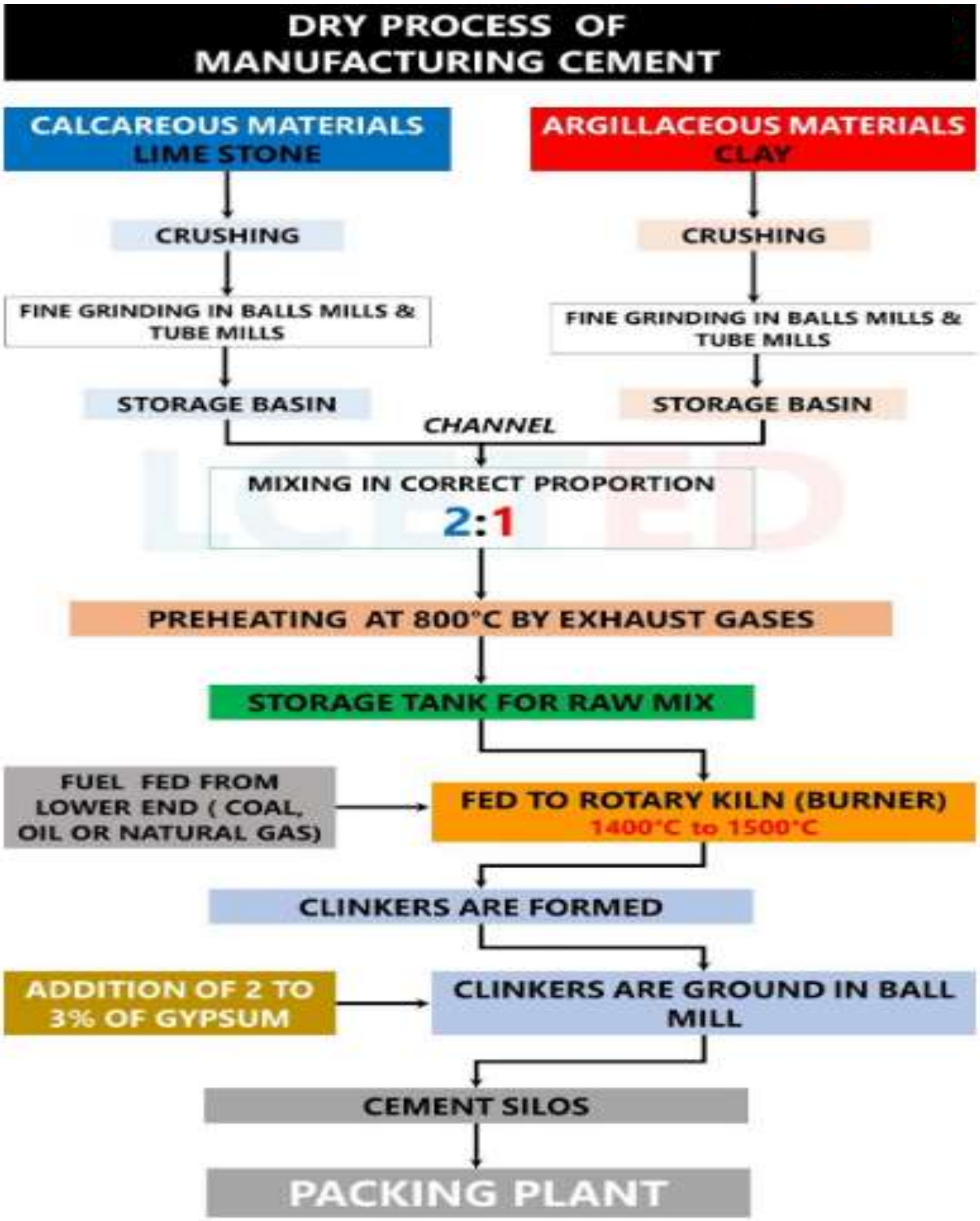


Figure 7. 16 Flowchart of Portland Cement manufacturing by Dry process

7.1.4.5. Comparison between Wet and Dry processes

Table 7. 2 Comparison between Wet and Dry processes

Wet process	Dry process
1-Moisture content of the slurry is about 32-40%	1-Moisture content of the pellets is 12%
2- Size of the kiln needed to manufacture the cement is bigger	2- Size of the kiln needed to manufacture the cement is smaller
3- The amount of heat required is higher, so the required fuel amount is higher	3- The amount of heat required is lower, so the required fuel amount is lower
4- Less economically	4- More economically
5- The raw materials can be mixed easily, so a better homogeneous material can be obtained	5- Difficult to control the mixing of raw materials process, so it is difficult to obtain a homogeneous material
6- The machinery and equipment do not need much maintenance	6- The machinery and equipment need more maintenance

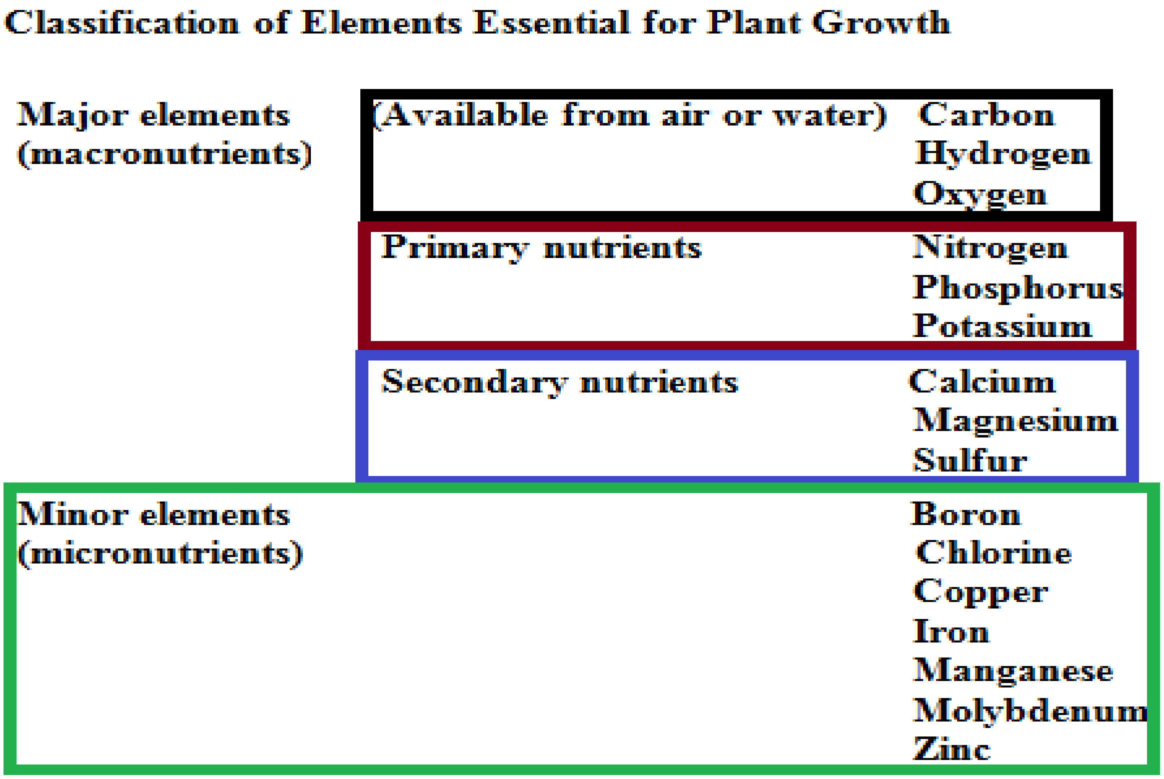
7.2. Fertilizers Production

A **fertilizer** is a material that includes one or more of the chemical elements necessary for the proper growth of plants.

Fertilizer product: (also called chemical or mineral fertilizer), is a material produced by industrial processes with the specific purpose of being used as a fertilizer.

Plant nutrients: chemical elements essential for the proper development and growth of plants.

Nitrate based mineral compound fertilizers: contain **Nitrogen** in Ammoniacal (NH_4) and Nitrate (NO_3) form, **Phosphorus** expressed as P_2O_5, and normally also **Potassium** expressed as K_2O. "NPK".



Classification of Elements Essential for Plant Growth

Major elements (macronutrients)	**(Available from air or water)**	**Carbon** **Hydrogen** **Oxygen**
	Primary nutrients	**Nitrogen** **Phosphorus** **Potassium**
	Secondary nutrients	**Calcium** **Magnesium** **Sulfur**
Minor elements (micronutrients)		**Boron** **Chlorine** **Copper** **Iron** **Manganese** **Molybdenum** **Zinc**

Figure 7. 17 Fertilizers production

These compound fertilizers are made by one of the two following important production routes:-

- The Nitric acid route or nitro-phosphate process.
- The Sulphuric acid route or mixed-acid process.

7.2.1. Nitro-Phosphate production process

1. Basic Concept

Nitro-phosphate process is a process which produces **compound fertilizers** containing Ammonium, Nitrate, Phosphate and Potassium salts. Phosphate sources (rock phosphate) must be converted into a form which can be taken up by plants.

- Dissolution of the rock phosphate in Nitric acid following the reaction:-

$$Ca_5F(PO_4)_3 + 10HNO_3 \longrightarrow 3H_3PO_4 + 5Ca(NO_3)_2 + HF$$

- Upon cooling, Calcium nitrate Tetra-hydrate (CNTH) crystallizes out following the reaction:-

$$H_3PO_4 + HNO_3 + Ca(NO_3)_2 + 4H_2O \longrightarrow H_3PO_4 + HNO_3 + Ca(NO_3)_2.4H_2O$$

The Nitro-phosphoric acid: The solution of Phosphoric acid, remaining Calcium nitrate and Nitric acid.

- The Nitro-phosphoric acid is then neutralized with Ammonia, mixed with Potassium/Magnesium salts, Sulphate and/or micro-nutrients and converted in a rotary granulation drum, fluidized bed or pug-mill to obtain solid compound fertilizers containing Nitrate.

- The separated Calcium nitrate crystals are treated with Ammonium Carbonate solution following the reaction:-

$$Ca(NO_3)_2 + (NH_4)_2\,CO_3 \longrightarrow CaCO_3 + 2NH_4NO_3$$

Calcium carbonate crystals are removed and used for the production of Calcium ammonium nitrate fertilizer. Dilute Ammonium nitrate solution is concentrated and used to produce Calcium ammonium nitrate fertilizer.

2. Technology of the Nitro-phosphate Process

A modern compound fertilizer plant, based on the Nitro-phosphate route, requires an integrated production complex of different units.

❑ Ammonia plant:

Ammonia is of importance in the Nitro-phosphate process because:-

- Liquid Ammonia is used in the Nitro-phosphoric acid section for cooling which is more economic than the use of cooling compressors with high energy consumption
- Gaseous Ammonia is used for the neutralization of the remaining acid.

❑ Nitric acid plant:

A Nitric acid plant on site is not a prerequisite because Nitric acid can be bought and stored without problems but there are important advantages from energy and environmental points of view if it is included in the integrated process:-

The Nitric acid plant provides surplus steam for concentration purposes in the other units and thus saves energy.

The Nitric acid plant can also process waste waters leading to a saving of expensive de-mineralized water and also saving energy.

❑ Nitro-phosphoric acid unit:

The production of Nitro-phosphoric acid takes place in a special unit.
Natural rock Phosphate, containing 30-40% P_2O_5, is first dissolved in about 60% HNO_3.

The reaction is exothermic. The temperature is controlled at about 70°C because of the high corrosion rate above 70-75°C.
The exothermic reaction leads to the emission of off-gases containing NOx and Fluorides. Such emission is controlled by collecting and combining the off-gases from the different vessels and treating them in a scrubbing unit before discharge to the atmosphere.
The resulting digestion solution contains different amounts of suspended solids, mostly quartz sand. The amount depending on the origin of the different rocks, is then treated to remove most of this sand by centrifuges.

Sand is undesirable and cause of equipment and piping damage by erosion.

The overflow solution flows into a storage tank and is subsequently used in the crystallization stage of the process.

The solution is cooled with water and liquid NH_3 to the required final crystallization temperature and most of the calcium crystallizes out as CNTH. These crystals are subsequently removed from the remaining solution by centrifuge.

The remaining nitro-phosphoric acid ("NP solution") having a 23% P_2O_5, 5.8% CaO, 6% NO_3-N and 33% H_2O, is the basic starting material for the production of nitrate containing compound fertilizers.

3. Compound fertilizer production unit:

Nitrate containing fertilizers can be produced from the nitro-phosphoric acid, by neutralizing with Ammonia and with the possible addition of Nitric acid, Ammonium sulphate or Sulphuric acid, Potassium and Magnesium salts and micronutrients. This production is carried out in three sections; neutralization, particle formation and conditioning.

❑ Neutralization:

The Nitro-phosphoric acid solution with a CaO/P_2O_5 ratio of 0.21-0.65 is neutralized with gaseous ammonia to around pH 5 in stainless steel reactors.

This reaction is very exothermic and raises the temperature to around the boiling point (125-145°C). The reaction heat is normally used for economic evaporation of the slurry and cooling the slurry.

Treatment with Ammonia and operate at high temperature, generating off-gases.

It is possible to use various condensing or scrubbing systems for off gases removal.

❑ Particle formation

Three types of processes are normally used for the production of NPK fertilizers; prilling, drum or pugmill granulation and Spheroids granulation.

❑ Conditioning

The commercial product is cooled in a fluidized bed, a bulk flow heat exchanger or rotating drum.

Off-gases from these latter stages, containing minor amounts of dust and generally no ammonia, are de-dusted in cyclones.

Finally, the product is cooled and coated before storage in order to minimize the subsequent caking of the material.

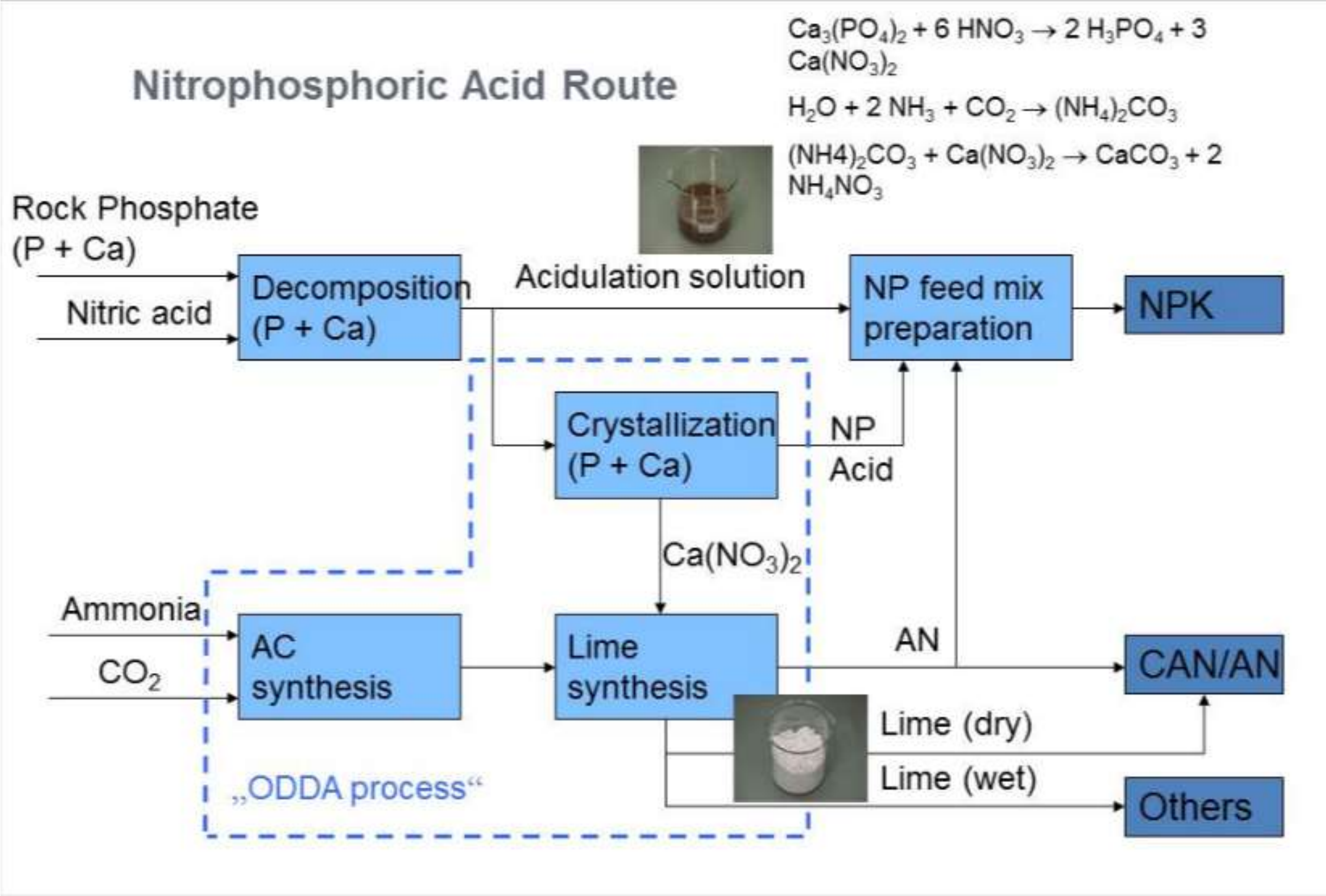


Figure 7. 18 Nitrophosphoric acid production - NPK Fertilizer

7.3. Production of Urea

Urea or Carbamide $CO(NH_2)_2$ is the Diamide of Carbonic acid. It is a concentrated Nitrogenous fertilizer (containing 46 percent Nitrogen) readily assimilable by plants.

Urea has a major outlet in industry for the production of Formaldehyde, condensation products-resins, plastics, lacquers, and adhesives. Urea also goes into the synthesis of medicinals (bromural, veronal, etc.), pharmaceuticals and cosmetics.

In **petroleum refining** Urea is employed for diesel duels. Urea is a good protein additive to food for ruminants.

The production of urea from ammonia obtained from refinery and casing-head gases and Carbon dioxide is one of the most important petrochemical processes. Urea synthesis proceeds in two stages:

1. **Formation of Ammonium carbamate**:

$$2NH_3 + CO_2 \leftrightarrow NH_2COONH_4 + 38{,}000\ \mathrm{cal/mole}$$

2. **Removal of a water molecule from the Carbamate to form Urea and water**

$$NH_2COONH_4 \leftrightarrow H_2O + NH_2 - CO - NH_2 + 6800\ \mathrm{cal/mole}$$

The formation of Ammonium carbamate is an exothermic reaction and the heat liberated is used up in the endothermic reaction of its dehydration.

The process includes Urea synthesis, distillation of Urea cake, and processing of Urea solution to form crystalline Urea.

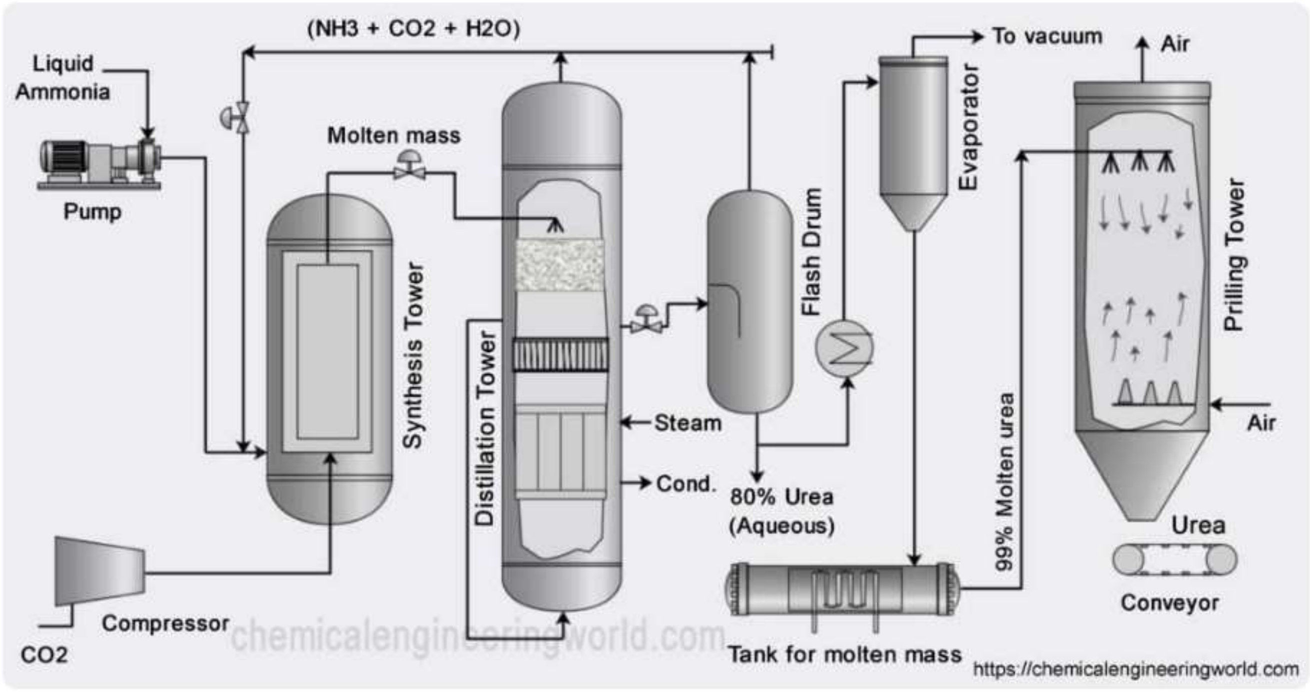
The synthesis is accomplished at 180-200℃ and 180-200 atm. The difficulties encountered in carrying out the process are due to the high corrosive action of the reagents, especially Ammonium carbamate. For this reason the equipment used must be made of special, preferably austenitic steels containing Chromium, Nickel, and Copper.

Reactors of various designs are used. There are reactors with special inserts serving as the reaction zone and precluding contact between the reaction products and the reactor walls.

These inserts are of high-alloy steels, making it possible to use cheaper alloy steel for the reactor body. Liquid Ammonia passes through the annular space between the insert and the body before entering the insert. As a result, only the insert corrodes, and is periodically replaced, while the autoclave body remains intact.

The reagent conversion per pass is 35-40 percent. The unreacted Carbon dioxide and Ammonia are returned to the process after separation from the Carbamide and Ammonium carbonates formed.

The process involving two-stage distillation of the cake is the more perfect one, because it enables more complete utilization of the initial reagents in the synthesis. In the two-stage distillation flow sheet the Ammonia given off during the first stage is recycled to the synthesis column, and only the minor amount of Ammonia liberated during the second stage is absorbed by Nitric acid. The yield of Ammonium nitrate obtained is 2-2.5 tons per ton of Ammonia.



https://chemicalengineeringworld.com

Figure 7. 19 Manufacture of urea from ammonia and carbon dioxide

Figure 7.19 represents a simplified flow sheet for the production of urea from Ammonia and Carbon dioxide.

Liquid Ammonia is pumped and Carbon dioxide is compressed and transported to the **reaction chamber**. Since this is where the reaction happens, it is the heart of the process. The pressure and temperature is maintained at 14 Mpa and 170-190°C for the first reaction to occur. As mentioned before, the reaction of Ammonia and Carbon dioxide is highly exothermic in nature. Most of the heat released is utilized in form of process steam wherever it is needed in to process.

The product from the first reaction flow into a **decomposer** where the second reaction occurs and it is endothermic reaction. It requires certain energy to begin. Biuret is also formed as a result of decomposition of Ammonium carbamate if temperature rise is excessive.

The conversion of the reactants to urea can be increased by increasing the amount of Carbon dioxide, if Carbon dioxide is present in excess then the conversion can be as high as 85% per pass but optimizing for the proper temperature, pressure and design is a challenge in itself hence usually per pass conversion are kept around 50%. The unreacted materials are recycled resulting in overall conversion of over 99%. This minimizes the effects on environment.

The major impurity in Urea is water and also unreacted Ammonia, Carbon dioxide and Ammonium carbamate. These are removed using distillation tower and evaporator. Essential condition is to keep temperature high and pressure low during stages of separation. At these conditions the Ammonium carbamate will be decomposed back to Ammonia and Carbon dioxide also some Carbon dioxide and Ammonia will flash off. The major process which happens in the evaporator is that of concentration. During concentration optimum temperature should be maintained so that the Urea remains in molten state and crystals are not formed inside the evaporator.

The molten Urea is passed through nozzles inside the **prilling tower**. Compressed air is passed in the tower so that its flow is counter current with respect to that of molten Urea. The Urea gets solidified in the prilling tower and air helps in shaping it in the form of prills or granules. The Urea is then stored and ready to be sold.

7.4. Natural gas

What is Natural Gas?

Natural gas: is a complex mixture of **hydrocarbon** and **non-hydrocarbon** constituents and exists as a gas under atmospheric conditions.

Natural gas is an odorless and colorless substance composed mostly of methane (94%), and small amounts of ethane, propane, butane, and pentane. Carbon dioxide, Hydrogen Sulphide and Nitrogen are the additional impurities that comprise a smaller percentage of natural gas' composition.

- There are two general types of Natural gas. **Biogenic gas** originates from marshes, bogs and landfills, where methanogenic organisms manufacture the gas. **Thermogenic** gas is what comes from deep beneath the earth, where buried organic material breaks down under high temperature and pressure.

- Methane, a combination of Hydrogen and Carbon, is formed when plants and animals (organic matter) are trapped beneath the sedimentary layers of the earth.

- In its original state, natural gas is odorless and colorless.

- Distribution companies add an odorant, Mercaptan, so that it is easily detectable in the event of leaks.

- For easy storage, chilling it to extremely cold temperatures can liquefy natural gas

Raw natural gas: typically consists primarily of **methane (CH_4),** the shortest and lightest hydrocarbon molecule.

Natural gas is responsible for approximately 23 percent of all energy produced in the world. It is generally considered as a non-renewable fossil fuel. It is called a fossil fuel because most scientists believe that natural gas was formed from the remains of tiny sea animals and plants that died 200-400 million years ago. Natural gas wells average 6000 feet deep.

Where is natural gas found?

The Natural gas that heats your home comes from deep beneath the earth, under several layers of rocks. The remains of plants and animals from millions of years ago were left buried under layers of rock and soil, before heat and pressure converted that matter into Natural gas and petroleum.

Once the gas has been created, it will attempt to migrate to a new location. The layers of the earth are molten rock, and those rocks can act as sponges for natural gas. Certain types of rocks within these layers contain large pores that act as storage units for Natural gas.

Like other fossil fuels, this is found deep underground. A rock formation called a **gas trap** allows the natural gas to form and collect. It contains three kinds of rocks:

- **The source rock** is the fossilized rock that produces the Natural gas.
- **The reservoir rock** is the porous rock that the Natural gas seeps into as it rises.
- **Cap rock**, or seal, is the layer of very dense rock above the reservoir rock that keeps the gas from leaking to the surface.

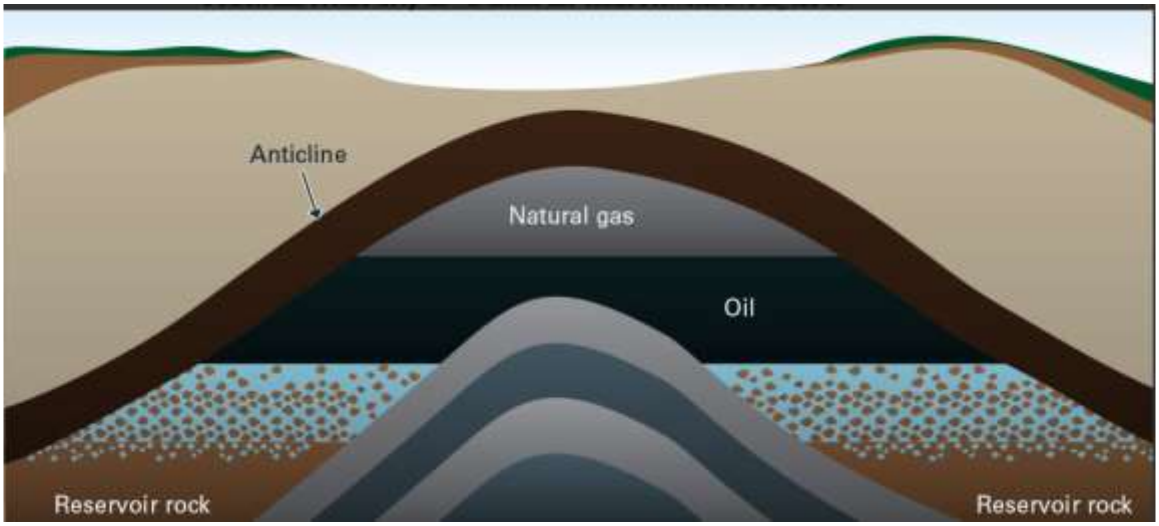


Figure 7. 20 Where is Natural gas found?

Petroleum occurs deep down under the earth between two layers of impervious rocks. Oil deposits are usually found mixed with water, sand and salts. Natural gas occurs above the petroleum oil trapped under the rocks.

To access these natural gases, companies drill hundreds of feet into the earth, pumping the gas into pipes. When piped to homes via boilers, furnaces or water heaters, this gas can serve to power ovens, gas-heated clothes dryers, central heating and cooling and more.

Natural gas classification:

Natural gas produced from geological formations comes in a wide array of compositions. The varieties of gas compositions can be broadly categorized into three distinct groups:

1. **Non-associated gas** that occurs in conventional gas fields,
2. **Associated gas** that occurs in conventional oil fields,
3. **Gas condensate** with high content of liquid hydrocarbon

Advantages of Natural gas

- **Economical: (**Natural gas is not as expensive as other burning fuels).
- **Clean:** Burns cleanly compared to other fossil fuels **(**Natural gas emits very less byproducts into the atmosphere as pollutants. This keeps the air we breathe cleaner**)**.
- **More heat/unit weight than any other fossil fuel**
- **More efficient: (**burning 10% energy loss only 60-year supply

at current rates)

Disadvantages of Natural gas

- Natural Gas is **Highly Combustible**
- **Long Processing Process**: (As Natural gas has other components that has to be removed before using it)
- **Leakage**: Even though it is lighter than air and can disperse easily
- **Storage**: Even though Natural gas is easier to store and transport, it has one big disadvantage. Its volume happens to be four times that of petrol which makes it more expensive to store since more needs to be spent on additional storage.

Major uses of Natural gas

- A **fuel source** domestically and around the world
- **Electricity Generation**
- **Heating**
- **Transportation**
- **Manufacturing:** Steel and paper production - petrochemicals, Hydrogen production, plastics, fertilizers, synthetic fibers, fabrics, glass, cosmetics, medicines and other products.

Typical Composition of Natural Gas:

It contains varying amounts of

- **Heavier gaseous hydrocarbons**: Ethane, Propane, n-Butane, iso-Butane, Pentanes and even higher molecular weight hydrocarbons. All of these are **NGL (Natural Gas Liquids)**.

- **Acid gases:** Carbon dioxide **(CO_2)**, Hydrogen sulfide **(H_2S)** and Mercaptans such as Methanethiol **(CH_3SH)** and Ethanethiol **(C_2H_5SH)**.
- **Other gases:** Nitrogen **(N_2)** and Helium **(He)**.
- **Water:** water vapor and liquid water.
- **Liquid hydrocarbons:** perhaps some Natural gas condensate.
- **Mercury:** very small amounts of mercury primarily in elementary form, but chlorides and other species are possibly present.

What are the Constituents of Natural Gas?

1. Compressed Natural Gas (CNG)

- When the Natural gas is compressed by increasing the pressure, it is called compressed natural gas (**CNG**).
- is an economical, clean burning, alternative fuel source for vehicles.
- The primary component of CNG is methane.

2. Liquid Natural Gas (LNG)

- LNG is Natural gas that has been cooled to –260° F (–162° C)
- Changing it from a gas into a liquid that is 1/600th of its original volume.
- This reduction allows it to be shipped safely and efficiently aboard specially designed LNG vessels.

Processing of Natural gas:

Is the treatment to remove the impurities and to recover the heavier hydrocarbons (heavier than methane).

For obtaining a sweet and dry Natural gas:

- Acid gases (CO_2 and H_2S) must be removed
- Water vapor reduced
- In addition, Natural gas with appreciable amounts of heavy hydrocarbons should be treated for their recovery as Natural gas liquids.

CO_2 and H_2S are very common contaminants in Natural Gas system

Reasons for CO_2 Removal for Gas Sweetening:

- When combined with water forms Carbonic Acid which is corrosive
- CO_2 reduces the calorific value of the gas
- If present in 2-3%, the gas is not saleable.
- Minimize operating and maintenance costs for fouling and corrosion control

Reasons for H_2S Removal for Gas Sweetening:

- Extremely toxic gas
- Highly corrosive

1) Acid Gas Treatment

The removal of acid gases (CO_2, H_2S and other sulfur components) from Natural gas is often referred to as gas **sweetening process**.

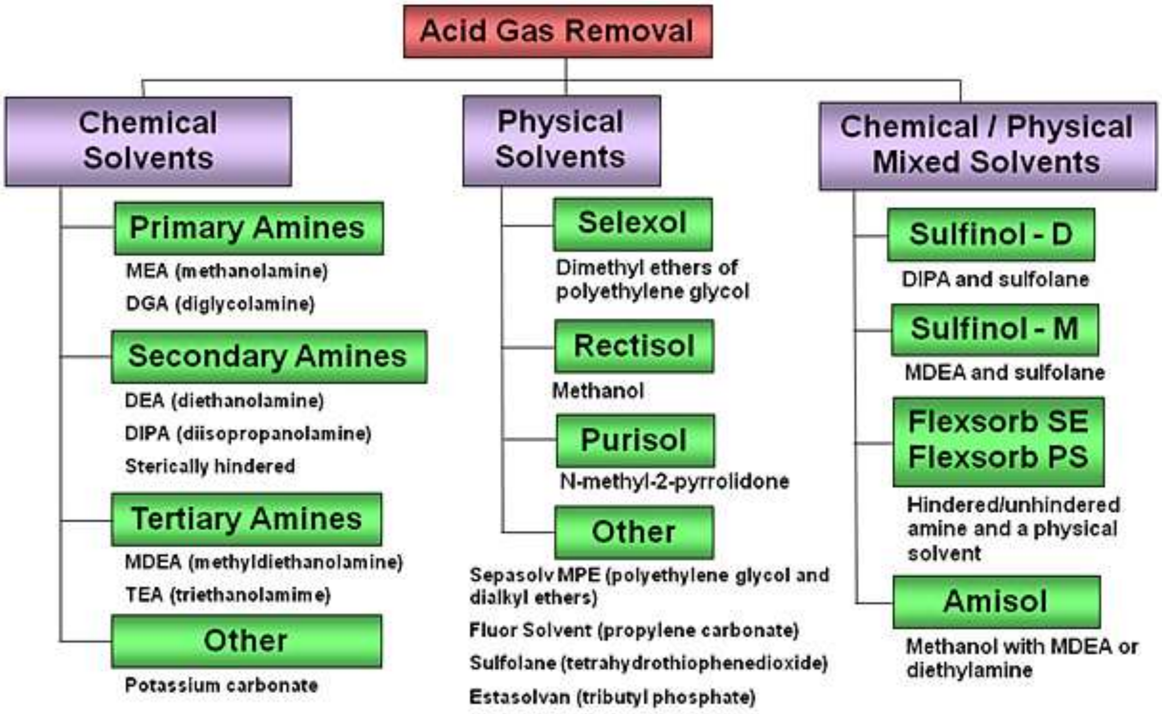


Figure 7. 21 Acid gases removal technologies

The major processes available can be grouped as follows:

- Physical absorption using a selective absorption solvent.
- Physical adsorption using a solid adsorbent.
- Physical Separation (Membrane).
- Chemical absorption where a solvent (a chemical) capable of reacting reversibly with the acid gases is used.

Physical absorption:

Selexol is the trade name for an acid gas removal solvent that can separate acid gases such as Hydrogen sulfide and Carbon dioxide from feed gas streams.

In these processes, no chemical reaction occurs between the acid gas and the solvent. The solvent (Dimethyl ether or Polyethylene glycol) is a liquid that selectively absorbs the acid gases and leaves out the hydrocarbons.

Raw Natural gas passes through the solvent. When the solvent becomes saturated with the acid gases, the pressure is reduced, and Hydrogen sulfide and Carbon dioxide are desorbed. The solvent is then recycled to the absorption tower.

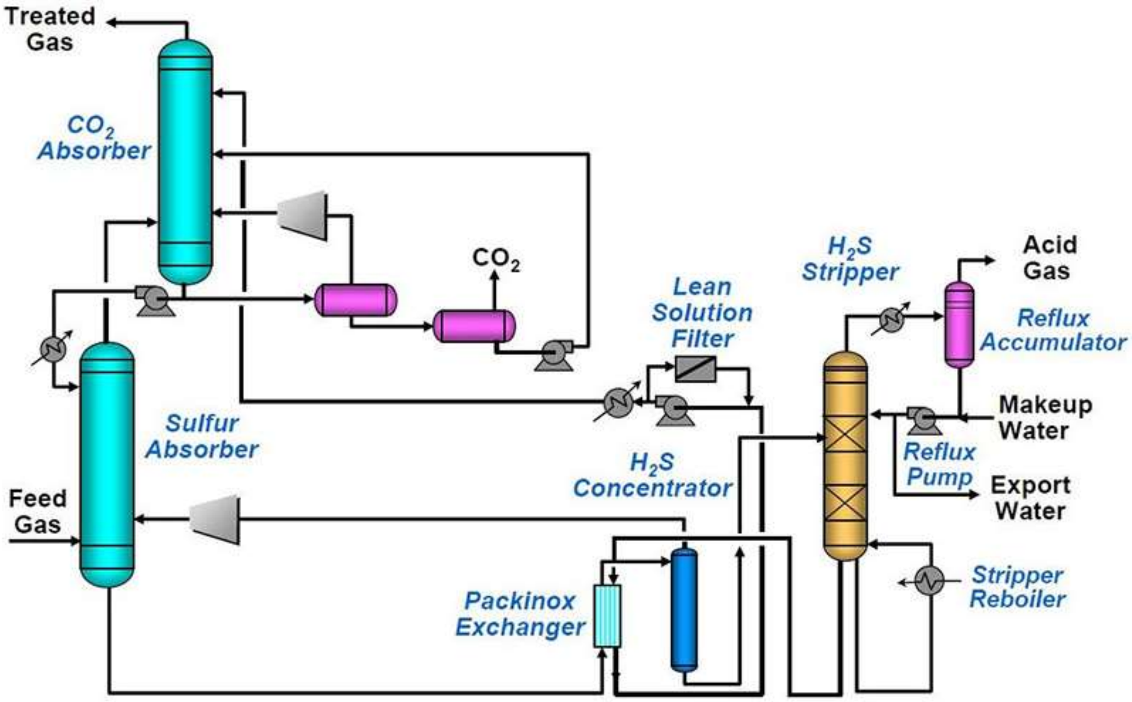


Figure 7. 22 Dual-stage Selexol flow diagram

❑ Physical adsorption:

In these processes, a solid with a high surface area is used. **Molecular sieves** (zeolites) are widely used and are capable of adsorbing large amounts of gases. In practice, more than one adsorption bed is used for continuous operation. One bed is in use while the other is being regenerated.

Regeneration is accomplished by passing hot dry fuel gas through the bed. Molecular sieves are also capable of adsorbing water in addition to the acid gases.

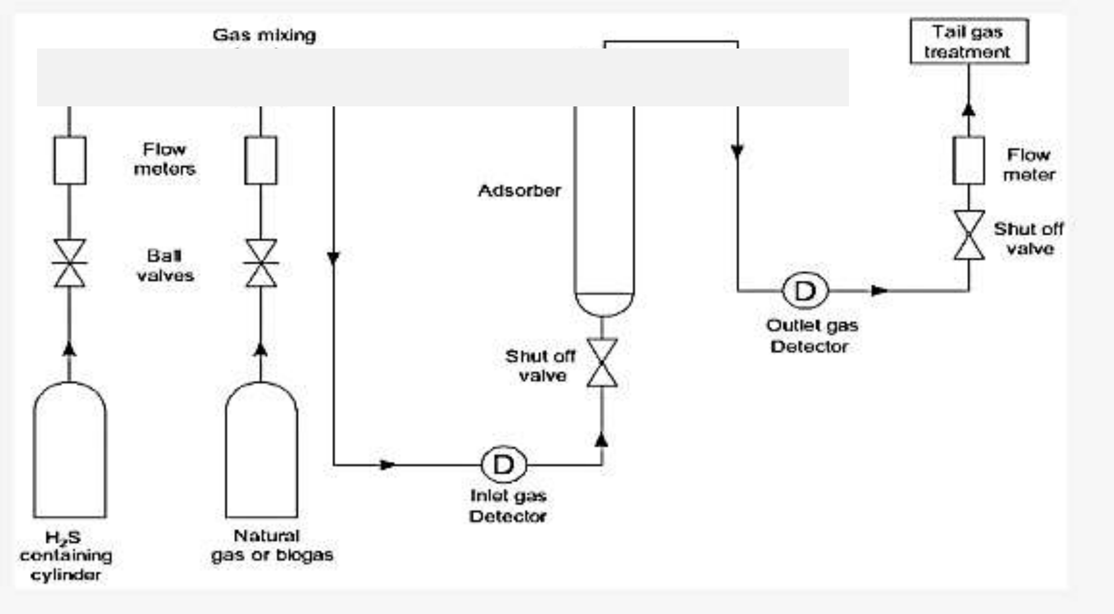


Figure 7. 23 Experimental set up for the removal of H_2S by Physical adsorption

❑ Chemical Absorption (Chemisorption):

Sweetening of Natural gas is one of the most important steps in gas processing and there are more than 30 processes of sweetening such as <u>Batch solid bed absorption</u> (for complete removal of H_2S at low Concentrations), <u>Reactive solvents</u> using MEA, DEA or MDEA (these solutions are used to remove large amounts of H_2S and CO_2 and the solvents are regenerated).

The concept: a solution of a relatively weak base, such as monoethanolamine is used. The acid gas (like H_2S and CO_2) forms a weak bond with the base which can be regenerated easily. Mono-and diethanolamines as well as diglycolamine (DGA) are frequently used for this purpose. Natural gas is passed through the amine solution where sulfides, carbonates, and bicarbonates are formed.

This process is characterized by a high capability of absorbing large amounts of acid gases.

Reasons for sweetening

- Safety and environmental protection
- Product specification
- Corrosion prevention
- Improved heating values
- CO_2 solid formation (Cryogenic operations)
- Economics (sometimes)

Acid gas removal processes utilize amines or specialty solvents to remove acid gases such as H_2S and/or CO_2 from **sour natural gas** in order to meet the gas quality specifications. These components are removed because they can form acidic solutions when they contact water, which will cause corrosion problems in gas pipelines.

The most widely method used for sweetening of natural gas is **reactive solvents (Amine)**. They are generally used for bulk removal of CO_2 and H_2S. The **low operating cost** and **flexibility of varying solvent composition to suit gas compositions** make this process one of most commonly selected.

The sour gas is contacted with **lean amine** in the contactor tower. An acid-base reaction occurs, binding the acid gases to the amine with a weak bond. The **rich amine** then flows to a regenerator, where heat breaks the weak bond between the amine and the acid gas, releasing the acid gas and regenerating the amine for re-use. The acid gases exit the top of the regenerator for further treatment while the lean amine is recirculated back to the contactor in a recirculating loop.

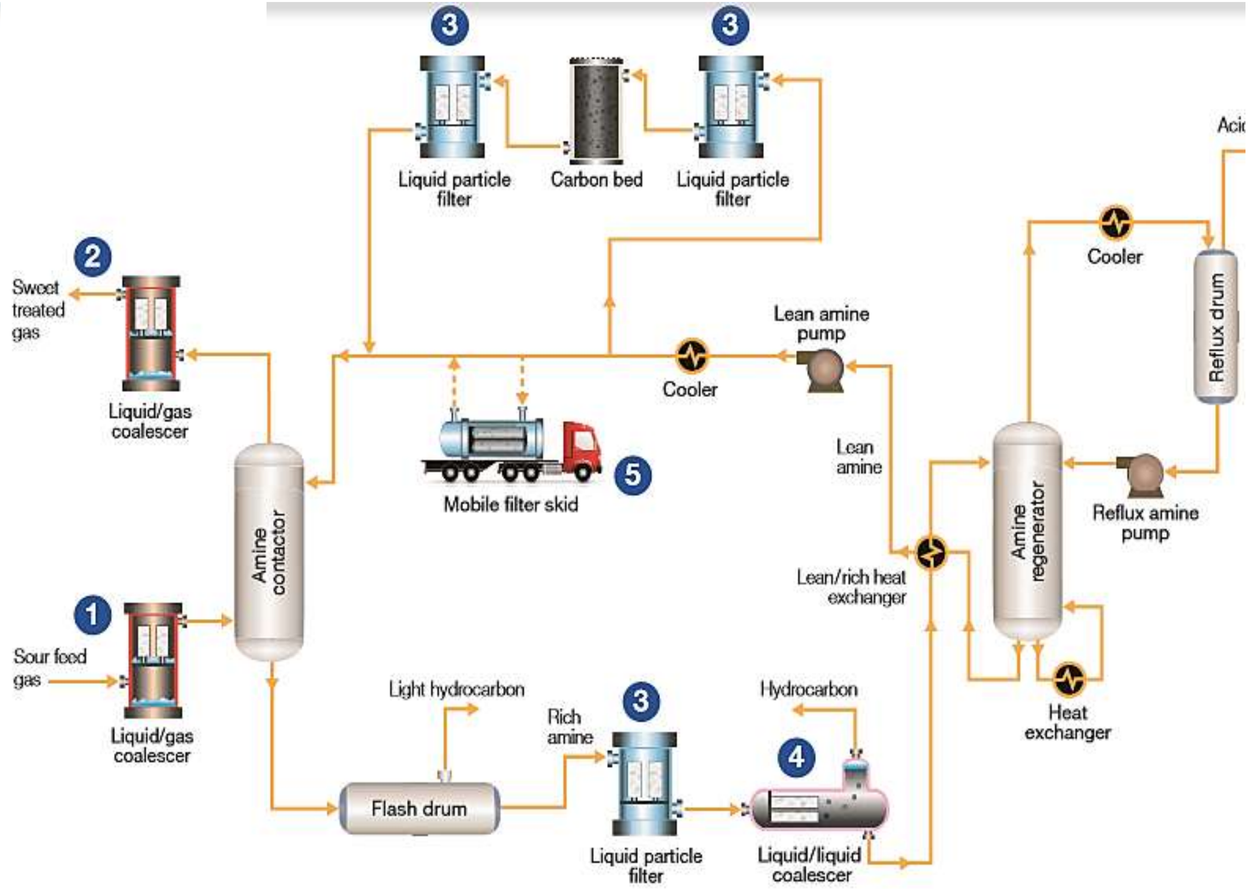


Figure 7. 24 Flow Diagram for the reactive solvent process for NG - Sweetening

2)Water Removal (Gas Dehydration):

Natural gas dehydration: is the process of removing water vapor from the gas stream to lower the dew point of that gas.

The dew point: is defined as the temperature at which water vapor condenses from the gas stream.

Dehydration prevents the formation of gas hydrates and reduces corrosion. Unless gases are dehydrated, liquid water may condense in pipelines and accumulate at low points along the line, reducing its flow capacity.

There are two ways to prevent hydrate formation

- **Treatment of Natural gas with glycols:** glycols like Ethylene glycol (EG), diethylene glycol (DEG), and triethylene glycol (TEG) are typical solvents for water removal which dissolve water efficiently.
- **Addition of Thermodynamic inhibitors:** chemicals can be injected into the production stream to depress the probability of significant hydrate formation. A Thermodynamic inhibitor alters the chemical potential of the hydrate phase such that the hydrate formation point is displaced to a lower temperature and/or a higher pressure.

Generally, an alcohol or one of the glycols—usually Methanol, Ethylene glycol (EG), or Diethylene glycol (DEG)—is injected as an inhibitor.

3)Separation of heavy hydrocarbons:

After the improvement of Natural gas sweet dry, hydrocarbons heavier than Methane that are present in Natural gases are valuable raw materials and important fuels and should be separated.

They can be recovered by oil extraction and heavy hydrocarbons are liquefied.

Natural gas liquids are normally fractionated to separate them into three streams:

- An ethane-rich stream, which is used for producing ethylene.
- Liquefied petroleum gas (LPG), which is a propane-butane mixture. It is mainly used as a fuel.
- Natural gasoline (NG) is mainly constituted of C5+ hydrocarbons and is added to gasoline to raise its vapor pressure.

Sheet no. (7)

1. **Define:**

Cement – wet process – dry process – sweetening process of Natural gas – uses of Natural gas – reasons for the liquefaction of Natural gas.

2. What are the types of materials necessary for the production of Portland Cement?

3. What is the importance of **gypsum** addition in Cement manufacturing?

4. Compare between wet process and dry process: Definition – reasons for using each method – economics – maintenance – size f kiln – moisture content – amount of heat required.

5. **Draw** and **explain** a flow sheet for manufacturing cement by wet process?

6. State the main reasons for **sweetening of Natural gas**.

7. What are the most widely methods used for sweetening of natural gas?

8. Natural gas is odorless and colorless but the companies added …………. to be easily detectable

9. **Choose the correct answer:**
   - **In cement production, 5% $CaSO_4$ added to:**

   a. Allow hardening
   b. Prevent hardening
   c. Control hardening

- **…………..is steel tube lined inside with free bricks. It is 90 to 120 meters long and from 2.5 to 3.5 meters in diameter.**

a. Rotary Kiln
b. Ball Mill
c. jaw crusher

- **The quality of cement is not so good in the ……………………**

a. Wet process
b. Dry process
c. Both (a) and (b)

- **$CaCO_3$ is called ………………..**

a. Silica
b. Clay
c. Lime stone

- **The selection of suitable process depends ………………**

a. Overall techno- economic feasibility
b. Availability and cost of utilities
c. all the above

- **Pick up the incorrect statement from the following:**

a. Dry process is more economical than wet process
b. Moisture content in dry process less than wet process
c. Size of kiln used in dry process is taller than wet process

- **CO_2 and H_2S are removed from Natural gas in**

a. Absorber
b. Regenerator
c. Distillation tower

- **Which of the following statements about volume comparison between NG and LNG is true?**

a. 1kg of Natural gas is 600 times smaller than 1kg of LNG
b. 1kg of Natural gas is 600 times larger than 1kg of LNG

c. 1kg of Natural gas is equal to 1kg of LNG

- **Which gas is present in compressed Natural gas (CNG)**

a. Oxygen
b. Methane
c. Carbon dioxide

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Appendix (A)

The term SI is from the International System of Units. There are 7 SI base quantities. It is the world's most widely used system of measurement, both in everyday commerce and in science. The system is nearly universally employed.

Length: measures distance between objects

1m = 100 cm
1cm= 10 mm
1 Km = 1000 m
1 ft = 0.2048 m

Mass: measures the amount of matter in an object

1 Kg = 1000 gm
1 Ib = 453.6 gm = 0.4536 Kg

Volume: measures the amount of space something takes up

1 m^3 = 1000 Liter
1 m^3 = 10^6 cm^3
1 Gallon = 3.785 Liter
1 Liter = 1000 cm^3
1 ml = 1 cm^3

Pressure: is the ratio of force to the area over which that force is distributed, and it is the amount of force acting per unit area.

1 atm = 760 mmHg

1 atm = 14.7 Psi
1 atm = 1.013×10^5 Pascal (N/m^2)
1 atm = 1.013 bar

Time: is Motion with Memory

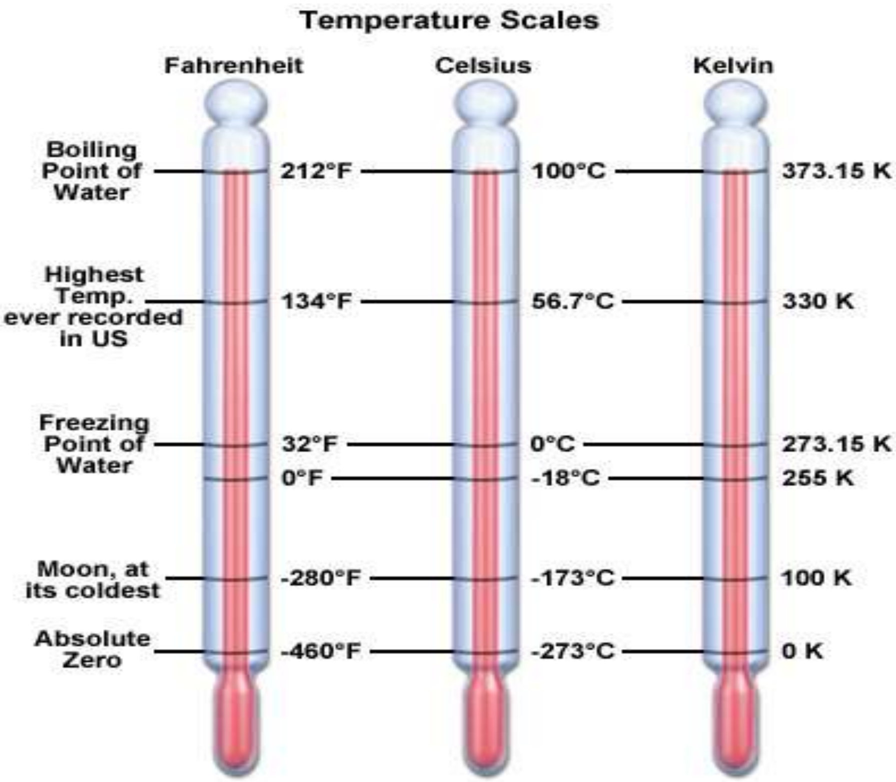
1 day = 24 hrs
1 hr = 3600 Seconds

Energy: is the process of changing one form of energy into another**.**

1 Btu = 252 Cal
1 Cal = 4.18 Joule

Temperature scales: Temperature is a measure of the kinetic energy of the atoms in an object.

- Temperature is measured with a thermometer and measured in Celsius or Kelvin.
- Celsius ranges from 0 (freezing) to 100 (boiling).
- The Kelvin scale begins at absolute zero, or 0 K. At 0 Kelvin no more heat can be removed from an object.



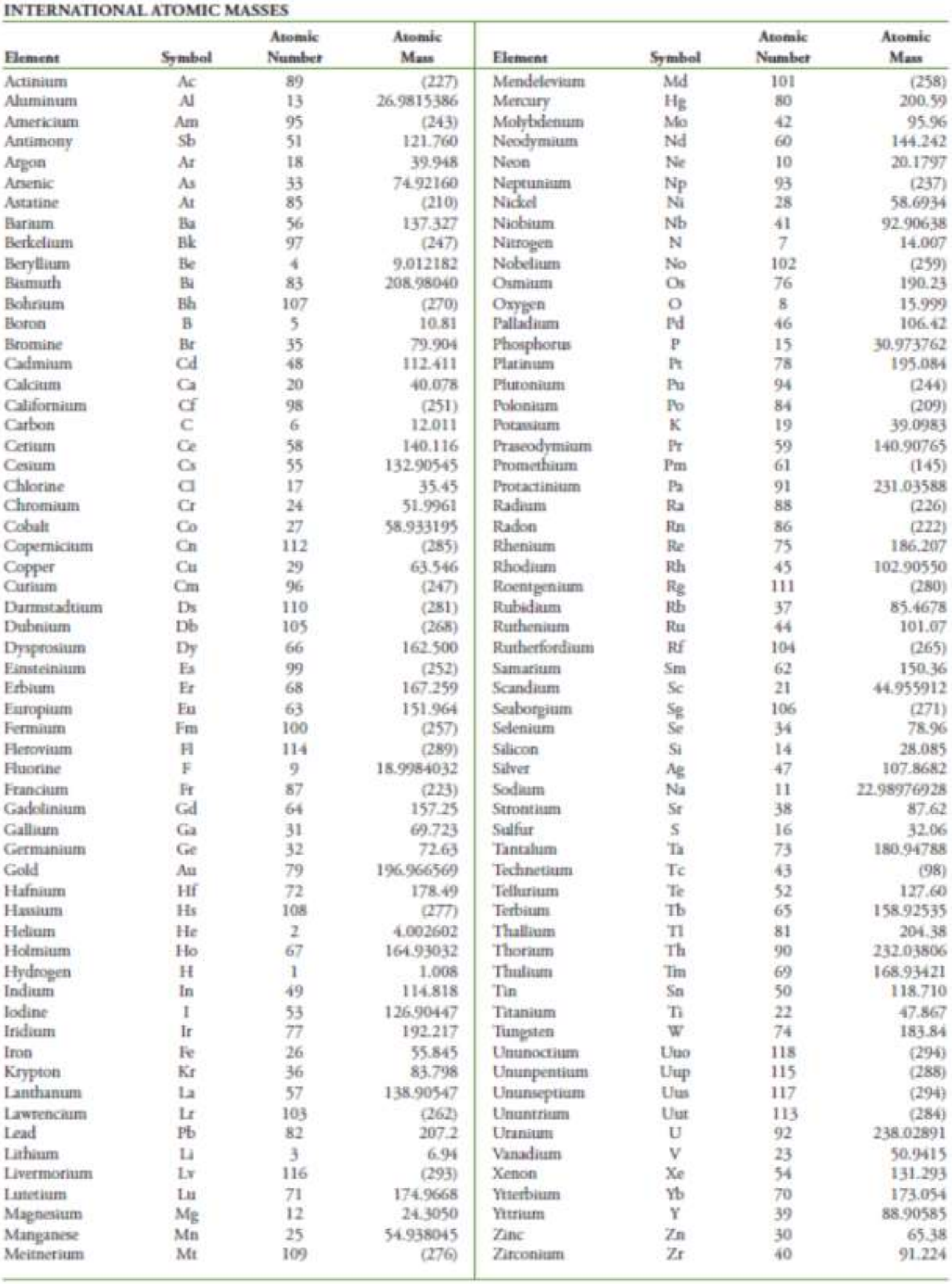
$T_F{}^{o} = 1.8\, T_C{}^{o} + 32$

$T_K = T_c{}^{o} + 273$

$\Delta T_C{}^{o} = \Delta T_K$

$\Delta T_F{}^{o} = 1.8\, \Delta T_C{}^{o}$

Appendix (B)



INTERNATIONAL ATOMIC MASSES

Element	Symbol	Atomic Number	Atomic Mass
Actinium	Ac	89	(227)
Aluminum	Al	13	26.9815386
Americium	Am	95	(243)
Antimony	Sb	51	121.760
Argon	Ar	18	39.948
Arsenic	As	33	74.92160
Astatine	At	85	(210)
Barium	Ba	56	137.327
Berkelium	Bk	97	(247)
Beryllium	Be	4	9.012182
Bismuth	Bi	83	208.98040
Bohrium	Bh	107	(270)
Boron	B	5	10.81
Bromine	Br	35	79.904
Cadmium	Cd	48	112.411
Calcium	Ca	20	40.078
Californium	Cf	98	(251)
Carbon	C	6	12.011
Cerium	Ce	58	140.116
Cesium	Cs	55	132.90545
Chlorine	Cl	17	35.45
Chromium	Cr	24	51.9961
Cobalt	Co	27	58.933195
Copernicium	Cn	112	(285)
Copper	Cu	29	63.546
Curium	Cm	96	(247)
Darmstadtium	Ds	110	(281)
Dubnium	Db	105	(268)
Dysprosium	Dy	66	162.500
Einsteinium	Es	99	(252)
Erbium	Er	68	167.259
Europium	Eu	63	151.964
Fermium	Fm	100	(257)
Flerovium	Fl	114	(289)
Fluorine	F	9	18.9984032
Francium	Fr	87	(223)
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.723
Germanium	Ge	32	72.63
Gold	Au	79	196.966569
Hafnium	Hf	72	178.49
Hassium	Hs	108	(277)
Helium	He	2	4.002602
Holmium	Ho	67	164.93032
Hydrogen	H	1	1.008
Indium	In	49	114.818
Iodine	I	53	126.90447
Iridium	Ir	77	192.217
Iron	Fe	26	55.845
Krypton	Kr	36	83.798
Lanthanum	La	57	138.90547
Lawrencium	Lr	103	(262)
Lead	Pb	82	207.2
Lithium	Li	3	6.94
Livermorium	Lv	116	(293)
Lutetium	Lu	71	174.9668
Magnesium	Mg	12	24.3050
Manganese	Mn	25	54.938045
Meitnerium	Mt	109	(276)
Mendelevium	Md	101	(258)
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.96
Neodymium	Nd	60	144.242
Neon	Ne	10	20.1797
Neptunium	Np	93	(237)
Nickel	Ni	28	58.6934
Niobium	Nb	41	92.90638
Nitrogen	N	7	14.007
Nobelium	No	102	(259)
Osmium	Os	76	190.23
Oxygen	O	8	15.999
Palladium	Pd	46	106.42
Phosphorus	P	15	30.973762
Platinum	Pt	78	195.084
Plutonium	Pu	94	(244)
Polonium	Po	84	(209)
Potassium	K	19	39.0983
Praseodymium	Pr	59	140.90765
Promethium	Pm	61	(145)
Protactinium	Pa	91	231.03588
Radium	Ra	88	(226)
Radon	Rn	86	(222)
Rhenium	Re	75	186.207
Rhodium	Rh	45	102.90550
Roentgenium	Rg	111	(280)
Rubidium	Rb	37	85.4678
Ruthenium	Ru	44	101.07
Rutherfordium	Rf	104	(265)
Samarium	Sm	62	150.36
Scandium	Sc	21	44.955912
Seaborgium	Sg	106	(271)
Selenium	Se	34	78.96
Silicon	Si	14	28.085
Silver	Ag	47	107.8682
Sodium	Na	11	22.98976928
Strontium	Sr	38	87.62
Sulfur	S	16	32.06
Tantalum	Ta	73	180.94788
Technetium	Tc	43	(98)
Tellurium	Te	52	127.60
Terbium	Tb	65	158.92535
Thallium	Tl	81	204.38
Thorium	Th	90	232.03806
Thulium	Tm	69	168.93421
Tin	Sn	50	118.710
Titanium	Ti	22	47.867
Tungsten	W	74	183.84
Ununoctium	Uuo	118	(294)
Ununpentium	Uup	115	(288)
Ununseptium	Uus	117	(294)
Ununtrium	Uut	113	(284)
Uranium	U	92	238.02891
Vanadium	V	23	50.9415
Xenon	Xe	54	131.293
Ytterbium	Yb	70	173.054
Yttrium	Y	39	88.90585
Zinc	Zn	30	65.38
Zirconium	Zr	40	91.224