# SUPPLEMENTARY MATERIAL

Unit V: *States of Matter*

5.7 KINETIC ENERGY AND MOLECULAR SPEEDS

Molecules of gases remain in continuous motion. While moving they collide with each other and with the walls of the container. This results in change of their speed and redistribution of energy. So the speed and energy of all the molecules of the gas at any instant are not the same. Thus, we can obtain only average value of speed of molecules. If there are n number of molecules in a sample and their individual speeds are $u_1, u_2, \ldots\ldots u_n$, then average speed of molecules u_{av} can be calculated as follows:

$$u_{av} = \frac{u_1 + u_2 + \ldots\ldots\ldots u_n}{n}$$

Maxwell and Boltzmann have shown that actual distribution of molecular speeds depends on temperature and molecular mass of a gas. Maxwell derived a formula for calculating the number of molecules possessing a particular speed. Fig. A(1) shows schematic plot of number of molecules vs. molecular speed at two different temperatures T_1 and T_2 (T_2 is higher than T_1). The distribution of speeds shown in the plot is called Maxwell-Boltzmann distribution of speeds.
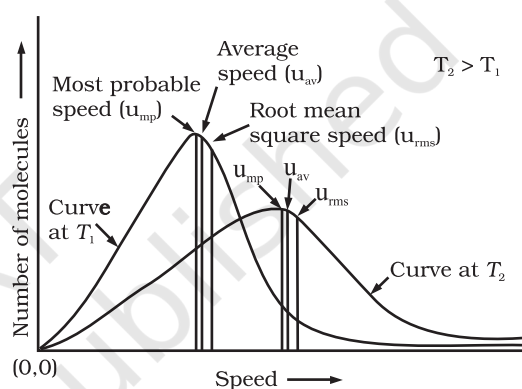
Fig. A(1) : *Maxwell-Boltzmann distribution of speeds*

The graph shows that number of molecules possessing very high and very low speed is very small. The maximum in the curve represents speed possessed by maximum number of molecules. This speed is called **most probable speed, u_{mp}**. This is very close to the average speed of the molecules. On increasing the temperature most probable speed increases. Also, speed distribution curve broadens at higher temperature. Broadening of the curve shows that number of molecules moving at higher speed increases. Speed distribution also depends upon mass of molecules. At the same temperature, gas molecules with heavier mass have slower speed than lighter gas molecules. For example, at the same temperature lighter nitrogen molecules move faster than heavier chlorine molecules. Hence, at any given temperature, nitrogen molecules have higher

value of most probable speed than the chlorine molecules. Look at the molecular speed distribution curve of chlorine and nitrogen given in Fig. A(2). Though at a particular temperature the individual speed of molecules keeps changing, the distribution of speeds remains same.
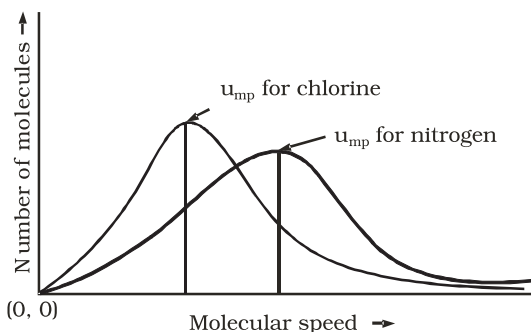
Fig. A(2): *Distribution of molecular speeds for chlorine and nitrogen at 300 K*

We know that kinetic energy of a particle is given by the expression:

$$\text{Kinetic Energy} = \frac{1}{2}mu^2$$

Therefore, if we want to know average translational kinetic energy, $\frac{1}{2}m\overline{u^2}$, for the movement of a gas particle in a straight line, we require the value of mean of square of speeds, $\overline{u^2}$, of all molecules. This is represented as follows:

$$\overline{u^2} = \frac{u_1^2 + u_2^2 + \ldots \ldots u_n^2}{n}$$

The mean square speed is the direct measure of the average kinetic energy of gas molecules. If we take the square root of the mean of the square of speeds then we get a value of speed which is different from most probable speed and average speed. This speed is called **root mean square speed** and is given by the expression as follows:

$$u_{rms} = \sqrt{\overline{u^2}}$$

Root mean square speed, average speed and the most probable speed have following

relationship:

$$u_{rms} > u_{av} > u_{mp}$$

The ratio between the three speeds is given below :

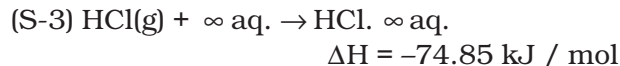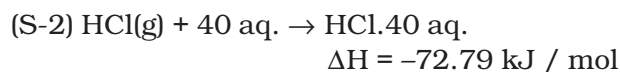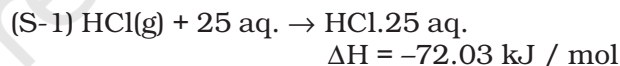$$u_{mp} : u_{av} : u_{rms} :: 1 : 1.128 : 1.224$$

UNIT VI: *Thermodynamics*

6.5(e) Enthalpy of Dilution

It is known that enthalpy of solution is the enthalpy change associated with the addition of a specified amount of solute to the specified amount of solvent at a constant temperature and pressure. This argument can be applied to any solvent with slight modification. Enthalpy change for dissolving one mole of gaseous hydrogen chloride in 10 mol of water can be represented by the following equation. For convenience we will use the symbol aq. for water

$HCl(g) + 10$ aq. $\rightarrow HCl.10$ aq.

$$\Delta H = -69.01 \text{ kJ / mol}$$

Let us consider the following set of enthalpy changes:

(S-1) $HCl(g) + 25$ aq. $\rightarrow HCl.25$ aq.

$$\Delta H = -72.03 \text{ kJ / mol}$$

(S-2) $HCl(g) + 40$ aq. $\rightarrow HCl.40$ aq.

$$\Delta H = -72.79 \text{ kJ / mol}$$

(S-3) $HCl(g) + \infty$ aq. $\rightarrow HCl. \infty$ aq.

$$\Delta H = -74.85 \text{ kJ / mol}$$

The values of ΔH show general dependence of the enthalpy of solution on amount of solvent. As more and more solvent is used, the enthalpy of solution approaches a limiting value, i.e, the value in infinitely dilute solution. For hydrochloric acid this value of ΔH is given above in equation (S-3).

If we subtract the first equation (equation S-1) from the second equation (equation S-2) in the above set of equations, we obtain–

$HCl.25$ aq. $+ 15$ aq. $\rightarrow HCl.40$ aq.

$\Delta H = [-72.79 - (-72.03)]$ kJ / mol
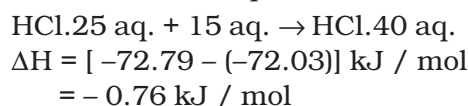
$\quad\quad = -0.76$ kJ / mol

This value (–0.76kJ/mol) of ΔH is enthalpy of dilution. It is the heat withdrawn from the

surroundings when additional solvent is added to the solution. The enthalpy of dilution of a solution is dependent on the original concentration of the solution and the amount of solvent added.

6.6(c) Entropy and Second Law of Thermodynamics

We know that for an isolated system the change in energy remains constant. Therefore, increase in entropy in such systems is the natural direction of a spontaneous change. This, in fact is the second law of thermodynamics. Like first law of thermodynamics, second law can also be stated in several ways. The second law of thermodynamics explains why spontaneous exothermic reactions are so common. In exothermic reactions heat released by the reaction increases the disorder of the surroundings and overall entropy change is positive which makes the reaction spontaneous.

6.6(d) Absolute Entropy and Third Law of Thermodynamics

Molecules of a substance may move in a straight line in any direction, they may spin like a top and the bonds in the molecules may stretch and compress. These motions of the molecule are called translational, rotational and vibrational motion respectively. When temperature of the system rises, these motions become more vigorous and entropy increases. On the other hand when temperature is lowered, the entropy decreases. **The entropy of any pure crystalline substance approaches zero as the temperature approaches absolute zero. This is called third law of thermodynamics.** This is so because there is perfect order in a crystal at absolute zero. The statement is confined to pure crystalline solids because theoretical arguments and practical evidences have shown that entropy of solutions and super cooled liquids is not zero at 0 K. The importance of the third law lies in the fact that it permits the calculation of absolute values of entropy of pure substance from thermal data alone. For a pure substance, this can be done by summing $\dfrac{\dot{q}_{rev}}{T}$ increments from 0 K to 298 K.

Standard entropies can be used to calculate standard entropy changes by a Hess's law type of calculation.

UNIT VII: Equilibrium

7.12.1 Designing Buffer Solution

Knowledge of pK_a, pK_b and equilibrium constant help us to prepare the buffer solution of known pH. Let us see how we can do this.

Preparation of Acidic Buffer

To prepare a buffer of acidic pH we use weak acid and its salt formed with strong base. We develop the equation relating the pH, the equilibrium constant, K_a of weak acid and ratio of concentration of weak acid and its conjugate base. For the general case where the weak acid HA ionises in water,

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$
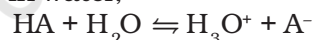
For which we can write the expression

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Rearranging the expression we have,

$$[H_3O^+] = K_a \frac{[HA]}{[A^-]}$$

Taking logarithm on both the sides and rearranging the terms we get -

$$pK_a = pH - \log \frac{[A^-]}{[HA]}$$

Or

$$pH = pK_a + \log \frac{[A^-]}{[HA]} \qquad \text{(A-1)}$$

$$pH = pK_a + \log \frac{[\text{Conjugate base, A}^-]}{[\text{Acid, HA}]}$$

$$\text{(A-2)}$$

The expression (A-2) is known as **Henderson–Hasselbalch equation.** The quantity $\dfrac{[A^-]}{[HA]}$ is the ratio of concentration of conjugate base (anion) of the acid and the acid present in the mixture. Since acid is a weak acid, it ionises to a very little extent and concentration of [HA] is negligibly different from concentration of acid taken to form buffer. Also, most of the conjugate base, [A⁻], comes from the ionisation of salt of the acid. Therefore, the concentration of conjugate base will be negligibly different from the concentration of salt. Thus, equation (A-2) takes the form:

$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

In the equation (A-1), if the concentration of [A⁻] is equal to the concentration of [HA], then pH = pK_a because value of log 1 is zero. Thus if we take molar concentration of acid and salt (conjugate base) same, the pH of the buffer solution will be equal to the pK_a of the acid. So for preparing the buffer solution of the required pH we select that acid whose pK_a is close to the required pH. For acetic acid pK_a value is 4.76, therefore pH of the buffer solution formed by acetic acid and sodium acetate taken in equal molar concentration will be around 4.76.

A similar analysis of a buffer made with a weak base and its conjugate acid leads to the result,

$$pOH = pK_b + \log \frac{[Conjugate\ acid, BH^+]}{[Base, B]}$$

$$(A-3)$$

pH of the buffer solution can be calculated by using the equation pH + pOH = 14.

We know that pH + pOH = pK_w and pK_a + pK_b = pK_w. On putting these values in equation (A-3) it takes the form as follows:

$$pK_w - pH = pK_w - pK_a + \log \frac{[Conjugate\ acid, BH^+]}{[Base, B]}$$

or

$$pH = pK_a + \log \frac{[Conjugate\ acid, BH^+]}{[Base, B]}$$

$$(A-4)$$

If molar concentration of base and its conjugate acid (cation) is same then pH of the buffer solution will be same as pK_a for the base. pK_a value for ammonia is 9.25; therefore a buffer of pH close to 9.25 can be obtained by taking ammonia solution and ammonium chloride solution of same molar concentration. For a buffer solution formed by ammonium chloride and ammonium hydroxide, equation (A-4) becomes:

$$pH = 9.25 + \log \frac{[Conjugate\ acid, BH^+]}{[Base, B]}$$

pH of the buffer solution is not affected by dilution because ratio under the logarithmic term remains unchanged.