

FEW ASPECTS ON THERMODYNAMICS OF CHEMICAL RELAXATION PROCESS

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Thermodynamics of chemical relaxation process like diffusion-limited reactions and enzyme reactions etc., have been discussed on the basis of the individual concentration changes of the components and the relative changes in the equilibrium constant.

In case of diffusion-limited reaction $\Delta F = \Delta H$, since $\Delta S = 0$ but for enzyme reaction the contribution of ΔS appears as a positive exponent, which aids the speed of the reaction. The entropy arises due to hydration in enzymes. In diffusion-limited reaction there is close relationship between the free energy function F and a_D (Debye variable distance), whereas in biomolecular reaction, F is closely related with bond distance.

In diffusion-limited reaction the variation of the ratio of fractional change in equilibrium concentration of reactants with the fractional change in equilibrium constant and the ratio of change in equilibrium concentration of the reactants with the equilibrium constant have been studied with the ratio of analytical concentration of reactants with equilibrium constant. In case of enzyme reaction, we have observed the effects of concentrations of substrate, enzyme and end products on the fractional change in the equilibrium concentration of reactants and the fractional change in equilibrium constant. In both reactions in forward and backward directions we have observed different behaviour.

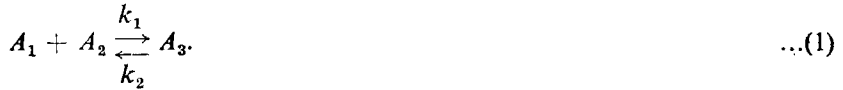
INTRODUCTION

THE chemical relaxation methods (Eigen 1954; Eyring & Eyring 1963; Czerlinski 1969; and Srivastava & Srivastava 1978) have played an important role in the theory of chemical kinetics. Generally, in this approach a chemical equilibrium is perturbed by some external or internal parameters like variation of temperature, individual concentrations of the reactants, enthalpy etc. Thus, the equilibrium constant is affected. For the existence of any relaxation process the change in enthalpy ΔH should not be zero.

In this paper, in case of diffusion limited reactions and enzyme reactions, we have discussed about some aspects on the thermodynamics on the basis of free energy and the individual concentration changes of the reactants for observing the corresponding changes in the equilibrium constants.

THEORY AND RESULTS.

A simple chemical equilibrium system is represented by



The rate constants k_1 and k_2 are related with equilibrium concentrations of the constituents $\bar{C}_i (i = 1, 2, 3)$ and equilibrium constant $K_{2,1}$ by

$$K_{2,1} = \frac{k_2}{k_1} = \frac{\bar{C}_1 \bar{C}_2}{\bar{C}_3}. \quad \dots(2)$$

For a diffusion-limited reaction the value of $K_{2,1}$ is given by (Czerlinski 1969; and Srivastava & Srivastava 1978)

$$K_{2,1} = n_1 \exp\left(\frac{n_2}{kT}\right), \quad \dots(3)$$

where the quantities n_1 and n_2 are given by

$$n_1 = \frac{3}{4 a_D^3 N_A}$$

$$n_2 = \frac{Z_1 Z_2 e_0^2}{4\pi \epsilon \epsilon_0 a_D} = \phi kT, \quad \dots(4)$$

where a_D is Debye effective reaction distance, ϕ is a constant quantity, e_0 is electronic charge, $\epsilon \epsilon_0$ is the dielectric permittivity of the medium, Z_1 and Z_2 are the valencies of the ions A_1 and A_2 , k is Boltzmann constant, T is absolute temperature and N_A is Avogadro number. The dependence of the equilibrium constant $K_{2,1}$ upon temperature is given by the equation of Van't Hoff :

$$\frac{\partial \ln K_{2,1}}{\partial T} = \frac{\Delta H_{2,1}}{RT^2}$$

i.e.,
$$\frac{\Delta K_{2,1}}{K_{2,1}} = \frac{\Delta H_{2,1}}{2.303 RT^2} \Delta T, \quad \dots(5)$$

where $\Delta H_{2,1}$ is enthalpy change. Eqn. (3) may be represented like

$$K_{2,1} = n_1 \exp\left(\frac{-\Delta H_{2,1}}{RT}\right). \quad \dots(6)$$

From thermodynamics of reversible reaction, it is well known that the change in entropy $\Delta S = 0$, which transforms above equation in the form

$$K_{2,1} = n_1 \exp\left(\frac{-\Delta F}{RT}\right), \quad \dots(7)$$

where ΔF is free energy change and is given by

$$\Delta F = -n_2 N_A$$

$$\text{i.e., } F = C \log \left(\frac{1}{a_D} \right); C = \frac{N_A Z_1 Z_2 e_0^2}{4\pi \epsilon \epsilon_0} \quad \dots(8)$$

For a monomolecular-type reaction



the rate constant k_1 is described by (Eigen 1954; and Pollard 1951)

$$\begin{aligned} k_1 &= \frac{kT}{h} \exp \left(\frac{-\Delta F}{RT} \right) \\ &= \frac{kT}{h} \exp \left(\frac{-\Delta H}{RT} \right) \exp \left(\frac{\Delta S}{R} \right), \end{aligned} \quad \dots(10)$$

where ΔS appears as a positive exponent, which aids the speed of the reaction. In case of the denaturation of proteins and inactivation of enzymes the values of ΔS come out of the order of 10-100 calories/mole/degree, which produces a drastic change in k_1 . A large part of the entropy of activation arises due to hydration like in enzymes while for dry substances (Pollard 1951) $\Delta S = 0$. Because of the great size of the molecules of enzymes, they diffuse slowly, a fact that separate them from readily diffusible substances by dialysis.

An aspect of the thermodynamics of diffusion-limited reactions and biomolecular reaction can be visualized in terms of free energy function F (see Fig. 1). For it, we have presented in Fig. 1(a) the behaviour of function F with bond distance in case of protein molecule on the basis of Eyring's theory (Glasstone *et al.* 1941). The representation of the curve of Fig. 1(b) for diffusion-limited reactions is followed by eqn. (8). In case of the curve of Fig. 1(a), there exists a second configuration separated by an intervening hump. For a large molecule to obtain the energy ΔF certainly involves many other bonds as well, so that ΔF includes the changes in covalent, helix and interhelix bonds. The enzymes possess many of the properties of proteins. It is the characteristic of a particular type of enzyme that it can affect only one particular type of chemical bond of a substance having a certain molecular pattern. In case of the curve of Fig. 1(b) of diffusion-limited reaction the maximum value of F lies in the range $0 < a_D < 0.1$. After the first maxima there is decay in the value of F and at $a_D = 1$ the free energy becomes zero. After this the free energy becomes negative and of decaying nature.

(a) Mathematical Analysis

We present here the changes near equilibrium in case of diffusion-limited reactions and enzyme reactions in terms of equilibrium concentration and analytical concentrations.

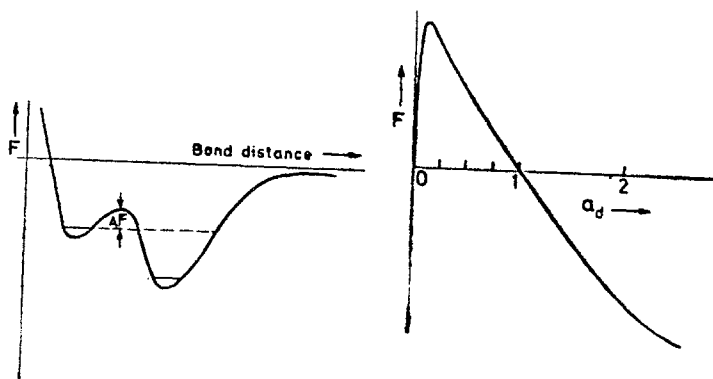


FIG. 1(a). Variation of free energy with bond distance in a biological molecule.
 1(b). Variation of free energy with a_D (Debye variable distance).

(i) *Analysis for diffusion-limited reactions* — For reaction represented by eqn. (1), we consider the symbol C as concentration of the constituents. In which the analytical concentrations of the constituents are defined by the superscript 0 and the equilibrium concentrations by putting the bar - over symbol C and the equilibrium concentration variable by $\bar{x} = -\bar{C}_3$ (therefore conservation laws), we obtain

$$C_1^0 + \bar{x} = \bar{C}_1$$

and $C_2^0 + \bar{x} = \bar{C}_2$... (11)

Thus the value of $K_{2,1}$ represented by eqn. (2) is given by

$$K_{2,1} = \frac{\bar{C}_1(C_2^0 - C_1^0 + \bar{C}_1)}{(C_1^0 - \bar{C}_1)},$$
 ... (12)

which presents a quadratic equation

$$(\bar{C}_1)^2 + (K_{2,1} + C_2^0 - C_1^0) \bar{C}_1 - K_{2,1} C_1^0 = 0.$$
 ... (13)

The solution of above equation is given by

$$\bar{C}_1 = -\frac{1}{2} \left\{ 1 + \left(\frac{C_2^0 - C_1^0}{K_{2,1}} \right) \right\} \left[1 \pm \left\{ 1 + \left\{ \frac{\left(\frac{4C_1^0}{K_{2,1}} \right)}{\left(1 + \left(\frac{C_2^0 - C_1^0}{K_{2,1}} \right) \right)^2} \right\} \right\} \right]$$
 ... (14)

For $C_2^0 = 2C_1^0$, one may obtain with the help of binomial expansion (leaving higher order term) with negative root, which is valid here $[C_2^0 + K_{2,1} > C_1^0]$

$$\frac{\bar{C}_1}{K_{2,1}} = \frac{\left(\frac{C_1^0}{K_{2,1}}\right)}{1 + \left(\frac{C_1^0}{K_{2,1}}\right)} \quad \dots(15)$$

The above equation represents a hyperbola having asymptotic behaviour at $C_1^0/K_{2,1} = -1$ as shown in Fig. 2. For positive values of $C_1^0/K_{2,1}$, the corresponding values of $\bar{C}_1/K_{2,1} < 1$.

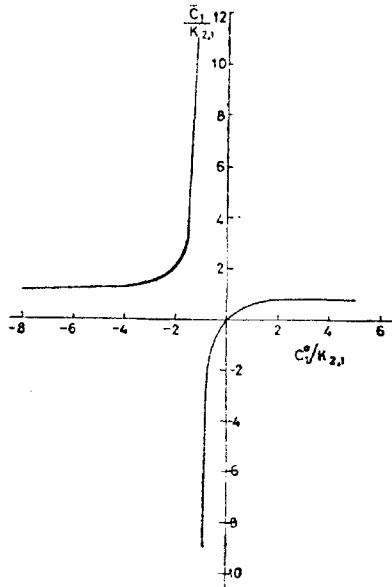


FIG. 2. $\bar{C}_1/K_{2,1}$ versus $C_1^0/K_{2,1}$ at $C_2^0 = 2 C_1^0$

With the help of eqns. (2) and (11), we obtain

$$\frac{\Delta K_{2,1}}{K_{2,1}} = \frac{\Delta \bar{C}_1}{\bar{C}_1} + \frac{\Delta \bar{C}_2}{\bar{C}_2} - \frac{\Delta \bar{C}_3}{\bar{C}_3} \quad \dots(16)$$

Again from the laws of conservation of mass and stoichiometry, we have

$$\Delta C_1 = - \Delta C_3.$$

and
$$\Delta C_1 = \Delta C_2. \quad \dots(17)$$

Hence
$$\Delta \bar{C}_2 = \Delta \bar{C}_1$$

and
$$\Delta \bar{C}_3 = - \Delta \bar{C}_1, \quad \dots(18)$$

where ΔC_1 and ΔC_2 are the instantaneous (time-dependent) concentration change. Using eqns. (15), (16), (17) and (18), for $C_2^0 = 2C_1^0$, we get

$$\frac{\frac{\Delta \bar{C}_1}{\bar{C}_1}}{\frac{\Delta K_{2,1}}{K_{2,1}}} = \left[1 + \left\{ 2 + \left(\frac{C_1^0}{K_{2,1}} \right) \right\}^{-1} - \left(\frac{C_1^0}{K_{2,1}} \right)^{-1} \right]^{-1} \quad \dots(19)$$

and

$$\frac{\frac{\Delta \bar{C}_1}{K_{2,1}}}{\frac{\Delta K_{2,1}}{K_{2,1}}} = \left[1 + \left(\frac{C_1^0}{K_{2,1}} \right)^{-1} \right]^{-1} \times \left[1 + \left\{ 2 + \left(\frac{C_1^0}{K_{2,1}} \right) \right\}^{-1} - \left(\frac{C_1^0}{K_{2,1}} \right)^{-1} \right]^{-1} \quad \dots(20)$$

The variations of

$$\frac{\frac{\Delta \bar{C}_1}{K_{2,1}}}{\frac{\Delta K_{2,1}}{K_{2,1}}} \text{ and } \frac{\frac{\Delta \bar{C}_1}{\bar{C}_1}}{\frac{\Delta K_{2,1}}{K_{2,1}}} \text{ vs. } \frac{C_1^0}{K_{2,1}}$$

have been presented in Figs. 3 and 4. Fig. 4 is of logarithmic plot. In Fig. 4, the values of $-.5 < C_1^0/K_{2,1} < .5$ are shown 2 times of the original values. The value of $C_1^0/K_{2,1} = -.1$ is shown 10 times of the original value. In Fig. 3, the graph is symmetrical about y-axis, if origin is displaced to point $C_1^0/K_{2,1} = -1$. Some important results of the Figs. are summarized as below :

About Fig. 3:

(i) For $C_1^0/K_{2,1} = 0$, $\frac{\Delta \bar{C}_1/\bar{C}_1}{\Delta K_{2,1}/K_{2,1}} = 0$.

(ii) For $C_1^0/K_{2,1} = -1$, $\frac{\Delta \bar{C}_1/\bar{C}_1}{\Delta K_{2,1}/K_{2,1}} = \infty$.

(iii) For $-100 < C_1^0/K_{2,1} > 1000$, $\frac{\Delta \bar{C}_1/\bar{C}_1}{\Delta K_{2,1}/K_{2,1}} \approx 1$.

(iv) In the region between $0.74 < C_1^0/K_{2,1} > 0.73$ there is a high fluctuation in the values of $\frac{\Delta \bar{C}_1/\bar{C}_1}{\Delta K_{2,1}/K_{2,1}}$, which shows the sensitivity of the region.

About Fig. 4:

(i) For $C_1^0/K_{2,1} = 0$, $\frac{\Delta \bar{C}_1/K_{2,1}}{\Delta K_{2,1}/K_{2,1}} = 0$

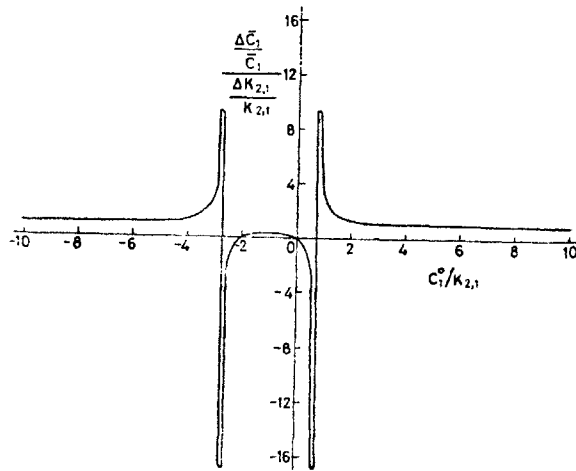


FIG. 3. $(\Delta \bar{C}_1 / \bar{C}_1) / (\Delta K_{2,1} / K_{2,1})$ vs. $C_1^0 / K_{2,1}$

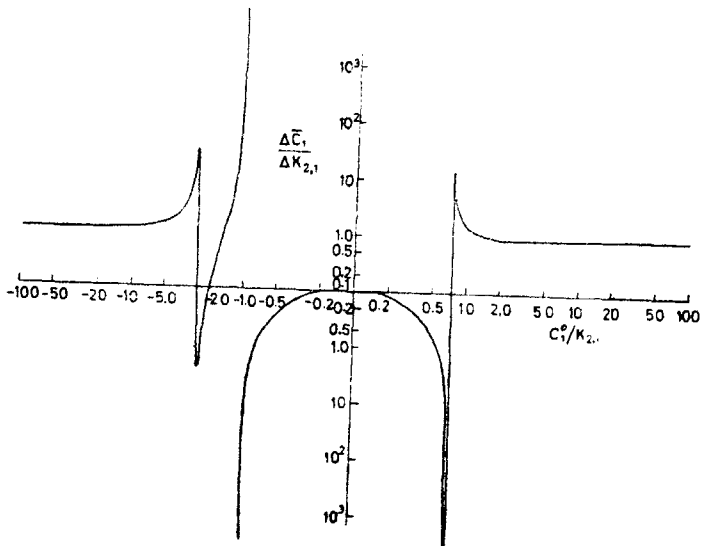


FIG. 4. $(\Delta \bar{C}_1 / \bar{C}_1) / (\Delta K_{2,1} / K_{2,1})$ vs. $C_1^0 / K_{2,1}$ (logarithmic plot).

(ii) For $C_1^0 / K_{2,1} = -1$, $\frac{\Delta \bar{C}_1 / K_{2,1}}{\Delta K_{2,1} / K_{2,1}} = \infty$

For positive values of $C_1^0 / K_{2,1}$, the general shape of the curves in Figs. 3 and 4 are the same. The magnitude of $\frac{\Delta \bar{C}_1 / K_{2,1}}{\Delta K_{2,1} / K_{2,1}}$ is larger due to the values of $\bar{C}_1 / K_{2,1}$.

Since

$$\left[\frac{(\Delta \bar{C}_1/\bar{C}_1)}{(\Delta K_{2,1}/K_{2,1})} \right] [\bar{C}_1/K_{2,1}] = \frac{(\Delta \bar{C}_1/K_{2,1})}{(\Delta K_{2,1}/K_{2,1})} \quad \dots(21)$$

i.e., eqn. (2) is the product of eqn. (15) and eqn. (19).

If now, we consider the analytical concentration of A_3 contained in the remaining two analytical concentrations of A_1 and A_2 , then doing similar treatment as for \bar{C}_1 , we obtain

$$\bar{C}_3 = \frac{1}{2} \{1 + (C_1^0 + C_2^0/K_{2,1})\} \left[1 \pm \left\{ 1 - \frac{4(C_1^0 C_2^0/K_{2,1})}{[1 + (C_1^0 + C_2^0/K_{2,1})]^2} \right\}^{1/2} \right] \quad \dots(22)$$

Since the second term under the root is always positive and always smaller than unity, there will always be only a real solution. Here we consider the negative root only. For $C_2^0 = 2C_1^0$ (same condition as for \bar{C}_1 case), we obtain

$$\bar{C}_3/K_{2,1} = \frac{2(C_1^0/K_{2,1})^2}{\{1 + 2(C_1^0/K_{2,1})\}} \quad \dots(23)$$

Using eqns. (16), (17), (18) and (23), we obtain

$$\frac{\Delta \bar{C}_3/\bar{C}_3}{\Delta K_{2,1}/K_{2,1}} = - \left[1 + 2(C_1^0/K_{2,1}) + \frac{2(C_1^0/K_{2,1})^2}{1 + 2(C_1^0/K_{2,1}) - 2(C_1^0/K_{2,1})^2} \right] \quad \dots(24)$$

and

$$\frac{\Delta \bar{C}_3/K_{2,1}}{\Delta K_{2,1}/K_{2,1}} = \frac{2(C_1^0/K_{2,1})^2}{1 + 2(C_1^0/K_{2,1})} \times \left[1 + 2(C_1^0/K_{2,1}) + \frac{2(C_1^0/K_{2,1})^2}{1 + 2(C_1^0/K_{2,1}) - 2(C_1^0/K_{2,1})^2} \right] \quad \dots(25)$$

The variations of $\frac{\Delta \bar{C}_3/K_{2,1}}{\Delta K_{2,1}/K_{2,1}}$ and $\frac{\Delta \bar{C}_3/\bar{C}_3}{\Delta K_{2,1}/K_{2,1}}$ vs. $C_1^0/K_{2,1}$ have been presented in Figs. 5 and 6. Some important results of these figures are summarized as below :

About Fig. 5:

- (i) for $C_1^0/K_{2,1} = 0$, $\frac{(\Delta \bar{C}_3/K_{2,1})}{(\Delta K_{2,1}/K_{2,1})} = 0$
- (ii) for $-30 < C_1^0/K_{2,1} < 30$, $\frac{(\Delta \bar{C}_3/\bar{C}_3)}{(\Delta K_{2,1}/K_{2,1})} \approx -\frac{1}{2}$
- (iii) The first minima occurs at $C_1^0/K_{2,1} \sim 2$ whereas first minima in negative side occurs at $C_1^0/K_{2,1} \sim -1$
- (iv) for the values $C_1^0/K_{2,1} > 4$ and $C_1^0/K_{2,1} < -1$ there is continuous decay in the curve.

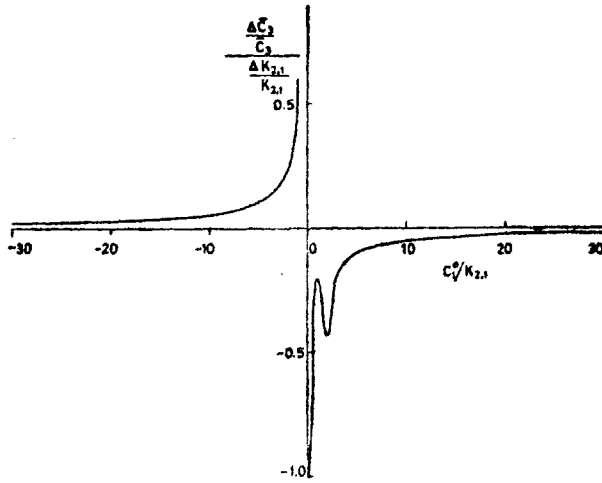


FIG. 5. $(\Delta \bar{C}_3/K_{2,1})/(\Delta K_{2,1}/K_{2,1})$ vs. $C_1^0/K_{2,1}$

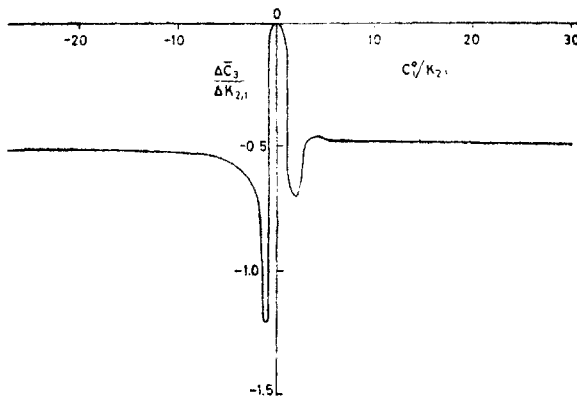


FIG. 6. $(\Delta \bar{C}_3/\bar{C}_3)/(\Delta K_{2,1}/K_{2,1})$ vs. $C_1^0/K_{2,1}$

About Fig. 6:

- (i) For $C_1^0/K_{2,1} = 0$, $\frac{(\Delta \bar{C}_3/\bar{C}_3)}{(\Delta K_{2,1}/K_{2,1})} = -1$
- (ii) The first maxima occurs at $C_1^0/K_{2,1} = 1$ and first minima at $C_1^0/K_{2,1} = 2$.
- (iii) For the values $C_1^0/K_{2,1} > 2$ and $C_1^0/K_{2,1} < -1$ there is a continuous decay in the curve.

Eqn. (24) may also be written as

$$\Delta \bar{C}_3/\bar{C}_3 = - \left[1 + \left(\frac{\bar{C}_1 + \bar{C}_2}{K_{2,1}} \right) \right]^{-1} \Delta K_{2,1}/K_{2,1} \quad \dots(26)$$

The above equation represents that the relative equilibrium concentration of L.H.S. quantity, which is also called as fractional change in the equilibrium concentration of \bar{C}_3 , is large if the equilibrium concentrations of $A_1(\bar{C}_1)$ and $A(\bar{C}_2)$ are small as compared to the equilibrium constant. This condition becomes the most favourable for the case whenever the equilibrium concentrations are in the neighbourhood of the equilibrium constant.

(ii) *Analysis for enzyme reactions* — For the case of mechanism of competitive inhibition, one may write in terms of enzyme reaction



and



where E represents the active site of an enzyme, S represents the substrate, ES represents an enzyme substrate complex, I represents an inhibitor, which may also be an indicating dye. An important characteristics of an enzyme is that it can only affect to different such substances which possess the common chemical bond.

The chemical equilibrium of above systems may be considered like eqn. (1) and all the above mathematical treatment also may be taken into account. During the study of enzyme reactions one should always consider that the concentration of free enzyme \bar{C}_E is relatively small as compared to \bar{C}_I and \bar{C}_{EI} . The reaction (27) is very fast as compared to reaction (28).

Similar to eqn. (16) related to eqn. (11) the corresponding eqns. for eqns. (27) and (28), we may write

$$\Delta K_{2,1}/K_{2,1} = \Delta \bar{C}_I/\bar{C}_I + \Delta \bar{C}_E/\bar{C}_E - \Delta \bar{C}_{EI}/\bar{C}_{EI} \quad \dots(29)$$

and

$$\Delta K_{4,3}/K_{4,3} = \Delta \bar{C}_S/\bar{C}_S + \Delta \bar{C}_E/\bar{C}_E - \Delta \bar{C}_{ES}/\bar{C}_{ES} \quad \dots(30)$$

From the laws of conservation of mass and stoichiometry, we have

$$\begin{aligned} \Delta C_I &= - \Delta C_{EI} \\ \Delta C_S &= - \Delta C_{ES} \\ \Delta C_E + \Delta C_{EI} &= - \Delta C_{ES} \\ \Delta C_E &= - \Delta C_{EI} \end{aligned} \quad \dots(31)$$

Concentration of end products : For fast relaxation process the eqn. (3) vanishes and for eqn. (29), we obtain

$$(\Delta \bar{C}_{EI}/\bar{C}_{EI})_1 = - \Delta K_{2,1}/K_{2,1} [1 + (\bar{C}_E + \bar{C}_I/K_{2,1})]^{-1}. \quad \dots(32)$$

If one determines the value of $(\Delta \bar{C}_{EI}/C_{EI})$ by considering the time range limit of the both eqns. (29) and (30) then first of all the time range of eqn. (29) [neglecting eqn. (30)] should be taken into account. The contribution of $(\Delta \bar{C}_{EI}/C_{EI})$ for first process [eqn. (29)] is called as $(\Delta \bar{C}_{EI}/\bar{C}_{EI})_1$. The time range of eqn. (30) provides the corresponding contribution as $(\Delta \bar{C}_{EI}/\bar{C}_{EI})_2$. The combined contribution of $(\Delta \bar{C}_{EI}/\bar{C}_{EI})_{total}$, for eqns. (29) and (30) by using eqn. (31), may be represented by

$$(\Delta \bar{C}_{EI}/\bar{C}_{EI})_{total} = (\Delta \bar{C}_{EI}/\bar{C}_{EI})_1 + (\Delta \bar{C}_{EI}/C_{EI})_2, \quad \dots(33)$$

where

$$\left(\frac{\Delta \bar{C}_{EI}}{C_{EI}} \right)_2 = \frac{\Delta K_{4,3}/K_{4,3} - \Delta K_{2,1}/K_{2,1}(1 + \bar{C}_E/\bar{C}_I + K_{2,1}/\bar{C}_I)^{-1}}{\{1 + (\bar{C}_E + \bar{C}_I/K_{2,1})\}[1 + (K_{4,3} + \bar{C}_E/\bar{C}_S) - \bar{C}_I/K_{2,1}]}, \quad \dots(34)$$

which on combining with eqn. (32) presents

$$(\Delta \bar{C}_{EI}/\bar{C}_{EI})_{total} = \frac{\Delta K_{4,3}/K_{4,3} [1 + \bar{C}_{ES}/\bar{C}_S + K_{4,3}/\bar{C}_S]^{-1} - \Delta K_{2,1}/K_{2,1}}{1 + \bar{C}_E/K_{2,1} + \bar{C}_I/K_{2,1} [1 + (1 + K_{4,3}/\bar{C}_S + \bar{C}_E/\bar{C}_S)^{-1}]} \quad \dots(35)$$

The limiting values for total, subscript 1 and subscript 2 are given by (Czerlinski 1969)

$$\begin{aligned} \lim_{C_S \rightarrow 0} (\Delta \bar{C}_{EI}/\bar{C}_{EI})_{total} &= - \Delta K_{2,1}/K_{2,1} [1 + (\bar{C}_E + \bar{C}_I/K_{2,1})]^{-1} \\ \lim_{C_S \rightarrow \infty} (\Delta \bar{C}_{EI}/\bar{C}_{EI})_{total} &= (\Delta K_{4,3}/K_{4,3} - \Delta K_{2,1}/K_{2,1}) \times \\ &\quad (1 + \bar{C}_E/K_{2,1})^{-1} \\ \lim_{C_S \rightarrow 0} (\Delta \bar{C}_{EI}/\bar{C}_{EI})_1 &= - \Delta K_{2,1}/K_{2,1} [1 + (\bar{C}_E + \bar{C}_I/K_{2,1})]^{-1} \\ \lim_{C_S \rightarrow \infty} (\Delta \bar{C}_{EI}/\bar{C}_{EI})_1 &= - \Delta K_{2,1}/K_{2,1} [1 + (\bar{C}_E + \bar{C}_I/K_{2,1})]^{-1} \\ \lim_{C_S \rightarrow 0} (\Delta \bar{C}_{EI}/\bar{C}_{EI})_2 &= 0 \\ \lim_{C_S \rightarrow \infty} (\Delta \bar{C}_{EI}/\bar{C}_{EI})_2 &= [\Delta K_{4,3}/K_{4,3} - \Delta K_{2,1}/K_{2,1}(1 + \bar{C}_E/\bar{C}_I + \\ &\quad K_{2,1}/\bar{C}_I)^{-1}] [1 + \bar{C}_E/K_{2,1}]^{-1} \quad \dots(36) \end{aligned}$$

Case—1:

When the free energy function F is same for both process eqn. (29) and eqn. (30), we obtain

$$\Delta K_{4,3}/K_{4,3} = \Delta K_{2,1}/K_{2,1}, \quad \dots(37)$$

which presents under condition $\bar{C}_L = \bar{C}_I$

$$\lim_{C_S \rightarrow \infty} (C_{EI}/\bar{C}_{EI})_{total} = 0 \quad \dots(38)$$

Case—II:

When $(\bar{C}_E + \bar{C}_I)/K_{2,1} = -1$, we obtain

$$\lim_{C_S \rightarrow 0} (\Delta \bar{C}_L/\bar{C}_{EI})_{total} = 0$$

Case—III:

For the values of $(\Delta \bar{C}_L/\bar{C}_{EI})_{total}$ to be equal in the limiting cases $C_S \rightarrow 0$ and $C_S \rightarrow \infty$, the following conditions are required

$$\begin{aligned} \bar{C}_I &= \bar{C}_E \\ \Delta K_{4,3}/\Delta K_{2,1} &= \Delta K_{2,1}/K_{2,1} \\ \bar{C}_I/K_{2,1} &= \frac{1}{2} \end{aligned} \quad \dots(39)$$

Concentration of Enzyme — For understanding the effect of variation of concentration of enzyme, we have determined here the ratio $\Delta \bar{C}_E/\bar{C}_L$ as below.

For the fast relaxation process eqn. (30) vanishes and for eqn. (29), we obtain

$$(\Delta \bar{C}_E/\bar{C}_L)_1 = \Delta K_{2,1}/K_{2,1} [1 + K_{2,1}/\bar{C}_I \{1 + (\bar{C}_{EI}/\bar{C}_I)\}]^{-1} \quad \dots(40)$$

Again considering the similar treatment of the time range limit of the both eqns. (29) and (30) as for the case of the concentration of end products, we finally write the corresponding value of $\Delta \bar{C}_E/\bar{C}_E$ as

$$(\Delta \bar{C}_E/\bar{C}_E)_{total} = (\Delta \bar{C}_E/\bar{C}_E)_1 + (\Delta \bar{C}_E/\bar{C}_E)_2, \quad \dots(41)$$

where

$$\begin{aligned} (\Delta \bar{C}_L/\bar{C}_E)_2 &= [\Delta K_{4,3}/K_{4,3} - \Delta K_{2,1}/K_{2,1} \times \\ &\quad \{1 + K_{2,1}/\bar{C}_I (1 + \bar{C}_{EI}/\bar{C}_I)\}^{-1} \times \\ &\quad \frac{(K_{2,1}/K_{4,3}) (\bar{C}_S/\bar{C}_I)}{(1 - K_{2,1}/\bar{C}_I + \bar{C}_{EI}/\bar{C}_I) +} \\ &\quad \frac{(K_{2,1}/K_{4,3}) (\bar{C}_S/\bar{C}_I)}{(1 + \bar{C}_E/K_{4,3})} \end{aligned} \quad \dots(42)$$

which on combining with eqn. (40) presents

$$\begin{aligned} (\Delta \bar{C}_E/\bar{C}_E)_{total} &= \\ &\frac{\Delta K_{2,1}/K_{2,1} + \Delta K_{4,3}/K_{4,3} [K_{2,1}/K_{4,3} + \bar{C}_E/K_{4,3}] \bar{C}_S/\bar{C}_I}{[1 + K_{2,1}/\bar{C}_I \{1 + \bar{C}_{EI}/\bar{C}_I\}] + \bar{C}_S/\bar{C}_I [K_{2,1}/K_{4,3} + \bar{C}_E/K_{4,3}]} \end{aligned} \quad \dots(43)$$

The limiting values of total, subscripts 1 and 2 are given by

$$\begin{aligned} \lim_{C_S \rightarrow 0} (\Delta \bar{C}_E / \bar{C}_E)_{total} &= \Delta K_{2,1} / K_{2,1} [1 + K_{2,1} / \bar{C}_I \{1 + (\bar{C}_{EI} / \bar{C}_I)\}]^{-1} \\ \lim_{C_S \rightarrow \infty} (\Delta \bar{C}_E / \bar{C}_E)_{total} &= \Delta K_{4,3} / K_{4,3} \\ \lim_{C_S \rightarrow 0} (\Delta \bar{C}_E / \bar{C}_E)_1 &= \Delta K_{2,1} / K_{2,1} [1 + K_{2,1} / \bar{C}_I \{1 + (\bar{C}_{EI} / \bar{C}_I)\}]^{-1} \\ \lim_{C_S \rightarrow \infty} (\Delta \bar{C}_E / \bar{C}_E)_1 &= \Delta K_{2,1} / K_{2,1} [1 + (K_{2,1} / \bar{C}_I) \{1 + (\bar{C}_{EI} / \bar{C}_I)\}]^{-1} \\ \lim_{C_S \rightarrow 0} (\Delta \bar{C}_E / \bar{C}_E)_2 &= 0 \\ \lim_{C_S \rightarrow \infty} (\Delta \bar{C}_E / \bar{C}_E)_2 &= \Delta K_{4,3} / K_{4,3} - \Delta K_{2,1} / K_{2,1} \times \\ &\quad [1 + K_{2,1} / \bar{C}_I \{1 + (\bar{C}_{EI} / \bar{C}_I)\}]^{-1} \quad \dots(44) \end{aligned}$$

Case — I :

When $\bar{C}_{EI} = -\bar{C}_I$

$$\lim_{C_S \rightarrow 0} (\Delta \bar{C}_E / \bar{C}_E)_{total} = \Delta K_{2,1} / K_{2,1} \quad \dots(45)$$

and

$$\lim_{C_S \rightarrow \infty} (\Delta \bar{C}_E / \bar{C}_E)_2 = \Delta K_{4,3} / K_{4,3} - \Delta K_{2,1} / K_{2,1} \quad \dots(46)$$

CONCLUSION

On the basis of present thermodynamical study, it is concludable that in diffusion-limited reactions only the change in enthalpy ΔH presents dominant contribution to the free energy function ΔF , while in biomolecular reactions like denaturation of proteins and inactivation of enzymes the change in entropy ΔS and change in enthalpy ΔH both presents significant contributions. It is reasonable, that in the dry state activation entropies are quite small, so that probably a very large part of the entropy of activation is concerned with hydration.

In case of diffusion-limited reactions the behaviour of free energy function F with a_D presents the value of F remains positive within range $0 < a_D \leq 0.1$ and after the first maxima (at $a_D = 0.1$) there is continuous exponential decay in the values of F as a_D varies. In biomolecular reactions there is oscillatory behaviour in the curve of F vs. bond distance [see Fig. 1(a)]. Also the first maxima in biomolecular curve describes the change in free energy ΔF , which includes the combined effect of covalent, helix and interhelix bonds.

The behaviour of the ratio of fractional change in equilibrium concentration of reactants and fractional change in equilibrium constant or the ratio of change in equilibrium concentration of the reactant and change in equilibrium constant

with the ratio of analytical concentration of reactant and equilibrium constant, is quite different in forward and backward reactions in case of diffusion-limited reactions.

In case of very fast relaxation process, eqn. (32) explains that as the fractional change in equilibrium concentration of end products increases the value of the fractional change in equilibrium constant decreases and as the fractional change in equilibrium concentration of end products decreases the value of the fractional change in equilibrium constant increases provided the equilibrium concentration of enzyme and inhibitor remains constant. Similarly, eqn. (40) explains that as the fractional change in equilibrium concentration of enzyme increases the value of the fractional change in equilibrium constant also increases and as the fractional change in equilibrium concentration of enzyme decreases the value of the fractional change in equilibrium constant also decreases provided the equilibrium constant of end products and inhibitor remains constant.

The behaviour of concentration of substrate with the fractional change in equilibrium concentration of end products in forward direction reaction and with the fractional change in equilibrium concentration of enzyme in backward direction reaction is quite different.

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