INTRODUCTION

The study of the rates of chemical reaction, which during the last few decades has excited the imagination of organic chemists, is the most useful tool available for the investigation of reaction mechanisms. A kinetic study has two complementary approaches, phenomnological and molecular. The former aspect is concerned with describing the behaviour and properties of the system in terms of macroscopically observable quantities, such as, pressure, temperature, composition, volume and time . It satisfies the goal of providing an empirical description and prediction of reacting systems and must of necessity precede other types of investigations. The results of such enquiries may be expressed in terms of general macroscopic variables (P, T and concentration etc.), "Chemical constants" which are specific for the particular system studied (e.g., specific rate constant, activation energy etc.) and time-dependent relations between the constants. On the other hand, the molecular aspect leads one to the understanding of the macroscopic properties of the systems in terms of their molecular structures. It describes the molecular and structural changes, involved in each step, with special reference to the nature of the activated complex. Any idea about the nature of the activated complex helps to throw light on the machanism of the reaction as a whole, and this idea can be had from the energy, entropy, enthalpy, heat capacity and volume of activation which are generally known as the activation parameters (or quasithermodynamic properties) of the reaction.

For many years, chemists have been familiar with the effects of temperature on the rates of chemical reactions. As a matter of fact, the entropy of activation, as derived from the temperature-coefficient of the reaction rate, had been used long since to elucidate the reaction mechanism. But it is only recently, since high pressure equipment has become cheap and readily available, that the analogous effects of pressure have been studied. The efffects can be as great and as varied as those caused by changes in temperature. A striking difference is that pressure may either increase or decrease the reaction rate.

Pressure affects both the kinetics and the equilibrium of a chemical reaction. In a gas phase reaction, the very large change in fugacity of the reactants makes it difficult to sort out any variation of the rate constant itself, and in a solid, the compression of the material produces local hot spots where the particles rub together, and the temperature effects at these sites can mask any changes due to the pressure alone. Liquid phase reactions seem to be the most suitable for the study under pressure because of the much lower compressibility of a liquid compared to that of a gas.

The effect of pressure on reaction rates in solution was first measured about 77 years back[1-3] and the earlier experiments could show that in certain cases, pressure had profound influence on the velocity of chemical reactions. Moesveld and de Meester[4] explained this on the basis of the changed association of solvents, but the extensive work of Cohen and Coworkers[5] led to the conclusion that pressure exerts a specific influence on reaction rates. Bridgman[6] made a complete review of the earlier works without offering any theoretical account for such changes.

The first theoretical interpretation of the effect of pressure on the rate of liquid phase reactions was put forward by Gibson and Fawcett[7,8] as well as by Evans and Polanyi[9]. The latter workers analyzed the data of the earlier workers[10,11] and suggested a theoretical explanation of the effect of pressure on the reaction velocity. On the basis of their theoretical calculations, they claimed that properties, such as dielectric polarisability, dipole moment, magnetic susceptibility etc. of the transition state could be calculated, though experimental verification of their claim has yet not been possible. Later Stearn and Eyring[12] derived an expression for the homogeneous liquid phase reactions from the absolute rate theory. However, Newitt and his collaborators[13] were, probably, the first to start a systematic study on the effect of pressure on the rate and activation parameters for liquid phase organic reactions.

Although, some of the early measurements have yielded many useful informations, it is only during the past few years that the results have been used to help in the elucidation of reaction mechanism. The interpretation of the measured volumes of activation in terms of reaction mechanism has been recently reviewed by a number of authors[14-19].

Theory of effect of pressure on reaction-rates:

The increase of pressure affects the rates of chemical reactions in several ways, as follows :-

(i) It changes the concentration of the reacting substances because of the resulting compression of the mixture. This is the most important effect of pressure up to several tens or a few hundred bars (atm) on simple reactions that involve gases. The magnitude of this effect is almost negligible for the liquid-phase reactions.

(ii) It alters the chemical equilibria and thereby changes the concentrations of the participants of the reaction. The variation of the equilibrium constant, K, with pressure is given by,

$$\left(\frac{\partial \ln K}{\partial P}\right)_T = -\frac{\Delta V^\circ}{RT}$$

where ΔV° is the difference between the partial molar volumes of the reactants and the products at the standard state.

(iii) It changes the rate at which reacting molecules diffuse together and newly produced molecules diffuse apart.

(iv) It may also affect the Arrhenius frequency factor(A) and thereby the rate at which the neighbouring molecules can react. It may also alter the energy of activation (E) of a reaction.

The existing explanations of the effects of hydrostatic pressure have stemmed from two main theories of reaction rates, namely the collision theory and the transition state theory. Both the theories are essentially equivalent,[20,21] but the transition state approach is considered to be better suited to an analysis of the role of pressure in chemical kinetics.

In the transition state theory,[22,23] a reaction of the general type,

$$aA + bB + \cdots \longrightarrow x^{*} \longrightarrow lL + mM + \cdots \qquad \ldots.\ (1)$$

is assumed to proceed through a state of maximum energy x^{*} which can be regarded as a definite molecular species in equilibrium with the reactants and the products. The rate constant, k, governing the appearance of the products is derived in the form.

$$k = \epsilon \frac{kT}{h} \cdot [K^{*'}] \qquad \ldots.\ (2)$$

where k is the Boltzmann constant, h is the Planck constant, and ϵ, the transmission coefficient, defined as the probability that the transition state will change in to the products rather than revert to the original species and is customarily taken to be unity. The quantity $K^{*'}$ is an equilibrium product for the formation of transition state uncorrected by activity coefficients and is expressed as ,

$$K^{*'} = \frac{[X^*]}{[A]^a [B]^b \ldots}$$

where the square brackets denote the concentrations.

Eqn.(2) can be used to estimate the effect of external variables governing the system such as temperature, pressure etc., on the rate constant, so long as the mechanism of the reaction is not altered. If α is a state variable of the system, then from eqn. (2),

$$\frac{\partial \ln k}{\partial \alpha} = \frac{\partial \ln T}{\partial \alpha} + \frac{\partial \ln K_X^{*'}}{\partial \alpha} \qquad \ldots\ldots \quad (3)$$

Taking external variable α as pressure, the eqn. (3) becomes,

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = \left[\frac{\partial \ln K_X^{*'}}{\partial P}\right]_T \qquad \ldots\ldots \quad (4)$$

By substituting $\ln K^{*'} = -\frac{\Delta \bar{G}^*}{RT}$ (where $\Delta \bar{G}^*$ is the standard partial molar free energy change when the transition state is formed from the reactants) and making use of the thermodynamic relation, $\left(\frac{\partial \Delta \bar{G}^*}{\partial P}\right)_T = \Delta \bar{V}^*$, eqn(4) gives

$$-RT.\left(\frac{\partial \ln k}{\partial P}\right)_T = \left(\frac{\partial \Delta \bar{G}^*}{\partial P}\right)_T = \Delta \bar{V}^* \qquad \ldots\ldots \quad (5)$$

$\Delta \bar{V}^*$, known as the volume of activation, is the excess of the partial molar volume of the transition state over the sum of the partial molar volumes of the reactants, all at the composition of the mixture. As it is a case of ideal solution, the partial molar volumes may be replaced by molar volumes. Eqn.(5) may be written as,

$$\left(\frac{\partial \ln k}{\partial P} \right)_T = \frac{-\Delta V^*}{RT} \quad \ldots\ldots \quad (6)$$

The above relation holds true only if the concentrations are expressed in molefraction or molality both of which are unaffected by pressure changes. Instead, if they are expressed in terms of molarity (moles/litre), even if the solution is nearly infinitely dilute and the activity coefficients of the solute species are unity, a correction term owing to the compressibility (κ_s) need to be introduced.

$$RT \left(\frac{\partial \ln k_c}{\partial P} \right)_T = -\Delta V^* + (1 - a - b)\, RT.\kappa_s \quad \ldots\ldots \quad (7)$$

For first order reactions (a=1, b,c .... = 0) the eqn. (7) is reduced to eqn. (6). The term RT.κ_s is about 1 $cm^3 mole^{-1}$ for water but may be 2 or 3 $cm^3 mole^{-1}$ for other solvents. As the errors involved in measuring rate constants under pressure are sufficient to introduce an uncertainly of few $cm^3 mole^{-1}$ into ΔV^*, it is a common practice to discuss experimental data on the basis of an assumed relation,

$$RT \left(\frac{\partial \ln k_c}{\partial P} \right)_T = -\Delta V^* \quad \ldots\ldots \quad (8)$$

Similarly taking volume as the external variable, the eqn.(3) results,

$$\left(\frac{\partial \ln k}{\partial V} \right)_T = \frac{\Delta P^*}{RT} \quad \ldots\ldots \quad (9)$$

where ΔP^* signifies the pressure of activation, i.e. the change of pressure when a fixed amount of transition state is formed at constant volume. Equations (8) and (9) contain essentially the same information but former is more useful, as the pressure is easier to measure and to control than the volume.

Again taking temperature as the external variable, the eqn. (3) gives a relation between the activation energy and the thermodynamic enthalpy change of reactions in solution,

$$E = RT^2 \left(\frac{\partial \ln k}{\partial T}\right)_P$$

$$= RT + \Delta H^* \qquad \ldots\ldots \quad (10)$$

Substituting the value of K^{*} as $e^{-\Delta G^*/RT}$ in the eqn. (2), the expression of rate constant derived as ,

$$k = \frac{kT}{h} \cdot e^{-\Delta G^*/RT}$$

$$\text{or,} \quad k = \frac{k.T}{h} \cdot e^{\Delta S^*/R} \cdot e^{-\Delta H^*/RT} \qquad \ldots\ldots \quad (11)$$

Hence the activation parameters such as E, ΔH^* , ΔS^* and ΔG^* can be determined measuring the rate constant at two or more than two different temperatures.

The relation between the various quantities of activation at constant pressure and at constant volume can be derived with the aid of the following operational equation,

$$\left(\frac{\partial}{\partial T}\right)_V = \left(\frac{\partial}{\partial T}\right)_P + \frac{\beta}{\kappa_s}\left(\frac{\partial}{\partial P}\right)_T \qquad \ldots\ldots \quad (12)$$

where β is the isopiestic thermal expansivity and is defined as,

$$\beta = 1/V \left(\frac{\partial V}{\partial T}\right)_P .$$

Equation (12) can be applied to any parameter that is a function of temperature and pressure only. The following relations can be derived with the help of equation (12)

$$\Delta H_p^* = \Delta U_V^* + T.\beta \frac{\Delta V^*}{\kappa_s} \qquad \ldots\ldots \quad (13)$$

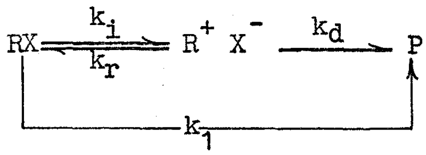
$$\Delta S_p^* = \Delta S_V^* + \beta \frac{\Delta V^*}{\kappa_s} \qquad \ldots\ldots \quad (14)$$

where ΔH_p^* is the enthalpy of activation at constant pressure, ΔS_p^* and ΔS_V^* are the entropies of activation at constant pressure and at constant volume respectively and ΔU_V^* is the intrinsic energy of activation at constant volume. The heat capacities of activation at constant pressure and at constant volume follow as :

$$\Delta C_p^* = \left(\frac{\partial \Delta H_p^*}{\partial T}\right)_P , \quad \Delta C_V^* = \left(\frac{\partial \Delta U_V^*}{\partial T}\right)_V \qquad \ldots\ldots \quad (15)$$

Among these parameters, derived above, eqn. (8) is particularly valuable as it relates the pressure dependence of the rate constant to a definite change in volume, the sign and magnitude of which have been interpreted mostly for the simple reactions having single, well defined, rate determining step. For simultaneous reactions, the volume of activation does not have any simple meaning because the term $- RT\left(\frac{\partial \ln k}{\partial P}\right)_T$ does not, in general, define a single volume but represent instead, the weighted sum of all the volumes of activation of all the rate controlling reactions. The volume of activation, involving equilibrium steps, is also a composite quantity. Under such conditions, it becomes the sum of the volume changes of each step, the equilibrium constant of which is involved in the final rate expression.[17]

The meaning of measured ΔV^* may be understood from the following example elucidated by leNoble.[17] An ionization reaction is taken in which an ion pair partly undergoes return and partly dissociation to separate ion.



If it is assumed that the ion pair concentration remains small throughout, the usual steady state approximation can be used to yield,

$$\text{Rate} = \frac{k_i . k_d}{k_r + k_d} [RX] = k_1 [RX]$$

Since $\Delta V_1^* = - \frac{RT \, \partial \ln k_1}{\partial P}$

$$\Delta V_1^* = \Delta V_i^* + \Delta V_d^* + RT . \partial \ln \left(\frac{k_r + k_d}{\partial P} \right)$$

If $k_d \gg k_r$ and ion pair formation is rate limiting, then

$$\Delta V_1^* = \Delta V_i^*$$

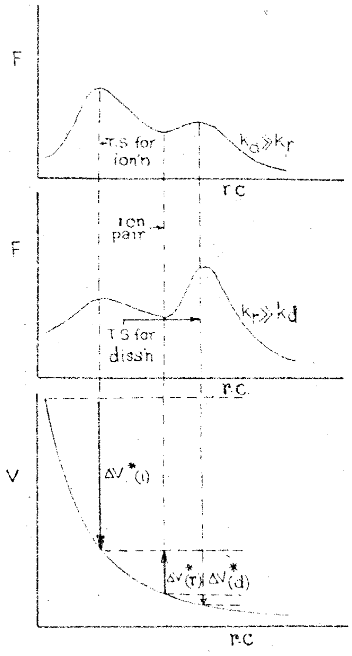


FIG. I—1. THE FREE ENERGY AND VOLUME DIAGRAMS OF THE IONIZATION PROCESS.

and if $k_d \ll k_r$ and ion pair dissociation is rate-controlling, then,

$$\Delta V_1^* = \Delta V_i^* - \Delta V_r^* + \Delta V_d^*$$
$$= \Delta V_K^* + \Delta V_d^*$$

these expressions are perhaps best explained by means of figure I-1. If k_d and k_r are comparable and ion pair return competes with solvolysis on a fairly even basis, ΔV_1^* will be somewhere between the two limiting cases and thus is more complex. If f_d is defined as the fraction of the ion pairs that dissociate, it is readily shown that,

$$\Delta V_1^* = \Delta V_i^* - RT \frac{\partial \ln f_d}{\partial P}$$

$(V_d^* - V_r^*)$ is a fairly small term, hence no large error is made in assuming that the correction term is linear in f_d, then

$$\Delta V_1^* = \Delta V_i^* + (1-f_d)\ (\Delta V_d^* - \Delta V_r^*).$$

There may be various other complicating possibilities in complex reactions which tend to confuse not only the significance of $\left(\frac{\partial \ln k}{\partial P}\right)_T$ but also its relation with the volume of activation.

Molecular models of the transition state :

The volume of activation at least for simple reactions could be in principle roughly calculated from a knowledge of the geometry of the initial state and the transition state.[14-16] In practice, there is usually insufficient information available about the configuration of the transition state so that approximate methods have been employed in attempts to predict the sign and the magnitude of ΔV^*.

Following the suggestions of Evans and Polanyi[9], ΔV^*, for reactions in solution, on molecular grounds, can be conveniently regarded as being made up of two terms : ΔV_r^*, the structural term which represents the change in volume of the reacting molecules directly due to the changing interaction of molecules with one another while a transition state is formed and ΔV_s^*, the solvation term, on the other hand representing the accompanying change in volume of the surrounding solvent, caused mainly by, among other reasons, changes in electrostricition. The second term i.e. ΔV_s^* is likely to be more pronounced when there is a very marked change in the intermolecular forces, arising, for instance, from the development or cancellation of ionic charges during the formation of the activated complex. The two terms, ΔV_r^* and ΔV_s^* are not completely separable, but the broad distinction between them has proved to be useful.

Factors influencing the value of ΔV_r^* (Structural term) :

ΔV_r^* is perceptible, essentially due to the changes in interatomic distances and van der Waals radii of the reacting molecules when transition state is formed. The bond distances are altered mainly (i) by conversion of an intermolecular interaction or valence bond into a partial valence bond (ii) through the variation of non-bonded interaction within a molecule which occurs when over crowding around the molecule is relaxed or enhanced, (iii) due to the changes in the distribution of electron-density around the nuclei or (iv) by the combined influence of all these factors. A rough idea of the magnitude of the change in volume, caused by a change in the intermolecular distance, can be obtained by multiplying the cross-section of the bond by the supposed change of internuclear distance.

A rough calculation of the contributions to ΔV^* due to bond rupture may be roughly calculated from the following equation :

$$\Delta V_b^* = \pi \left(r_A^2 + r_B^2 \right) \frac{\delta l}{2}$$

where δl is the elongation of a bond whose initial length is l, r_A and r_B are the van der Waals radii of the atoms. A similar equation to calculate the contribution to ΔV^* due to the bond-formation follows as :

$$\Delta V_f^* = -\pi \left[r_A^2 + r_B^2 \right] \left[r_A + r_B - l - \delta l \right] / 2$$

In 1940, Ri and Eyring[24] from the calculations of potential surfaces for activated complex, stated that the atomic distances which change during the formation of activated complex (in a dissociation reaction) are often around 10% larger than the normal distances. Stearn and Eyring[12] later incorporated this idea in a treatment of pressure effects, and on this basis, the value of ΔV_b^* for unimolecular dissociation was calculated to be about 2-3 cm^3 $mole^{-1}$. In rough agreement with this, the volumes of activation of a number of reactions, that are thought to be essentially unimolecular decompositions, are close to zero, though observed deviations are many.[16] Similarly a rough estimation of ΔV_f^* can be made in case of bond formation. When two molecules combine, a van der Waals interaction which causes an inter-molecular separation of, say, 3.6 A° , is converted to a partial valence bond in the transition state. If a C-C or C-O bond is formed, the internuclear separation in the transition state is roughly 1.7 A° . If the cross-sectional areas at the place where the bond being formed is 10 A°, the contribution to the volume of activation due to the shortening of the bond is around - 12 cm^3 $mole^{-1}$.[14]

When the activation step for a reaction involves simultaneous formation of one bond and rupture of another, ΔV_f^* generally predominates over ΔV_b^* , as a result of which ΔV_r^* becomes negative.

The formation or destruction of intramolecular empty - space, that is too small to be occupied by a solvent molecule, does also affect the magnitude of ΔV_r^* . This possibility becomes more predominant in the reactions involving formation or destruction of rings,[25,26,27,28] and also when the transition state is cyclic.[29]

Sometimes steric-hindrance may also be significant in determining the magnitude of ΔV_r^* .[30-34]

Factors influencing the value of ΔV_S^* (solvation term) :

Electrostriction is, no doubt, the principal factor contributing to ΔV_S^* , but recent evidences indicate that it is not the only one. The interaction between a molecule and its solvent is very complicated and cannot yet be expressed with any accuracy by any detailed molecular theory. However, it can, in principle, be roughly related to forces of dispersion, repulsion, electrostatic interaction etc. The existence of dipole may also give rise to the same phenomenon. The change, ΔV_S^*, can arise because either the solvent molecules rearrange their packing, for purely steric reasons, to accommodate the changed shape of the reacting molecules, or there is tightening or loosening of electrostatic bonds between the solvent and the reacting species.

Studies of ionic equilibria have shown that when a small spherical molecule in a liquid dielectric medium acquires a full electronic change, there is an accompanying decrease in volume lying between 12 and 30 $cm^3 mole^{-1}$ for most solvents. The volume change for a pair of singly charged ions, according to a simple form of the theory of electrostriction, is expressed by the following equation.[15]

$$\Delta V_{el} = - \frac{z^2 . e^2}{2r \epsilon^2} . \frac{\partial \epsilon}{\partial p} + \frac{z^2 e^2}{2r^2} \left(1 - \frac{1}{\epsilon}\right) . \frac{\partial r}{\partial p}$$

where ΔV_{el} denotes the contraction (electrostriction) of a medium of dielectric constant, ϵ, around a sphere of radius r carrying a change ze, e being the electronic change and z an integral number.

It has been observed that the dissociation of a neutral molecule into two free ions involves a contraction which may be as great as 28 $cm^3 mole^{-1}$ in water and 45 $cm^3 mole^{-1}$ in methanol. This clearly indicates that ΔV_s^* is as important as ΔV_r^* particularly in reactions which produce or remove electrical charges. Highly polar or partially ionic transition state is formed in a solvolytic reaction where as ionization involves a complete separation of two free ions. However, it is a general observation that ΔV^* for the former is more negative than that of the latter. The reasons have been discussed by leNoble.[17]

The relative importance of ΔV_r^* and ΔV_s^* cannot be assessed theoretically since how fully developed are the charges in the activated complex cannot be predicted with certainty. However, the individual contributions of ΔV_r^* and ΔV_s^* can be easily identified studying the pressure-effect on the reactions for which one or the other is the only important contributor.

Recently, attempts have been made to determine the influence of the solvents on ΔV^* by measuring the pressure-effect on the rates of reactions in different solvents[35,36] (of varying polarity). Since ΔV_r^* , is by definition, independent of the medium surrounding the reacting molecules, any change of ΔV^* with solvent must be ascribed to a change in ΔV_s^* . This aspect of solvent effect on ΔV^* has been studied in details for Menschutkin reactions[32] in which the transition states are more strongly solvated than the initial reactants. Harris and Weale[32] found that for the reaction between N,N-dimethyl aniline and ethyl iodide, the acceleration due to pressure was almost twice in methanol solution than in nitrobenzene, the respective values of ΔV^* (at 1 atmosphere) being -34 and -20 $cm^3 mole^{-1}$. Similarly, Brower[38] observed that the value of ΔV^* for the reaction of pyridine with butyl bromide decreased from -26 cm^3-$mole^{-1}$ in ethanol-water to -42 $cm^3 mole^{-1}$ in toluene. From these informations, Gonikberg and Elyanov[39(a,b)] made an attempt to estimate roughly the number of solvent molecules incorporated in the activated state complex. They assumed that the solvent molecules are incompressible compared to the bulk solvent and the ΔV_r^* (structural contribution) is constant in the pressure range considered. The pressure equivalent to the electrostriction around an ion has been estimated[40] to be of the order of 10,000 atmosphere. Then the solvent part of the volume of activation may be expressed as :

$$\Delta V_s^* = -n\ (V_{s.p} - V_{s.10{,}000})$$

where , n = no. of solvent molecules attached to the transition state.
= -slope.

$V_{s.p}$ = molar volume of the solvent at pressure, P.

$V_{s.10{,}000}$ = molar volume of the solvent at $(P+10^4)$ atmospheres.

According to the above equation, a plot of ΔV^{*} at various pressure, P, against the molar volume of the solvent at the same pressures should be a straight line with a slope (=-n). Hence the information regarding the variation of rate with change in solvent may provide new insight to the transition state of solvation and hence on the mechanism of the reaction.

The relationship between the volume of activation and the Reaction Mechanism :

In many cases, the knowledge of volume of activation, ΔV^{*}, is very helpful in elucidating the reaction mechanisms, when it is interpreted in terms of the structure of the transition state. The significance of the volume of activation can be more easily understood at an elementary level than that of free energy, enthalpy or entropy of activation, because ΔV^{*} is determined, primarily, by nuclear positions of the constituent atoms of the activated complex, while the others are all governed by the interatomic forces and vibrations also.

Whalley and his collaborators[41] have made outstanding contributions to the mechanistic studies of acid-base-catalyzed reactions by extending the concepts of activation-volume and entropy of activation to such reactions. The experimental values of ΔV^{*} and ΔS^{*} taken together, have often made it possible to distinguish between the different mechanisms that could not have been otherwise resolved. The positive value of ΔV^* for the hydrolysis of acetals and formals provides unambiguous evidence that the slow step, in such reactions, is a unimolecular decomposition of the protonated substrate and not a bimolecular reaction. In this instance, the entropy of activation alone, was insufficient to distinguish between the two possible mechanisms.

From the studies on the effect of pressure on equilibria and kinetics of simple reactions and from the density and parachor data of stable compounds, investigated by various workers to the present day, leNoble[17] has summarized the following approximate contributions of the principal mechanistic features to the volume of activation.

Table : I-1

Mechanistic features and their contributions to ΔV^*

Mechanistic feature	Contribution, cm^3/mole.
Bond cleavage	+10
Bond deformation	~ 0
Bond formation	-10
Displacement	- 5
Diffusion control	> +20
Cyclization	~ 0
Ionisation	-20
Steric hindrance	- 0
Neutralization	+20
Charge dispersal	+ 5
Charge concentration	- 5

In many cases, it is quite possible that the correct mechanism of a reaction can be ascertained with the aid of these concepts.

The compressibility of the transition state :

Since ΔV^* is not independent of pressure, the interpretation of eqn. (6) is not straight forward. The initial state and the transition state usually have different compressibilities. A change of pressure affects the interaction between the transition state and the solvent and hence, changes the nature of the transition state, itself. Consequently, graphs of lnk against pressure are frequently markedly curved.[42] For the purpose of determining the mechanism, the volume of activation at zero pressure (ΔV_0^*), which for all intents and purposes, is same as the volume at 1 atm, is determined from the slope of the plot of lnk against pressure. The use of ΔV_0^* has the advantage that one can make comparison with molar volumes of substances similar to the transition state in some way, without taking their compressibilities into account.

In 1962, Benson and Berson[43] criticized the above procedure on the ground that proper weightage is not given to the high pressure data. They suggested that atleast for non-ionic reactions, the treatment of the data could be improved by considering the compressibilities of both the initial and transition states according to Tait's equation, and thereby agreeing to the fact that lnk is an explicit function of P. The integrated form of the isothermal Tait's equation can be written as,

$$V_P = V_1 \left[1 - C.\log_{10}\left(\frac{B + P}{B + 1} \right) \right]$$

where V_P and V_1 denote the volumes of the substance at pressures P atm. and 1 atm. respectively, C is a dimensionless constant, and B is a constant in units of pressure. Both B and C are positive quantities. These authors, after a long mathematical calculations and further simplification, arrived at a result requiring $1/P \log(k_p/k_o)$ to be linear function of $p^{0.523}$. ΔV_o^* and B^*, the Tait's parameter for the transition state, can be calculated from the slope and intercept of this plot.

This treatment has been, recently, much criticized by Hamann[16] and Walling[44]. Although it may be justifiable to assume 44 that initially the reacting molecules obey Tait's equation of state, it is by no means clear why the transition state complex should also do so. There is no reason to believe that the compressibility of the transition state along its reaction coordinate should be governed by the equation of state applicable for ordinary molecules. Moreover, Tait's equation is an empirical one, without having much theoretical significance and hence much reliance on it is not justified.

If ΔV^* does not vary rapidly, a suitable nonlinear least squares procedure[14], usually of the following form, is adopted.

$$\ln k = a + b.p + c.p^2 .$$

If the curvature of a plot of lnk against pressure is not small, or if there are too few points for the above equation to be fitted numerically, a graphical method is probably the best. If the rate constants at suitably spaced pressures, $p_1, p_2, \ldots\ldots p_n$ etc. are $k_1, k_2, \ldots\ldots k_n$ etc., a plot of $\ln \frac{k_{n+1}}{k_n}$ against $\frac{1}{2}(p_n + p_{n+1})$ should, when extrapolated to zero pressure, give a reasonably good value of $\partial \ln k/\partial p$ at zero pressure.

Actually, the estimation of ΔV_0^* poses no serious difficulty, if the rate-measurements are made at reasonably small pressure intervals. Brower has measured ΔV^* for a number of reactions in the range zero to 1000 atmospheres with small pressure increments and observed that ΔV^*, as a rule, is approximately constant in this region at least at low temperatures.

Scope of the present work :

In the light of the above theoretical discussion, it seems clear that the volume of activation, ΔV^*, as measured from the pressure-coefficient of reaction-rate, may be quite satisfactorily correlated with the structure of the activated complex and hence with the mechanism of simple reactions.[41] Recently, Whalley, Hamann, Weale, Gonikberg and many others have studied the kinetics of a large number of liquid-phase reactions under pressure to ascertain their mechanisms from the knowledge of activation-volume. In order to extend the application of volume of activation and other parameters to the study of reaction-mechanism, the following reactions, under high-pressure, have been exhaustively investigated.

(1) Acid-catalyzed hydration of acrylic acid to β-hydroxypropionic acid and the reverse reaction.

(2) Hydrolysis of α-bromopropionate ion to lactate ion in dilute alkaline solution.

Besides the kinetic order, the activation parameters, E, ΔV^* and ΔS^* of the reaction (1) are determined. The experimental observations are discussed in the light of the modern concepts of acid-catalysis. With the help of the observed activation parameters, in conjunction with Bunnett's parameters, an attempt is made to throw light on the plausible configuration of the transition state. Finally various possible mechanisms for the reaction are discussed.

As the reaction (2) had been studied in detail by several workers, a short review of the earlier work is made. From the pressure-coefficient of the reaction-rate, the volume of activation is determined. On the basis of the experimental value of ΔV^*, an endeavour is also made to arrive at an unambiguous decision among the various mechanisms, proposed earlier by different workers.

The scope and the advantages of the present method will be better understood from the discussion of different methods, to follow in the subsequent chapters, employed for predicting the mechanism of chemical reactions.