STUDY MATERIAL

VIVEKANANDA COLLEGE
THAKURPUKUR

NAAC Accredited Grade—A

Subject: Physical Chemistry

Topic: Introduction of Liquid State and Fick's Law of Diffusion

Name of the Techer: Dr. Sanjib Kumar Bhar *

*Associate Professor, Department of Chemistry, Vivekananda College, Thakurpukur.

Introduction of Liquid State and Fick's Law of Diffusion

Liquid state is the intermediate state between the gas and solid because on cooling, a gas changes into the liquid state and on further cooling, it transforms into solid. In fact, a liquid possesses some of the properties of the solid and some of the properties of gases.

In the case of solid state, we find the presence of strong cohesive forces among the molecules and hence molecules are tied together in a regular pattern and free motion except oscillation is forbidden. In the gaseous state, molecules are in random due to very little cohesive forces and their potential energy is also negligible. In liquid, we do not find random movement of molecules (like gas) nor have the perfect ordering arrangement (like solid). In liquid, molecules have intermediate order of potential energies and cohesive forces.

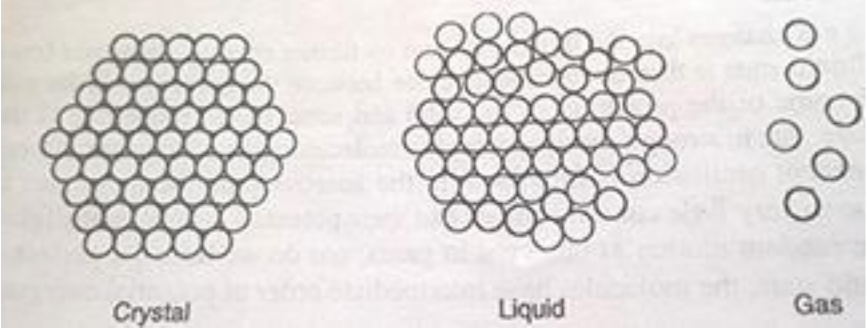
Experimental observations indicate that there is a relatively small increase in volume during the fusion of a solid. This means that at least near about the melting point, the density or volume of the liquid does not appreciably alter from that of the solid. Again, the latent heat of fusion is much less than the latent heat of vaporisation. The specific heats of a substance in the liquid and in the solid-state approach each other at the neighbourhood of the freezing point (Table1). This implies that arrangement of molecules in the liquid state is more or less similar to that of the solid state. The low latent heat of fusion value hints that the cohesive forces between the molecules decrease to a little extent when the solid is transformed into its liquid state.

The resemblance between the solids and the liquids is their relative incompressibility compared to gases. The compressibility's of solids and gases are of the order of 10^{-6} and 10^{-5} per atmosphere whereas compressibility of gas is the reciprocal of the pressure. On the other hand, the lack of rigidity is the most noticeable resemblance between the liquids and the gases.

Table 1

Substance	Density		Latent Heat		Specific Heat	
	Solid (gm/cc)	Liquid (gm/cc)	Fusion (cal/g K)	Vaporisation (cal/g K)	Solid (cal/g)	Liquid (cal/g)
Na	0.97	0.93	630	23300	7.6	8
Hg	14.19	19.6	560	14200	6.7	6.7
Zn	7.14	6.93	1800	27700	7.2	7.9

In a crystal, we find a perfect and well-ordered arrangement of molecules throughout the entire mass and each molecule is surrounded by other molecules in a particular symmetrical pattern. Since on melting a crystal expands about 10% in volume or in 3% intermolecular spacing, so we can conclude that a molecule in the liquid state must remain in the vicinity of some molecules surrounding it.



Therefore, the ordered arrangement is not completely destroyed when a solid is liquefied. The crystal structure of a particular solid involves rigorous geometrical order. The thermal energy introduces a disorder of a smaller region in a crystal and that causes disturbance in the entire region of a crystal and destroy the crystalline arrangement. This explains why a crystalline solid possesses sharp melting point. As for example a small disorder is introduced in the liquid by permitting only five surrounding atoms to an atom instead of six atoms as provided in the solid. The remaining circles then drawn in the utmost possible order arrangement. Thus, the result shows that the disorder must appear in long ranges in the diverse directions. Thermal motion which causes disorder in one region, it spreads into all directions and destroy the regular pattern. The liquid is therefore considered to have a structure like that of a solid except that well-ordered arrangement over a shorter range. This is called short range order and long-range disorder of a liquid.

Study of X- ray diffraction of liquid supports short range ordered arrangement as X- ray diffraction pattern of liquid shows the presence of a few number of peaks with maxima and minima, indicating the existence of partial regular or order arrangement as compared to the case of the solid for which peaks with minima and maxima are very large in numbers. Thus, presence of short range order and long-range disorder of a liquid is experimentally verified by X- ray diffraction studies.

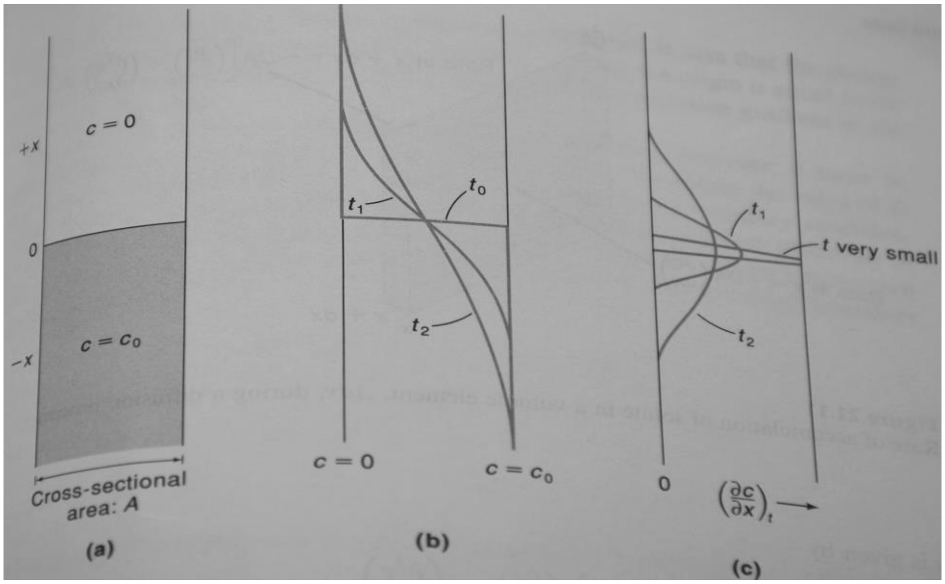
Transport Properties:

Whenever a system is not at equilibrium state, we can say that either matter or energy or both one being transported between the system and surroundings or between one part of the system and another. Such process is called transport process. Examples are - the flow of fluids is the subject of fluid dynamics, when an electric field is applied to a system, electrically charged particles (electrons and ions) experience a force and move through the system, producing an electric current. If temperature differences exist between the system and surroundings or within the system, then it is not in thermal equilibrium and heat energy flows. If differences in concentrations of substances exist between different regions of a system, the system not in material equilibrium and material flows until the concentrations and chemical potentials have been equalised. This flow differs from the bulk flow that arises from pressure differences and is called diffusion.

Diffusion is the process for which concentration gradients in a solution spontaneously decrease until a uniform homogeneous distribution is obtained. This diffusion is important to many chemical and biological systems. For example, it is the major mechanism by which carbon dioxide reaches the sites of photosynthesis in chloroplasts. Understandingly the transportation of solute molecules across the cell membranes also requires a detailed knowledge of diffusion phenomenon. So, diffusion plays an important role in determining the molar mass of macromolecules.

Fick’s Law of Diffusion:

Imagine a container with a solution on the bottom and the pure solvent on the top.

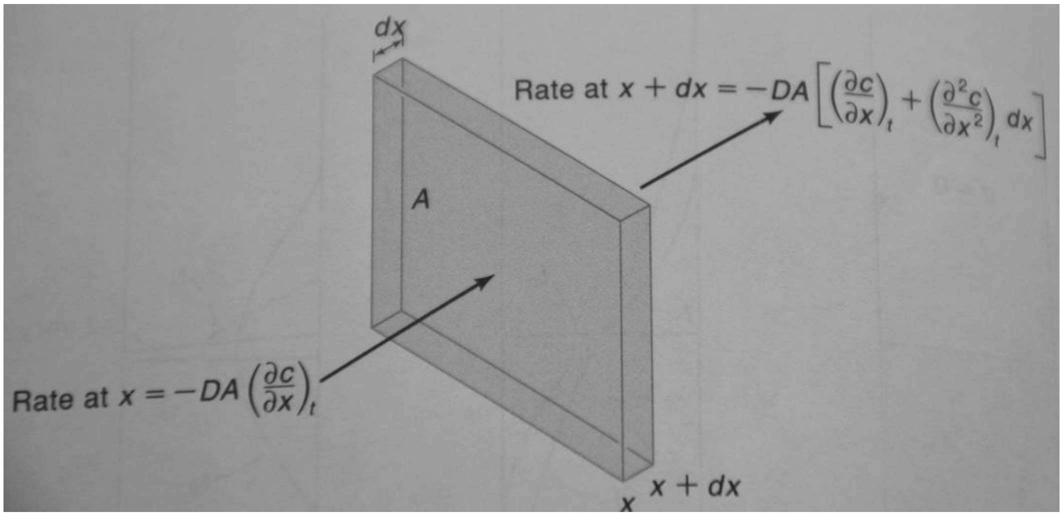


Initially, there is a sharp boundary between the solution and the solvent. As time progresses, solute molecules gradually move upward by diffusion. The process continues until the entire system becomes homogeneous. German physiologist Adolf Eugen Fick studied the diffusion phenomenon and found that the flux (J) that is the net amount of solute diffuses through a unit area per unit time is proportional to the concentration gradient in one dimension along the X axis.

So, we can write $J \infty - (\partial c/\partial x)_t$

$$J = -D\,(\partial c/\partial x)_t \qquad \text{.......... ...} \quad ①$$

Equation ① is known as Fick’s first law of diffusion where $(\partial c/\partial x)_t$ is the concentration gradient along x axis in one dimension. D is the diffusion coefficient and its unit are m^2s_{-1} in S.I unit and $cm^2\ s^{-1}$ in cgs unit. The negative sign indicates that diffusion proceeds from higher to lower concentration in the direction of diffusion at time t. Thus, the flux is positive quantity. Let us investigate the diffusion process in a little more detail. Consider a volume element (A.dx) where A is the area of cross section, x is the distance measured from the original boundary, Thus the rate of solute molecules entering through the volume element is $- D\,A\,(\partial c/\partial x)_t$.



Rate at x = $-DA(\partial c/\partial x)_t$

Rate at x+dx = $-DA[(\partial c/\partial x)_t + (\partial^2 c / \partial x^2)_t\, dx]$

Rate at which the concentration gradient changes with x is given by

$\partial/\partial x\ [(\partial c/\partial x)_t] = (\partial^2 c / \partial x^2)_t$ = the rate of solute leaving the volume element , after having travelled distance dx is

$$-D.A(\partial c/\partial x)_t - -DA(\partial^2 c / \partial x^2)_t\, dx$$

$$=-D.A[(\partial c/\partial x)_t + (\partial^2 c / \partial x^2)_t\, dx]$$

Thus, the rate of accumulation of solute molecules in the volume element A. dx

= (the rate solute molecules entering in the volume element) – (rate of solute molecules leaving in the volume element)

$= -DA(\partial c/\partial x)_t + DA[(\partial c/\partial x)_t + (\partial^2 c / \partial x^2)_t\, dx]$

$= DA(\partial^2 c / \partial x^2)_t\, dx$ ....②

So, there is another way of approaching at an expression for the accumulation. As time goes on, the concentration of solute in the volume element is steadily increasing as a result of diffusion. The rate of increase is given by the product of the volume element and the change in concentration with time that is

$(\partial c/\partial t)_x$ (A. dx) ....③

Equating ② and ③ these two rates of solute accumulation, we obtain

$$(\partial c/\partial t)_x = D\,(\partial^2 c / \partial x^2)_t \text{ ....④}$$

Equation ④ is known as Fick's second law of diffusion which implies that the change of concentration with time at a certain distance x, from the origin is equal to the diffusion coefficient and the change of concentration gradient in the direction x at time t.

References:

1. Physical Chemistry; G.W. Castellan.
2. Physical Chemistry for the Chemical and Biological Sciences; Raymond Chang.
3. Physical Chemistry; I.N. Levine.
4. Physical Chemistry; P.C. Rakshit.