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FACULTY OF SCIENCE
DEPARTMENT OF CHEMISTRY
CHEM111 LECTURE NOTE

- GASES -

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INTRODUCTION

This part of the course intends to introduce students to the chemistry of the three states of matter being Solids, Liquids and Gases.

GASES

Gases are treated under three different categories. These are; Ideal Gas, Kinetic Gas and the Real Gas. They obey different mathematical equations.

IDEAL GASES

An Ideal Gas is any gas whose pressure P , volume V , and temperature T are related by the ideal gas law/equation of state $PV = nRT$.

where n is the number of moles of the gas, R is the ideal gas constant.

DERIVATION OF IDEAL GAS EQUATION

The ideal gas equation is derived by combining Boyle's law, Charles' law and Avogadro's law.

Boyle's Law + Charles' Law + Avogadro's Law = Ideal Gas Equation

Boyle's Law

Volume is inversely proportional to pressure at constant temperature and a fixed amount of gas. $V \propto \frac{1}{P}$ (T, n constant) (i)

Charles' Law

Volume is directly proportional to absolute temperature at constant pressure and a fixed amount of gas. $V \propto T$ (P, n constant) (ii)

Avogadro's Law

Volume is directly proportional to the amount of gas at constant pressure and temperature. $V \propto n$ (P, T constant) (iii)

These three laws can be combined into a single more general gas law:

$$V \propto \frac{nT}{P} \quad (\text{iv})$$

Equation (4) is called the **Universal Gas Law**. It is also called **Ideal Gas Law** as it applies to all gases which exhibit ideal behaviour i.e., obeys the gas laws perfectly. The **Ideal Gas Law** may be stated as: "the volume of a given amount of gas is directly proportional to the number of moles of gas, directly proportional to the absolute temperature, and inversely proportional to the pressure". Introducing the proportionality constant **R** (called, the Gas constant) in equation (iv), we can write

$$V = R \frac{nT}{P} \quad \text{OR} \quad PV = nRT \quad (v)$$

Equation (5) is called the **Ideal Gas Equation**. It is also called an **Equation of State** for a gas, because it contains all the variables (T , P , V and n) which describe completely the condition or state of any gas sample. If we know the three of these variables, it is enough to specify the system completely because the fourth variable can be calculated from the ideal-gas equation.

The Numerical value of R: From the ideal-gas equation, we can write

$R = \frac{PV}{nT}$ We know that one mole of any gas at STP occupies a volume of 22.4 litres. Substituting the values in the above expression, we have

$$R = \frac{1\text{ atm} * 22.4\text{ dm}^3}{1\text{ mole} * 273\text{ K}} = 0.0821 \text{ atm dm}^3 \text{ mol}^{-1} \text{ K}^{-1}$$

Other values of **R** include

- $8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$
- $62.364 \text{ Torr dm}^3 \text{ mol}^{-1} \text{ K}^{-1}$
- note: $8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$ is the SI unit for the gas constant.

Hints:

Because of the various value of **R** one can use to solve a problem, it is crucial to match your units of pressure, volume, number of mole, and temperature with units of **R**.

If you use the first value of **R**, which is $0.0821 \text{ atm dm}^3 \text{ mol}^{-1} \text{ K}^{-1}$, your unit for Pressure must be atm, for Volume must be litre, for Temperature must be Kelvin.

□ If you use the second value of R, which is $62.364 \text{ Torr dm}^3 \text{ mol}^{-1} \text{ K}^{-1}$, your unit for pressure must be torr, for volume must be litre, for Temperature must be Kelvin.

CALCULATING THE NUMBER OF MOLES, n

$$\text{Number of moles} = \frac{\text{Mass}}{\text{Molar Mass}}$$

□ Example: 1

Calculate the number of moles of the following gases,

- (1) 5.6g of Nitrogen gas, $\text{N}_2(\text{g})$ (2) 1.32g of $\text{CO}_2(\text{g})$

Solution:

$$(1) n\text{N}_2(\text{g}) = (5.6/28)\text{mol} = 0.20\text{mol} \quad (2) n\text{CO}_2(\text{g}) = (1.32/44)\text{mol} = 0.03\text{mol}$$

The usefulness of the ideal gas equation is that it relates the four variables, P, V, n and T, that describe a sample of gas at one set of conditions.

□ Example: 2

What pressure, in atmosphere is exerted by 54.0g of Xe in a litre flask at 293K?
(Xe = 131.38)

Solution:

$$V = 1.0\text{L}, n = 0.411\text{mol}, T = 293\text{K} \text{ and } P = ?$$

Solving, $PV = nRT$ for P and substituting gives

$$P = nRT/V = (0.411\text{mol})(0.0821 \text{ atm dm}^3 \text{ mol}^{-1} \text{ K}^{-1})(293\text{K})/1.0\text{L}, P = 9.89\text{atm}$$

□ Example: 3

5.0g of neon is at 256mmHg and at a temperature of 35°C. What is the volume?

Solution:

$$P = 256\text{mmHg}, m = 5.0\text{g}, T = 35^\circ\text{C}, R = 0.0821 \text{ atm dm}^3 \text{ mol}^{-1} \text{ K}^{-1}, V = ?$$

Convert as necessary: Pressure: $256\text{mmHg} \times (1\text{atm}/760\text{mmHg}) = 0.336\text{atm}$

Moles: $5.0\text{g Ne} \times (1\text{mol}/20.1797\text{g}) = 0.25\text{ mol Ne}$, Temperature: $35^\circ\text{C} + 273 =$

308K

Plug in the variables into the appropriate equation

$$V = (nRT/P)$$

$$V = \frac{(0.25\text{mol})(0.0821\text{atm}\text{dm}^3\text{mol}^{-1}\text{K}^{-1})(308\text{K})}{0.3368\text{atm}} = 19\text{L}$$

Example: 4

What is the gas' temperature in Celsius when it has a volume of 25 dm^3 , 203 mol , 143.5 atm ?

Solution:

$$P = 143.5\text{ atm}, n = 203\text{ mol}, V = 25\text{ dm}^3, R = 0.0821\text{ atm dm}^3\text{mol}^{-1}\text{K}^{-1}, T = ?$$

$$T = PV/nR$$

$$T = \frac{(143.5\text{ atm})(25\text{ dm}^3)}{(203\text{ mol})(0.0821\text{ atm dm}^3\text{mol}^{-1}\text{K}^{-1})} = 215.4\text{ K}$$

Converting the temperature to Celsius, gives: $215.4\text{ K} - 273\text{ K} = -57.4^\circ\text{C}$

EXPRESSING $PV = nRT$ IN TERMS OF DENSITY, ρ

Density is defined as mass per unit volume i.e., $\rho = m/V$ (i)

For an ideal gas $PV = nRT$

$$V = nRT/P \quad (\text{ii})$$

Put eqn (ii) in (i), we have

$$\rho = Pm/nRT \quad (\text{iii})$$

$$\text{But } n = \text{mass/molar mass} = m/M \quad (\text{iv})$$

Put eqn (iv) in (iii)

$$\rho = PM/RT \quad (\text{v})$$

Example: 5

Calculate the density of Ammonia (NH_3) in gL^{-1} at 0.989 atm and 55°C .

Solution:

$$P = 0.989\text{ atm}, T = 328\text{ K}, R = 0.0821\text{ atm dm}^3\text{mol}^{-1}\text{K}^{-1}$$

The molar mass of NH_3 is 17.03 g mol^{-1}

$$\rho = PM/RT = (0.989\text{ atm})(17.03\text{ g mol}^{-1}) / (0.0821\text{ atm dm}^3\text{mol}^{-1}\text{K}^{-1})(328\text{ K})$$

$$\rho = 0.625\text{ g L}^{-1}$$

Example: 6

What is the density of nitrogen gas (N_2) at 248.0 Torr and 18°C.

Solution:

$$P = 248.0 \text{ Torr}, R = 0.0821 \text{ atmLmol}^{-1}\text{K}^{-1}, T = 18^\circ\text{C}, V = ?, n = ?$$

$$\text{Convert as necessary: } (248 \text{ Torr}) \times \frac{1 \text{ atm}}{760 \text{ Torr}} = 0.3263 \text{ atm}$$

$$18^\circ\text{C} + 273 = 291 \text{ K}$$

Using the equation, $\rho = PM/RT$, gives

$$\rho = \frac{(0.3263 \text{ atm})(2 * 14.01 \text{ g mol}^{-1})}{(0.0821 \text{ atm L mol}^{-1} \text{ K}^{-1})(291 \text{ K})} = 0.3828 \text{ g/l}$$

DALTON'S LAW OF PARTIAL PRESSURE

It states that: the total pressure of a mixture of gases is equal to the sum of the partial pressures of all gases present. Mathematically the law can be expressed as:

$$P_{\text{total}} = P_1 + P_2 + P_3 + \dots + P_n \quad (1)$$

where P_1 , P_2 and P_3 are partial pressures of the three gases 1, 2 and 3; and so on. Dalton's Law of partial pressures, followed by application of the ideal-gas equation $PV = nRT$ separately to each gas of the mixture. Thus we can write the partial pressures P_1 , P_2 and P_3 of the three gases

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

Where n_1 , n_2 and n_3 are moles of gases 1, 2 and 3. The total pressure, P_{total} of the mixture is

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

In other words, the total pressure of the mixture is determined by the total number of moles present, whether of just one gas or a mixture of gases.

□ Example: 7

What pressure is exerted by a mixture of 2.00g of H_2 and 8.00g of N_2 at 273K in a 10litre vessel?

Solution:

$$\text{Moles of H}_2 = 2.00/2.02 = 0.990 \text{ moles},$$
$$\text{Moles of N}_2 = 8.00/28 = 0.286 \text{ moles}.$$
$$n_{\text{total}} = 1.276 \text{ mol}$$

Therefore, $P_{\text{total}} = (n_{\text{He}} + n_{\text{N}_2}) \left(\frac{RT}{V} \right)$

$$P_{\text{total}} = (0.990 \text{ mole} + 0.286 \text{ mole}) \left(\frac{(0.0821 \text{ atm L mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{10.0 \text{ litres}} \right) = 31.218 \text{ atm}$$

For the individual pressures,

$$\text{Partial pressure of nitrogen} = \frac{n_{\text{N}_2}}{n_{\text{total}}} \times P_{\text{total}} = 0.286 \div 1.276 \times 31.21 \text{ atm} = 6.99 \text{ atm}$$

$$\text{Partial pressure of Helium} = \frac{n_{\text{He}}}{n_{\text{total}}} \times P_{\text{total}} = 0.990 \div 1.276 \times 31.21 \text{ atm} = 24.21 \text{ atm}$$

□ MOLE FRACTIONS

By definition, $n_A + n_B = n_{\text{total}}$

Divide eqn. 1 through by n_{total} .

$$\frac{n_A}{n_{\text{total}}} + \frac{n_B}{n_{\text{total}}} = \frac{n_{\text{total}}}{n_{\text{total}}} = 1$$

$X_A + X_B = 1$, where $X_A = n_A/n_{\text{total}}$, the mole fraction of A and $X_B = n_B/n_{\text{total}}$, the mole fraction of B.

The sum of the mole fractions of the components of a mixture is equal to 1.

□ Example: 8

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

Solution:

The solution contains 36g of HCl and 64g of H₂O

$$\text{number of mol of HCl} = (36 \text{ g}) \left(\frac{(1 \text{ mol})}{35.5 \text{ g mol}^{-1}} \right) = 1.01$$

$$\text{number of mol of H}_2\text{O} = (64 \text{ g}) \left(\frac{(1 \text{ mol})}{18 \text{ g mol}^{-1}} \right) = 3.55$$

$$X_{\text{HCl}} = \left(\frac{\text{mol of HCl}}{\text{mol of HCl} + \text{mol of H}_2\text{O}} \right) = \left(\frac{1.01}{3.55 + 1.01} \right) = 0.221$$

Example: 9

0.100 mole of NaCl is dissolved into 100g of pure H₂O. What is the mole fraction of NaCl?

Solution

We calculate the number of moles of water

$$\left(\frac{100\text{ g}}{18\text{ g/mol}} \right) = 5.56 \text{ moles of H}_2\text{O}$$

add that to the 0.100 mol of NaCl = 5.56 + 0.100

$$= 5.66. \text{ Now, mol fraction of NaCl} = \left(\frac{0.100\text{ mol}}{5.66\text{ mol}} \right) = 0.0177$$

$$\text{mol fraction of H}_2\text{O} = \left(\frac{5.56\text{ mol}}{5.66\text{ mol}} \right) = 0.982$$

RELATIONSHIP BETWEEN PARTIAL PRESSURE, MOLE FRACTION AND TOTAL PRESSURE

Consider an ideal gas mixture (binary) of A and B. From the ideal gas equation $PV = nRT$;

$$P_A = n_A RT/V \quad \dots \dots \dots \text{i}$$

$$P_{\text{total}} = n_{\text{total}} RT/V \quad \dots \dots \dots \text{ii}$$

Divide eqn (i) by eqn (ii)

$$P_A / P_{\text{total}} = n_A / n_{\text{total}} = X_A \quad \dots \dots \dots \text{iii}$$

$$P_A = X_A P_{\text{total}} \quad \dots \dots \dots \text{iv}$$

The partial pressure of a particular component is equal to its mole fraction multiplied by the total pressure.

Example: 10

A mixture of gases contains 2.1 moles of Argon (Ar) and 1.6 moles of Xenon (Xe). Calculate the partial pressures of the gases if the total pressure is 2.00 atm.

Solution:

Firstly, Calculating the mole fraction

$$X_{Ar} = \frac{n_{Ar}}{n_{Ar} + n_{Xe}} = \frac{2.1}{2.1 + 1.6} = 0.567$$

$$X_{Xe} = \frac{n_{Xe}}{n_{Ar} + n_{Xe}} = \frac{1.6}{2.1 + 1.6} = 0.432$$

The partial pressure will be

$$P_{Xe} = x_{Xe} P_T = 0.432 * 2.00 \text{ atm} = 0.864 \text{ atm}$$

$$P_{Ar} = x_{Ar} P_T = 0.567 * 2.00 \text{ atm} = 1.134 \text{ atm}$$

KINETIC MOLECULAR THEORY OF GASES

Maxwell and Boltzmann (1859) developed a mathematical theory to explain the behaviour of gases and the gas laws.

It is based on the fundamental concept that a gas is made of a large number of molecules in perpetual motion. This theory is called the Kinetic Molecular Theory or the Kinetic Theory of Gases.

Assumptions of the KMT

- 1) A gas consists of extremely small discrete particles called molecules dispersed throughout the container. It means that the actual volume of the molecules is negligible compared to the total volume of the gas. The molecules of a given gas are identical and have the same mass (m).
- 2) Gas molecules are in constant random motion with high velocities. They move in straight lines with uniform velocity and change direction on collision with other molecules or the walls of the container.
- 3) The distance between the molecules is very large and it is assumed that van der Waals attractive forces between them do not exist. Thus the gas molecules can move freely, independent of each other.
- 4) All collisions are perfectly elastic. Hence, there is no loss of the kinetic energy of a molecule during collision.
- 5) The pressure of a gas is caused by the hits recorded by molecules on the walls of the container.
- 6) The average kinetic energy ($\frac{1}{2}mv^2$) of the gas molecules is directly proportional to absolute temperature. This implies that the average kinetic energy of molecules is the same at a given temperature.

on substitution we have $E = \frac{3}{2} * 2.0\text{mol} * 8.314\text{JK}^{-1}\text{mol}^{-1} * 300\text{K} = 7482.6\text{J}$
 Therefore the kinetic energy of two moles of N_2 is 7482.6J.

DEDUCTION OF GAS LAWS FROM THE KINETIC GAS EQUATION

1) Boyle's Law

According to the Kinetic Theory, there is a direct proportionality between absolute temperature and average kinetic energy of the molecules i.e.

$$T \propto \frac{1}{2} m N u^2$$

$$\frac{1}{2} m N u^2 = k T$$

$$* \frac{1}{2} m N u^2 = k T$$

$$\frac{1}{3} m N u^2 = \frac{2}{3} k T$$

Substituting the above value in the kinetic gas equation

$PV = \frac{1}{3} m N u^2$ we have $PV = \frac{2}{3} k T$. The product PV, therefore, will have a constant value at a constant temperature. This is Boyle's Law.

2) Charles' Law:

As derived above, $PV = \frac{2}{3} k T$ (i)

Divide both sides of equation (i) by P,

$$V = \frac{2}{3} * \frac{k}{P} T \quad \text{At constant Pressure, P.}$$

$$V = k' T \text{ where } k' \text{ is also a constant}$$

Therefore

$$V \propto T \quad \text{.....(ii)}$$

Eqn (ii) is Charles' law

This implies that, at constant Pressure, volume of a gas is proportional to Kelvin temperature and this is Charles Law.

3) Avogadro's Law:

Consider equal volume of 2 gases at the same pressure.

$$PV = \frac{1}{3} m_1 N_1 u_1^2 \quad \text{(i) kinetic eqn of 1st gas}$$

$$PV = \frac{1}{3} m_2 N_2 u_2^2 \quad \text{(ii) kinetic eqn of 2nd gas}$$

Therefore

$$\frac{1}{3}m_1N_1u_1^2 = \frac{1}{3}m_2N_2u_2^2 \dots \dots \dots \quad (iii)$$

When the temperature (T) of both the gases is the same, their mean kinetic energy per molecule will also be the same.

$$i.e \frac{1}{3}m_1u_1^2 = \frac{1}{3}m_2u_2^2 \dots \dots \dots \quad (iv)$$

Dividing (iii) by (iv), we have

$$N_1 = N_2$$

Or, under the same conditions of Temperature and Pressure, equal volumes of the two gases contain the same number of molecules. This is Avogadro's Law.

4) Graham's Law of Diffusion:

If m_1 and m_2 are the masses and u_1 and u_2 the velocities of the molecules of gases 1 and 2, then at the same pressure and volume,

$$\frac{1}{3}m_1N_1u_1^2 = \frac{1}{3}m_2N_2u_2^2 \dots \dots \dots \quad (1)$$

$$N_1 = N_2 \dots \dots \dots \quad (2)$$

$$m_1u_1^2 = m_2u_2^2 \dots \dots \dots \quad (3)$$

If M_1 and M_2 represent the molecular masses of gases 1 and 2, then

$$\left(\frac{u_1}{u_2}\right)^2 = \frac{M_2}{M_1}$$

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

The rate of diffusion (r) is proportional to the velocity of molecules (u), therefore,

$$\frac{\text{rate of diffusion of gas 1}}{\text{rate of diffusion of gas 2}} = \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

This is Graham's law of diffusion.

ROOT MEAN SQUARE VELOCITY

If $V_1, V_2, V_3, \dots, V_n$ are the velocities of n molecules in a gas, U^2 , the mean of the squares of all the velocities is:

$$U^2 = \frac{V_1^2 + V_2^2 + V_3^2 + \dots + V_n^2}{n}$$

Taking the square root, we have,

$$U = \sqrt{\frac{V_1^2 + V_2^2 + V_3^2 + \dots + V_n^2}{n}}$$

U is thus the Root Mean Square Velocity or RMS velocity. It is denoted by U . The value of the RMS velocity U , at a given temperature can be calculated from the kinetic gas equation,

$$PV = \frac{1}{3}mNu^2$$

$$U^2 = \frac{3PV}{mN} \text{ For one mole of ideal gas, } PV = RT \text{ therefore } U^2 = \frac{3RT}{mN} \text{ OR } U^2 = \frac{3RT}{M}$$

Where M = molar mass

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

By substituting the values of R, T and M, the value of U (RMS velocity) can be determined. RMS velocity is superior to the average velocity considered earlier. With the help of U, the total kinetic energy of a gas sample can be calculated.

REAL GAS

Distinction between Ideal and Real gases

1. An ideal gas is infinitely compressible; a real gas will condense to a liquid at some pressure.
2. The particles of an ideal gas lose no energy to its container. A real gas conducts and radiates heat, thereby losing energy.
3. There is no attraction between the molecules of an ideal gas. A real gas has particle attractions.
4. An ideal gas can follow the formula $PV = nRT$. A real gas does not follow this formula

DEVIATIONS FROM IDEAL BEHAVIOUR

An ideal gas is one which obeys the gas laws or the gas equation $PV = RT$ at all pressures and temperatures. However, no gas is ideal. Almost all gases show significant deviations from the ideal behavior. Thus the gases H₂, N₂ and CO₂ which fail to obey the ideal gas equation are termed non ideal or real gases.

COMPRESSIBILITY FACTOR

This is a quantity that measures the deviation of a real gas from ideal behaviours. It is defined by the equation; $z = \frac{PV_m}{RT}$

Where Z = compression factor, $V_m = \frac{V}{n}$ = Molar Volume of gas

P, R and T have their usual meanings.

$\Rightarrow Z = 1$ at all conditions.

For a real gas, Z depends on the value of PV_m relative to RT.

At high pressures $PV_m > RT$ so that $Z > 1$. The gas is said to deviate positively from ideality and is less compressible than an ideal gas.

At low pressure, $PV_m < RT$. So that $Z < 1$. The gas deviates negatively from ideality and is more compressible than an ideal gas.

CONCLUSIONS

From the above discussions, it can be concluded that:

1. At low pressures and fairly high temperatures, real gases show nearly ideal behavior and the ideal gas equation is obeyed.
2. At low temperatures and sufficiently high pressures, a real gas deviates significantly from ideality and the ideal gas equation is no longer valid.
3. The closer the gas is to the liquefaction point, the larger will be the deviation from the ideal behavior.

EXPLANATION OF DEVIATION – VANDER WAALS EQUATION

Van der Waals (1873) attributed the deviations of real gases from ideal behavior to two erroneous postulates. These are:

- i. The molecules in a gas are point masses and possess no volume.
- ii. There are no intermolecular attractions in a gas.

Therefore, the ideal gas equation $PV = nRT$ derived from kinetic theory could not hold for real gases. Van der Waals pointed out that both the pressure (P) and volume (V) factors in the ideal gas equation need to be corrected in order to make it applicable to real gases.

Volume Correction

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

The volume of a real gas is, therefore, ideal volume minus the volume occupied by gas molecules. If b is the effective volume of molecules per mole of the gas, the volume in the ideal gas equation is corrected as: $(V - nb)$
 For n moles of the gas, the corrected volume is $(V - nb)$
 Where, b is termed the excluded volume which is constant and characteristic for each gas. Excluded volume is four times the actual volume of molecules.
 Therefore, excluded volume is not equal to the actual volume of the gas molecules.

Pressure Correction

A molecule in the interior of a gas is attracted by other molecules on all sides. The attractive forces cancel out. But a molecule about to strike the wall of the vessel is attracted by molecules on one side only. Hence it experiences an inward pull.

A molecule about to strike the wall has a net inward pull;

A molecule in the interior of gas has balanced attractions; therefore, it strikes the wall with reduced velocity and the actual pressure of the gas, P , will be less than the ideal pressure. If the actual pressure P , is less than P_{ideal} by a quantity p , we have $P = P_{\text{ideal}} - p$ or $P_{\text{ideal}} = P + p$. P is determined by the force of attraction between molecules (A) striking the wall of container and the molecule (B) pulling them inward. The net force of attraction is, therefore, proportional to the concentration of (A) type molecules and also of (B) type molecules. That is,

$$P \propto C_A * C_B \text{ OR } P \propto \frac{n}{V} * \frac{n}{V} \Rightarrow P = \frac{an^2}{V^2}$$

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

$$\left(P + \frac{an^2}{V^2} \right) \text{ For } n \text{ moles of gas}$$

VAN DER WAALS EQUATION

Substituting the values of corrected pressure and volume in the ideal gas equation, $PV = nRT$, we have

$\left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT$ This is known as Vander Waals equation for n moles of a gas. For 1 mole of a gas ($n=1$), Vander Waals equation becomes

$$\left(P + \frac{a}{V^2} \right) (V - b) = RT$$

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

DETERMINATION OF a AND b

From the expression $P = \frac{an^2}{V^2}$ the value of a is given by the relation

$a = \frac{Pn^2}{V^2}$ atm mol 2 litre $^{-2}$ if the pressure is expressed in atmosphere and volume in litres. Thus a is expressed in atm mol 2 litre $^{-2}$ units. Since nb is excluded volume for n moles of gas, $b = \frac{\text{volume}}{n} = \frac{\text{litre}}{\text{mole}}$ its volume is expressed in litres, b is in litre mol $^{-1}$ units.

SI Units of a and b

$$a = \frac{(\text{pressure})(\text{volume})^2}{(\text{mole})^2} = \frac{(Nm^{-2})(m^3)^2}{(\text{mole})^2} = Nm^4 \text{mol}^{-2}$$

$$b = \text{Volume mol}^{-1} = m^3 \text{mol}^{-1}$$

□ Example: 12

One mole of diethyl ether occupies 15 litres at 227°C. Calculate the pressure if van der Waals constant for diethyl ether are $a = 17.38 \text{ atmL}^2 \text{mol}^{-2}$ and $b = 0.134 \text{ Lmol}^{-1}$.

Solution:

Formula used:

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

Quantities given:

$$n = 1 \text{ mol} \quad V = 15 \text{ L} \quad R = 0.0821 \text{ atmLmol}^{-1}\text{K}^{-1}$$

$$a = 17.38 \text{ atmL}^2 \text{mol}^{-2} \quad T = 500 \text{ K} \quad b = 0.134 \text{ Lmol}^{-1}$$

Substituting, gives $P = 2.68376 \text{ atm}$

□ Example: 13

Calculate the pressure exerted by 1.00 mole of methane (CH_4) in a 250mL container at 300K using Van der Waals equation. What pressure will be predicted by ideal gas equation? Take $a = 2.253 \text{ atmL}^2 \text{mol}^{-2}$, $b = 0.0428 \text{ Lmol}^{-1}$ and $R = 0.0821 \text{ atmLmol}^{-1}\text{K}^{-1}$.

Solution:

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

Making P the subject and substituting the values, gives
 $P = 82.8 \text{ atm}$.

While,

The ideal gas equation predicts that
 $P = nRT/V = 98.5 \text{ atm}$.

LIMITATION OF VAN DER WAALS EQUATION

Van der Waals equation explains satisfactorily the general behavior of real gases. It is valid over a wide range of pressures and temperatures. However it fails to give exact agreement with experimental data at very high pressures and low temperatures.

EXERCISES

- 1) One mole of $\text{CO}_2(\text{g})$ occupies $0.382 \times 10^3 \text{ m}^3$ at 40°C . Calculate the pressure that the gas would exert assuming ideal behavior. Take $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
- 2) Convert the following Physical quantities to the required units: 365 cm to m , 22400 cm^3 to dm^3 then to m^3 and 760 torr to Nm^{-2}
- 3) The hottest place on record in North America is Death Valley in California. It reached a temperature of 134°F in 1913. What is this temperature reading in degrees Celsius? In Kelvins?
- 4) The total pressure exerted by a mixture of 2 gases A & B is 76.2 cmHg . The number of moles of the 2 gases is 0.0075 and 0.0040 respectively. Calculate the partial pressures of the 2 gases.
- 5) Nitric acid, a very important industrial chemical, is made by dissolving the gas $\text{NO}_2(\text{g})$ in water. Calculate the density of NO_2 gas, in g/L , at 1.24 atm and 50°C .
- 6) A sample of hydrogen gas (H_2) has a volume of 8.56 L at a temperature of 0°C and a pressure of 1.5 atm . Calculate the moles of H_2 molecules present in this gas sample.
- 7) What is the volume of a gas balloon filled with 4.00 moles of He when the atmospheric pressure is 748 torr and the temperature is 30°C ?
- 8) Calculate the root mean square speed of O_2 molecules in a cylinder at 21°C and 15.7 atm .

- 9) The density of a gas was measured at 1.50 atm and 27 °C and found to be 1.95 g/L. Calculate the molar mass of the gas.
- 10) Calculate the pressure exerted by 1.0 mole of methane, in a 500 mL vessel at 25 °C assuming a) Ideal behavior and b) Non-Ideal behavior.
- 11) Define the compressibility factor of a gas. The compressibility factors of 2 gases are $Z_A = 0.65$ and $Z_B = 1.23$ (i) state the nature of deviation of each gas from ideality. (ii) How does the ease of compression of each gas compare with that of an ideal gas?

SOLIDS

A solid is a material that retains both its shape and volume over time. Of the three states of matter, solids possess the most structural diversity.

Types of Solids

Crystalline Solids: Is a solid which composed of atoms, ions, or molecules arranged in a pattern that is repeated in three dimensions eg Iron Metal, Diamond, Table Salt (NaCl) and Sugar ($C_{12}H_{22}O_{11}$)

Amorphous Solids: If there is no long-range structural order throughout the solid, the material is best described as amorphous eg Synthetic Fibers, Plastics, and Glasses,

Polycrystalline Solids: It may not be completely crystalline due to more complicated structure but there is high degree of order over many atomic or molecular dimensions. The ordered regions vary in size and orientation with respect to one another. The single crystalline regions are called grains.

DEFINITION OF TERMS

The Unit Cell: Is a small volume of crystals that can be used to reproduce the entire crystal; unit cells can be seen as building blocks to construct the whole crystal

Crystal Lattice: The periodic arrangement of atoms, ions, or molecules in a crystal is called lattice

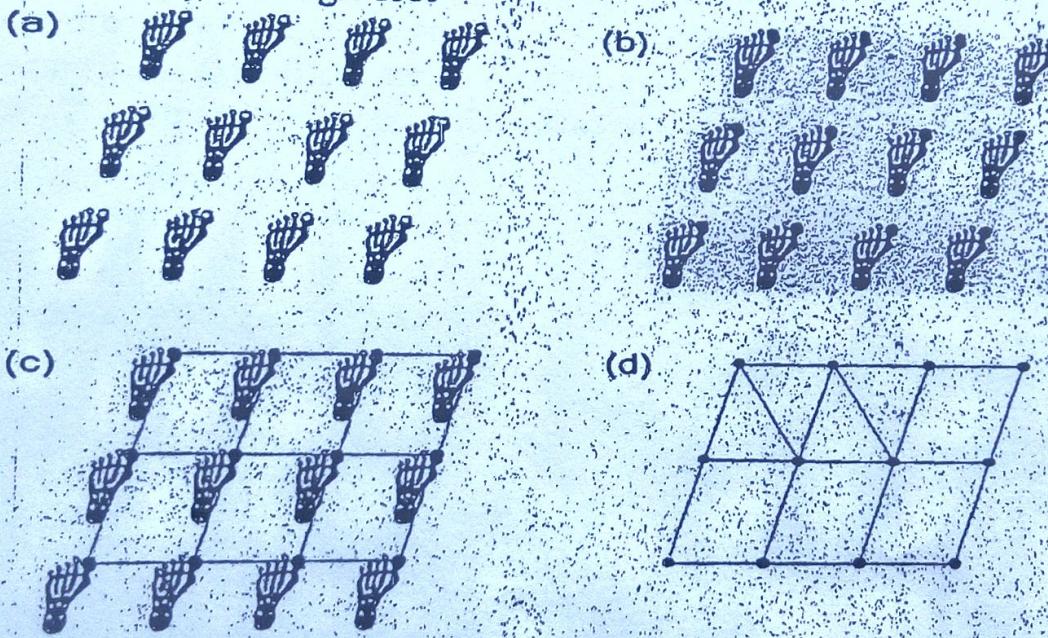
Lattice Points: A dot used to present a particular atomic array

Coordination Number: The number of atoms that surround a central atom in a solid is called coordination number

THE CRYSTALLINE STATE

Single crystals comprise an infinite array of ions, atoms, or molecules, known as a crystal lattice. The strength of the interactions between the species comprising the crystal is known as the lattice energy. Crystalline solids have patterns that repeat. This is called translational symmetry because by translating an original object you come to an identical object. (Translate just means to slide the object without rotating it). In order to describe translational symmetry you don't have to know what the objects are, just where they are located. In crystalline solids, the actual object that is being translated is represented by a point called a **lattice point**. The lattice point might represent a single atom, a single molecule, or a collection of atoms or molecules – whatever it represents repeats by translational symmetry. The collection of lattice points that describes the crystalline solid defines a crystal lattice. The lattice points can be used to draw boxes called unit cells, and another way of looking at the translational symmetry is to imagine using the unit cells as building blocks to construct the whole crystal.

In two dimensions, this is illustrated in the following figure, where the repeat unit shown in (a) is a single foot

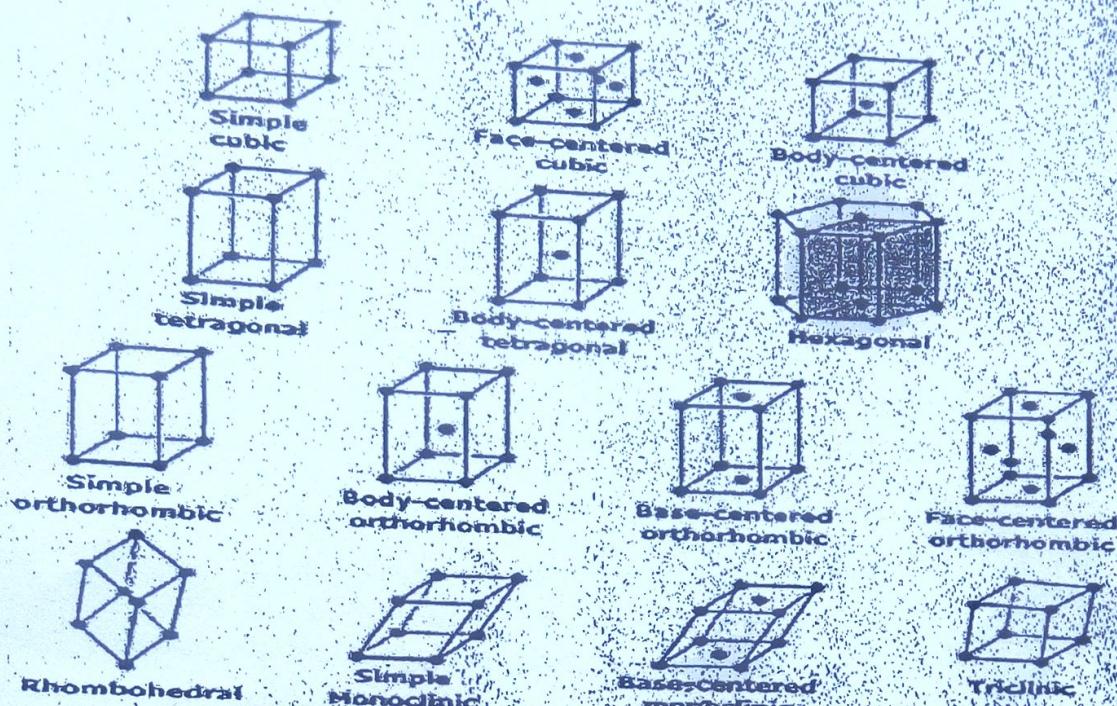


There are only 12 feet shown in the array, but imagine that the pattern repeats to cover a plane that contains Avogadro's number of feet. In order to represent the translational symmetry, the lattice points must have identical environments in the pattern and therefore be in the same place relative to each foot. In (b), a lattice point is arbitrarily placed on each big toe. In (c), the lattice points are connected to

form unit cells. Because each lattice point is shared by 4 cells and each cell has a lattice point in each of its 4 corners, there is one lattice point per unit cell ($4 \times \frac{1}{4} = 1$). There is one foot per lattice point and one lattice point per unit cell so there is one foot per unit cell, although to get a whole foot the pieces of the three feet that enter a single unit cell must be added. In (d), the lattice points show the translational symmetry without showing the object being translated. Notice that while the relative positions of the lattice points are uniquely determined by the underlying translational symmetry, there is more than one unit cell that can be drawn. A different choice of the unit cell is outlined in black in (d). Also, if you imagine sliding the lattice in (d) over the feet in (a), you can see that the lattice points could have been chosen in spaces between the feet, with one whole foot in each unit cell.

For actual crystals, we are interested in three dimensions. It turns out that nature doesn't use many different kinds of translational symmetry, so that in three dimensions the translational symmetry in all crystalline solids can be described for the 7 existing crystal systems with just 14 patterns called Bravais lattices. With all of the complexity found in crystalline solids, this is pretty amazing. But remember that the objects represented by the lattice points can be very complex and can have internal symmetry.

The least symmetrical crystal system is triclinic; all cell edges unequal and all angles between the edges not equal to each other and not equal to 90° . The most symmetrical crystal system is cubic; all cell edges equal and all angles equal to 90° . The remaining five crystal systems run the gamut in between.



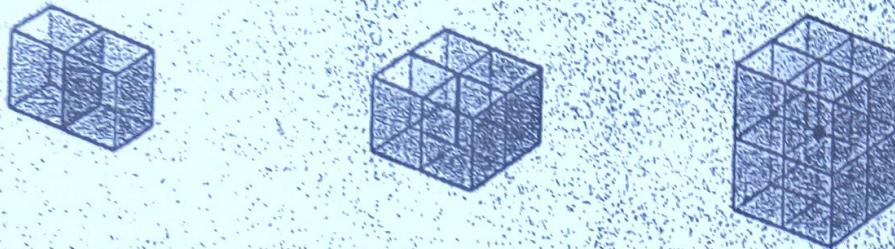
Classification of space lattices by crystal system

| Crystal system | Axial lengths and interaxial angles | Space lattices |
|----------------|---|---|
| Cubic | Three equal axes at right angles $a = b = c, \alpha = \beta = \gamma = 90^\circ$ | Simple cubic Body-centered cubic Face-centered cubic |
| Tetragonal | Three axes at right angles, two equal $a = b \neq c, \alpha = \beta = \gamma = 90^\circ$ | Simple tetragonal Body-centered tetragonal |
| Orthorhombic | Three unequal axes at right angles $a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$ | Simple orthorhombic Body-centered orthorhombic Base-centered orthorhombic Face-centered orthorhombic |
| Rhombohedral | Three equal axes, equally inclined $a = b = c, \alpha = \beta = \gamma \neq 90^\circ$ | Simple rhombohedral |
| Hexagonal | Two equal axes at 120° , third axis at right angles $a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$ | Simple hexagonal |
| Monoclinic | Three unequal axes, one pair not at right angles $a \neq b \neq c, \alpha = \gamma = 90^\circ \neq \beta$ | Simple monoclinic Base-centered monoclinic |
| Triclinic | Three unequal axes, unequally inclined and none at right angles $a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$ | Simple triclinic |

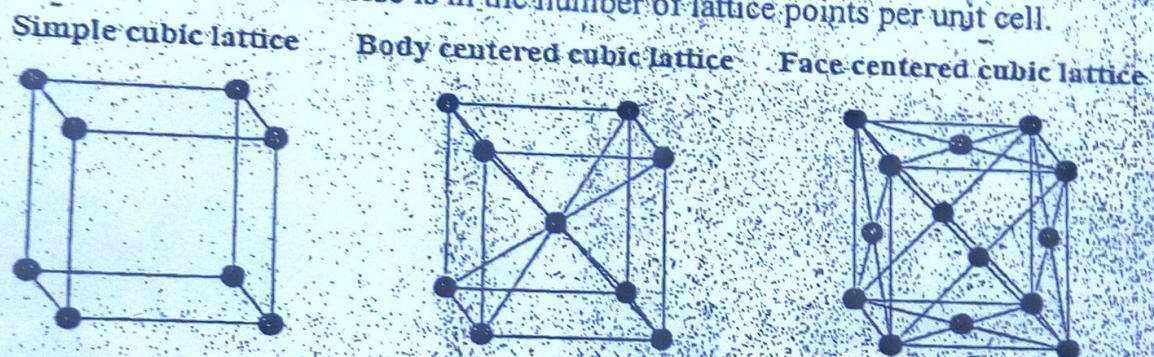
The 14 Bravais lattices and the summary of their properties

Since cubes serve as the unit cells in the systems that we will be examining, it is useful to visualize their features and what happens when identical cubes pack.

together to fill space. An isolated cube has 12 edges, 6 faces and 8 corners. When identical cubes are packed together, each face of a cube is shared by two cubes; each edge of a cube is shared by 4 cubes, and each corner of a cube is shared by 8 cubes. Also notice that six cube edges come together at each corner.

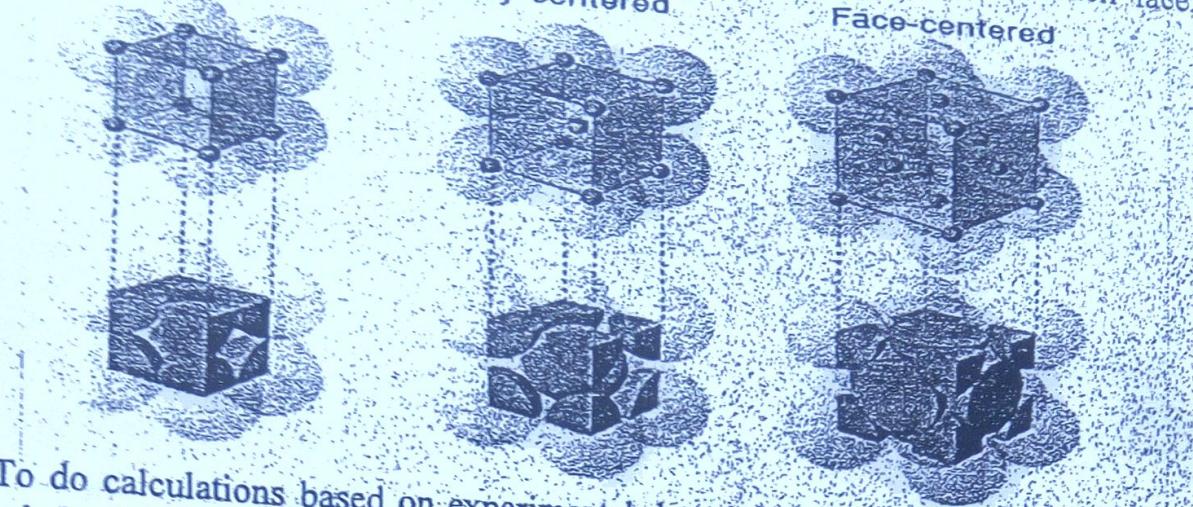


There are three possible Bravais lattices for the cubic system. These are shown in the following figure, where the spheres represent lattice points: simple or primitive cubic (P), body-centered cubic (BCC) and face-centered cubic (FCC). The difference between these is in the number of lattice points per unit cell.

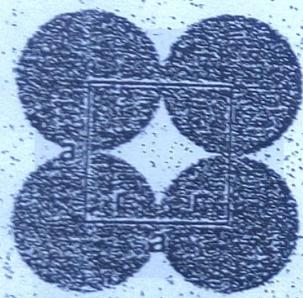


In the simple cubic lattice, each of the eight corners of the unit cell contains a lattice point which is shared by the 8 unit cells that meet at each corner. Therefore, the 8 corner lattice points account for only 1 whole lattice point for each unit cell ($8 \times 1/8 = 1$). In the body-centered cubic cell, in addition to the one lattice point from the corners, there is a lattice point in the center of the cube to give a total of two lattice points per unit cell. This means that whatever is represented by the lattice point at the corner of the cube is also found at its center. In a face-centered cubic cell, in addition to the lattice point associated with the corners, there is a lattice point in the center of each of the 6 faces. Since each face is shared by two cells, $\frac{1}{2}$ of each face lattice point is assigned to each cell, and the six faces contribute 3 lattice points ($6 \times \frac{1}{2} = 3$) per cell for a total of four lattice points per unit cell. In a face-centered cubic cell, whatever motif is associated with the lattice

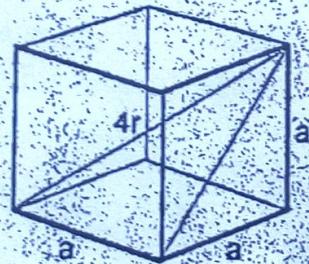
points at the corners of the unit cell also appears in the center of each face.



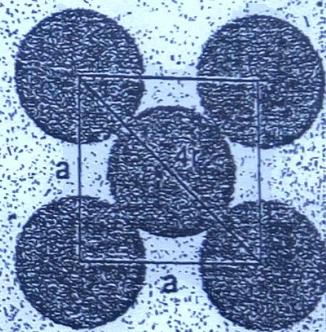
To do calculations based on experimental data, it is often necessary to know the relationship between the edge length of the unit cell, a , and the radius of the atoms, r , that comprise it. Because the contact between atoms is different for each of the three types, the relationship between the edge length and the atom radius is also different for each. In the simple cubic cell, where the atoms meet along the edge of the cell, the edge of each cell is twice the radius of the atom: $a=2r$.



Simple



Body-centered



Face-centered

In the face-centered cell, the contact is along the face diagonal. A face diagonal passes through the diameter of the atom in its face (a distance of $2r$) and half way through each of two corner atoms for a distance of r from each. The total distance along the face diagonal is therefore $4r$ and each edge has a length of a . From the Pythagorean theorem, $a^2 + a^2 = (\text{face diagonal})^2$ or face diagonal = $a\sqrt{2} = 4r$.

In the body-centered cell, the atoms meet along the body diagonal. The diagonal passes through the diameter of the atom in the center of the cell, but also passes half way through each of the corner atoms. The contribution from each of the two corner atoms is r , and the contribution from the center atom is $2r$, so that the entire

body diagonal has a length of $4r$. In this case the right triangle for the calculation is composed of the body diagonal ($4r$), an edge (a) and a face diagonal ($a\sqrt{2}$), outlined in red in the figure above, to give $a^2 + (a\sqrt{2})^2 = (4r)^2$ or $a\sqrt{3} = 4r$. The results for all three are summarized in the following table and are valid for atomic substances that crystallize in cubic lattices with one atom per lattice point, where a is the edge length of the unit cell and r is the radius of the atom.

| Lattice Structure | Atom per Unit Cell | a to r relationship | r to a factor | Coordination No. |
|-------------------|--------------------|-------------------------|-------------------|------------------|
| Simple Cubic | 1 | $a = 2r$ | $r = 0.5a$ | 6 |
| Face-Centered | 4 | $a\sqrt{2} = 4r$ | $r = 0.35355a$ | 12 |
| Body-centered | 2 | $a\sqrt{3} = 4r$ | $r = 0.43301a$ | 8 |

EXAMPLE PROBLEM : Atomic Solids

1. Relationship between Edge Length and Atomic Radius

Metallic uranium crystallizes in a body-centered cubic lattice, with one U atom per lattice point. How many atoms are there per unit cell? If the edge length of the unit cell is found to be 343 pm, what is the metallic radius of U in pm?

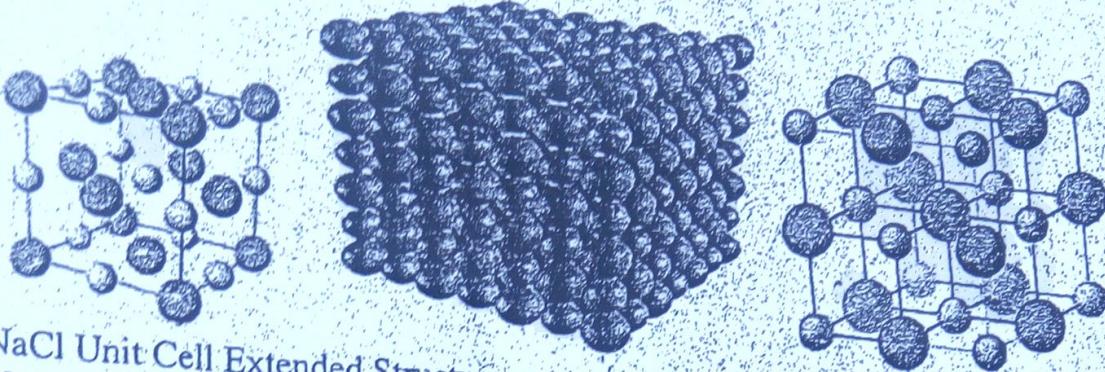
Solution: For a body-centered cubic lattice with one atom per lattice point, there are 2 atoms per unit cell. For this type of lattice the atoms are in contact along a body diagonal and $4r = a\sqrt{3}$, where r is the metallic radius and a is the edge length of the cell.

$$\text{Thus, } r = 0.433a = 0.433 \times 343 \text{ pm} = 149 \text{ pm}$$

The NaCl Structure.

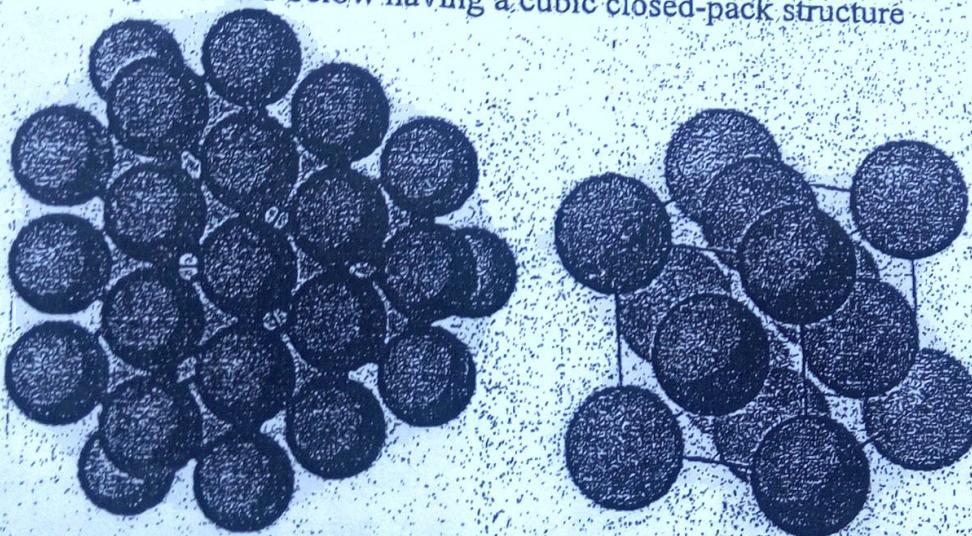
The sodium chloride structure is another cubic structure commonly adopted by 1 to 1 salts. A model of the sodium chloride unit cell is shown below, where the sodium ions are represented by white spheres and the chloride ions by ash spheres. The structure is face-centered cubic, with one sodium ion and one chloride ion per lattice point. Since there are 4 lattice points per unit cell this gives a total of 4 NaCl molecules per unit cell. You can come to the same conclusion by counting spheres in the unit cell. Notice that the ash-colored chloride ions have the same arrangement as in a face-centered metal with a cubic close-packed structure. Therefore there are a total of 4 chloride ions per cell (1 from the 8 corners plus 3 from the 6 faces). The sodium ions (white spheres) occupy the octahedral holes created by the chloride ions. This alone tells you there are 4 per cell. Or you can

count: there is a sodium ion on each of the cell edges and one in the center of the cell, for a total of 4 sodium ions per unit cell. Notice that the ratio of Na^+ to Cl^- is 4:4 or 1:1.



NaCl Unit Cell Extended Structure

If the positions of the sodium ions and the chloride ions were interchanged, the same extended structure would result, and the sodium chloride structure is sometimes described as two interpenetrating face-centered cubic lattices. This can be seen by inspecting the extended structure to the right of the unit cell. Finally, both the cation and the anion have a coordination number of 6, as each is surrounded by an octahedron of counter-ions. This is a similar case with copper which is presented below having a cubic closed-pack structure.

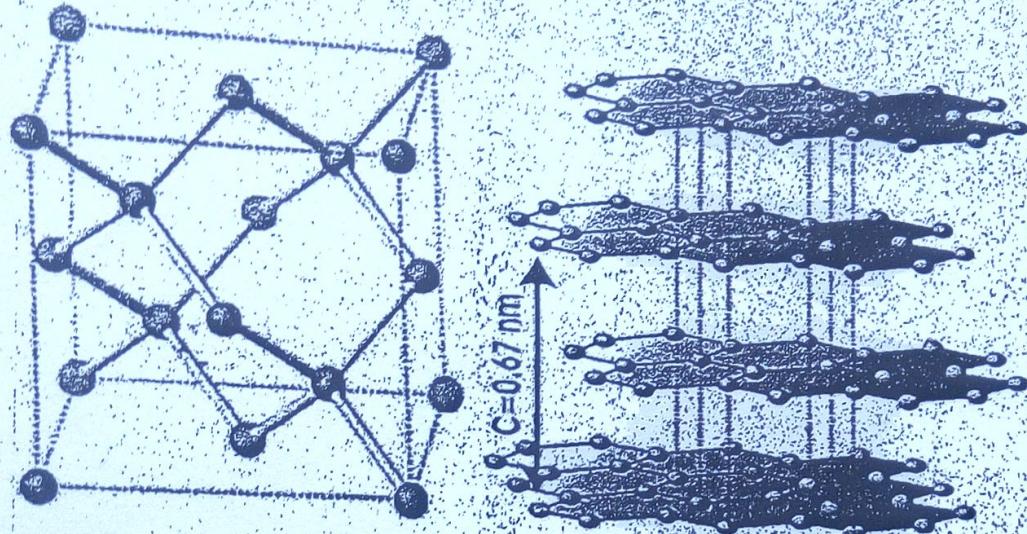


Diamond and graphite

Diamond crystal: is octahedral in shape. It is actually a giant molecule in which the carbon atoms are loosely packed and held together by strong covalent bonds. In diamond each carbon is bonded to four other C atoms ($\text{C.N}=4 = sp^3$ hybridized) as such no electron is left unbonded making diamond to be the hardest substance.

known and it does not conduct electricity, it also shows excellent resistance to high temperature and chemical attack. Its unit cells are FCC.

Graphite: Has hexagonal structure, covalently bonded sp^2 orbitals and weak secondary bonds between planes. It is soft and flexes easily because of its layered crystalline structure. It has high melting point but less dense than diamond, it conducts electricity, and it can be oxidized unlike diamond.



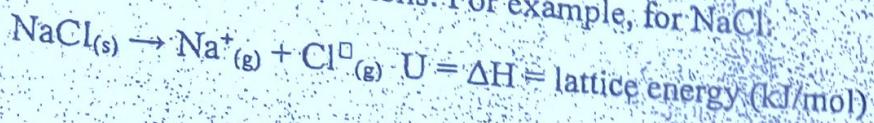
Lattice Energy

We have said that ionic solids are held together by the strong attractive forces between oppositely charged ions. Coulombs law in this context can be written:

$$E = a \frac{q_1 q_2}{r}$$

where a is a constant, q_1 and q_2 are the charges on the ions and r is the distance between their centers. If the details of how the ions are packed together in the solid are known, it ought to be possible to use Coulombs law to calculate the energy released when molar quantities of the isolated ions in the gas phase (zero interaction energy) come together to form a mole of crystalline solid. In such a calculation the strongest attractive forces would be between nearest neighbors of opposite charge, but it would be necessary to sum up all of the attractive and repulsive forces, including those operating at a distance. Summations like this are done, and give calculated values of the binding energy in crystals. These values can also be determined experimentally. The binding energy in a crystalline lattice is called the **lattice energy** and is given the symbol U . It is the energy required to separate one mole of a crystalline ionic solid into its gaseous ions. Alternatively it

can be defined as the energy released when one mole of a crystalline ionic solid forms from its gaseous ions. For example, for NaCl:



2

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ABUBAKAR TAFAWA BALEWA UNIVERSITY, BAUCHI #20
FACULTY OF SCIENCE
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NOTES FOR FIRST SEMESTER 2018/2019 SESSION.

EQUILIBRIUM.

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CHAPTER ONE

1.0 CHEMICAL EQUILIBRIUM

1.1 The concept of equilibrium

1.2 Reversible reactions

These are reactions which proceed in two alternative directions depending on the prevailing conditions or proceed in either direction; i.e. can move forward or backward directions. The symbol \rightleftharpoons is used to represent the reversibility of the reaction. They can be homogeneous or heterogeneous.

1.2.1 Homogeneous reaction: in homogeneous reaction, all reactants and products are in the same phase. For example, the reaction of $H_2(g)$ and $I_2(g)$ to give $HI(g)$ is a homogeneous gaseous reaction. It is represented as;



Esterification of $C_2H_5OH(l)$ and $CH_3COOH(l)$ is a homogeneous liquid reaction as shown below; $C_2H_5OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$.

1.2.2 Heterogeneous reaction: in heterogeneous reaction, two or more phases are involved. For example, thermal decomposition of $CaCO_3(s)$ is a heterogeneous reaction as can be seen below; $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

1.2.3 Dynamic equilibrium: consider the thermal decomposition of N_2O_4 represented by the equation. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$.

Suppose the reaction takes place in a closed vessel; a point will be reached at which the rates of the forward and backward reactions will be equal. Under this condition, the reaction is said to be at equilibrium. The equilibrium is dynamic because the reaction still continues.

Other properties of a dynamic equilibrium are as follows:

1. It can be approached from either direction. For example, an equilibrium of N_2O_4 / 2NO_2 system can be established either by decomposition of the colourless N_2O_4 to dark brown NO_2 or vice versa.

2. Concentrations and pressures of the reacting substances remain constant at equilibrium.

1.2.4 The law of mass action: this law helps to establish the relationship between the concentrations of the reactants and the products at equilibrium.

The law states that the rate at which a substance reacts is proportional to its active mass provided that the temperature remains constant i.e. Rate \propto active mass. Rate $\propto a$, where 'a' is active mass = CF :

C = molar concentration, F = activity coefficient, for reactions involving solutions and gases, $F = 1$.

1.2.5 Equilibrium constant (K): for a reaction $aA + bB \rightleftharpoons cC + dD$, the ratio of the activities of products to the activities of reactants each raised to the power of its stoichiometric coefficient is called the equilibrium constant (K). Mathematically as $K = (C)^c(D)^d/(A)^a(B)^b$; where a, b, c , and d are the activities of A, B, C , and D respectively. If activity is replaced by concentration, K is now known as concentration equilibrium constant (K_c). It can be represented as shown below;

$$K_c = [C]^c [D]^d / [A]^a [B]^b. \text{ Where } [] \text{ stands for concentration.}$$

Again, if the activity is also replaced by pressure, K is called pressure equilibrium constant (K_p). Mathematically as shown below;

$$K_p = (P_C)^c (P_D)^d / (P_A)^a (P_B)^b. \text{ Where } P \text{ stands for partial pressure.}$$

Some properties of the equilibrium constant (K) are;

1. A large value of the equilibrium constant (K) shows that large amounts of products are formed from reactants.
2. The value of K for a reaction is not affected by changes in concentration or pressure of the reacting system, but it only changes by changing the temperature.
3. The equilibrium constant (K) does not give any information on the rate of reaction.

Decrease in pressure will shift the position of equilibrium to the left thereby converting some of the SO_2 and Cl_2 into SO_2Cl_2 . $[\text{SO}_2\text{Cl}_2]$ increases whereas $[\text{SO}_2]$ and $[\text{Cl}_2]$ decreased.

1.27.4 Effects of temperature changes: the effect of temperature change on equilibrium of a system depends on the nature of the reaction.

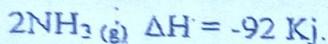
For example, exothermic reactions are favoured by a decrease in temperature

Reactants

forward reaction produces heat so, it is favoured by low pressure

backward reaction absorbs heat so, it is favoured by high pressure

Products



Since the reaction is exothermic, a decrease in temperature will shift the equilibrium position forward, consequently concentration of NH_3 will increase while concentrations of N_2 and H_2 molecules will decrease. The equilibrium constant (K) will increase with decrease in temperature.

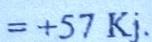
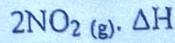
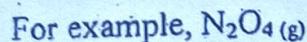
While in the case of endothermic reaction, increase in temperature will favour the reaction.

Reactants

forward reaction absorbs heat so, it is favoured by high temp.

backward reaction produces heat so, it is favoured by low temp.

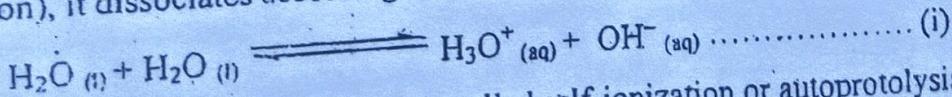
Products



The reaction is endothermic; an increase in temperature will shift the equilibrium forward to consume the added heat. Hence, $[\text{NO}_2]$ will increase and $[\text{N}_2\text{O}_4]$ will decrease. The equilibrium constant (K) will increase with increase in temperature.

1.2.8 IONIC EQUILIBRIUM

Water is amphiprotic (i.e. any substance which has the ability to accept or donate a proton), it dissociates according to the following equation:



This reaction of equation (i) is called self-ionization or autoprotolysis of water,

The concentration equilibrium constant (K_c) for the reaction is:

$$K_c = [\text{product}] / [\text{reactant}] = [\text{H}_3\text{O}^{\text{(aq)}}][\text{OH}^{-\text{(aq)}}] / [\text{H}_2\text{O}^{\text{(l)}}]^2 \quad (\text{ii})$$

$$K_c [\text{H}_2\text{O}^{\text{(l)}}]^2 = [\text{H}_3\text{O}^{\text{(aq)}}][\text{OH}^{-\text{(aq)}}] \quad (\text{iii})$$

A very small fraction of water molecule is ionised at equilibrium, the concentration of water molecule remain virtually unchanged.

Therefore, $K_c [\text{H}_2\text{O}^{\text{(l)}}]^2$ is constant, the ionic product constant of water symbolized as K_w which is the combination of both the constant for $[\text{H}_2\text{O}^{\text{(l)}}]^2$ and K_c , $K_w = K_c [\text{H}_2\text{O}^{\text{(l)}}]^2$ (iv)

Substituting equation (iv) into (iii)

$$K_w = [\text{H}_3\text{O}^{\text{(aq)}}][\text{OH}^{-\text{(aq)}}] \quad (\text{v})$$

Recall that, the value of K_w is 1.00×10^{-14} mol²dm⁻⁶ at 25 °C, like any equilibrium constant, K_w varies with temperature.

$$\text{In aqueous solution } [\text{H}_3\text{O}^{\text{(aq)}}] = [\text{H}^{\text{(aq)}}] \quad (\text{vi})$$

Substituting equation (vi) into (v)

$$\text{Therefore, } K_w = [\text{H}^{\text{(aq)}}][\text{OH}^{-\text{(aq)}}] \quad (\text{vii})$$

In pure water at 25 °C, these ions are produced in equal numbers i.e

$$[\text{H}^{\text{(aq)}}] = [\text{OH}^{-\text{(aq)}}] = 1.00 \times 10^{-7} \text{ mol dm}^{-3} \quad (\text{viii})$$

Substituting equation (viii) into (vii)

$$K_w = (1.00 \times 10^{-7})^2 = 1.00 \times 10^{-14} \text{ mol}^2 \text{dm}^{-6} \quad (\text{ix})$$

Note that, in acidic solution, $[\text{H}^{\text{(aq)}}] > [\text{OH}^{-\text{(aq)}}]$, in a basic solution, $[\text{OH}^{-\text{(aq)}}] > [\text{H}^{\text{(aq)}}]$, and in neutral solution, $[\text{OH}^{-\text{(aq)}}] = [\text{H}^{\text{(aq)}}]$.

Equation (vii) can be used to calculate the $[\text{H}^{\text{(aq)}}]$ or $[\text{OH}^{-\text{(aq)}}]$ of a solution as in the example below:

Example 1

The concentration of OH^- ions in a certain household ammonia cleaning solution is 0.0025 mol dm⁻³, calculate the concentration of H^+ ions?

Answer

Recall that $K_w = 1.00 \times 10^{-14}$ mol²dm⁻⁶

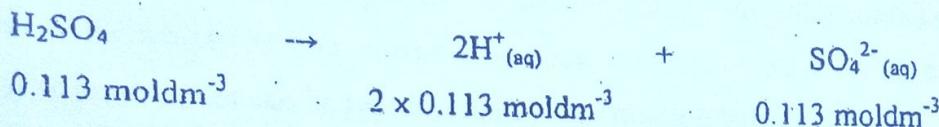
$$K_w = [\text{H}^{\text{(aq)}}][\text{OH}^{-\text{(aq)}}], \text{ making } [\text{H}^{\text{(aq)}}] \text{ the subject formula}$$
$$[\text{H}^{\text{(aq)}}] = K_w / [\text{OH}^{-\text{(aq)}}] = 1.00 \times 10^{-14} \text{ mol}^2 \text{dm}^{-6} / 0.0025 \text{ mol dm}^{-3} = 4.00 \times 10^{-12} \text{ mol dm}^{-3}$$

Example 2

Calculate the H^+ and OH^- ions concentrations of a $0.113 \text{ mol dm}^{-3}$ H_2SO_4 ?

ANSWER

Remember that for strong acid, the concentration of the ions will be equal to the concentration of an acid. H_2SO_4 is a strong acids, its ionises completely according to the following equation:



$$\text{Thus, } [\text{H}^+_{(\text{aq})}] = 2 \times 0.113 \text{ mol dm}^{-3} = 0.226 \text{ mol dm}^{-3}$$

$$\text{From } K_w = [\text{H}^+_{(\text{aq})}][\text{OH}^-_{(\text{aq})}], \quad [\text{OH}^-_{(\text{aq})}] = K_w / [\text{H}^+_{(\text{aq})}] = 1.00 \times 10^{-14} \text{ mol}^2 \text{dm}^{-6} / 0.226 \text{ mol dm}^{-3} = 4.425 \times 10^{-14} \text{ mol dm}^{-3}$$

Exercises

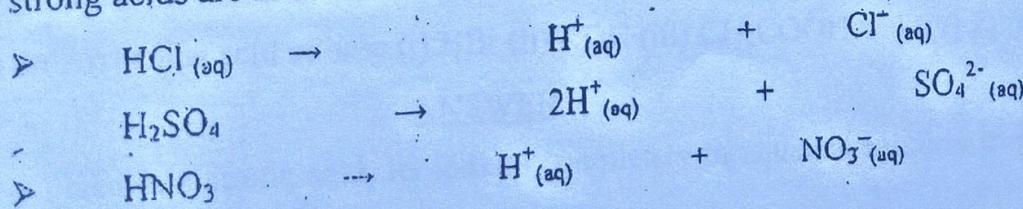
1. Calculate the concentration of OH^- ions in 0.10M HCl
2. In 0.010 M NaOH, calculate the concentration of H^+ ions
3. Calculate the concentration of H^+ ions in:
 - (a.) 0.75 M solution of Nitric acid (HNO_3), (b.) 2.0 M solution of potassium hydroxide (KOH), (c.) 0.05 M solution of sulphuric acid (H_2SO_4), and (d.) 0.002 M solution of calcium hydroxide [$\text{Ca}(\text{OH})_2$].

CHAPTER TWO

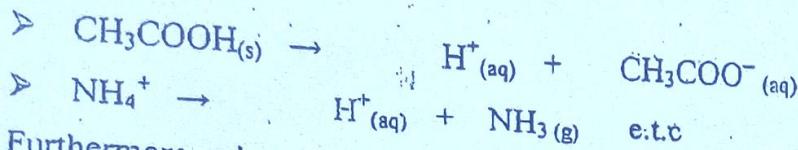
2.0 Concept of acids and bases

2.1 Arrhenius concept of acids and bases

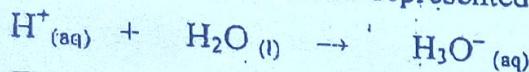
According to Arrhenius, an acid is any substance which dissociates or ionises in aqueous solution to liberate hydrogen ion (H^+) as the only positive charge. Strong acids are completely dissociated into positive and negative charges respectively, examples of strong acids are as follows:



While weak acids are only partially ionised with high proportion or percentage of the acid remaining in the undissociated form (i.e negative part of the substance). Examples,



Furthermore, when hydrogen ion associated itself with polar molecule e.g water (i.e a molecule which contain atleast one polar bond) formed what is called Oxonium or hydronium ion as can be represented by the equation below:



The ionisation of acids in water are:

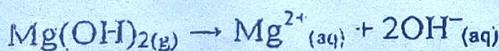
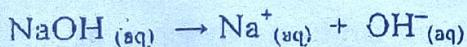
- ❖ $\text{HCl}_{(s)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{H}_3\text{O}^+_{(aq)} + \text{Cl}^-_{(aq)}$
- ❖ $\text{H}_2\text{SO}_4_{(aq)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{H}_3\text{O}^{+2}_{(aq)} + \text{SO}_4^{2-}_{(aq)}$
- ❖ $\text{CH}_3\text{COOH}_{(s)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{H}_3\text{O}^+_{(aq)} + \text{CH}_3\text{COO}^-_{(aq)}$

An Arrhenius base (A-base) is any substance which reacts with H^+ ions to form water.

Examples

- $\text{CuO}_{(s)} + 2\text{H}^+_{(aq)} \rightarrow \text{Cu}^{2+} + \text{H}_2\text{O}_{(l)}$
- $\text{Ca}(\text{OH})_2_{(s)} + 2\text{H}^+_{(aq)} \rightarrow \text{Ca}^{2+}_{(aq)} + 2\text{H}_2\text{O}_{(l)}$

Alkali (soluble bases) are regarded as substances which dissociate in water to produce hydroxyl ions (OH^-). E.g



NB: Basicity is decreasing across the period on the periodic table i.e oxides of group I and II members are more basic than the rest members across the period because they have large atomic and ionic radii.

Example 1.

Write down a chemical equation to show how each of the following substances behaves as an Arrhenius acid or base (i) HBr (ii) KOH (iii) CH_3COOH and (iv) $\text{Zn}(\text{OH})_2$.

ANSWER

- (i) HBr is a strong acid, its ionises completely in aqueous solution to produce H_3O^+ ion. The chemical equation is as follows:

- (ii) $\text{HBr}_{(\text{aq})} + \text{H}_2\text{O}_{(l)} \rightarrow \text{H}_3\text{O}^{+}_{(\text{aq})} + \text{Br}^{-}_{(\text{aq})}$
 KOH is an alkali, it is also ionises completely in aqueous solution to liberate an OH^{-} ion as can be seen below:
- $$\text{KOH}_{(\text{aq})} \rightarrow \text{K}^{+}_{(\text{aq})} + \text{OH}^{-}_{(\text{aq})}$$
- (iii) $\text{CH}_3\text{COOH}_{(\text{s})}$ is a weak acid,
- $$\text{CH}_3\text{COOH}_{(\text{s})} + \text{H}_2\text{O}_{(l)} \rightarrow \text{H}_3\text{O}^{+}_{(\text{aq})} + \text{CH}_3\text{COO}^{-}_{(\text{aq})}$$
- (iv) $\text{Zn}(\text{OH})_2$ is a weak base, $\text{Zn}(\text{OH})_2 + 2\text{H}^{+}_{(\text{aq})} \rightarrow \text{Zn}^{2+}_{(\text{aq})} + 2\text{H}_2\text{O}_{(l)}$

2.1.1 Advantages of Arrhenius theory are:

- It recognises the role of polar molecule (water) as a solvent in the dissociation of acids.
- It also explains why substances such as hydrogen chloride HCl, (strong acid) and ethanoic acid CH_3COOH , (weak acid) can only show their acidic properties in the presence of water.

2.1.2 Limitations of Arrhenius theory

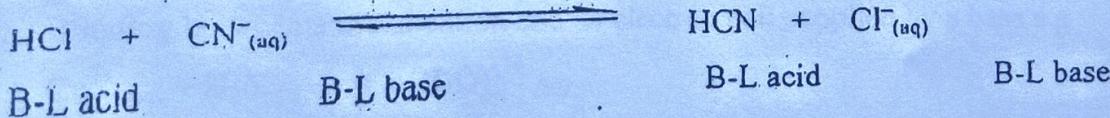
The Arrhenius theory does not provide a satisfactory definition of an acids and a bases because:

- It can be applied only to aqueous solution
- It is restricted to a base which react with H^{+} ion only.

2.2 Bronsted-Lowry concept of acids and bases

In order to broad (cover) the scope of an acid-base reaction to include non-aqueous system and to include a wide range of base, Bronsted-Lowry independently put forward the following definition:

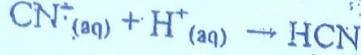
A Bronsted-Lowry (B-L) acid is a proton donor, while a Bronsted-Lowry (B-L) base is a proton acceptor. A proton-transfer reaction is a B-L reaction. Examples



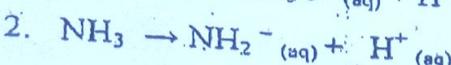
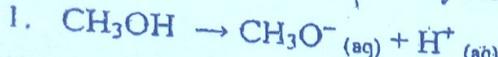
2.2.1 the conjugate acids and bases

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A conjugate acid is formed by adding a proton to a base. E.g CN^- is a base, adding a H^+ to it will give the conjugate acid of CN^- base.

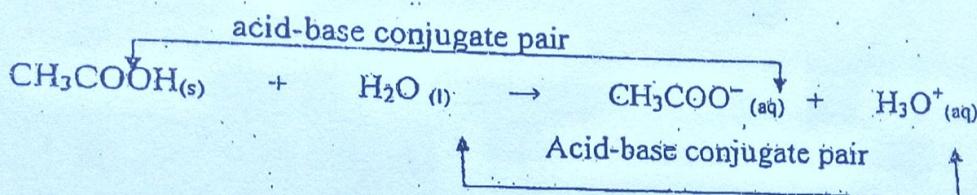


A conjugate base is obtained by removing a proton from an acid e.g



Where $\text{CH}_3\text{O}^-_{(\text{aq})}$ and $\text{NH}_2^-_{(\text{aq})}$ are the conjugate bases.

An acid-base conjugate pair; is any two substances which differ in chemical composition by a proton. Example



According to the Bronsted-Lowry theory, an acid salt such as KHSO_4 and NH_4^+ ions are recognised as acids along side hydrochloric acid and ethanoic acid, whereas the definition of a base includes all anions, H_2O , NH_3 and hydroxide ions.

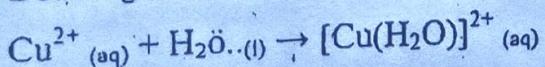
2.3 Lewis concept of acids and bases

According to the Lewis definition, a Lewis acid is an electron pair acceptor while a base is an electron pair donor. The Lewis theory is a more general concept that satisfies the requirements of the Arrhenius and the Bronsted-Lowry concept. It also involves other substances not covered by Arrhenius and Bronsted-Lowry theories.

For example HCl is an Arrhenius and Bronsted-Lowry acid as well as a Lewis acid, thus, AlCl_3 is Lewis acid, but it is not an Arrhenius or Bronsted-Lowry acids.

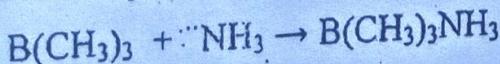
2.3.1 Types of Lewis acid-base interactions

- Bonding between a metal cation and an electron pair supplied by a base e.g



L.A L.B

- A molecule with an incomplete octet can complete its octet by accepting an electron pair. E.g



|3

L.A

L.B

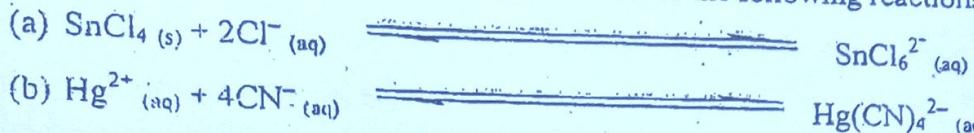
- A molecule or ion expanding its octet by accepting an electron pair. E.g
 $\text{SiF}_4 + 2\text{F}^- \rightarrow [\text{SiF}_6]^{2-}$

L.A

L.B

Example 1.

Identify the Lewis acid and Lewis base in each of the following reactions:



ANSWER

- (a) SnCl_4 accepts two electron pair from Cl^- ions, therefore SnCl_4 is the Lewis acid (i.e electron pair acceptor) and Cl^- is the Lewis base (i.e electron pair donor).
(b) Hg^{2+} accepts four pairs of electrons from the CN^- ions. Hence Hg^{2+} is the Lewis acid and CN^- is the Lewis base.

Example 2.

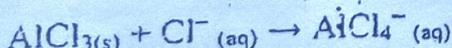
Classify each of the following species as an acid or Lewis base: (a) CO_2 (b) H_2O
(c) I^- (d) NH_3 (e) OH^- (f) H^+ (g) BCl_3 .

ANSWER

| <u>Lewis acid</u> | <u>Lewis base</u> |
|---|---|
| (a) CO_2 , (f) H^+ , (g) BCl_3 | (b) H_2O (c) I^- (d) NH_3 (e) OH^- |

Example 3.

Describe the following reaction in terms of the Lewis theory of acid and base.



LA

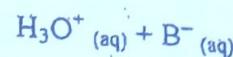
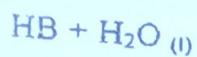
LB

ANSWER

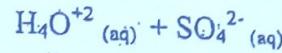
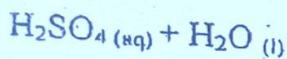
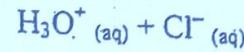
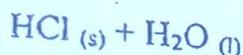
AlCl_3 used its empty $3p_x$ orbital to accept electron pair from Cl^- , therefore AlCl_3 is the Lewis acid and Cl^- is the Lewis base.

2.4 Relative strength of acids and bases

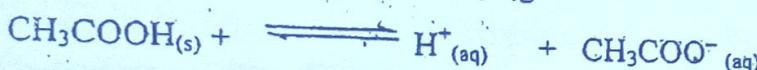
The dissociation of an acid HB in water is given by the following equilibrium:



Acids differ in their ability to donate protons to water in aqueous solution, strong acids donate all their protons to water molecule so, that the equilibrium will completely shift to the right as can be represented below:

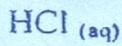
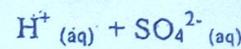


If an acid is weak, for example, ethanoic acid; its conjugate base is strong since it must have a strong affinity for protons, e.g



Strong conjugate base of weak acid
↓

Similarly, if acid is strong for instance, H_2SO_4 , its conjugate base is weak because it does not have most affinity for protons. E.g



Where $SO_4^{2-}_{(aq)}$ and $Cl^-_{(aq)}$ are the weak conjugate bases of strong acids

Acid strength: is a measure of how dissociate it is in water or how readily or quickly it donates a proton compared to water. Note that this is not the same how concentrated it is. Concentration: is a measure of how many moles are dissolved in enough water to form one dm³ or litre.

Table 1:0 show the relative strength of some acids and bases

| S/N | NAME OF ACID | ACID | $H^+ +$ BASE | NAME OF BASE |
|-----|-----------------------|-----------------------------------|--------------|---------------|
| 1. | Ethanol | $C_2H_5OH \rightleftharpoons H^+$ | $C_2H_5O^-$ | Ethoxide |
| 2. | Water | $H_2O \rightleftharpoons H^+$ | OH^- | Hydroxide |
| 3. | Ammonium | $NH_4^+ \rightleftharpoons H^+$ | NH_3 | Ammonia |
| 4. | Hydrogen Sulphide | $H_2S \rightleftharpoons 2H^+$ | S^{2-} | Sulphide |
| 5. | Ethanoic acid | $CH_3COOH \rightleftharpoons H^+$ | CH_3COO^- | Ethanoate |
| 6. | Trioxosulphate (iv) | $H_2SO_3 \rightleftharpoons 2H^+$ | SO_3^{2-} | Sulphate (iv) |
| 7. | Hydroxonium | $H_3O^+ \rightleftharpoons H^+$ | H_2O | Water |
| 8. | Tetraoxosulphate (vi) | $H_2SO_4 \rightleftharpoons 2H^+$ | SO_4^{2-} | Sulphate (vi) |



NB: acid strength increases down while base strength decreases down

Acid-base reaction: is a competition between bases for protons. E.g. when dilute hydrochloric acid is added to a solution of sodium benzoate, a white precipitate of benzoic acid appears.



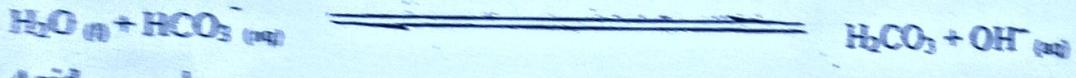
but when ethanoic acid is added to $\text{C}_6\text{H}_5\text{COONa}$ solution, no reaction occurs because ethanoic acid cannot protonate benzoate ion due to its weak ability.



Any substance which has the capacity to act as an acid as well as a base is known as amphoteric. E.g bicarbonate ion (HCO_3^-), H_2O , NH_3 etc.



Acid base



Acid base

There are two important factors in determining the relative strength of acid, these are as follow:

- One factor is the polarity of the bond to which the hydrogen atom is attached. The hydrogen atom will have a partial positive charge while the other will have a partial negative charge as shown below:

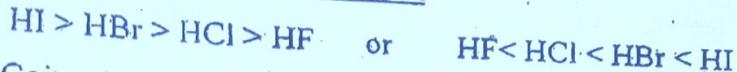


The more polarized the bond, the more easily the proton is removed and the greater the acid strength. C — H, H — Cl.

- The second factor is the strength of the bond i.e how firmly or tightly the proton is held. This depends on the size of an atom X, the larger the atom X, the weak the bond and the greater the acid strength. Going down a group on the periodic table, the atomic size or radius increases markedly and the

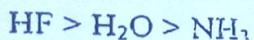
H—X bond strength decreases. One can easily predict the acidic strength of the following acids made up of elements from group 17 as follow: HF, HCl, HI, and HBr.

ANSWER



Going across a period on the periodic table of elements, the polarity of the H—X bond becomes the dominant factor. As electronegativity from left to right across the period on the periodic table, the polarity of the H—X bond increases and the acidic strength increases. One can predict the following order of acidic strength of H_2O , HF, and NH_3 .

ANSWER



2.5 pH

pH of a solution is defined as the negative logarithm of the molar hydrogen ion (H^+) concentration. Mathematical expression: $\text{pH} = -\log_{10}[\text{H}^+]$.

Example 1.

Calculate the pH of a solution in which the hydrogen ion concentration is 1.0×10^{-3} .

ANSWER

$$\text{pH} = -\log_{10}[\text{H}^+] = -\log_{10}(1.0 \times 10^{-3}) = 3.00. \text{ The pH has no unit.}$$

2.5.1 pH of solutions

In a neutral solution, the hydrogen ion concentration is 1.0×10^{-7} M, therefore pH is equal to 7.00. For acidic solutions, the hydrogen ion concentration is greater than 1.0×10^{-7} M, so the pH is less than 7.00. Similarly, a basic solution, has a pH greater than 7.00. Remember that a strong acid has a low pH value.

Example 2.

A sample of an orange has a hydrogen ion concentration of 2.9×10^{-4} M. What is the pH?

ANSWER

$$\text{Recall that } \text{pH} = -\log_{10}[\text{H}^+] = -\log_{10}(2.9 \times 10^{-4}) = 3.54.$$

2.5.2 The pOH

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The pOH of a solution is defined as the negative logarithm of the molar hydroxide ion concentration.

$$pOH = -\log_{10} [OH^-]$$

Example 1.

A solution has a hydroxide ion concentration of 1.9×10^{-3} M. what is the pOH of the solution.

Answer

$$pOH = -\log_{10} [OH^-] = -\log_{10} (1.9 \times 10^{-3}) = 2.72$$

the relation between pH and pOH of a solution is derived as follow:

By definition, $[H^+] [OH^-] = 1.00 \times 10^{-14}$ mol²dm⁻⁶, take negative log of each side

$$-\log \{[H^+] [OH^-]\} = -\log(1.00) -\log(10^{-14})$$

$$pH + pOH = 0 + 14$$

$$pH + pOH = 14.$$

Using this equation, pH of the solution in example (1) above can be evaluated as follow;

$$pH + pOH = 14$$

$$pH = 14 - pOH, pH = 14 - 2.72 = 11.28$$

2.5.3 pH calculations of strong acids and bases

2.5.3.1 for a strong acid (SA)

$$[H^+] = [SA] \times \text{number of ionisable hydrogens}$$

The pH of the acid is calculated by taking the negative logarithm of $[H^+]$.

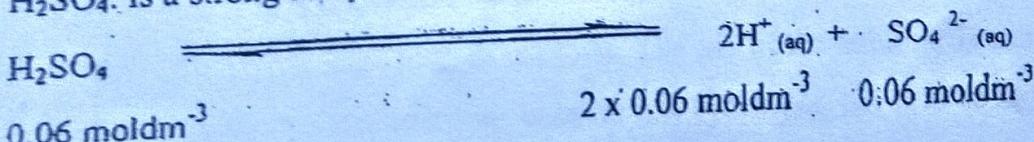
The pOH of the acid is obtained from the equation $pOH = 14 - pH$.

Example

Calculate the pH and pOH of a 0.06moldm⁻³ H₂SO₄.

Answer

H₂SO₄. Is a strong acid, its ionises completely in solution as shown below:



$$[H^+] = 2 \times 0.06 \text{ moldm}^{-3} = 0.12 \text{ moldm}^{-3}$$

$$\text{Therefore, } pH = -\log[H^+] = -\log(0.12) = -\log(1.2 \times 10^{-1}) = -\log(1.2) -\log(10^{-1})$$

$$= -0.08 + 1.00 = 0.92$$

{\\$}

$$pOH = 14 - 0.92 = 13.08$$

2.5.3.2 for a strong base (SB)

$$[OH^-] = [SB] \times \text{number of ionisable OH groups}$$

The pOH of the base is calculated by taking the negative logarithm of $[OH^-]$.

The pH of the base is evaluated from the equation $pH = 14 - pOH$.

Example

Calculate the pH and pOH of 2.22g of $Ca(OH)_2$ in 250cm^3 solution.

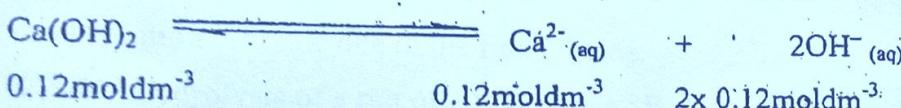
Answer

$$\text{Number of moles of } Ca(OH)_2 = 2.22\text{g}/74 \text{ g mol}^{-1} = 0.03 \text{ mol.}$$

$$\text{Volume of solution (dm}^3) = 250 \text{ cm}^3 \times 1 \text{ dm}^3/1000 \text{ cm}^3 = 0.25 \text{ dm}^3$$

$$[Ca(OH)_2] = \text{no. of mol. / vol. in (dm}^3) = 0.03\text{mol}/0.25 \text{ dm}^3 = 0.12 \text{ mol dm}^{-3}$$

$Ca(OH)_2$ ionises in solution according to the equation below:



$$[OH^-] = 2 \times 0.12\text{mol dm}^{-3} = 0.24\text{mol dm}^{-3}$$

$$pOH = -\log (0.24) = 0.62$$

$$pH = 14 - pOH = 14 - 0.62 = 13.38$$

EXERCISE

Calculate the pH and pOH of the following solution:

(1) 0.025 mole H_2SO_4 in 500ml solution.

(2) 5.985g $Ba(OH)_2$ in 662ml solution ($H=1$, $O=16$, $Ba=137$)

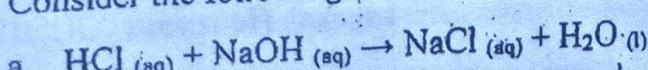
(3) $[H^+] = 4.56 \times 10^{-8} \text{ mol dm}^{-3}$

(4) $[OH^-] = 0.0055 \text{ mol dm}^{-3}$

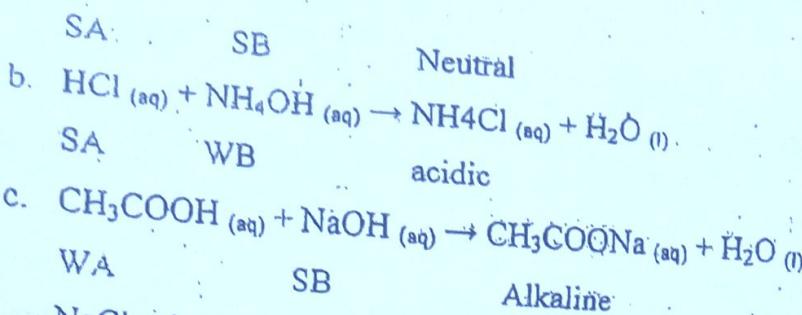
2.6 Hydrolysis of salt

Hydrolysis: can be defined as the interaction of an ion with water molecules to release free H^+ or OH^- ions in solution. The pH of the solution is usually affected. Ion of a strong acid or a strong base do not hydrolyse; ion of a weak acid produce OH^- ions in solution while a weak base ion hydrolyses to form H^+ ions in solution.

Consider the following neutralisation reactions:



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NaCl solution is neutral, it is a salt of a strong acid and a strong base

NH₄Cl solution is acidic, it is a salt of a strong acid and a weak base

CH₃COONa solution is alkaline, it is a salt of a weak acid and a strong base

2.6.1 Hydrolysis of a salt of a SA with a WB

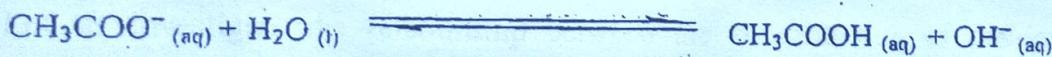
A typical example of a salt of a SA with a WB is NH₄Cl. Cl⁻ does not hydrolyse. The interaction of NH₄⁺ with H₂O yielded the following equation:



The solution is acidic due to the free H⁺ ions.

2.6.2 Hydrolysis of a salt of a WA with a SB

A typical example of a salt of a WA with a SB is CH₃COONa. Na⁺ does not hydrolyse, the hydrolysis of CH₃COO⁻ is given by the equation:



The solution is alkaline due to the free OH⁻ ions.

2.7. Buffer solution:

Buffer solution: refers to a solution of either a weak acid and its conjugate base or a weak base and its conjugate acid which has the ability to resist changes in pH upon addition of small amount of either an acid or a base.

Example are:

1. A solution containing a weak acid and its conjugate base (i.e CH₃COOH and CH₃COO⁻)

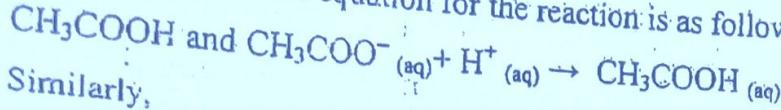
2. Also a solution containing weak base and its conjugate acid (i.e NH₃ and NH₄⁺).

Example 1.

Explain how a Buffer solution of weak acid and its conjugate base (i.e CH₃COOH and CH₃COO⁻) resist pH changes

Q20

If an acid is added to the solution, the H^+ ion will be utilized by conjugate base (CH_3COO^-), and the equation for the reaction is as follow:

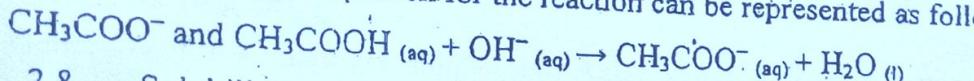


Similarly,

Explain how a Buffer solution of weak base and its conjugate acid (CH_3COO^- and CH_3COOH) resist pH changes

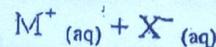
Answer

If a base is added to the solution, the OH^- ions will be consumed by the acid (i.e. CH_3COOH), and the equation for the reaction can be represented as follow:



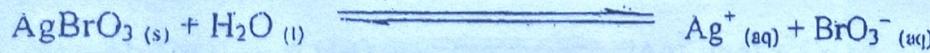
2.8 Solubility equilibria

Solubility of sparingly soluble ionic solids in water, a sparingly soluble ionic solid is one which dissolves to a small extent in solution. In a saturated solution, the undissolved solute is in equilibrium with its ions. E.g. $MX \xrightarrow{(s)} + H_2O \xrightarrow{(l)}$



Let us investigate the relationship between the concentration of the ions and the undissolved solute at equilibrium.

Consider the equilibrium between pure $AgBrO_3 \xrightarrow{(s)}$ and its ions



The table below shows equilibrium concentrations of Ag^+ and BrO_3^- formed from $AgBrO_3 \xrightarrow{(s)}$ and $AgBrO_3 \xrightarrow{(s)}$ formed from different initial concentrations of $AgNO_3$ and $KBrO_3$ at $16^\circ C$

| $Ag^+ \xrightarrow{(aq)}$ (mol dm ⁻³) | $BrO_3^- \xrightarrow{(aq)}$ (mol dm ⁻³) | $[Ag^+ \xrightarrow{(aq)}][BrO_3^- \xrightarrow{(aq)}]$ (mol dm ⁻³) |
|---|--|---|
| 0.0144 | 0.0024 | 3.45×10^{-5} |
| 0.0081 | 0.0041 | 3.32×10^{-5} |
| 0.0058 | 0.0058 | 3.36×10^{-5} |

The products of the equilibrium concentrations of Ag^+ and BrO_3^- are constant as shown on the table 2.0 above, we can therefore, write for this equilibrium

Q.L

$$[\text{Ag}^+_{(\text{aq})}][\text{BrO}_3^-_{(\text{aq})}] = 3.38 \times 10^{-5} \text{ mol}^2 \text{dm}^{-6} \text{ at } 25^\circ\text{C}$$

The equilibrium constant for the reaction



$$K_c = [\text{Ag}^+_{(\text{aq})}][\text{BrO}_3^-_{(\text{aq})}] / [\text{AgBrO}_3_{(\text{s})}] \quad \text{Ag}^+_{(\text{aq})} + \text{BrO}_3^-_{(\text{aq})} \text{ is}$$

$$K_c [\text{AgBrO}_3_{(\text{s})}] = [\text{Ag}^+_{(\text{aq})}][\text{BrO}_3^-_{(\text{aq})}] \quad (2)$$

Recall that the concentration of a pure solid is constant, then $K_c [\text{AgBrO}_3_{(\text{s})}] = \text{new constant}$ (3)

This new constant is called the solubility product; (K_{sp}).

Substituting equation (3) into (2)

$$K_{\text{sp}} = [\text{Ag}^+_{(\text{aq})}][\text{BrO}_3^-_{(\text{aq})}] \quad (4)$$

Generally, for a sparingly soluble salt AxBy which ionises in water according to the equation: $\text{AxBy}_{(\text{s})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons x\text{A}^{y+}_{(\text{aq})} + y\text{B}^{x-}_{(\text{aq})}$

$$\text{Therefore, } K_{\text{sp}} = [\text{A}^{y+}_{(\text{aq})}]^x + [\text{B}^{x-}_{(\text{aq})}]^y$$

Example 1.

Write an expression for K_{sp} and its unit for each of the following sparingly soluble salts

- (a) AgCl (b) Ag_2CrO_4

Answer

(a) $\text{AgCl}_{(\text{s})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons \text{Ag}^+_{(\text{aq})} + \text{Cl}^-_{(\text{aq})}$, $K_{\text{sp}} = [\text{Ag}^+_{(\text{aq})}][\text{Cl}^-_{(\text{aq})}]$ and the unit of $K_{\text{sp}} = \text{mol}^2 \text{dm}^{-6}$.

(b) $\text{Ag}_2\text{CrO}_4_{(\text{s})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons 2\text{Ag}^{2+}_{(\text{aq})} + \text{CrO}_4^{2-}_{(\text{aq})}$, $K_{\text{sp}} = [\text{Ag}^{2+}_{(\text{aq})}]^2 + [\text{CrO}_4^{2-}_{(\text{aq})}]$ and the unit of $K_{\text{sp}} = \text{mol}^2 \text{dm}^{-6}$.

The solubility product of a salts can be calculate from its solubility as shown in the following examples,

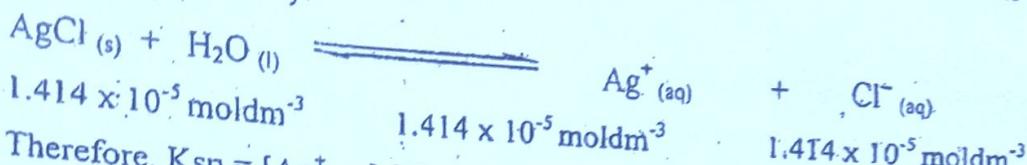
Example 2.

Calculate the solubility product of AgCl if its solubility in pure water at 25°C is $1.414 \times 10^{-5} \text{ mol dm}^{-3}$.

Answer

✓

If the solubility of AgCl is $1.414 \times 10^{-5} \text{ mol dm}^{-3}$, then in a saturated solution, $1.414 \times 10^{-5} \text{ mol dm}^{-3}$ of AgCl will dissolve to give the same concentration of each of Ag^+ and Cl^- ions respectively.



$$\text{Therefore, } K_{\text{sp}} = [\text{Ag}^+_{(aq)}][\text{Cl}^-_{(aq)}] = (1.414 \times 10^{-5} \text{ mol dm}^{-3})^2 = 2.00 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$$

Note that, if the solubility of a salt is given in g dm^{-3} , it is first converted to mol dm^{-3} as given in the example below:

Example 3.

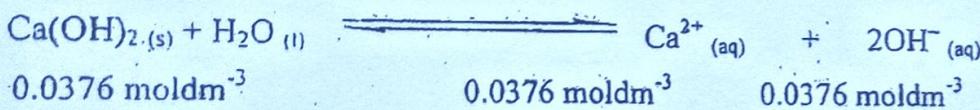
The solubility of Calcium hydroxide in water at 20°C is 2.78 g dm^{-3} . Calculate the:

- Solubility of its ions in a saturated solution at this temperature.
- Solubility product (K_{sp}) given that ($\text{H} = 1$, $\text{O} = 16$, $\text{Ca} = 40$)

Answer

First convert the unit of solubility from g dm^{-3} to mol dm^{-3}

(a) Solubility of $\text{Ca}(\text{OH})_2$ in mol dm^{-3} = solubility in g dm^{-3} / molar mass = $2.78 \text{ g dm}^{-3} / 74 \text{ gmol}^{-1} = 0.0376 \text{ mol dm}^{-3}$



$$[\text{OH}^-] = 2 \times 0.0376 \text{ mol dm}^{-3} = 0.0752 \text{ mol dm}^{-3}$$

$$K_{\text{sp}} = [\text{Ca}^{2+}_{(aq)}][\text{OH}^-_{(aq)}]^2 = (0.0376 \text{ mol dm}^{-3})(0.0752 \text{ mol dm}^{-3})^2$$

$$K_{\text{sp}} = (0.0376 \text{ mol dm}^{-3})(0.00566 \text{ mol}^2 \text{ dm}^{-6}) = 2.13 \times 10^{-4} \text{ mol}^3 \text{ dm}^{-9}$$

2.9 Common ion effect

Two or more salts in a given solution may contain a like ion. This like ion is called a common ion. Example, in a solution containing $\text{Mg}(\text{OH})_2$ and NaOH , OH^- is the common ion. The presence of a common ion in a solution decreases significantly the solubility of a sparingly soluble salt. This effect is called the common ion effect.

CHAPTER THREE

3.0 Quantitative aspect of electrolysis

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3.1 Electrolysis:

first of all, we need to understand the meaning of the following terms before going further into it;

1. **Electrolysis:** is the process by which a chemical compound decomposes when an electric current is passed through either solution or in molten state.
2. **Electrolyte:** is a compound which in solution or molten form conducts electricity and get decomposed in the process.
3. **Electrodes:** are conductors in the form of wires, rods, or plates through which an electric current enters or leaves the electrolyte.
4. **Anode:** is the positive electrode by which the conventional current enters the electrolyte or by which electrons leaves the electrolyte.
5. **Cathode:** is the negative electrode by which the conventional current leaves the electrolyte or by which electrons enters the electrolyte.

3.2: The process of electrolysis

From the above figure, when an electric current is passed through an electrolyte;

- Positive ions are forced to move towards the negative electrode (i.e cathode) where they are reduced.

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- Negative ions are attracted towards the positive electrode (i.e anode) where they are oxidised.

3.3 Preferential discharge of ions in electrolysis:

The discharge of ions during the electrolysis is governed by three conditions as listed below;

- Position of the ions in the electrochemical series
- Concentration of the ions in the electrolyte
- Nature of the electrode

3.3.1 Position of the ions in the electrochemical series: if all other factors are constant, the lower the position of a cation in the electrochemical series, the greater is the tendency of the ion to be discharged in preference to other ions.

Preferential discharge for cations follows the reverse order for anions.

For example, H^+ is discharged in preference to Zn^{2+} , Na^+ , e.t.c similarly, OH^- is discharged in preference to NO_3^- , SO_4^{2-} , e.t.c in the series as shown below;

Cations

K^+
 Na^+
 Ca^{2+}
 Mg^{2+}
 Al^{3+}
 Zn^{2+}
 Fe^{2+}
 Sn^{2+}
 Pb^{2+}
 H^+
 Cu^{2+}
 Hg^{2+}
 Ag^+
 Au^+

Anions

OH^-
 I^-
 Br^-
 Cl^-
 NO_3^-
 SO_4^{2-}
 F^-

3.3.2 Concentration of ions: if other conditions are equal, increasing the concentration of a given ion tends to promote its discharge from the solution. Example during the

electrolysis of dilute NaCl solution, oxygen is produced at the anode, if the solution is concentrated, chlorine will be evolved instead of oxygen.

3.3.3 Nature of electrode: the preference for ionic discharge also depends on the nature of electrodes used.

Inert electrodes are those that do not take part in the electrolytic reaction. Examples are platinum and carbon (graphite). However, platinum is attracted by liberated chlorine and carbon by oxygen.

An electrode which has a strong affinity for a certain ion will promote the discharge of the ion. Example, in the electrolysis of aqueous sodium chloride using platinum electrodes, $H_2(g)$ is produced at the cathode. If a mercury cathode is used, sodium amalgam, Na/Hg is formed. This is because mercury has a strong affinity for sodium.

An electrode which has a lower discharge ability or potential than the species in solution will dissolve instead of the solution.

The discharge potential or ability of some species are given below:

| Half equation | discharge potential (V) |
|---------------|-------------------------|
| Cu | -0.34 |
| $2H_2O$ | -1.23 |
| $2SO_4^{2-}$ | -2.00 |

in the electrolysis of $CuSO_4$ solution using platinum electrodes, H_2O will be oxidised at the anode in preference to SO_4^{2-} . If a copper anode is used, it will dissolve in preference to the oxidation of H_2O .

3.4 Predicting the products of aqueous electrolysis:

the following observations were made from the results of several experiments conducted in aqueous solutions:

3.4.1 Cations:

- H^+ , Hg^+ , or Cu^{2+} is reduced at the cathode in preference to H_2O
- In the absence of H^+ , Hg^+ , or Cu^{2+} , water is reduced in preference to any other cation present.

3.4.2 Anions:

- Br^- , or I^- is oxidised at the anode in preference to water (H_2O)
- In the absence of Br^- , or I^- , water is oxidised in preference to any other anion present.
- Cl^- is a borderline case. In a dilute solution, water is oxidised in preference to Cl^- . In a concentrated solution, Cl^- is oxidised instead of water.

3.5 Examples of electrolysis:

3.5.1 Electrolysis of molten or fused electrolytes.

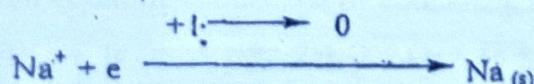
If the ions present at the electrodes (i.e anode and cathode) come from the electrolyte only, then there is no comparative discharge.

3.5.2 Electrolysis of fused sodium hydroxide using iron cathode and nickel anode:

The ions present are Na^+ and OH^- only

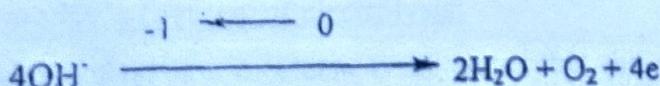
3.5.2.1 Reaction at the cathode:

Na^+ is reduced and it is oxidising agent



3.5.2.2 reaction at the anode:

OH^- is oxidised and it is reducing agent

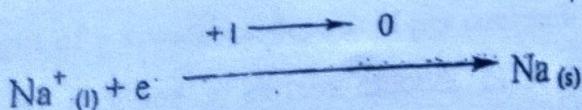


Note: carbon anode cannot be used because it is attacked by $\text{O}_2(g)$.

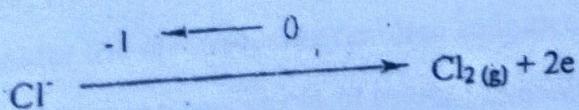
3.5.3 Electrolysis of molten sodium chloride using carbon electrodes:

The ions present are Na^+ and Cl^-

3.5.3.1 reaction at the cathode:



3.5.3.2 reaction at the anode:



or
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Note: platinum anode cannot be used because it is attacked by Cl_2 gas.

3.5.4 Electrolysis of aqueous electrolyte solutions:

In aqueous solutions competitive discharge occurs due to the oxidation and reduction of both water and the solute.

3.5.4.1 Electrolysis of acidified water (i.e. dilute H_2SO_4):

The species present are H^+ , OH^- , and SO_4^{2-} .

1. Reaction at the anode:

Where OH^- is discharged instead of SO_4^{2-}



2. Reaction at the cathode: H_2 is evolved



The overall equation is obtained by combining the two half equations together.



Michael Faraday was the first to describe the quantitative relationship between the amount of electricity and the chemical change produced in an electrolysis.

3.6 Faraday's first law of electrolysis:

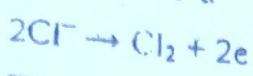
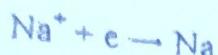
Faraday's first law of electrolysis: states that the mass (m) of an element discharged during an electrolysis is directly proportional to the quantity of electricity (Q) passed through it. Mathematical expression,

$$M \propto Q \text{ or } m = zQ \quad \text{(1)}$$

where $Z = m/Q$ is called the electrochemical equivalent of the material. It is defined as the weight of a substance deposited per coulomb of electricity. The amount of electricity needed to produce a certain amount of a substance can be calculated from the appropriate electrode reaction.

Consider the electrolysis of molten sodium chloride

| Electrode reaction | No. of moles of electrons | product |
|--------------------|---------------------------|---------|
| | | 6.2 |



1 mole of electrons 1 mol Na = 23.0 g

2 moles of electrons 1 mol Cl₂ = 71.0 g

The quantity of electricity (Q) is related to the current (I) and time (t) by the equation: Q = It

SI unit of charge = SI unit of current (I) x SI unit of time (t)

Coulomb = Ampere x Second, C = AS

The quantity of charge carried by 1 mole of electron is calculated as follow:

Charge carried by 1 mole of electrons = no of electrons in 1 mole x charge by a single electron.

$$= (6.0225 \times 10^{23}) (1.60219 \times 10^{-19} \text{ C}) = 96492 \text{ C.}$$

The charge is called the Faraday constant, F in honour of Michael Faraday. For most calculation, F is rounded off to 96500 mol⁻¹.

The charge (Q) is also related to the number of electrons by the expression:

$$Q = nF (2)$$

Example 1.

Calculate the amount of charge required to liberate 23 g of Na and 71 g of Cl₂ in the electrolysis of molten NaCl.

Answer

23 g of Na is deposited by 1 mole of electron, recall that, Q = nF,

$$Q = nF = (1 \text{ mole}) \times (96500 \text{ mol}^{-1}) = 96500 \text{ C}$$

Similarly, 71 g of Cl₂ is deposited by 2 moles of electrons, Q = nF,

$$Q = (2 \text{ moles}) \times (96500 \text{ mol}^{-1}) = 2 \times 96500 = 193000 \text{ C.}$$



Example 2.

In the electrolysis of molten NaCl, a current of 50.0 A is passed for 1.00 hr. calculate:

- The amount of charge passed
- The number of electrons
- The weights of Na and Cl₂ liberated

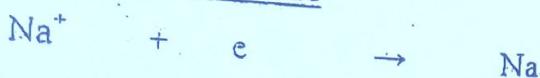
Answer

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(a) Quantity of charge (Q) = $50.0 \text{ A} \times (1 \text{ C}/1 \text{ AS}) \times 1 \text{ hr} \times (60 \text{ mins}/1 \text{ hr}) \times (60 \text{ s}/1 \text{ mins})$
= 180,000 C.

(b) $N = Q/F = 180,000 \text{ C} / 96500 \text{ C mol}^{-1}$ = 1.87 mole of electrons

(c) (i) reaction at cathode



1 mol of electrons deposit 23 g of Na

Therefore, 1.87 mol of electrons will deposit X g of Na

$$X \text{ g of Na} = 1.87 \text{ mol} \times 23 \text{ g} / 1 \text{ mol} = 43.0 \text{ g of Na}$$

So, 1.87 mol of electrons deposited 43.0 g of Na.

(ii) reaction at anode



2 moles of electrons deposited 71.0 g of Cl₂

Therefore, 1.87 moles of electrons will deposit x g of Cl₂

$$X \text{ g of Cl}_2 = 1.87 \text{ mol} \times 71.0 \text{ g of Cl}_2 / 2 \text{ mol} = 66.4 \text{ g of Cl}_2$$

EXERCISE

- What mass of aluminium will be produced in 1.00 hr by the electrolysis of molten AlCl₃ using a current of 10.0 A? given that F = 96500 C mol⁻¹
- What volume of chlorine at S.T.P is produced when a current of 20.0 A is passed through molten sodium chloride for 2.00 hrs? F = 96500 C mol⁻¹.
- Calculate the electrochemical equivalent of Copper if 63.5 g is deposited by 193000 C.

3.6.1 Faraday's second law of electrolysis

Faraday's second law of electrolysis states that when the same quantity of electricity is passed through different electrolytes, the number of moles of elements discharged are inversely proportional to the charges on the ions. For example, when the same quantity of electricity is passed through a solution containing Al³⁺ and Cu²⁺ ions,

$$\text{No of moles of Al} / \text{No of moles of Cu} = \text{charge on Cu}^{2+} \text{ ion} / \text{charge on Al}^{3+} = 2$$

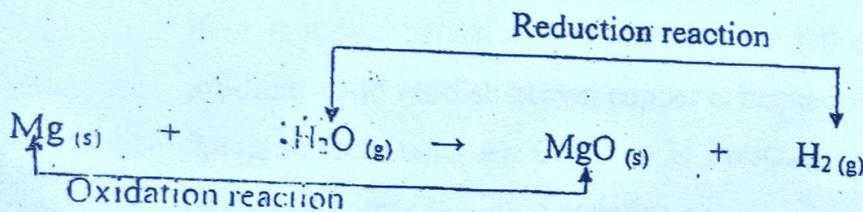
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CHAPTER FOUR

4.0 Redox reaction

The words red derived from reduction, and ox from oxidation, redox reaction: is the reaction involves the simultaneous occurrence of reduction and oxidation reactions. Oxidation is described as addition of oxygen or removal of hydrogen, and reduction as addition of hydrogen or removal of oxygen. E.g take the reaction between heated magnesium and steam

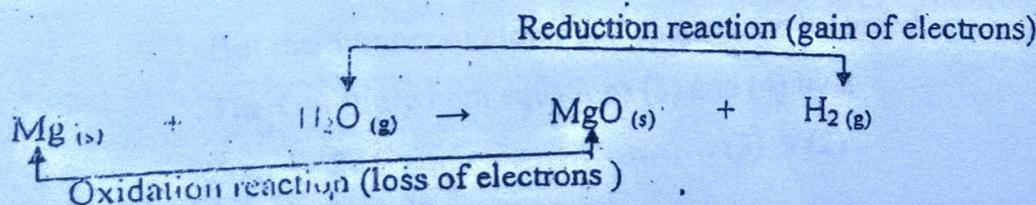


In the reaction above, magnesium is oxidised as oxygen is added to it, as it undergoes oxidation. Water is reduced as oxygen is removed from it, as it undergoes reduction. Reducing Agent oxidised while oxidising agent reduced

4.1 In terms of electron transfer

Chemical reactions often involve the rearrangement of the outermost shell electrons of the reacting species. They either transfer or share electrons in order to gain higher stability.

Consider the chemical reaction between magnesium and steam again



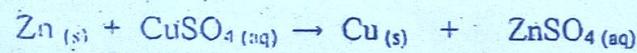
atoms are reduced. The total increase in O.N for Mg (+2) is exactly the same as the total decrease in O.N for H (-1 x 2).

4.3 Balancing redox reactions

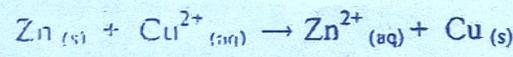
To balance redox reactions, we can use the half equations method:

1. Write the reducing Agent, oxidising agent and their corresponding products for each half reaction.
2. Write separate half equations for oxidation and reduction, balance each half equation with respect to number of atoms and charges
3. Multiply each balanced half equation by a number such the number of electrons gain in the oxidation half equation is equal to that lost from the reduction half equation.
4. Combine the half equations and eliminate electrons, the overall equation can be obtained. For example,

In a reaction between Zinc and Copper (ii) sulphate solution, Zinc dissolves gradually and reddish brown copper is displaced as shown below:



We can express the ionic equation as:



In the reaction, Zn is oxidised as it loses 2 electrons to form Zn^{2+} while Cu^{2+} is reduced as it gain 2 electrons to form Cu.

The above equation can be balance as:

Zn is the reducing agent (1)

Cu^{2+} is the oxidising agent (2)

Oxidation half equation: $\text{Zn}_{(s)} \rightarrow \text{Zn}^{2+}_{(aq)} + 2e$ (3)

Reduction half equation: $\text{Cu}^{2+}_{(aq)} + 2e \rightarrow \text{Cu}_{(s)}$ (4)

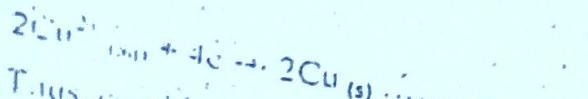
But the number of atoms and charges are balanced.

Then multiply both equations (3) and (4) by 2

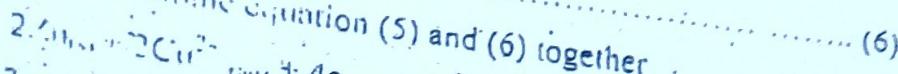
$\text{Zn}_{(s)} \rightarrow \text{Zn}^{2+}_{(aq)} + 2e$ (3) x (2)

$2\text{Zn}_{(s)} \rightarrow 2\text{Zn}^{2+}_{(aq)} + 4e$ (5)

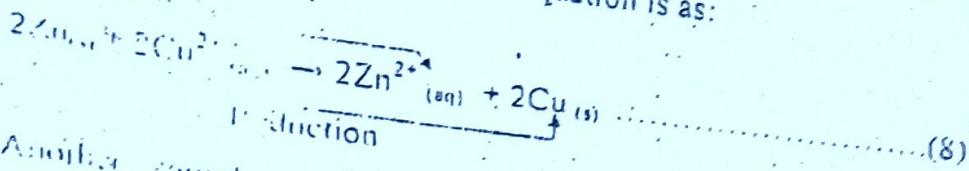
$\text{Cu}^{2+}_{(aq)} + 2e \rightarrow \text{Cu}_{(s)}$ (4) x (2)



Thus, combine equation (5) and (6) together.



Therefore, the overall redox ionic equation is as:



Another example:

Is the redox reaction between $\text{Mg}_{(\text{s})}$ and $\text{H}^{+}_{(\text{aq})}$.

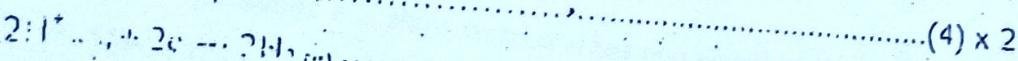
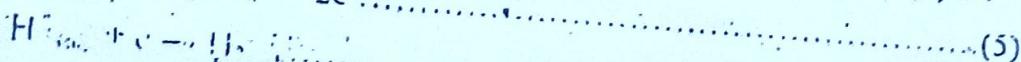
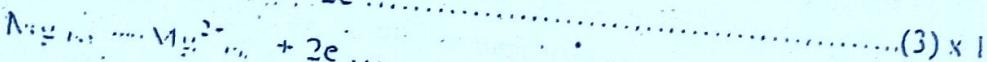
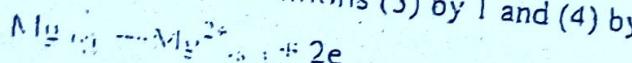
$\text{Mg}_{(\text{s})}$ is the reducing agent.

$\text{H}^{+}_{(\text{aq})}$ is the oxidising agent.

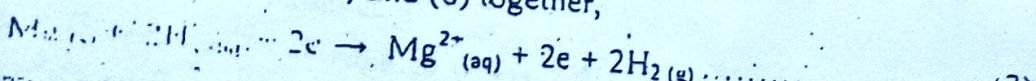
Oxidation half-equation: $\text{Mg}_{(\text{s})} \rightarrow \text{Mg}^{2+}_{(\text{aq})} + 2\text{e}$

Reduction half-equation: $\text{H}^{+}_{(\text{aq})} + \text{e} \rightarrow \text{H}_2_{(\text{g})}$

Then multiply equations (3) by 1 and (4) by 2

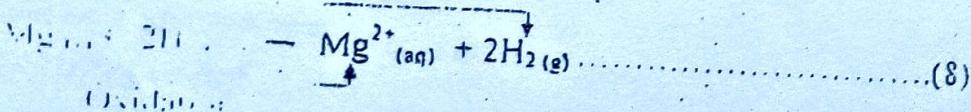


Combine equations (5) and (6) together,



Therefore, the overall ionic equation is:

Reduction

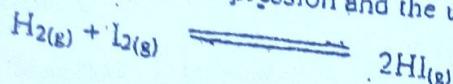


EXERCISE

Chlorine reacts with iron (II) sulphate solution to give chloride ions and iron (III) sulphate. Write the two half-equations and hence, the overall equation for the reaction. State the reducing agent and oxidising agent. Explain your answer.

Example 1.

Write the K_c expression and the unit for the following reaction;



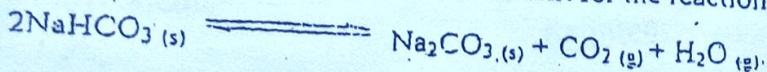
Solution.

By definition, $K_c = [HI]_{}^2 / [H_2]_{} [I_2]_{}^{}.$ Unit of $K_c = (\text{mol l}^{-1})^2 / (\text{mol l}^{-1})(\text{mol l}^{-1}) =$ no unit.

Note: in any reaction, where the total number of moles of reactants is equal to the total number of moles of products, K_c or K_p has no unit.

Example 2.

Write down the K_c expression and its unit for the reaction;



Solution.

By definition, $K_c = [Na_2CO_{3(s)}] [CO_{2(g)}] [H_2O_{(g)}] / [NaHCO_{3(s)}]^2 = 1 \times [CO_{2(g)}] [H_2O_{(g)}] / l^2, K_c = [CO_{2(g)}] [H_2O_{(g)}];$ unit of $K_c = (\text{mol l}^{-1})(\text{mol l}^{-1})$ or $(\text{mol l}^{-1})^2$ or $\text{mol}^2 \text{l}^{-2}$.

Note: concentration of a solid is taken as 1 mol l⁻¹ in mass action expression.

Example 3.

Express the K_p for the following reaction and show whether it has unit or not; $P_4O_{10(g)} +$



Solution.

By definition, $K_p = (P_{POCl_3})^{10} / (P_{P_4O_{10}}) (P_{PCl_5})^6;$ unit of $K_p = (\text{atm})^{10} / (\text{atm})(\text{atm})^6 = (\text{atm})^{10} / (\text{atm})^{1+6} = (\text{atm})^{10-7} = (\text{atm})^3.$

1.2.6 Relationship between K_p and K_c for a reaction:

Generally, for a reaction; $aA + bB \rightleftharpoons cC + dD.$

By definition, $K_c = [C]^c [D]^d / [A]^a [B]^b \dots \dots \dots \text{i}$

$K_p = (P_C)^c (P_D)^d / (P_A)^a (P_B)^b \dots \dots \dots \text{ii}$

Again by definition, the pressure exerted by a gas is a product of its concentration, temperature, and molar gas constant, R. therefore, the partial pressures of A,B,C and D

are; $P_A = [A] (RT)$ (iii), $P_B = [B] (RT)$ (iv), $P_C = [C] (RT)$ (v), $P_D = [D] (RT)$ (vi).

Substitute equations (iii), (iv), (v), (vi) in (ii);

$$K_p = [C]^c (RT)^c [D]^d (RT)^d / [A]^a (RT)^a [B]^b (RT)^b = [C]^c [D]^d / [A]^a [B]^b \times (RT)^{c+d} / (RT)^a (RT)^b$$

$$K_p = K_c (RT)^{(c+d)-(a+b)}$$

$$\text{Where } \Delta n = (c+d)-(a+b), (c+d) = \text{total moles of products and } (a+b) = \text{total moles of reactants.}$$

Example 1:

Given that, K_p for the reaction; $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is 40.7 atm^{-2} at 400 K . Calculate K_c at this temperature.

Solution:

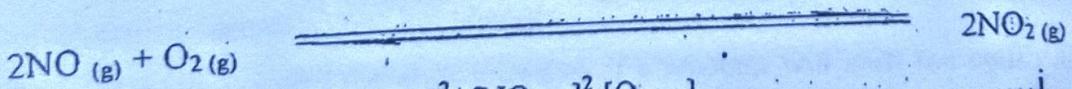
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, given that; $T = 400 \text{ K}$, $K_p = 40.7 \text{ atm}^{-2}$, $R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$, recall that ; $K_p = K_c (RT)^{\Delta n}$ from equation (viii) above, therefore, $K_c = K_p / (RT)^{\Delta n}$, from equation of the reaction above, $\Delta n = 2 - (1+3) = -2$. Thus, $K_c = 40.7 \text{ atm}^{-2} / (0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 400 \text{ K})^2 = 4.4 \times 10^4 \text{ mol}^2$.

Example 2.

Show that $K_p = K_c / RT$ for the reaction of nitric oxide with oxygen molecule to give nitrogen (iv) oxide as shown by the equation below;



Solution:



$$\text{By definition, } K_c = [NO_2]^2 / [NO]^2 [O_2] \quad \text{i}$$

$$K_p = (P NO_2)^2 / (P NO)^2 (P O_2) \quad \text{ii}$$

Again by definition, the pressure exerted by a gas is a product of its concentration, temperature, and molar gas constant, R. therefore, the partial

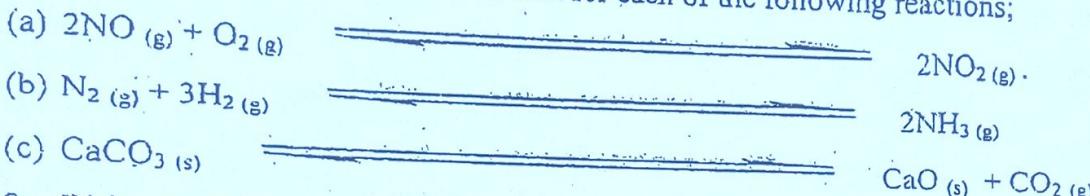
pressures of $\text{NO}_{(g)}$, $\text{O}_{2(g)}$ and $\text{NO}_{2(g)}$ are; $P_{\text{NO}_{(g)}} = [\text{NO}_{(g)}] \cdot (RT)$, (iii), $P_{\text{O}_{2(g)}} = [\text{O}_{2(g)}] \cdot (RT)$, (iv), $P_{\text{NO}_{2(g)}} = [\text{NO}_{2(g)}] \cdot (RT)$, (v).
 Substitute equations (iii), (iv), (v), in (ii),

$$K_p = [\text{NO}_{2(g)}]^2 \cdot (RT)^2 / [\text{NO}_{(g)}]^2 \cdot (RT)^2 \cdot [\text{O}_{2(g)}] \cdot (RT) = [\text{NO}_{2(g)}]^2 / [\text{NO}_{(g)}]^2 \cdot [\text{O}_{2(g)}] \cdot (RT)^2 / (RT)^2 \cdot (RT), K_p = K_c \cdot (RT)^{2(2+1)} = K_c \cdot (RT)^{-1},$$

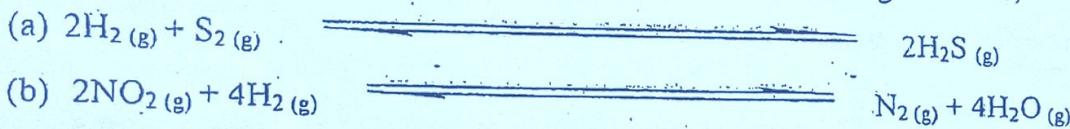
Therefore, $K_p = K_c / RT$.

Exercises

1. Write the K_c expression and its unit for each of the following reactions;



2. Write the K_p expression and its unit for each of the following reactions;



3. At 100°C , $K_p = 6.5 \times 10^{-2} \text{ atm}^{-1}$ for the reaction $\text{N}_{2}\text{O}_{4(g)} \rightleftharpoons 2\text{NO}_{2(g)}$. What is the value of K_c at this temperature? Given that $R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$.

1.2.7 Factors affecting equilibria:

1.2.7.1 Lechatelier's principle: states that if a stress or a disturbance or constraint is applied to a system at equilibrium, the system will respond in such a way to remove or neutralize the effect of the stress or constraint or disturbance.

1.2.7.2 Effect of concentration change: a change in concentration of a system at equilibrium, changes the position of equilibrium. But the numerical value of the equilibrium constant does not change.

Generally, increasing the concentration of a reactant will shift the equilibrium towards the products, and vice versa

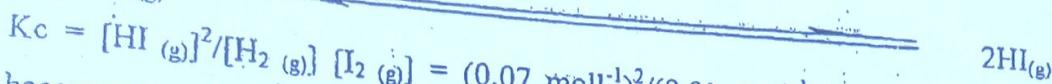
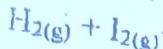
Reactants

forward reaction forms products

backward reaction forms reactants

Products

For example, consider an equilibrium mixture of HI , H_2 and I_2 in which $[\text{HI}] = 0.07 \text{ mol l}^{-1}$, $[\text{H}_2] = 0.01 \text{ mol l}^{-1}$, $[\text{I}_2] = 0.01 \text{ mol l}^{-1}$



because the units have cancelled out.

Let us consider the effect of doubling the initial $[\text{H}_2]$. By lechatelier's principle, the system is under a stress, this can be removed by reaction of H_2 and I_2 to give more HI .

1.2.7.3 Effect of pressure changes: the effect of pressure changes apply mainly to gaseous reactions. It affect the equilibrium position, but not the value of equilibrium constant. Generally, the effect of pressure changes depends on the stoichiometry of the reaction.

Reactants

forward reaction favoured by high pressure

backward reaction favoured by low pressure

Products

The total number of molecules in the system decreases when reactants are converted to products, an increase in pressure will shift the position of equilibrium towards the products.



When the pressure is increased, the system will received the effect by shifting the position of equilibrium towards the product side, some of the reactants (i.e $\text{SO}_2(\text{g})$ and $\text{O}_2(\text{g})$) are converted into $\text{SO}_3(\text{g})$. so, concentration of $\text{SO}_3(\text{g})$ increases while concentrations of $\text{SO}_2(\text{g}) + \text{O}_2(\text{g})$ decreased.

The total number of molecules in the system increases when the products are converted into reactants, decrease in pressure will shift the position of equilibrium towards the reactants.

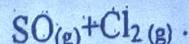
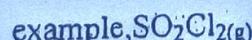
Reactants

forward reaction favoured by high pressure

backward reaction favoured by low pressure

Products

For



COLLIGATIVE PROPERTIES

Colligative properties are properties of solutions that depend on the ratio of the number of solute particles to the number of solvent molecules in a solution, i.e. they depend upon the concentration of solute molecules or ions, but they do NOT depend upon the identity of the solute or the type of solute particles.

SOME COLLIGATIVE PROPERTIES

Dilute solution containing non-volatile solutes exhibit the following properties:

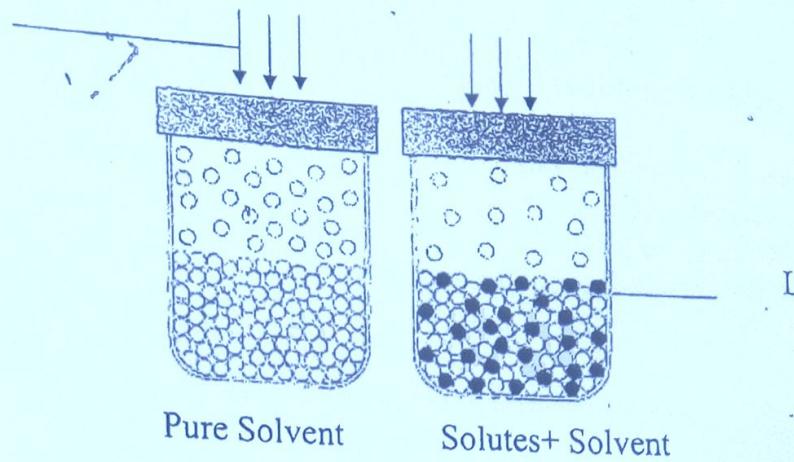
1. Vapour pressure lowering
2. Boiling point elevation
3. Freezing point depression
4. Osmotic pressure

1. VAPOUR PRESSURE LOWERING

When a non-volatile solute was added to a volatile solvent it is observed that there is a decrease in vapour pressure of the solution. This decrease in vapour pressure can be quantitatively used to measure several properties of liquid solution. Thus, the vapour pressure of solution is lower than that of the pure liquid. More correctly, the vapour pressure of solution containing a non volatile (zero-Vapour Pressure) solute is lower than that of the pure solvent. So, if salt was dissolved into water, the vapour pressure of the solution (salt + water) is lower than that of pure water.

The logo for Dominion Center, featuring the word "Dominion" in a large, bold, serif font and "Center" in a slightly smaller, bold, sans-serif font to its right. A stylized graphic element resembling a bridge or arches is positioned to the left of the text.

Atmospheric pressure



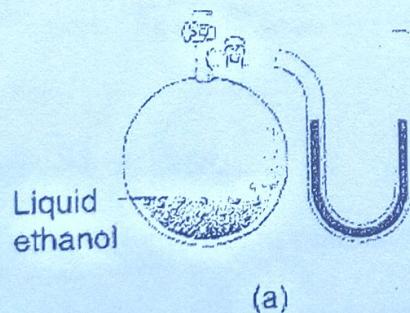
Lower Vapour Pressure

Pure Solvent

Solutes + Solvent

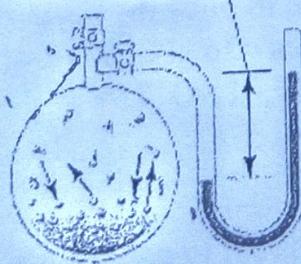
From the figure above there is a relative lowering of vapour pressure because fewer surfaces are available for solvent molecules to escape out. The vapour pressure of a solvent is lowered when a non-volatile solute is added into it. This is called "lowering of vapour pressure".

The French chemist Francoise – marie Raout's observed that the concentration of solute particles is mainly responsible for the lowering of vapour pressure and also discovered the relation between vapour pressure of solution, vapour pressure of pure solvent and mole fraction of solute and solvent. That is, the vapour pressure is directly proportional to the mole fraction of the solute.



(a)

$$P_{\text{gas}} = \text{Equilibrium vapor pressure}$$



(b)

From the figures above, the vapour pressure decrease as solute is added into pure solvent.

As a result of extensive experimentation results, Raoult (1886) gave an empirical relation connecting the relative lowering of vapour pressure and the concentration of the solute in solution. This is now referred to as Raoult's law. It states that: "The relative lowering of the vapour pressure of a dilute solution is equal to the mole fraction of the solute present in dilute solution"

Mathematical expression of Raoult's law:

For a solution with a solvent (A) and one non-volatile solute (B)

$$P_B = 0 \text{ and } P = P_A^o \times X_{\text{solvent}}$$

$$P_{\text{solution}} = X_{\text{solvent}} \times P_A^o \text{ solvent} \quad (1)$$

Where: P_A^o solvent is the vapour pressure of the pure solvent.

X_{solvent} is the mole fraction of the solvent.

Since this is a two-component system (solute and solvent), then

$$X_{\text{solvent}} + X_{\text{solute}} = 1 \quad (2)$$

Where: X_{solvent} is the mole fraction of the solvent

X_{solute} is the mole fraction of the solute

The change in vapour pressure (ΔP) can be expressed as

$$\Delta P = P_{\text{solvent}}^o - P_{\text{solution}}$$

$$\Delta P = P_{\text{solvent}}^o - X_{\text{solvent}} P_{\text{solvent}}^o \quad (3)$$

Or

$$\Delta P = (1 - X_{\text{solvent}}) P_{\text{solvent}}^o$$

By making X_{solute} the subject in equation (2),

$$\text{We have } \Delta P = X_{\text{solute}} P_{\text{solvent}}^o \quad (4)$$

Example 1:

- Calculate the vapour pressure of a solution made by dissolving 50.0g glucose ($C_6H_{12}O_6$) in 500g of water. The vapour pressure of pure water is 47.1 torr at 37°C. (C=12, O=16; H=1).

Solution

Lets calculate the mole fraction of the solvent, which is water as follows

$$X_{\text{solvent}} = \frac{\text{Mole of solvent}}{\text{Mole solute} + \text{mole of solvent}}$$

$$\text{But } n_{\text{water}} = \frac{500\text{g}}{18\text{g/mol}} = 27.7\text{mol}$$

$$\text{And } n_{\text{Glucose}} = \frac{50\text{g}}{180.\text{g/mol}} = 0.277\text{mol}$$

$$X_{\text{solvent}} = \frac{27.7\text{mol}}{0.277\text{mol} + 27.7\text{mol}} = 0.99$$

The pressure of solution is then calculated via Raoult's equation

$$P_{\text{solution}} = 0.99 \times 47.1 = 46.63 \text{ torr}$$

Example 2:

The vapour pressure of an aqueous solution is found to be 24.90mmHg at 25°C. What is the mole fraction of solute in this solution? The vapour pressure of water is 25.756mmHg at 25°C.

Solution

Using Raoult's equation

$$P_{\text{solution}} = X_{\text{solvent}} P_{\text{solvent}}^0$$

$$24.90\text{mmHg} = (x) (25.756\text{mmHg})$$

$$X = 0.966765 \text{ (but this is the solvent mole fraction)}$$

To find the solute mole fraction:

$$X_{\text{solvent}} + X_{\text{solute}} = 1$$

$$\text{Therefore } X_{\text{solute}} = 1 - X_{\text{solvent}}$$

$$X_{\text{solute}} = 1 - 0.966765 = 0.033235$$

$$X_{\text{solute}} = 0.03324$$

Exercise

Calculate the vapour pressure lowering caused by the addition of 100g of sucrose (molar mass = 342) to 1000g of water if the vapour pressure of pure water at 25°C is 23.8mmHg.

2. BOILING POINT ELEVATION

When a liquid is heated, its vapour pressure rises and when it equals the atmospheric pressure, the liquid boils. The addition of a non-volatile solute lowers the vapour pressure and consequently elevates the boiling point as the solution has to be heated to a higher temperature to make its vapour pressure becomes equal to atmospheric pressure. Therefore on addition of non-volatile solute in a solvent, the vapour pressure of the solution decreases. However the boiling point of the solution is greater than that of the pure solvent, this is because vapour pressure is directly proportional to temperature. And in order to boil a solution, there is a need to raise the boiling point of the solution to a certain temperature. This rise in temperature is called elevation of boiling point, and just like the relative lowering of vapour pressure it also depends on solute particles in the solution.

Water boils at 100°C and 1 atm of pressure, but a solution of salt water does not. When table salt is added to water the resulting solution has higher boiling point than the water. The ions form an attraction with the solvent particles that then prevent the water molecules from going into the gas phase. Therefore, the salt-water solution will not boil at 100°C, but above 100°C. This is true for any solute added to a solvent. The more solute dissolved, the greater the effect. An equation has been developed for this behavior:

$$\Delta T_b = i k_b M$$

The above equation is derived mathematically: if T_b^0 is the boiling point of pure solvent and T_b denotes boiling point of the solution, then elevation in boiling point (Denoted by ΔT_b) is

$$\Delta T_b = T_b - T_b^0$$

Experimentally it has been found that elevation in boiling point in dilute solution is directly proportional to molality 'M' of solute present in a solution. \propto

$$\Delta T_b \propto M$$

$$\Delta T_b = K_b M$$

If T_b^0 is the boiling point of pure solvent and T_b is boiling point of the solution, then elevation in boiling point is given by

$$\Delta T_b = T_b - T_b^0$$

Experimentally, it has been found that elevation in boiling point in dilute solutions is directly proportional to molality 'm' of solute present in solution. The term molality 'M' denotes the number of moles of solute present in 1000g or 1kg of solvent. The standard unit of molality or molal elevation constant K_b is Kkg/mol. Let m_1 and m_2 be the given masses of solvent and solute respectively. And molar masses of solute by N_2 and that of solvent is N_1 , then molality can be evaluated from the relation

$$M = \frac{\frac{m_2}{N_2}}{\frac{m_1}{1000g}} = \frac{1000 \times m_2}{N_2 \times m_1}$$

Putting the value of molality in the boiling point elevation relation, we get,

$$\Delta T_b = \frac{K_b \times 1000 \times m_2}{N_2 \times m_1}$$

Example:

1. The boiling point of a pure liquid is 353.23k, if 2.70g of a non-volatile solute was added in 90g of liquid, the boiling of the solution rises to 354.11k. what will be the molar mass of non-volatile solute? Take the value of K_b of liquid to be 2.53Kkg/mol.

Solution

$$T_b^0 = 353.23k$$

$$T_b = 354.11k$$

$$m_2 = 2.70g$$

$$K_b = 2.53\text{Kkg/mol}$$

$$m_1 = 90g$$

The elevation in boiling point

$$\begin{aligned}\Delta T_b &= T_b - T_b^0 \\ &= 354.11k - 353.23k = 0.88\end{aligned}$$

Using the above relation

$$\Delta T_b = \frac{K_b \times 1000 \times m_2}{N_2 \times m_1}$$

$$0.88 = \frac{2.53 \times 1000 \times 2.70}{N_2 \times 90}$$

Ans $N_2 = 86.25g$, hence molar mass of solute is 86.25g

2. Acetone boils at 56.38°C and a solution of 1.41g of an organic solid in 20g of an Acetone boils at 56.88°C . if K_b for acetone is 16.7, calculate the mass of one mole of the organic solid.

3) DEPRESSION OF FREEZING POINT:

When the vapour pressure of a solution is reduced, the freezing of the solution decreases. The freezing point of a solution is defined as the temperature at which vapour pressure of its substance become equal in liquid and vapour phase. If the vapour pressure of the solution equals to vapour pressure of the pure solvent, Then the solution will be frozen.

According to Raoult's law when non-volatile solute is added to a solvent, the freezing point of a solution is slightly less than that of the pure solvent. This is called depression of freezing point.

The freezing point of depression is denoted by

$$\Delta T_f = T_f^0 - T_f$$

The freezing point depression of dilute solution is directly proportional to molality of the solute just like the boiling point elevation, that is

$$\Delta T_f \propto M$$

$$\Delta T_f = K_f M$$

The proportionality constant K_f is called molal depression constant and is also known as cryoscopic which depends constant upon the nature of the solvent.

$$\text{Molality } M = \frac{1000 \times m_2}{N_2 \times m_1}$$

Putting the value of molality in above equation we get depression in freezing point as

$$\Delta T_f = K_f M$$

$$\Delta T_f = \frac{K_f \times 1000 \times m_2}{N_2 \times m_1}$$

Further investigation was made by Raoult's using non-aqueous solvents and H_2O . These results confirmed that various solutions of molar concentration produce the same depression in any particular solvent. The depression of freezing point produced when one mole of any solute is dissolved in 1000g (1kg) of a given solvent is known as the molecular depression constant or the cryoscopic constant (K). The depression of freezing point has been found to be depended upon the nature of the solvents and on the concentration of the solvent particles. Therefore, the lowering of the freezing point in dilutes solution has been found to be proportional to the solutes or molal concentration i.e

$$\Delta T \propto M \text{ where } M = \text{molal concentration or molality}$$
$$\Delta T = K \cdot M \quad \dots \dots \dots (1)$$

And molality is the mole of the solvent present in 1kg or 1000g of the solvent

$$\Delta T = K \times \frac{m_1}{M} \text{ where } m_1 = \text{mass of solute}$$

M = molar mass of the solute in 1kg of solvent.

Example:

1. A solution of concentrated sugar containing 2.50g in 100g of water begins to freeze at -0.1350°C. Given that the cryoscopic constant of H₂O (1Kg) is 1.86, calculate the molar mass of the concentrated sugar

Solution

Using $\Delta T = K \times \frac{m_1}{M}$

$$m_1 = 2.5$$

$$K = 1.86$$

$$\Delta T = 0.1350^\circ\text{C} (-ve is ignored)$$

100g of H₂O = mass of solvent and

$$1000g \longrightarrow 1\text{kg}$$

$$100g \longrightarrow X\text{kg}$$

$$X\text{kg} = \frac{100}{1000} \times 1 = 0.1\text{kg}$$

$$1000$$

$$100g = 0.1\text{kg}$$

$$0.10\text{kg of H}_2\text{O} = \frac{m_1}{M} \quad (\text{since molality is mole of solute present in 1kg of solvent})$$

From definition of molality

$$1\text{kg of H}_2\text{O} = \frac{2.5}{M} \div 0.10\text{kg}$$

$$= \frac{2.5}{M} \times \frac{1}{0.10g}$$

Molality = $\frac{2.5}{0.10M}$

From the formula

$$0.135 \times 0.10 \times M = 1.86 \times 2.50$$

$$M = \frac{1.86 \times 2.50}{0.135 \times 0.10}$$

$$M = 344.44 \text{ g/mol.}$$

2. 0.440g of substance dissolved in 22.2g of benzene lowered the freezing point of benzene by $0.567 \text{ }^{\circ}\text{C}$. calculate the molecular mass of the substance. ($k_f = 5.12 \text{ }^{\circ}\text{C mol}^{-1}$)

4) OSMOSIS AND OSMOTIC PRESSURE

Let us consider a pure solvent and solution separated by a membrane which permit the passage to solvent molecules but to solute molecules. Only the solvent will diffuse through the membrane into solution. A membrane which is permeable to solvent and not to solute, is called a semi-permeable membrane.

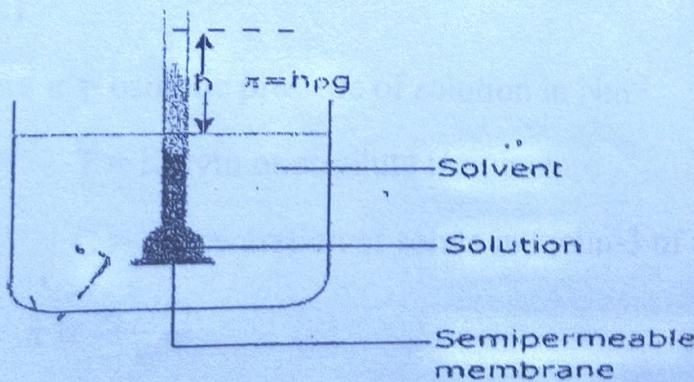


Fig (3) is the illustration of the process of osmosis. The solvent molecules can pass through the membrane from either side of the semi-permeable membrane. There is a net flow of solvent from the dilute solution to the concentrated solution. It shows up in the rise of level in the concentrated solution compartment.

If a solution is separated from its pure solvent by a semi-permeable membrane, then a net flow of solvents take place into the solution. This phenomenon is what is referred to as osmosis, by definition, osmosis is referred to as the movement of solvent molecules from region of lower concentration to higher concentration through a semi-permeable membrane.

A semi-permeable membrane is one that allows the passage of solvent molecules through it, but not the passage of solute.

Osmotic pressure, this is best defined as the pressure that is needed to prevent osmosis from taking place. "for example, a given solution standing

$$\pi \propto C \quad \dots \quad (1)$$

The above equation is derived from the laws of osmosis.

- 1) Which says that at a constant temperature, the osmotic pressure of a solution is proportional to the concentration of the solute molecules.
- 2) States that; the osmotic pressure of a solution is proportional to its absolute temperature.

Mathematically:

$$\pi \propto T(K) \quad \dots \quad (2)$$

The above two laws can be summarized as follows:

1. $\pi \propto C \quad \dots \quad (1)$
2. $\pi \propto T(K) \quad \dots \quad (2)$

Combining equation (1) and (2) we have

$$\pi \propto CT(K)$$

Where π = osmotic pressure of solution in Nm^{-2}

T = Kelvin or absolute temperature

C = concentration of solute in $mol m^{-3}$ of the solution

$$\pi \propto \frac{n_2 T(K)}{V}$$

$$\pi = R \frac{n_2 T(K)}{V} \quad \dots \quad (3)$$

Where R is the molar or universal gas constant ,which is equals to $8.314 J K^{-1} mol^{-1}$

But $1J = 1Nm$

NB: R is also $= 8.314 \text{ NmK}^{-1} \text{ mol}^{-1}$

$$\pi V = \frac{m}{M} RT \quad \dots \quad (4)$$

Where m is the mass of solute and M is the molar mass (g/mol) of the solute.

$$\pi = \frac{m}{V} \times \frac{RT}{M}$$

$$\pi = \frac{CRT}{M} \quad \dots \quad (5)$$

Reciprocal of M as subject, we have

$$\frac{1}{M} = \frac{\pi}{CRT}$$

Example:

- Calculate the molar mass of an unknown compound (solute), if its solutions contains 75 gdm^{-3} and they carries pending osmotic pressure is $4.85 \times 10^5 \text{ NM}^{-2}$ at 10°C .

Solution

Using the ideal equation of solution

$$\frac{1}{M} = \frac{\pi}{CRT}$$

$$M = \frac{CRT}{\pi}$$

$$\pi = 4.85 \times 10^5 \text{ NM}^{-2}, R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1},$$

$$T = 283 \text{ K}, C = 75 \text{ g dm}^{-3} \neq 75 \times 10^3 \text{ gm}^{-3}, M = ?$$

$$\text{Therefore } M = \frac{75 \times 10^3 \times 8.314 \text{ Nm K}^{-1} \text{ mol}^{-1} \times 283 \text{ K}}{4.85 \times 10^5 \text{ N mm}^{-2}} = 363.8 \text{ g mol}^{-1}$$

Therefore molar mass = 364 g/mol

DETERMINATION OF MOLECULAR WEIGHT OR MOLAR MASS.

Relative molecular mass: molecules also have mass since they consist of atoms called molecular mass, and it is expressed in terms of C-12.

The relative molecular mass (R.M.M) of a molecule is the number of times the average mass of one molecule is heavier than one-twelfth the mass of an atom of C-12.

Thus, relative molecular mass: the sum of R.A.M of the individual atoms present in one molecule of a given substance (compound).

Example:

1. Calculate the relative molecular mass of CaCO_3 given that Ca = 40, C = 12, O = 16.

Solution

Recall that, one molecule of CaCO_3 consists of 1Ca, 1C, and 3O atoms hence,

$$\text{R.M.M} = (1 \times \text{R.A.M of Ca}) + (1 \times \text{R.A.M of C}) + (3 \times \text{R.A.M of O})$$

$$\text{R.M.M} = [(1 \times 40) + (1 \times 12) + (3 \times 16)]$$

$$= 40 + 12 + 48 = 100\text{g}$$

Therefore R.M.M of CaCO_3 = 100g

But, the molecular weights of polymers (macromolecular compounds) can be determined by chemical or physical methods.

The chemical method includes functional group analysis (end-group assay) while the physical methods include:

Colligative properties, light scattering, ultracentrifugation and dilute-solution viscosity.

The methods used to determine the molar mass M are either relative or absolute. Relative method requires calibration with samples of known M and include viscosity and vapour pressure osmometry. The absolute methods are often classified by the types of averages they yield, for example colligative techniques yield M_n (number averages) light scattering and ultracentrifuge yield higher averages M_w (weight averages).

Assignment

Briefly explain the physical and chemical methods of determining the molecular weight/molar mass of high molecular compounds, with examples.

CHARACTERISTICS OF THE SOLID STATE

Gases and liquids can flow and take up the shape of their container. Solids, on the other hand have a definite volume and shape. They are rigid and lack the ability to flow.

In both gases and liquids, atoms, ions and molecules continually move. They translate randomly as well as rotate and vibrate. This determines the ability of gases and liquids to flow. In solids, atoms, ions and molecules are held together by relatively strong chemical forces : ionic bond, covalent bond, or by intermolecular vander waals forces. They do not translate although they vibrate to some extent in their fixed positions. The solid are characterized by incompressibility rigidity and mechanical strength. The molecules, atoms and ions in solids are closely packed, i.e they are held together by strong forces and they can not move about at random. Thus, solid have definite volume, shape, slow diffusion, low vapour pressure and posses the unique property of being rigid, such solid are known as true solid. E.g NaCl, KCl, sugar, Ag, Cu, e.t.c

On the other hand, the solid which loses shape on long standing, flows under its own weight and is easily distorted by even mild distortion force is called pseudo solid e.g glass, pith e.t.c

Some solid such as a NaCl, Sugar, sulphur e.t.c have properties not only of rigidity and imcompressibility but also of having typical geometrical forms. These solids are called crystalline solids. In such solids there is definite arrangement of particles (atoms, ions or molecules) throughout the entire three dimensional network of a crystal. This is named as long-range order

This three dimensional arrangement is called crystal lattice or space lattice. Other solid such as glass, rubber, plastics e.t.c which have rigidity and incompressibility to a certain extent but they do not have definite geometrical forms or do not have long-range order are known as amorphous solid.

TYPES OF SOLIDS

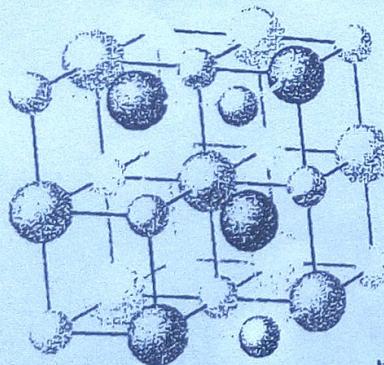
Solids are of two types

- a. Cysatalline solid
- b. Amorphous solid
- a. A crystalline solid exists as small crystals, each crystal having a characteristic geometrical shape. In a crystal, the atoms, molecules or ions are arrange in a regular, repeating three-dimensional pattern called the crystal lattice. Sugar, and salt are crystalline solids.
- b. An amorphous solid has atoms, molecules or ions arranged at random and lacks the order crystalline lattice. Examples are rubber, plastics and glass.

LATTICE STRUCTURE

- Crystals: are types of a solid material composed of atom or group of atoms that are arrange in a three-dimensional pattern that is very ordered. In a crystal, the groups of atoms are repetitive at evenly spaced intervals, all maintaining their orientation to one another. In other words, the geometric shape of a crystal is highly symmetrical.
- A crystal lattice: is the arrangement of these atoms, or groups of atoms, in a crystal. These atoms or groups of atoms are commonly referred to as points within a crystal lattice site. These point simply points "in space" oriented in such a way to build a lattice structure.

CRYSTAL LATTICE STRUCTURE



Example of a crystal lattice structure

The pattern of arrangement of each point as well as their symmetry of the crystal lattice structure site's are only viewed microscopically and are invisible to the naked eye. In order to view these structures, it has to be placed under a microscope.

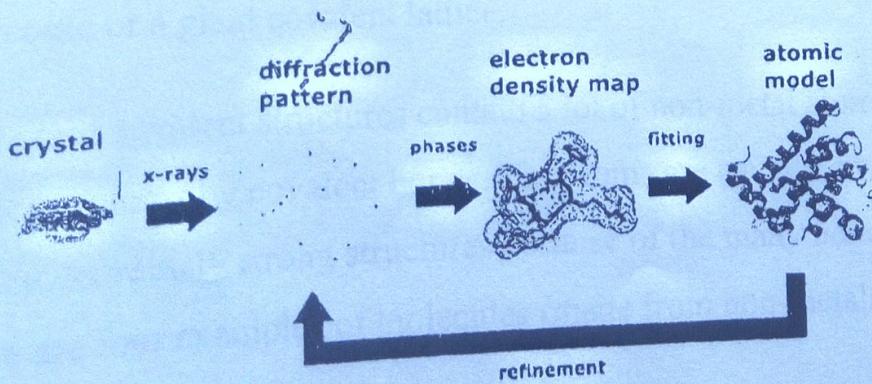
A crystal lattice is the arrangement of atoms in a crystal (the black and white points in the example above are atoms). This arrangement can be defined as the intersection of these parallel planes.

X-RAY DIFFRACTION

x-ray crystallography: is a technique used for determining the atomic and molecular structure of a crystal, in which the crystalline atoms cause a beam of incident x-rays to diffract into many specific directions. By measuring the angles and intensities of these diffracted beams, a crystallographer can produce a three-dimensional picture of the density of electrons within the crystals. From this electron density, the mean positions of the atoms in the crystal can be determined as well as their chemical bonds, their disorder, and various other information.

A crystal lattice is considered to be made up of regular layers or planes of atoms equal distance apart. Since the wavelength of x-rays is comparable to the interatomic distances, crystal can act as grating to x-rays. Thus, when a beam of x-rays is allowed to fall on a crystal, a large number of images of different intensities are formed. If the diffracted waves are in the same phase, they reinforce each other and a series of bright spots are produced on a photographic plate placed in their path. On the other hand, if the diffracted waves are out of phase, dark spots are caused on the photographic plate. The study of crystal structure with the help of x-ray diffraction is called x-ray crystallography

Lecture 53: X-ray crystallography



ISOMORPHISM

Isomorphism is an identity or close similarity in the crystalline form of substances usually containing different element but having similar composition. Such substances are called isomorphs or isomorphous to each other.

CHARACTERISTICS OF ISOMORPHOUS SUBSTANCES

- The crystal of isomorphous substances have the same shape.
- If crystal of one substance are suspended in a saturated solution of another, the former continues to grow as latter is deposited all over it. Thus, they form overgrowth on each other
- They can form a mixed crystal with each other

Examples:

- Ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and magnesium sulphate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$),
- Potassium perchlorate (KClO_4) and potassium permagnate (KMnO_4)

GIANT MOLECULE

A covalently bonded substance containing a huge number of atoms is called a giant molecule or a giant covalent lattice.

The giant covalent structures contain a lot of non-metal atoms, each joined to adjacent atoms by covalent bonds. The atoms are usually arranged into giant lattice, extremely strong structures because of the many bonds involved. There are four examples of molecules (made from non-metals) which form giant structure. They are:

Silicon, silicon dioxide and two forms of the element carbon called diamond and graphite.

Carbon and silicon are both in group 4 of the periodic table. They both need to form 4 bonds with themselves or other elements they have valency of 4.

When two or more forms of an element exist in the same physical state, they are called allotropes. Diamond and graphite are allotropes of carbon.

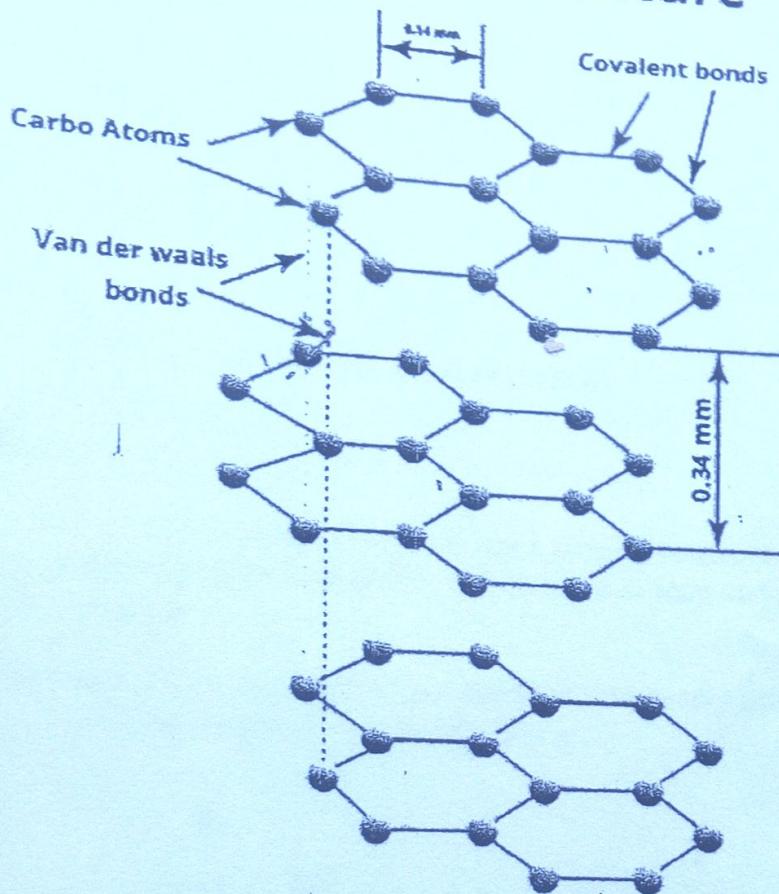
PROPERTIES OF GIANT STRUCTURE

- Very high melting points: substances with giant covalent structures have very high melting point because a lot of strong covalent bonds must be broken. Graphite for example has a melting point of more than $3,600^{\circ}\text{C}$.
- Variable conductivity: diamond does not conduct electricity. Graphite contains free electrons, so it does conduct electricity. Silicon is semi-conductor. That is, midway between non-conductive and conductive.

GRAPHITE:

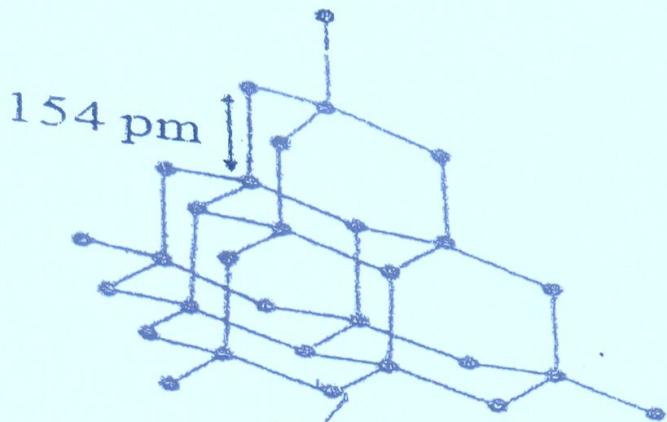
Graphite is a form of carbon in which the carbon atoms form layers. These layers can slide over each other, so graphite is much softer than diamond, it is used in pencils and as a lubricant. Each carbon atom in a layer is joined to only three other carbon atoms. Graphite conducts electricity.

Graphite Structure



DIAMOND:

Diamond is a form of carbon in which each carbon atom is joined to four other carbon atoms, forming a giant covalent structure. As a result, diamond is very hard and has a high melting point. It does not conduct electricity.

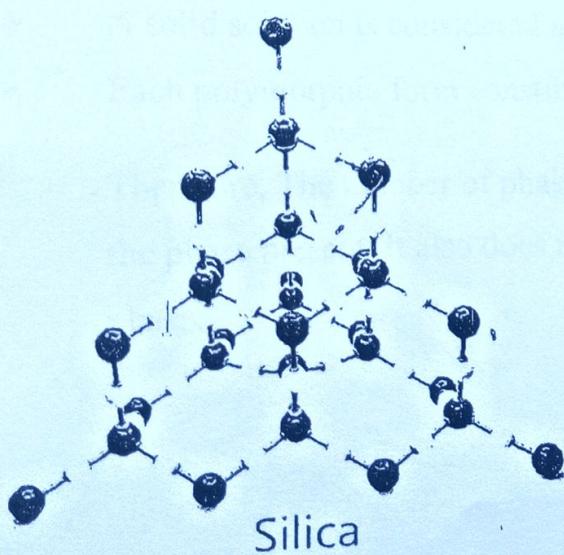


Structure of diamond

SILICA:

Silica, which is found in sand has a similar structure to diamond. It is also hard and has a high melting point, but contains silicon and oxygen atoms, instead of carbon atoms.

The fact that it is a semi-conductor makes it immensely useful in the electronics industry: most transistors are made of silica's.



PHASE EQUILIBRA

Phase: a phase is a form of matter that is homogenous in chemical composition and physical state. It refers to any part of a system which is physically separated from other part of the system by a distinct boundary.

A phase can be a solid, liquid, vapour (gas) or aqueous solution which is uniform in both chemical constitution and physical state. Two immiscible liquid (or liquid mixtures with different composition) separated by a distinct boundary are counted as two different phase as are two immiscible solids.

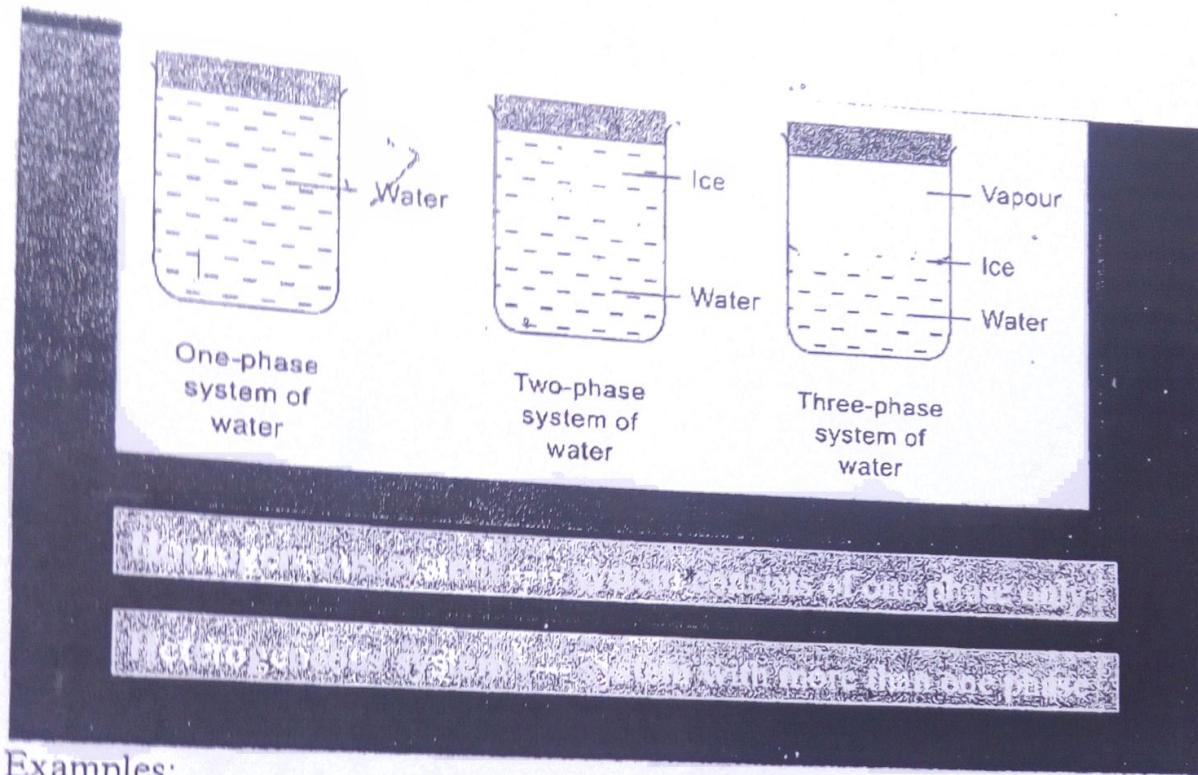
- A phase may be gas, liquid or solid
- A gas or a gaseous mixture is a single phase
- In an immiscible liquid system, each layer is counted as a separate phase
- Every solid constitutes as a single phase except when a solid solution is formed.
- A solid solution is considered as a single phase
- Each polymorphic form constitutes as a separate phase.

Therefore, The number of phase does not depend on the actual quantities of the phase present. It also does not depend on the state of subdivision of phase.

PHASE OF DIFFERENT SYSTEMS

| S/No | System | Examples | Number of phase |
|------|------------------------------------|---|---------------------------------------|
| 1. | Mixture of gases | Air (mixture of N ₂ , O ₂ , CO ₂) | 1 gaseous phase |
| 2. | Mixture of two miscible liquids | Ethanol and water | 1 liquid phase |
| 3. | Mixture of two immiscible liquids | Oil and water | 2 liquid phases |
| 4. | Mixture of two solids | Salt and sand | 2 solid phase |
| 5. | Mixture of a solid and liquid | Ice and water | 1 solid phase and 1 liquid phase |
| 6. | Mixture of a solid, liquid and gas | Ice, water and vapour | 1 solid, 1 liquid and 1 gaseous phase |
| 7. | Mixture of 2 solids and a gas | CaCO ₃ , CaO and CO ₂ | 2 solid phases and 1 gaseous phase |

A system with more than one phase is described as a heterogeneous system, while a homogeneous system consists of one phase only.



Examples:

Containing the number of phases.

- Liquid water, pieces of ice and water vapour are present together. The number of phase is 3 as each form is a separate phase. Ice in the system is a single phase even if it is present as a number of pieces.
- Calcium carbonate undergoes thermal decomposition. The chemical reaction is;



Number of phase = 3

This system constitute of 2 solid phase, CaCO_3 and CaO and are gaseous phase, that of CO_2

- Ammonium chloride undergoes thermal decomposition the chemical reaction is:



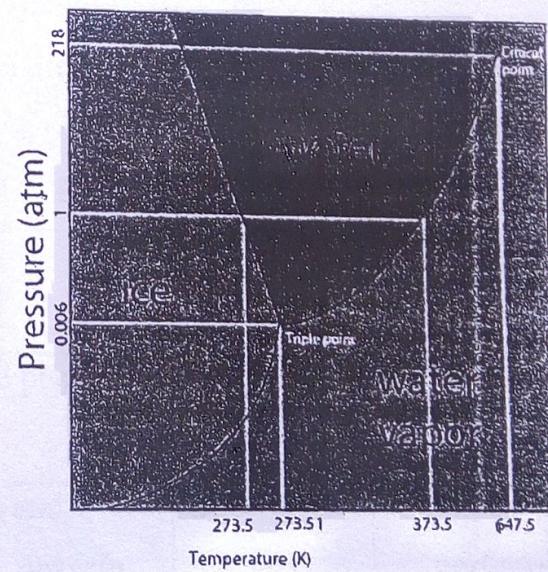
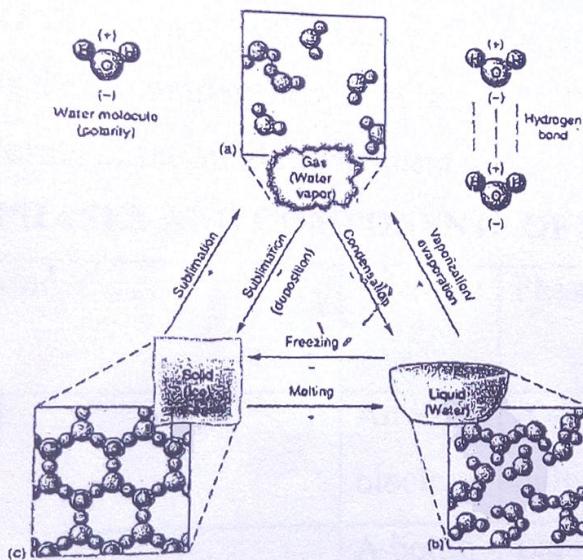
Number of phase = 2

- d. This system has two phases, one solid, NH_4Cl and one gaseous, a mixture of NH_3 and HCl
 A solution of NaCl in water
 Number of phase = 1

PHASE EQUILIBRIUM

This is a balance between phases that is the co-existence of two or more phases in a state of dynamic equilibrium. In other words, the relative quantity or composition of each phase remains unchanged unless the external condition is altered.

Examples of a phase transition below;



<http://www.sci.uidaho.edu/~scrinter/cecn100/>

A phase transition occurs when the external condition is altered.

Phase equilibrium are classified according to the number of components present in a system

COMPONENTS:

The number of components of a system at equilibrium is a smallest number of independently varying chemical constituents using which the composition of each and every phase in the system can be expressed, OR A component is a chemical species which may be used to specify the composition of a system. A system may have one or more components. It should be noted that the term 'constituents' is different from "components" which has a special definition. When no reaction is taking place in the system, the number of components is the same as the number of components is the same as the number of constituents. For example, pure water is a one component system because all the different phase can be expressed in terms of the single constituent water.

PHASES AND COMPONENTS OF DIFFERENCES

| s/no | Example | Phase | Number of components | Components |
|------|---------------------|---|----------------------|------------|
| 1 | An ice block | A solid phase only | One | water |
| 2 | A bottle of perfume | Liquid and vapour phase(a small amount of perfume vapour over liquid per) | One | perfume |
| 3 | A small amount | Solid and liquid phases(A small | Two | |

| | | | | |
|--|---|---|--|---------------------------|
| | of sodium chloride is added to a saturated sodium chloride solution | amount of undissolved is found in solution) | | Sodium-chloride and water |
|--|---|---|--|---------------------------|

Example

Counting the number of component

- a. A mixture of ethanol and water is an example of a two component system.
We need both ethanol and water to express its composition.
- b. An example of a system in which a reaction occurs and equilibrium is established is the thermal decompositions of solid CaCO_3 . In this system, there are three distinct phases. Solid CaCO_3 , solid CaO and gaseous CO_2 . though there are 3 species present, the number of component is only two, because of the equilibrium



Any two of the three constituent may be chosen as the component. If CaO and CO_2 are chosen the composition of the phase CaCO_3 is expressed as one mole of component CO_2 plus one mole of component CaO . If on the other hand CaCO_3 and CO_2 were chosen, the composition of the phase CaO would be described as one mole of CaCO_3 minus one mole of CO_2 .

PHASE RULE

The phase rule; also known as the gibbs phase rule.

Phase Rule: when a heterogeneous system in equilibrium at a definite temperature and pressure, the number of degrees of freedom is equal to $b - 2$ the difference in the number of components and the number of phases provided the equilibrium is not influenced by external factors such as gravity, electricity or magnetic forces surface tension e.t.c

Mathematically, the rule is written as

$$F = C - P + 2$$

Where:

F = number of degrees of freedom

C = number of component

P = number of phases of the system

For understanding the various applications of phase rule a clear understanding of the various terms: phase (P), components(C) and degrees of freedom (F) present in the phase rule

NOTE: phase(P) and components(C) explained above:

Degrees of Freedom:

The smallest number of independently variable factors such as temperature, pressure and concentration which must be required in order to define the system completely are called the degree of freedom. Degree of freedom of a system is also known as variance.

- When a system having no degree of freedom

$F = 0$ it is called non-variant system or invariant system

- When a system having only one degree of freedom,

$F = 1$ it is called invariant or monovariant

- A system having two degree of freedom

$F = 2$ is a Bavarian system e.t.c.

Example

a. The system ice water vapour has no degree of freedom (i.e $F = 0$). Because the three phases of water i.e ice, liquid water and vapour can exist together in equilibrium only at a particular temperature and pressure (corresponding to the freezing point) and no factor is necessary to be specified to define the system. Hence, a system consisting of ice, water and vapour in equilibrium has no degree of freedom i.e is a non-varient or invariant system.

Ice_(s) water_(l) vapour_(g)

Number of phase = 3

Number of component = 1

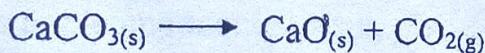
$$F = C - P + 2$$

$$F = 1 - 3 = 2$$

$$F = -2 + 2 = 0$$

Degree of freedom $F \leq 0$

2. Calculate the degree of freedom F of the following equation at equilibrium.



Solution

There are also three different chemical constituents, but the number of components is only two because any two constituents completely define the system in equilibrium. Any third constituent may be determined if the concentration of the other two is known.

Number of phases (P) = 3

Number of component (C) = 2

$$F = C - P + 2$$

$$F = 2 - 3 + 2 = 1$$

Therefore, only one variable, either temperature or pressure, can be changed independently. (the number of components is not always easy to determine at first glance, and it may require careful examination of the physical conditions of the system at equilibrium).

PHASE DIAGRAM FOR ONE COMPONENT SYSTEM

The least number of phases possible in any system is one. So, according to the phase rule equation, a one-component system should have a maximum of two degrees of freedom.

Where $C = 1, P = 1$

$$F = C - P + 2 = 1 - 1 + 2 = 2$$

Hence a one-component system requires a maximum of two variables are temperature and pressure. Therefore the phase diagram for one component system can be obtained by plotting PVST.

A phase diagram is a graph summarizing the conditions of pressure and temperature under which a particular phase (Solid, Liquid, or Vapour) can remain stable, and also the conditions that brings about the phase changes.

In case of a one-component system, phase diagram consists of areas, curves or lines and points which provide the following information regarding the system:

- Point on a phase diagram represent a non-varient system
- Area represent a bivariant system
- Curve or line represents a univariant system.

A typical phase diagram of vapour pressure against temperature is illustrated below and the general features of a phase diagram is summarized in Table below:

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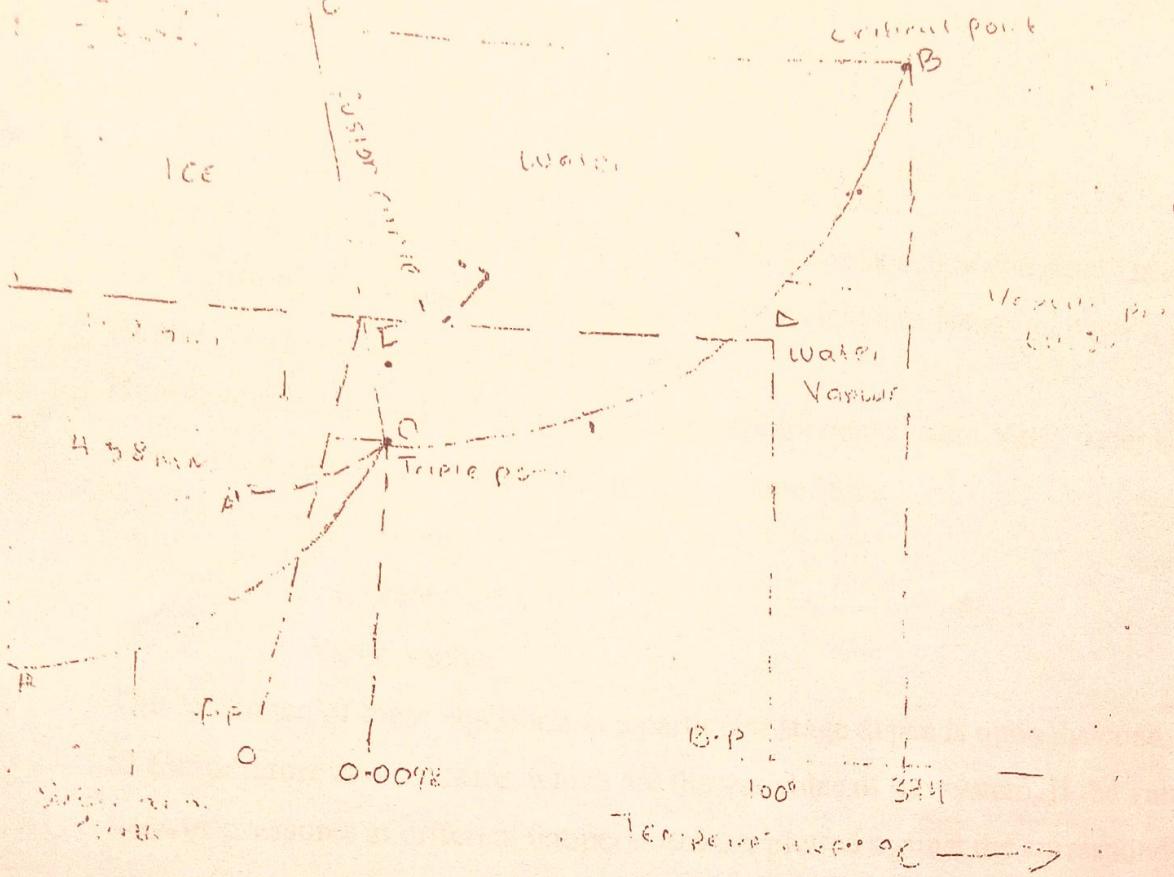
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GENERAL FEATURES OF A PHASE DIAGRAM

| Area/line/point | Name | Dynamic equilibrium |
|-----------------|----------------------------|---|
| Area | Solid | Only solid phase can exist |
| | Liquid | Only liquid phase can exist |
| | Vapour | Only vapour phase can exist |
| Line | S - L (fusion curve) | Solid & liquid phases in equilibrium |
| | L - V (vaporization curve) | Liquid & vapour phases in equilibrium |
| | S - V (sublimation curve) | Solid & vapour phases in equilibrium |
| Point | T (triple point) | Solid, liquid & vapour phases in equilibrium |
| | C (critical point) | Liquid phase is indistinguishable from vapour phase |

ONE COMPONENT SYSTEM – WATER

Water is a one component system which is chemically a single compound involved in the system. The three possible phases in this system are: ice (solid phase), water (liquid phase) and vapour (gaseous phase).

Hence, water constitutes a three-phase, one-component system, since water is a three phase system, it can have the following equilibria:

Ice vapour

Ice water

Water vapour

The existence of these equilibria at a particular stage depends upon the conditions of temperature and pressure, which are the variables of the system. If the values of vapour pressures at different temperatures are plotted against the corresponding temperature, the phase diagram of the system is obtained.

The phase diagram of the water system and the explanation are as follows:

a. Curves

The phase diagram of the water system consists of three stable curves and one metastable curve which are explained as follow:

1. Curves OB: The curve OB is known as vapour pressure curve of water and tells about the vapour pressure of water at different temperatures. Along this curve, the two phase- water and vapour exist together in equilibrium.

At point D; the vapour pressure of water become equal to the atmospheric pressure (100°C), which represent the boiling point of water. The curve OB finishes at point B (temp 374°C and pressure 218 atm) where the liquid water and vapour are indistinguishable and the system has only one phase. This point is called the critical point.

Applying the phase rule on this curve

$$C=1 \text{ and } P=2$$

$$F=C-P+2=1-2+2=1$$

Hence, the curve represents a univariant system. This explain that only one factor (either temperature or pressure), is sufficient to be fixed in order to define the system.

2. Curve OA: it is known as sublimation curve of ice and gives the vapour pressure of solid ice at different temperatures. Along sublimation curve, the two phases ice and vapour exist together in equilibrium. The lower end of the curve OA extends to absolute zero (-273 °C) where no vapour exists.

| s/no | Area | Phase exists | Components |
|------|----------------|--------------|------------------|
| i. | Area AOC | Ice | H ₂ O |
| ii. | Area COB | Water | H ₂ O |
| iii. | Area below BOA | Vapour, | H ₂ O |

Thus, for every area contains

$$C=1 \text{ and } P=1$$

Therefore applying phase rule on areas

$$F = C - P + 2 = 1 - 1 + 2 = 2$$

Hence, each area is a bivariant system. So, it becomes necessary to specify both the temperature and the pressure to define a one-phase system.

TWO -COMPONENT SYSTEMS

When the two independent components are present in a heterogeneous system, the system is referred to as a two-component system. Hence, according to the phase rule, for a two-component system having one phase.

$$F = C - P + 2 = 2 - 1 + 2 = 3$$

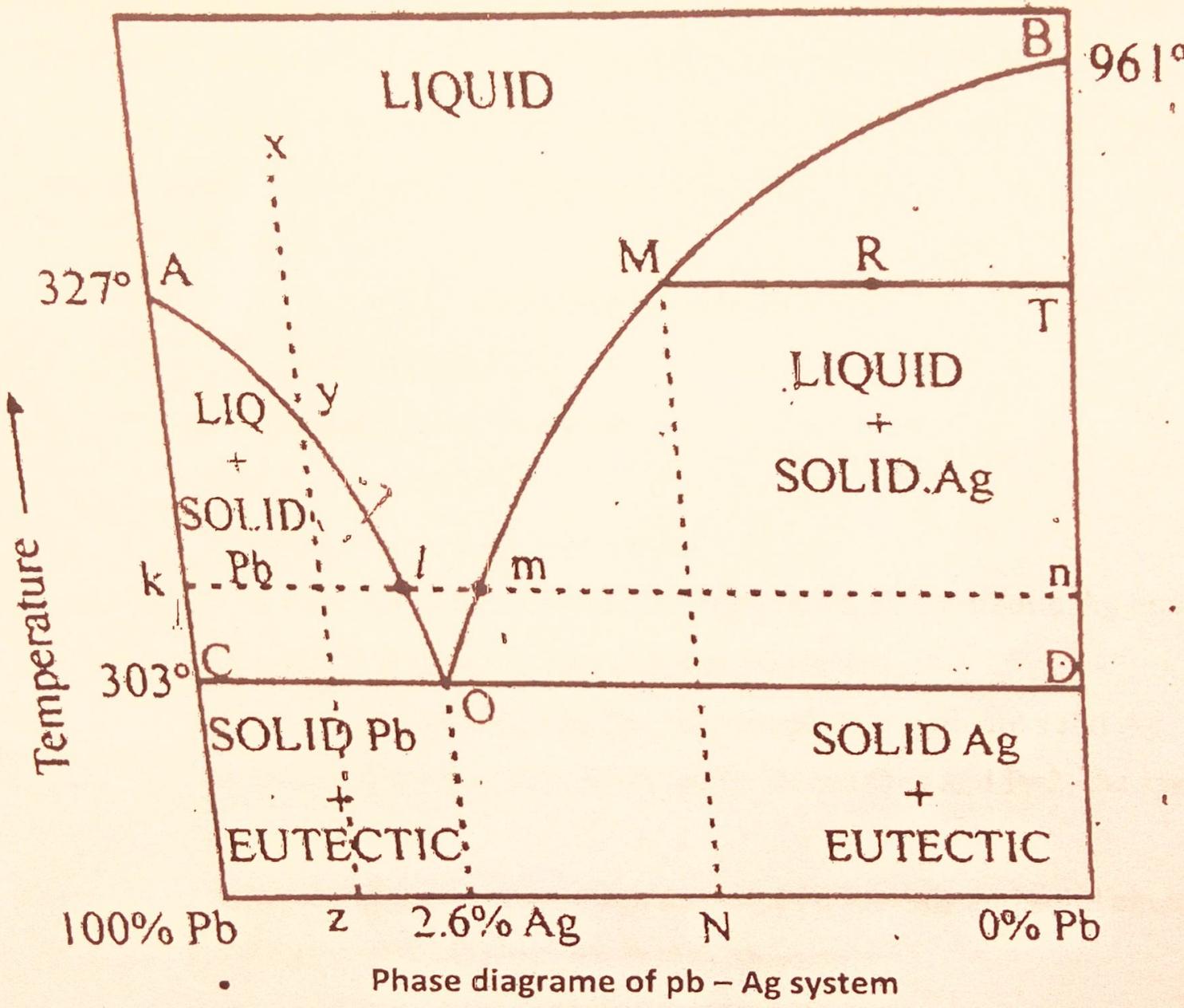
Therefore, the two-component system having one phase will have three degree of freedom or three variables would be required to define the system. The three

variables are: pressure (P), temperature (T) and concentration (C). This will require a three-dimensional phase diagram for the study of a two-component system. However, in order to simplify the study, a two component system is usually studied in the form of a condensed system. A condensed system can be studied by reducing a comparatively less important variable. This reduces the degree of freedom of the system by 1 and the system can easily be studied with the help of two-dimensional phase diagram.

It can have a maximum of the following four phases: solid lead, solid silver, solution of molten silver & lead and vapour.

The boiling point of silver and lead are considerably high and the vapour pressure of the system is very low. Therefore, the vapour phase can be ignored and the system can be studied as a condensed system. This system thus, can be easily studied with the help of a two-dimensional T-C diagram and the reduced phase rule equation;

$$F^* = C - P + 1, \text{ can be used. This system is generally studied at constant pressure.}$$



the phase diagram of the lead - silver system consists of the following curves, which are explained as follows:

- i. curve AC (freezing point curve of lead): the AC curve shows the variation of the melting point of lead on addition of silver. The pure lead melts at 327°C (Point A). Addition of silver lowers its melting point along curve AC. The added silver dissolves in molten lead to form Ag-Pb solution which with the separation of some part of solid lead. Therefore, the two phases, solid lead and Ag-Pb solution remain together in equilibrium along the curve AC.

HENCE

$$P=2, (\text{solid Pb and melt of Ag-Pb})$$

$$C=2 (\text{Pg and Ag})$$

On apply the reduced phase rule

$$F^1 = C - P + 1 = 2 - 2 = 1 = 1$$

Therefore the system is univariant.

- ii. Area BCF: the area consists of two phases which are solid Ag and a solution of Pb and Ag. Hence it also univariant.
- iii. Area DCFH: This area also has the two phases which are solid Ag crystals and solid entectic crystals. Hence $C=2$ and $P=2$, the system is univariant.
- iv. Area CEGD: the area also has the solid Pb crystals and solid entectic crystals phases. The system is also univariant.

THREE- COMPONENT SYSTEM

System having 3 phase, i.e $P=3$

$$F=3, P=3-3=0$$

The system is univariant and three phase can exist in equilibrium only at definite values of temperature and pressure. The three phases in equilibrium

with each other may be solid- liquid-vapour, solid-solid-liquid and solid-solid-vapour.