CHAPTER 5

Reaction Mechanism: Ligand Substitution, Isomerisation and Racemisation Reactions of Metal Complexes

5.1 ENERGETICS OF REACTIONS (IN GENERAL) AND DIFFERENT TYPES OF REACTIONS OF METAL COMPLEXES

5.1.1 Energetics of Reactions (in General)

For any reaction to occur, ΔG (Gibbs free energy charge under the given conditions) must be negative. **It is the thermodynamic condition**, however, the reaction may be kinetically disfavoured. At this point, we shall pay attention to only the thermodynamic requirements of a reaction to occur.

$$\Delta G = \Delta H - T\Delta S < 0$$

i. If $\Delta H < 0$ (exothermic reaction) and $\Delta S > 0$, the reaction will occur at all temperatures ($\Delta G < 0$) as **both the enthalpy and entropy drive the reaction**.
ii. If $\Delta H > 0$ (endothermic reaction) and $\Delta S < 0$, the reaction is **nonspontaneous at all temperatures** ($\Delta G > 0$).
iii. If $\Delta H > 0$ (endothermic reaction) and $\Delta S > 0$, the reaction is spontaneous only at **higher temperature** under the condition, $|T\Delta S| > |\Delta H|$, *i.e.* the reaction will be **entropy driven** under the condition.
iv. If $\Delta H < 0$ and $\Delta S < 0$, the reaction is only spontaneous at low temperature ($|T\Delta S| < |\Delta H|$), and the reaction is **enthalpy driven** under the condition.
v. If $\Delta H = 0$ (*e.g.* racemisation reaction), the reaction is **entropy driven under the condition $\Delta S > 0$.**

Note: $\Delta G < 0$ (spontaneous process), > 0 (nonspontaneous process) $= 0$ (process at equilibrium). $\Delta G = \Delta G^\circ + RT \ln K^o_{eq}$, where ΔG° = standard free energy change when the reactants and products at their equilibrium states (P = 1 bar at T of interest), K^o_{eq} = thermodynamic equilibrium constant, a dimensionless quantity. At equilibrium, $\Delta G = 0 = \Delta G^\circ + RT \ln K^o_{eq}$ and $\Delta G^\circ = -RT \ln K^o_{eq}$.

The **thermodynamic equilibrium constant** (K^o_{eq}) is related to the standard free energy change (ΔG°) as $\Delta G^\circ = -RT \ln K^o_{eq}$. To make K^o_{eq} **dimensionless**, in the expression of equilibrium constant, each concentration term is divided by the unit quantity (*i.e.* 1.0 mol dm^{-3} denoted by C_o, standard concentration). It is illustrated for $A + B \rightleftharpoons C$ or $K_{eq} = \frac{[C]}{[A][B]}, K^o_{eq} = \frac{([C]/C_o)}{([A]/C_o)([B]/C_o)}$. K_{eq} (**stoichiometric equilibrium constant**, *i.e.* **concentration quotient**) is expressed by the concentration terms expressed in mol dm^{-3}. The unit of K_{eq} in the given reaction is $mol^{-1}\ dm^3$. To make it dimensionless,

each concentration term is divided by the **unit quantity** C_o (= 1.0 mol dm^{-3}, **standard state concentration**). Thus the numerical values of both K_{eq} and K^o_{eq} are the same but K^o_{eq} is dimensionless. Thus to express K^o_{eq}, concentration of each **reactant** and **product is to be measured with respect to the standard state of concentration** C_o (= 1.0 mol dm^{-3}).

A. Let us illustrate some reactions to understand the effects of enthalpy change (ΔH) (*i.e.* **enthalpy driven reactions)**

a. **Lewis acid-base adduct formation:** A + :B → AB (*e.g.* BF_3 + :NH_3 → F_3B←:NH_3), ΔS < 0, the reaction to occur must be enthalpy driven (*i.e.* ΔH < 0).

b. **Acid dissociation:** A–H + :B → BH^+ + A^- (*e.g.* $H_3CO_2H + H_2O \rightarrow CH_3CO_2^- + H_3O^+$), ΔS < 0 (**effect of electrorestriction of the ionic products on solvent**, ΔS refers to $\Delta S_{universe}$), the reaction to be spontaneous, ΔH must be negative to satisfy the condition $|\Delta H| > |T\Delta S|$. However, if proton transfer neutralises the charge, then ΔS becomes positive (*i.e.* electrorestriction over the solvent is reduced).

$$NH_4^+(aq) + PO_4^{3-}(aq) \rightarrow NH_3(aq) + HPO_4^{2-}(aq),\ \Delta S > 0$$

ΔH change in a reaction can be calculated from the involved **Born-Haber cycle** (see Vol. 3A). For the Lewis acid-base adduct formation, ΔH can be calculated by using the **Drago-Wayland equation** (see Vol. 3A).

c. **Solubilisation of ionic compounds in polar solvents like water** is basically an enthalpy driven process (see Sec. 11.7, Vol. 2).

d. Let us take the following electron transfer reaction occurring through the inner-sphere mechanism.

$$SO_3^{2-}(aq) + ClO_3^-(aq) \rightarrow SO_4^{2-}(aq) + ClO_2^-(aq)$$

$$\Delta H^\circ = -251\ kJ,\ \Delta S^\circ = -88\ J\ K^{-1},\ \Delta G^\circ \approx -224\ kJ\ at\ 25^\circ C$$

The reaction is **entropically disfavoured** but the reaction is **enthalpy driven**, *i.e.* $|\Delta H^\circ| > |T\Delta S^\circ|$.

e. **Formation of ionic compounds** (*e.g.* $Na(s) + 0.5Cl_2(g) \rightarrow NaCl(s)$, lattice energy driven process), **electrode potentials** of different redox couples (*e.g.* M/M^{n+}, etc.) are the classic examples of enthalpy driven reactions (see Sec. 12.6, Vol. 3A for more details).

B. Let us illustrate the **entropy driven reactions**. In the cases where ΔH ≈ 0 or ΔH > 0, the reaction to be spontaneous, it must satisfy the following condition, $|T\Delta S| > |\Delta H|$, (of course ΔS refers to $\Delta S_{universe}$).

a. **Solubilisation of nonpolar solutes in nonpolar solvents** (see Sec. 11.7, Vol. 2 for more details). In the ideal mixture (assuming no interaction between the solvent and solute), the entropy change is given by:

$$\Delta S_{mix} = -\sum n_i R \ln x_i = -R(n_1 \ln x_1 + n_2 \ln x_2),\ (\Delta H_{mix} = 0)$$

x_1 and x_2 denote the mole fractions of solute and solvent respectively. For $n_1 = n_2 = 1$ and $x_1 = x_2 = 0.5$, ΔS = +1.7 kJ mol^{-1} (*cf.* **spreading of a gaseous substance** in air is an example of entropy driven process).

b. **Clathrate or cage compound formation** is basically an entropy driven process (see Sec. 11.3.2, Vol. 2).

c. **Crystal defect formation** is also an entropy driven process (see Sec. 12.15, Vol. 3A for more details).

d. **Chelate effect** and **macrocyclic effect** to increase the stability of the complex are basically the entropy driven processes (see Vol. 4).

e. Thermal decomposition of a compound producing specially the gaseous substances (see Sec. 12.8.2, Vol. 3A for details) is entropy driven.

$$MCO_3(s) \xrightarrow{\Delta} MO(s) + CO_2(g),\ \Delta G = \Delta H - T\Delta S\ (\Delta H = +ve,\ \Delta S = +ve)$$

Decomposition temperature (T_d) is obtained as follows:

$$\Delta G = 0 = \Delta H_d - T_a \Delta S_d,\ i.e.\ T_d = \frac{\Delta H_d}{\Delta S_d}$$

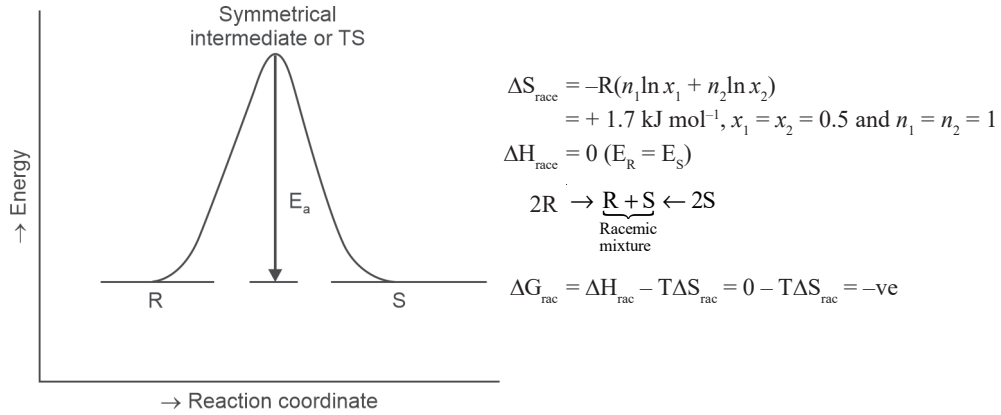


Fig. 5.1.1.1: Energy profile diagram of a racemisation reaction

Note: An **isomerisation reaction** producing a mixture of *cis*- and *trans*-isomers (*i.e.* geometric isomers) makes $\Delta S > 0$ but $\Delta H \neq 0$ as the stabilities of the geometric isomers are different (*i.e.* one form is generally more stable)

f. **Explosives** produce a large volume of gaseous substances to favour the explosion process entropically (see Appendix 16A, Vol. 3B).
g. Importance of entropy effect has been illustrated in **Ellingham diagram** (see Vol. 3B).
h. **Racemisation reaction** ($\Delta H = 0$) is purely an **entropy driven process** (see Fig. 5.1.1.1). It propduces a mixture of R- and S-conformations to increase the overall entropy of the process. If the **activation energy barrier** (E_a) is very small, then the optical isomers (*i.e.* enantiomers) cannot be separated at ordinary condition (*i.e.* room temperature). The inversion process of chiral amines and phosphines through the planar intermediate/TS (transition state) has been discussed in Sec. 10.9.1, Vol. 2 (*cf.* phosphine derivatives having the higher E_a-values are optically more stable).

5.1.2 Different Types of Reactions of Metal Complexes

Different types of reactions of metal complexes are as follows:

- ligand substitution reactions
- metal substitution reactions
- isomerisation and recemisation reactions
- redox (*i.e.* electron transfer) reactions
- reactions of coordinated ligands (*i.e.* activation of ligands).

5.2 CLASSIFICATION OF SUBSTITUTION REACTION

These are classified as follows:

- nucleophilic substitution (S_N)
- electrophilic substitution (S_E)

In **nucleophilic substitution reactions, a nucleophile** (*i.e.* Lewis base) donates its electron cloud to a positively charged centre, *i.e.* nucleus (*i.e.* Lewis acid) through the replacement of another nucleophile.

$$M—X + Y \rightarrow M—Y + X \ (S_N)$$

(Charges not shown)

Here both *X* and *Y* are the nucleophiles (*i.e.* ligands). *Y* is the *entering* or *incoming nucleophile* while *X* is the *leaving group* or *leaving nucleophile.* The metal centre (*i.e. M*) is the Lewis acid. Thus in a nucleophilic substitution reaction, one Lewis base (*i.e.* ligand) displaces another Lewis base from a Lewis acid (*i.e.* metal centre).

Thus the ligand substitution reaction is a case of nucleophilic substitution reaction. In ligand substitution reactions, other ligands (*i.e. nonleaving groups)* are called the **spectator ligands**.

$$L_5M—X + Y \rightarrow L_5M—Y + X$$

Here the ligands denoted by L_5 are called the *spectator ligands that may influence the rate and process of the substitution reaction through the steric and electronic effects.*

In an electrophilic substitution reaction, the metal centres (*i.e.* electron seeking, Lewis acids) are replaced, *i.e.* one metal centre replaces another one. In metal complexes, the *ligand substitution* (*i.e.* nucleophilic substitution) reactions are abundant while the *metal substitution* (*i.e.* electrophilic substitution) reactions are relatively rare.

5.3 DIFFERENT TYPES OF LIGAND SUBSTITUTION REACTIONS

These are illustrated with some specific examples.

Acid hydrolysis: The leaving group is replaced by H_2O (*i.e.* solvent in aqueous media) in acidic condition.

$$[Co(NH_3)_5X]^{2+} + H_2O \rightarrow [Co(NH_3)_5(OH_2)]^{3+} + X^-$$

This is also called the *aquation* or simply the *dissociation* reaction.

Base hydrolysis: The leaving group is replaced by OH^- group in aqueous media. This is also a case of dissociation reaction.

$$[Co(NH_3)_5X]^{2+} + OH^- \rightarrow [Co(NH_3)_5(OH)]^{2+} + X^-$$

Anation: The coordinated solvent molecule (*i.e.* H_2O in aqueous media) is replaced by an anion (X^-).

$$[Co(NH_3)_5(OH_2)]^{3+} + X^- \rightarrow [Co(NH_3)_5X]^{2+} + H_2O$$

This is also described as the *formation reaction*.

Solvent exchange: This is illustrated below.

$$[M(OH_2)_n] + H_2O^* \rightarrow [M(OH_2)_{n-1}(^*OH_2)] + H_2O, \text{ (in aqueous solvent)}$$

Ligand exchange: This is illustrated below.

$$[PtCl_2(py)_2] + 2^*Cl^- \rightarrow [Pt(^*Cl)_2(py)_2] + 2Cl^-$$

Formation reaction: Replacement of a coordinated solvent molecule by a ligand other that the solvent itself.

$$[M(OH_2)_n] + L \rightarrow [M(OH_2)_{n-1}(L)] + H_2O$$

Solvolysis reaction (*cf.* Hydrolysis reaction): Replacement of a ligand by the solvent itself.

$$M—L + S \text{ (solvent)} \rightarrow M—S + L$$

5.4 THERMODYNAMIC AND KINETIC STABILITY: LABILITY AND INERTNESS (*cf.* Sec. 4.1)

Thermodynamic stability of a complex is determined by β_n called **thermodynamic stability constant** (a dimensionless quantity).

$$M + nL \rightleftharpoons ML_n, \beta_n = \frac{[ML_n]/(C_o)}{([M]/C_o)([L]/C_o)^n} \text{ and } \beta_{n(C)} = \frac{[ML_n]}{[M][L]^n}$$

$C_o = 1.0$ mol dm^{-3} (**standard state concentration**), a unit quantity. $\beta_{n(C)}$ called **stoichiometric stability constant** (concentration quotient), where the concentrations are expressed in the unit mol dm^{-3}. To obtain β_n (dimensionless) from $\beta_{n(C)}$, each concentration term is divided by the unit quantity C_o (= 1.0 mol dm^{-3}) (see Sec., 5.1.1).

The higher value of β_n indicates its higher thermodynamic stability. Thus it gives the measure of the extent to which the equilibrium can proceed but it cannot say anything regarding the speed with which the equilibrium is attained. Thus the thermodynamic and kinetic stability are not necessarily correlated. A thermodynamically stable complex may react slowly or fast depending on the condition. This can be illustrated by considering the different cyanido complexes which are extremely stable (*i.e.* very high value of β_n) but they behave quite differently in terms of the rate of exchange of the radiocarbon labelled cyanide.

$$\left[Hg(CN)_4\right]^{2-} + 4^{14}CN^- \rightleftharpoons \left[Hg(^{14}CN)_4\right]^{2-} + 4CN^-, \textbf{ very fast}$$

$$\left[Ni(CN)_4\right]^{2-} + 4^{14}CN^- \rightleftharpoons \left[Ni(^{14}CN)_4\right]^{2-} + 4CN^-, t_{1/2} \approx 30\,s, \textbf{ very fast}$$

$$\left[Pt(CN)_4\right]^{2-} + 4^{14}CN^- \rightleftharpoons \left[Pt(^{14}CN)_4\right]^{2-} + 4CN^-, t_{1/2} \approx 1\,min$$

$$\left[Mn(CN)_6\right]^{3-} + 6^{14}CN^- \rightleftharpoons \left[Mn(^{14}CN)_6\right]^{3-} + 6CN^-, \; t_{1/2} \approx 1\,h$$

$$\left[Cr(CN)_6\right]^{3-} + 6^{14}CN^- \rightleftharpoons \left[Cr(^{14}CN)_6\right]^{3-} + 6CN^-, t_{1/2} \approx 24\,d,$$

$$\left[Fe(CN)_6\right]^{3-/4-} + 6^{14}CN^- \rightleftharpoons \left[Fe(^{14}CN)_6\right]^{3-/4-} + 6CN^-, \textbf{ (very slow)}$$

All the above complexes are thermodynamically very stable (*cf.* $[Ni(CN)_4]^{2-}$, log $\beta_4 \approx 29$; $[Pt(CN)_4]^{2-}$, log $\beta_4 \approx 40$; $[Hg(CN)_4]^{2-}$, log $\beta_4 \approx 42$; $[Fe(CN)_6]^{3-}$, log $\beta_6 \approx 44$; $[Fe(CN)_6]^{4-}$, log $\beta_6 \approx 37$; etc.) but their kinetic stabilities differ widely. *The thermodynamically stable complexes like* $[Ni(CN)_4]^{2-}$, $[Hg(CN)_4]^{2-}$, etc. *react fast in the ligand exchange reactions but* $[Cr(CN)_6]^{3-}$ *which is also thermodynamically stable reacts slowly* and $[Fe(CN)_6]^{4-}$ also reacts very slowly.

Between $[Fe(CN)_6]^{4-}$ (t_{2g}^6) and $[Fe(CN)_6]^{3-}$ (t_{2g}^5), $[Fe(CN)_6]^{3-}$ is relatively more labile. In fact, slow aquation of $[Fe(CN)_6]^{3-}$ produces $[Fe(CN)_5(OH_2)]^{2-}$ to release CN^- **that can induce toxicity**. In fact, **ferricyanide solution is more poisonous than ferrocyanide solution in terms of CN^- poisoning.** The lability or inertness of the complexes and the pathway of ligand substitution can be interpreted in terms of crystal field activation energy (**CFAE**) discussed later.

- For some **square planar Pt(II) – complexes**, experiencing the **associative pathway of ligand substitution,** the lability and thermodynamic stability follow the same sequence, *i.e.* **the most stable complex is the most labile one** in the corresponding ligand exchange reaction.

Complex:	$[PtCl_4]^{2-}$	$[PtBr_4]^{2-}$	$[PtI_4]^{2-}$	$[Pt(CN)_4]^{2-}$
~ logβ_4:	17	20	30	40
~ $t_{1/2}$ (min):	850	6	4	1

Increasing lability $(cf.$ Secs. 5.30.5,6$)$ **and stability** →

- **Dissociation of $[Co(NH_3)_6]^{3+}$** in aqueous acidic media is thermodynamically highly favoured but the process is kinetically highly disfavoured.

$$\left[Co(NH_3)_6\right]^{3+} + 6H_3O^+ \rightleftharpoons \left[Co(OH_2)_6\right]^{3+} + 6NH_4^+, \; \log K_{eq} \approx 25.0$$

The tremendous thermodynamic driving force for the forward reaction arises from the protonation of the basic NH_3 ligands, but the complex remains unchanged in a fairly strong acidic medium for weeks at room temperature. In fact, the salt $[Co(NH_3)_6]Cl_3$ can be crystallised from a hot aqueous solution of HCl without any noticeable decomposition. Thus, *stability of the complex arises not from the thermodynamic stability but from the kinetic stability.*

- **$[M(en)_3]^{3+}$ and $[M(bigH)_3]^{3+}$** (M = Cr, Co): The biguanide complex is more stable than the ethylenediamine complex but with respect to the acid catalysed dissociation reaction, $[M(bigH)_3]^{3+}$ reacts much faster than the $[M(en)_3]^{3+}$ complex.

$$\left[M(en)_3\right]^{3+} \xrightarrow{H_3O^+} \left[M\left(OH_2\right)_6\right]^{3+} + 3enH^+$$

$$\left[M(bigH)_3\right]^{3+} \xrightarrow{H_3O^+} \left[M\left(OH_2\right)_6\right]^{3+} + 3bigH_2^+$$

  In fact, $[Co(bigH)_3]^{3+}$ undergoes dissociation in an acidic medium at a measureable rate at 30°C (*cf*. D. Banerjea *et al*, *J. Inorg. Nucl. Chem.,* **26,** 1233, 1964) and $[Co(en)_3]^{3+}$ remains completely unchanged in l M $HClO_4$ at room temperature even for months.

  Note: The kinetic favour for dechelation of the biguanide ring arises from the *its possibility of protonation before ring opening* but such a protonation cannot occur prior to opening of the chelate ring for the ethylenediamine complex.

- To differentiate between the thermodynamic stability and kinetic stability, H. Taube has coined the kinetic terms: **lability** and **inertness.** The kinetically stable complexes are called the **inert complexes** while the kinetically unstable complexes are called the **labile complexes.** The simple terms — stable and unstable refer to the thermodynamic parameters.
- In ligand substitution reactions, the rate can span a very wide range of time scale — **nanosecond (ns) to years**.

$$[Cu(aq)]^{2+} + 4NH_3 \rightarrow \underset{\text{(blue purple)}}{[Cu(NH_3)_4]^{2+}},\ \textbf{(instantaneous)}$$

  $[Co(NH_3)_6]^{3+}$ or $[Co(en)_3]^{3+} \rightarrow$ Hydrolysis or aquation **(years)**

- *There is no sharp border line to distinct between the labile and inert complexes.* However, H. Taube has described the complexes as the **labile complexes** having $t_{1/2}$ (substitution half life) ≤ 30 s in a particular reaction while the complexes with $t_{1/2} > 30$ s as the **inert complexes.** Rate process for the inert complexes can be followed by the conventional techniques while for the labile complexes, it requires some special techniques (*e.g. stopped flow, P–jump, T–jump,* etc.). This is why, more information is available for the inert complexes.
- The lability or inertness depends on the **activation energy,** *i.e.* high activation energy imparts the inertness while low activation energy imparts the lability (*cf.* Fig. 4.1.1). The inertness or lability is determined by $\Delta G^{\neq}$ (**free energy of activation**).

  $\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$, $\Delta H^{\neq}$ = enthalpy of activation, $\Delta S^{\neq}$ = entropy of activation.

  The stability of a complex is determined by the free energy change (ΔG^{o}) (*cf.* Fig 4.1.1) in a reaction.

$$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o} = -RT \ln K_{eq}$$

  $\Delta G^{\neq}$ depends on the reaction pathway (*i.e.* reaction mechanism) while ΔG^{o} depends on the difference in standard free energy of the reactant and product.

Labile and inert complexes of 3*d*–series

It depends on the d^n–configuration for a particular oxidation state.

Labile centres: d^0, d^1, d^2, d^4 (h.s.), d^5 (h.s.), d^6 (h.s.), d^7, d^8, d^9

Inert centres: d^3, d^4 (l.s.), d^5 (l.s.), d^6 (l.s.)

These can be explained by CFT. These aspects will be discussed later.

5.5 NUCLEOPHILICITY *vs.* BASICITY; ELECTROPHILICITY

- It has been already mentioned that the nucleophiles are basically the Lewis bases but the term **basicity** (measured with respect to H^+ in terms of the pK_a value of the corresponding conjugate

acid, YH^+) refers to the thermodynamic concept (*i.e.* equilibrium concept). The analogous kinetic term is called **nucleophilicity** (nucleophile = nucleus loving). In an associative pathway, the entering nucleophile (*i.e.* entering ligand) makes a bond with the metal centre in producing the **activated complex or transition state**. The *kinetic ease* with which a nucleophile can attack the metal centre to produce the activated complex gives the measure of its nucleophilicity. Relative nucleophilicity of a particular ligand L is measured with reference to that of a standard ligand L^0 by comparing their rates of substitution reaction (occurring through the **associative process**) at a chosen metal centre, *i.e.*

$$\text{Nucleophilicity of } L = \frac{\text{rate of substitution by } L}{\text{rate of substitution by } L^0}$$

The details of nucleophilicity scale will be discussed later (*cf.* Sec. 5.30.5)

The Lewis acids act as *electrophiles.*

- **Acidity** is a thermodynamic term while the analogous kinetic term is **electrophilicity** (electrophile = electron loving). The rate of reaction of a Lewis acid (*i.e.* metal centre in the complexes) with the Lewis bases (*i.e.* entering ligands or entering nucleophiles) gives the measure of the electrophilicity of the Lewis acid. Just like the relative nucleophilicity scale, a relative electrophilicity scale can be generated.

5.6 METHODS OF FOLLOWING KINETICS (*i.e.* RATE MEASUREMENT)

(1) For the inert systems, conventional techniques like: UV-visible spectroscopic method, potentiometry, conductometry, polarography, polarimetry, titrimetry, etc. can be used to follow the rate process. In fact, reactions of the complexes of Cr(III), Co(III), Rh(III), Ir(III), Pt(II), Pt(IV), some complexes of Ni(II), etc. can be studied by the conventional techniques. Some examples are given below.

- **Direct chemical analysis:** Direct chemical estimation of either the reactants or products at regular intervals during the progress of reaction is possible in many cases.

(a) $[PtCl(NH_3)_3]^+ + H_2O \rightarrow [Pt(NH_3)_3(OH_2)]^{2+} + Cl^-$

(b) $[CoCl_2(en)_2]^+ + H_2O \rightarrow [CoCl(en)_2(OH_2)]^{2+} + Cl^-$

(c) $[Co(NCS)(NH_3)_5]^{2+} + OH^- \rightarrow [Co(NH)_5(OH)]^{2+} + SCN^-$

(d) $[Co(NH_3)_5(S_2O_3)]^+ + L \rightarrow [Co(L)(NH_3)_5]^{n+} + S_2O_3^{2-}$

(L = different nucleophiles)

Here, we shall illustrate the direct chemical estimation of one of the products in the above reactions.

In the reactions (a) and (b), the released Cl^- can be estimated by *argentometry* (*i.e.* titration by $AgNO_3$) or by *potentiometry* (using an electrode reversible with respect to Cl^-, *e.g.* Ag/AgCl electrode). However, there is a possibility by the *direct attack* of Ag^+ *on the bound* Cl^- (*i.e.* overestimation of Cl^-) in the *argentometry method*. This can be minimised, if it is carried out at low temperature and in a mixed solvent like acetone-water mixture. In the reaction (c), released SCN^- can be also estimated similarly by titration with $AgNO_3$. In the reaction (d), the released $S_2O_3^{2-}$ can be estimated iodimetrically as usual.

- **Spectrophotometric method:** Generally, the coordination compounds are coloured and concentration of a coloured coordination compound can be determined from the optical density measurement at a suitable wavelength (A = optical density = εCl, ε = molar extinction coefficient, C = molar concentration, l = optical path length). Generally, in a particular reaction, the absorption spectra of the product and reactant are different and the most suitable wavelength for the optical density measurement is the wavelength at which absorption of the reactant and product differs most.

If the measured optical density (*OD*) is due to a particular compound whose formation or decay experiences a first order kinetics then the plot of $\log\frac{A_0 - A_\infty}{A_t - A_\infty}$ *vs.* t (time) will give the first order rate constant.

$A_t = OD$ at time t; $A_0 = OD$ at zero time; $A_\infty = OD$ at infinity (*i.e.* at the end of the reaction).

Note: For a first-order reaction, we can write:

$$C_t = C_0 \exp(-kt), \textit{ i.e. } \ln\frac{C_t}{C_0} = -kt \text{ or, } 2.303\log\frac{C_t}{C_0} = -kt \text{ and } k = \frac{2.303}{t}\log\frac{a}{a-x}$$

$C_0 = a$ = initial concentration (*i.e.* $t = 0$), $C_t = (a - x)$
= concentration at t.

If a physical property P (like *OD*), directly proportional to its concentration is available, then we can write:

$$k = \frac{2.303}{t}\log\frac{P_0 - P_\infty}{P_t - P_\infty}\text{ ; slope of the plot, } \log\frac{P_0 - P_\infty}{P_t - P_\infty} \textit{ vs. } t \text{ is } \frac{k}{2.303}$$

● **Electrometric method** (*i.e.* measurement of conductance, emf, pH, etc.): In the following aquation reactions, conductance increases remarkably during the progress of reaction.

$$[CoCl_2(en)_2]^+ + H_2O \rightarrow [CoCl(en)_2(OH_2)]^{2+} + Cl^-$$
$$[PtCl(NH_3)_3]^+ + H_2O \rightarrow [Pt(NH_3)_3(OH_2)]^{2+} + Cl^-$$

Thus conductance measurement with time can be practised to study the above reactions. The rate of Cl^- release can also be measured potentiometrically by using an electrode sensitive to Cl^-.

In the following reaction, during the progress of reaction, pH decreases due to the release of H^+ ion.

$$M^{2+} + LH \rightarrow ML^+ + H^+$$

Thus the pH measurement with time can evaluate the rate constant of the process.

● **Polarimetric method:** The measurement of optical rotation with time can be used to determine the rate constant of a racemisation processes.

$$\Delta\text{-}\left[Co\left(big\,H\right)_3\right]^{3+} \rightleftharpoons \Lambda\text{-}\left[Co\left(big\,H\right)_3\right]^{3+}$$

It should be taken into consideration that the light used in the optical rotation measurements may accelerate the isomerisation process in some cases. In such cases, the method becomes erratic.

● **Isotope tracer technique:** The electron exchange reactions in the couples like $[Ru(NH_3)_6]^{3+}/[Ru(NH_3)_6]^{2+}$, $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$, $[Fe(OH_2)_6]^{3+}/[Fe(OH_2)_6]^{2+}$, etc. may be followed by using the labelled isotope (see Secs. 6.1, 6.3.2). Isotopic tracer techniques may also be used to follow the metal exchange and ligand exchange reactions (see Sec. 5.12).

(2) For following the fast reactions of labile centres, it needs some special techniques like stopped-flow spectrophotometry, T–jump, P–jump, NMR, etc. depending on the $t_{1/2}$ of the reactions.

● **Stopped-flow spectrophotometry:** In the stopped-flow technique, the mixing time between the reactants is about 1 ms (*i.e.* 10^{-3} s) and the reactions faster than the mixing time cannot be studied by the stopped-flow spectrophotometry. In the stopped-flow spectrophotometry, after mixing of the reactants within the reaction cell, progress of the reaction can be followed spectrophotometrically with the help of a fast recorder device.

● **Perturbation technique (*i.e.* T–jump, P–jump):** This technique is applicable for the reactions of $t_{1/2}$ in the time scale of μs (= 10^{-6} s). In this technique, the equilibrium is perturbed suddenly (within a fraction of a μs or less) by a temperature change, *ca.* 5 – 10°C (in T–jump) or a pressure change, *ca.* a few hundred atmospheres (in P–jump). This change of temperature or pressure directs the equilibrium in a direction as demanded by *Le Chatelier's principle.* **This relaxation of the system towards the**

new equilibrium position can be followed spectrophotometrically by using a fast recorder device. This is why, this perturbation technique is referred to as the **relaxation technique.**

It measures the **relaxation time** (τ) which is the time required for a reaction to cover a certain fraction of the path towards the new equilibrium state. For the following type of reaction, we have:

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B,\ \Delta x_t = \Delta x_0 \exp(-t/\tau),\ \text{where } \tau = \frac{1}{k_1 + k_{-1}}$$

Here Δx_o is the perturbation or departure from the equilibrium immediately after the T-jump and Δx_t measures the departure from the new equilibrium state at the time t after the perturbation of the old equilibrium state (see Fig. 5.6.1). **Whatever may be the order of the reaction, relaxation towards the new equilibrium state always occurs exponentially like a first order reaction**.

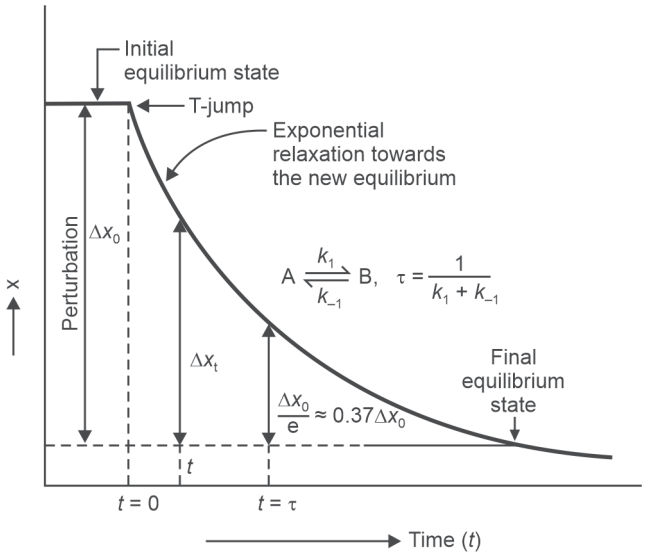


Fig. 5.6.1: Illustration of the exponential relaxation towards the new equilibrium after a perturbation as in a T-jump technique. Here x is a measurable quantity like absorbance that varies linearly with the composition of the system

Relaxation time (τ) corresponds to $\Delta x_0/\Delta x_t = e$, *i.e.* $\ln(\Delta x_0/\Delta x_t) = 1$. Thus relaxation time is the time taken by the system to drop the deviation (Δx_t) to $1/e$ (≈ 0.368) times the initial deviation (Δx_o). The expression of τ depends on the nature of reaction. By using the T-jump technique, the following reaction has been studied.

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

After T-jump, **conductivity** increases with time and the relaxation process can be followed by measuring the conductivity ($\tau \approx 3.7 \times 10^{-5}$ s at 25°C). From this τ value, the second order rate constant for the combination of H_3O^+ and OH^- is found to be 1.4×10^{11} dm^3 mol^{-1} s^{-1} which is a very high value (the **fastest reaction in solution phase**). This is, in fact, a diffusion controlled process.

It may be mentioned that the T–jump technique can be applied to all systems (assuming $\Delta H° \neq 0$) but the P-jump technique can only be applied to the systems where there is a change in the number of species in the reaction (more correctly, **where there is a molar volume change**). P-jump technique has been utilised for the rate constant measurement of the reaction, $H^+ + OH^- \rightarrow H_2O$ ($k = 1.5 \times 10^{11}$ M^{-1} s^{-1}, 25°C). **This is the fastest reaction known in solution** and it is controlled by the rate of diffusion of the involved ions in solution. This is why, reaction between the strong acid and strong base occurs in no time.

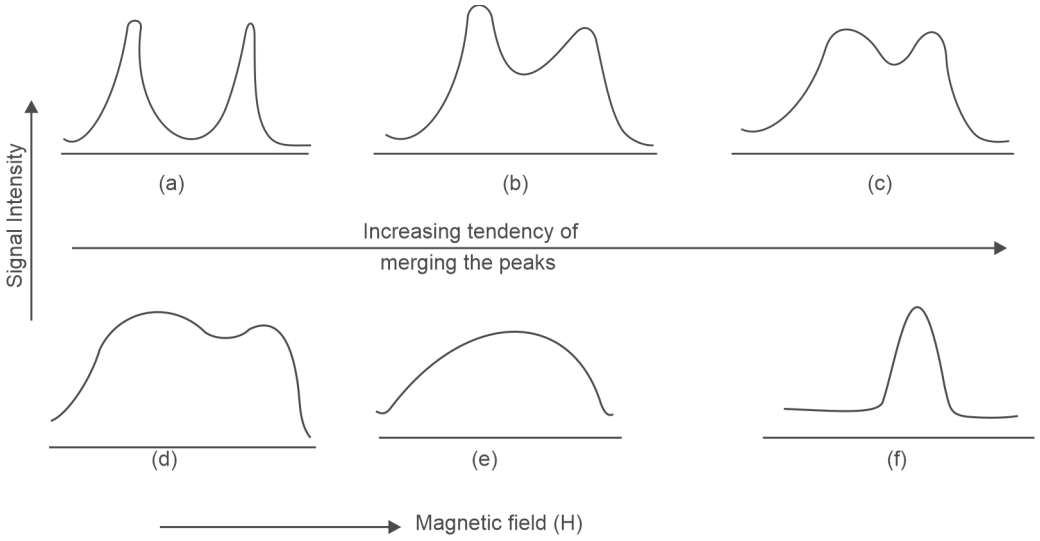


Fig. 5.6.2: Change of the NMR signals with the gradual increase of exchange rates (*e.g.* PMR signals in the proton exchange process between the two sites X—H and Y—H) from (a) → (f). (a) Exceedingly slow exchange rate (*i.e.* practically no exchange); (b) to (e) Gradually increasing rate; (f) Very rapid exchange rate (*see* Sec. 3.15, Fig. 3.15.1 in Vol. 7).

Temperature dependence of the equilibrium constant can be expressed by **van't Hoff relation** (see Sec. 5.19.3)

$$\frac{d \ln K_{eq}}{dT} = \frac{\Delta H^\circ}{RT^2}, \textit{ i.e. } \ln K_{eq} = -\frac{\Delta H^\circ}{RT} + \text{constant}$$

$$\text{or} \quad \ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H^\circ}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\Delta G^\circ = -RT \ln K_{eq} = \Delta H^\circ - T\Delta S^\circ$$

$$\text{or} \quad \ln K_{eq} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} = -\frac{\Delta H^\circ}{RT} + \text{constant}$$

● **NMR technique** (*cf.* Sec. 3.15, Vol. 7): For the studies of *fast exchange reactions* (both ligand exchange and metal exchange), the NMR method is very much important. For the studies of water exchange reactions, $^{17}OH_2$ is used. The NMR spectra of a particular NMR-active centre depends on its chemical environment. Thus the NMR spectra of ^{17}O are different for metal bound $^{17}OH_2$ and free $^{17}OH_2$ present in bulk solvent. If the water exchange rate is slow, then the NMR signals of ^{17}O for two different chemical environments are quite distinct. *But with the increase of exchange rate, the signals will move to merge or overlap* (*i.e.* the peak will be broadening). If the exchange rate is extremely fast, then a single peak is noticed. Thus from the nature of merging the peaks, it is possible to determine the exchange rate constant. Merging of peaks due to an exchange reaction is qualitatively shown in Fig. 5.6.2.

5.7 MECHANISM OF LIGAND SUBSTITUTION REACTION: INTIMATE AND STOICHIOMETRIC MECHANISM

● **Stoichiometric mechanism:** It deals with the *sequence of elementary steps* leading to a chemical reaction. It looks at the *reactants, products* and *intermediates* but not at the transition states. Thus the stoichiometric mechanism looks at the species residing at the **potential minima** along the reaction

coordinates. Consideration of the involved elementary steps can lead to the rate law. There are three types of stoichiometric mechanism of ligand substitution reaction. These are:

Dissociative (*D*), Interchange (*I*) and Associative (*A*)

Dissociative and associative reactions are the **two-step reactions** passing through an **intermediate,** while interchange reaction is a **one-step reaction** without the formation of a **true intermediate.**

● **Intimate mechanism:** It deals with the *activation process* leading to the formation of an activated complex at the rate determining step. It looks at the species residing at **the highest point (***i.e.* activated complex or transition state) on the reaction coordinate. Thus it considers the *energetics of the formation of the activated complex* and *consequently the rate.*

If the rate of formation of the activated complex at the **rate determining step** (*rds*) (*i.e.* slowest reaction step) depends strongly on the nature of the entering ligand (say *L*) then it indicates that the entering ligand makes a new bond to a significant extent to generate the activated complex. Thus the *activation process* is **associative (*a*)**. On the other hand, if the reaction rate is strongly dependent on the nature of the leaving group (say *X*) and almost independent of the nature of enterging group (*L*), then it indicates that bond breaking by the leaving group is important (*i.e. rds*) to generate the activated complex. Thus the *activation process* is ***dissociative* (*d*)**.

Here it is worth mentioning that the **associative activation** and **dissociative activation** are denoted by ***a*** and ***d*** respectively (not by ***A*** and ***D*** which denote the stoichiometric associative and dissociative reaction mechanisms respectively).

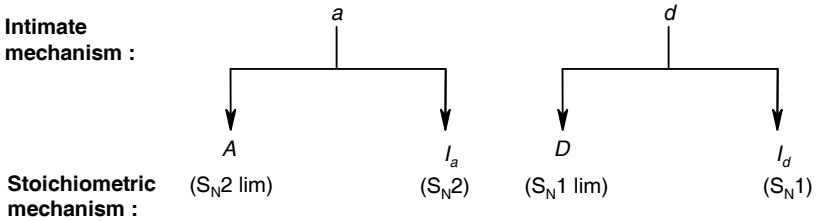
● **Relationship between the stoichiometric and intimate mechanism: *D* mechanism** must involve the **dissociative** (***d***) **activation** while ***A* mechanism** must involve the **associative** (***a***) **activation. *I* mechanism** involves **both the dissociative and associative activation,** *i.e.* both bond breaking by the leaving group and bond formation by the entering group contribute to the rate determining step. If in this process of activation, bond breaking (*i.e.* dissociative activation) is the predominant factor then it is referred to as I_d. On the other hand, if in the interchange process, bond formation (*i.e.* associative activation) by the entering group is the predominant factor then it is referred to as I_a.

Thus the **combined notations** describing both the stoichiometric and intimate mechanisms are:

$$\boldsymbol{A, I_a, I_d, D}\ \textbf{(Langford-Gray notation)}$$

● **Relationship between Langford-Gray notation and Hughes-Ingold notation used in organic chemistry:** According to Basolo and Pearson, *A mechanism* is equivalent to $\mathbf{S_N2}$ **lim**. (*i.e.* limiting situation of S_N2) while *D mechanism* is equivalent to $\mathbf{S_N1}$ **lim**. I_a and I_d correspond to S_N2 (not limiting) and S_N1 (not limiting) respectively.

Note: $S_N1 \Rightarrow$ substitution nucleophilic unimolecular; $S_N2 \Rightarrow$ substitution nucleophilic bimolecular.



● For both the ***D*** and $\boldsymbol{I_d}$ processes, the intimate mechanism is ***d*** (*i.e.* ***d***-activation) but for the *D*–process, the intermediate (*i.e.* **long life time**) of lower coordination number is detectable while the intermediate is not detectable (*i.e.* **very small life time**) for the I_d process. Thus their stoichiometric mechanisms (*i.e.* sequence of elementary steps) differ, *i.e.* single step (I_d) *vs.* two steps (*D*) (cf. Fig. 5.8.1)

● Similarly for both the ***A*** and $\boldsymbol{I_a}$ processes, the intimate mechanism is ***a*** (*i.e.* ***a***–activation). The intermediate of higher coordination number is detectable for the ***A***–pathway but not for the I_a–pathway. Thus their stoichiometric mechanisms (*i.e.* sequence of elementary steps) differ, *i.e.* single step (I_a) *vs*. two steps (*A*) (*cf*. Fig. 5.8.1).

● **Cases involving a fast *pre-equilibrium step* followed by the rate determing step (*rds*):** The fast pre-equilibrium step may lead to the formation of reactive intermediates like **ion pair (IP), conjugate base (CB), conjugate acid (CA),** etc. and then these reactive intermediates participate at the rate determining steps. In such cases, notation of the reaction mechanism depends on both the nature of the reactive intermediate (formed in a rapid pre-equilibrium step) and the nature of rate determining step (*rds*) involving the reactive intermediate. This aspect is illustrated below.

$$\text{Reactants} \rightleftharpoons \text{Intermediate} \left(\text{fast pre-equilibrium}\right)$$
$$\Big\downarrow rds$$
$$\text{Product}$$

Notation of the mechanism: Nature of the rds (*i.e. A* or *D* or *I*) – nature of the intermediate (*i.e.* IP or CA or CB).

If the intermediate is *IP*, and the rds is an *A*–pathway, then the mechanism is designated by ***A–IP*** (*i.e.* ***S_N2–IP*** in old nomenclature). Similarly, we can have:

***D–IP* (*i.e.* S_N1 lim*–IP,* in short S_N1*–IP*)** meaning *IP* as the reactive intermediate, and rds as the *D*-pathway;

***D–CA* (*i.e.* S_N1 lim*–CA,* in short S_N1*–CA*)** meaning *CA* as the reactive intermediate and rds as the *D*-pathway;

***D–CB* (*i.e.* S_N1 lim*–CB,* in short S_N1*–CB*)** meaning *CB* as the reactive intermediate, and rds as the *D*-pathway;

Similarly, we can write: ***I_d–CB, I_d–IP, I_a–IP***, etc.

● **Pre-equilibrium step *vs*. steady-state (*i.e.* stationary-state) approximation:** In a consecutive reaction, steady-state approximation is applied under the condition: **rate of formation of the reactive intermediate is much slower than the rate of disappearance of the reactive intermediate**. Under this condition, the intermediate disappears as soon as it is formed and consequently, **there is no build-up of the concentration of the intermediate**. In other words, it finds no time to get accumulated during the reaction. Consequently, **very small concentration of the intermediate is assumed to remain constant** so long the formation of the intermediate continues.

On the other hand, if **the rate of formation of the intermediate is faster than the rate of its disappearance**, then there is a gradual build-up of its concentration in the system and very soon, it attains an equilibrium condition with the reactants. The intermediate remaining in an equilibrium transforms into the product slowly. Under this condition, during the progress of reaction at any time, concentration of the intermediate can be considered as the **equilibrium concentration of the intermediate** and its concentration can be expressed in terms of the equilibrium constant (K_{eq}) and concentration of the reactants. This is described as the **pre-equilibrium concept**.

Let us consider the following consecutive reaction to illustrate the pre-equilibrium concept and steady-state approximation for the concentration of the intermediate (*C*).

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C \xrightarrow{k_2} \text{product}$$

Pre-equilibrium step: If k_1 and k_{-1} are much higher than k_2, then the first step is called the **pre-equilibrium step** and concentration of the intermediate (*C*) remaining in an equilibrium with the reactants *A* and *B* is expressed as follows:

$$K_{eq} = \frac{[C]}{[A][B]}$$ (assuming the forward and backward reactions to be the **elementary reactions** to express $K_{eq} = k_1/k_{-1}$

Rate of the reaction = $k_2[C] = k_2K_{eq}[A]$ [B]

Here $[A]$, $[B]$ and $[C]$ denote their respective equilibrium concentrations that can be expressed in terms of the initial concentrations of A and B, *i.e.* $[A]_0$ and $[B]_0$ respectively.

From the **mass balance relation**, we can write from the stoichiometry of the reaction:

$$[A]_0 = [A] + [C] \text{ and } [B]_0 = [B] + [C]$$

i.e. $$[A] = [A]_0 - [C] \text{ and } [B] = [B]_0 - [C]$$

Under the condition, $[A]_0 \gg [B]_0$, we can reasonably write:

$$[A]_0 \approx [A] \text{ and } [B] = [B]_0 - [C]$$

$$K_{eq} = \frac{[C]}{[A][B]} = \frac{[C]}{[A]_0\{[B]_0 - [C]\}}$$

i.e. $K_{eq}[A]_0[B]_0 - K_{eq}[A]_0[C] = [C]$

or $$[C] = \frac{K_{eq}[A]_0[B]_0}{1 + K_{eq}[A]_0}$$

$$\text{Rate} = k_2[C] = \frac{k_2 K_{eq}[A]_0[B]_0}{1 + K_{eq}[A]_0}$$

Steady-state or stationary-state approximation: If k_2 is comparable to k_1 and k_{-1}, then steady-state approximation can be applied to express the concentration of the intermediate (C) whose **very small concentration remains constant during the reaction**.

$$\frac{d[C]}{dt} = 0 = k_1[A][B] - k_{-1}[C] - k_2[C], \; i.e. \; [C] = \frac{k_1[A][B]}{k_{-1} + k_2}$$

$$\text{Rate} = k_2[C] = \frac{k_1 k_2[A][B]}{k_{-1} + k_2}$$

Under the condition, $k_{-1} \gg k_2$, we can write:

$$\text{Rate} = \frac{k_1 k_2[A][B]}{k_{-1} + k_2} \approx \left(\frac{k_1}{k_{-1}}\right) k_2[A][B] = K_{eq} k_2[A][B]$$

Thus, the **rate equation of steady-state approximation transforms into the rate equation for the pre-equilibrium concept under the condition,** $k_{-1} \gg k_2$.

The rate equation for the steady-state approximation can be expressed in terms of the initial concentrations of the reactants, *i.e.* $[A]_0$ and $[B]_0$.

Under the condition, $[A]_0 \gg [B]_0$ we can write:

$$[A]_0 = [A] + [C] \approx [A] \text{ and } [B]_0 = [B] + [C], \; i.e. \; [B] = [B_0] - [C]$$

$$\frac{d[C]}{dt} = 0 = k_1[A][B] - k_{-1}[C] - k_2[C], \text{ or } k_1[A][B] = [C](k_{-1} + k_2)$$

or $$k_1[A]_0\{[B]_0 - [C]\} = [C](k_{-1} + k_2)$$

or $$k_1[A]_0[B]_0 = [C](k_{-1} + k_2) + k_1[C][A]_0$$

or $$[C] = \frac{k_1[A]_0[B]_0}{k_1[A]_0 + (k_{-1} + k_2)}$$

$$\text{Rate} = k_2[C] = \frac{k_1 k_2[A]_0[B]_0}{k_1[A]_0 + (k_{-1} + k_2)}$$

(*cf.* **Michaelis-Menten equation** in enzyme kinetics)

● **Derivation of rate equation for a reversible reaction:** Let us first consider the following 1st order reversible reaction.

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} P,\ K_{eq} = \frac{k_1}{k_{-1}} = \frac{[P]_e}{[A]_e}$$

$$\frac{d[P]}{dt} = -\frac{d[A]}{dt} = k_1[A] - k_{-1}[P],$$

$$[A]_0 + [P]_0 = [A]_t + [P]_t = [A]_e + [P]_e \text{ (mass balance)}$$

Combining the above relations, we can write:

$$[A]_t + [P]_t = [A]_e + [P]_e$$

or
$$[A]_t = [A]_e + [P]_e - [P]_t$$
$$= [A]_e + \frac{k_1}{k_{-1}}[A]_e - [P]_t$$

i.e.
$$[P]_t = [A]_e\left(1 + \frac{k_1}{k_{-1}}\right) - [A]_t$$

$$-\frac{d[A]_t}{dt} = k_1[A]_t - k_{-1}[P]_t$$
$$= k_1[A]_t - k_{-1}\left\{[A]_e\left(1 + \frac{k_1}{k_{-1}}\right) - [A]_t\right\}$$
$$= k_1[A]_t - k_{-1}[A]_e - k_1[A]_e + k_{-1}[A]_t$$
$$= [A]_t(k_1 + k_{-1}) - [A]_e(k_1 + k_{-1})$$
$$= ([A]_t - [A]_e)(k_1 + k_{-1})$$

or
$$-\frac{d[A]_t}{([A]_t - [A]_e)} = (k_1 + k_{-1})dt$$

Integration of the above equation gives:

$$-\ln([A]_t - [A]_e) = (k_1 + k_{-1})t + I \text{ (constant of integration)}$$

Under the boundary condition: at $t = 0$, $[A]_t = [A]_0$

i.e.
$$I = -\ln([A]_0 - [A]_e)$$

It gives: $$\ln\left(\frac{[A]_t - [A]_e}{[A]_0 - [A]_e}\right) = -(k_1 + k_{-1})t$$

Negative slope of the linear plot of $\ln([A]_t - [A]_e)$ *vs.* t) (time) gives the observed rate constant (k_{obs}) as:

$$-\text{slope} = k_{obs} = k_1 + k_{-1}$$

Now let us consider the following complex formation reaction.

$$M + L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ML,\ K_{eq} = \frac{k_1}{k_{-1}} = \frac{[ML]_e}{[M]_e[L]_e}$$

Under the **pseudo-first order condition**, $[L]_0 \gg [M]_0$, we can write:

$$[M]_0 + [L]_0 + [ML]_0 = [M]_t + [L]_t + [ML]_t = [M]_e + [L]_e + [ML]_e$$
$$\text{and} \quad [L]_0 \approx [L]_t \approx [L]_e \text{ (mass balance)}$$

$$[M]_t = [M]_e + [L]_0 + [ML]_0 - [L]_0 + [ML]_t$$

$$= [M]_e + \frac{k_1}{k_{-1}}[M]_e[L]_e - [ML]_t$$

$$\text{or } [ML]_t = [M]_e + \frac{k_1}{k_{-1}}[M]_e[L]_e - [M]_t$$

$$\frac{d[ML]_t}{dt} = -\frac{d[M]_t}{dt} = k_1[M]_t[L]_t - k_{-1}[ML]_t$$

$$i.e. -\frac{d[M]_t}{dt} = k_1[M]_t[L]_t - k_{-1}\left\{[M]_e + \frac{k_1}{k_{-1}}[M]_e[L]_e - [M]_t\right\}$$

$$= k_1[M]_t[L]_t - k_{-1}[M]_e - k_1[M]_e[L]_e + k_{-1}[M]_t$$

$$= [M]_t(k_1[L]_t + k_{-1}) - [M]_e(k_1[L]_e + k_{-1})$$

$$= ([M]_t - [M]_e)(k_1[L]_0 + k_{-1}), [L]_t \approx [L]_0 \approx [L]_e$$

$$\text{or } -\frac{d[M]_t}{([M]_t - [M]_e)} = (k_1[L]_0 + k_{-1})dt$$

Integration of the above equation leads to:

$$\ln\frac{[M]_t - [M]_e}{[M]_0 - [M]_e} = k_1[L]_0 + k_{-1}$$

Negative slope of the linear plot of ln ($[M]_t - [M]_e$) *vs*. *t* (time) gives the k_{obs} under the given pseudo-first order condition.

$$\text{slope} = k_{obs} = k_1[L]_0 + k_{-1}$$

From the plot of k_{obs} *vs*. $[L]_0$, the forward and backward rate constants can be calculated (Fig. 5.7.1). For this purpose, using different concentration of $[L]_0$ under the condition, $[L]_0 \gg [M]_0$, k_{obs} values are to be determined.

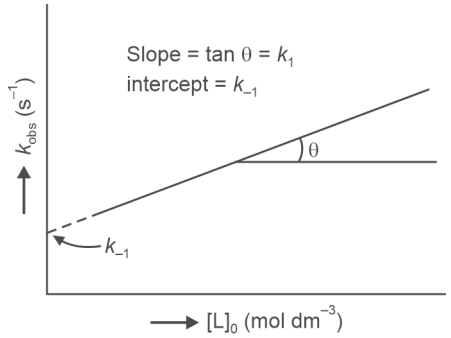


Fig. 5.7.1: Evaluation of forward and backward rate constants in a typical complexation reaction

5.8 ENERGY PROFILE DIAGRAMS FOR DIFFERENT STOICHIOMETRIC MECHANISMS

Energy profile (also known as **reaction profile)** diagram represents the plot, energy of the system *vs*.. **reaction coordinate** that indicates the extent to which the reaction process has occurred (simply, the progress of the reaction). The energy profile diagram indicates the positions of reactants, transition states, intermediates and products.

A. Associative (A) process: Two step reaction with two transition states and one intermediate

$$L_5M - X \xrightarrow[(rds)]{+Y} L_5M\begin{matrix}X\\ \diagup\\ \diagdown\\ Y\end{matrix} \xrightarrow[(\text{fast})]{-X} L_5M-Y$$

The entering ligand (Y) makes a new bond with the metal centre at the rate determining step (*rds*) to **increase the coordination number by unity.** In attaining this intermediate of higher coordination number, there is no bond breaking by the leaving group (X). After the rate determining step (rds), the leaving group (X) is lost from the intermediate at a faster step.

The reaction pathway involves the formation of a **single intermediate** ($Y—ML_5—X$) and **two transition states (T.S.)** — one for the formation of the intermediate and another for the decomposition of the intermediate to the product. The activation energy barrier for the decomposition of the intermediate is relatively lower.

B. Dissociative (*D*) process: Two step reaction with two transition states and one intermediate

$$L_5M - X \xrightarrow[(rds)]{-X} L_5M \xrightarrow[(fast)]{+Y} L_5M - Y$$

The leaving group (X) is lost at the rate determining step (*rds*) through the rupture of the $M—X$ bond to generate an intermediate (L_5M) with **a lower coordination number** (*i.e.* coordination number decreases by unity for the unidentate leaving group). At this stage of generation of the intermediate, there is no interaction with the entering ligand (Y). After the rate determining step, the entering group enters into the coordination sphere at a faster step to give the final product.

As in the *A* process, in the *D*–process also, there is **a single intermediate** but of lower coordination number, and **two transition states –** one leading to the formation of the intermediate and the other leading to the product from the intermediate. The activation energy barrier leading to the formation of the intermediate is higher.

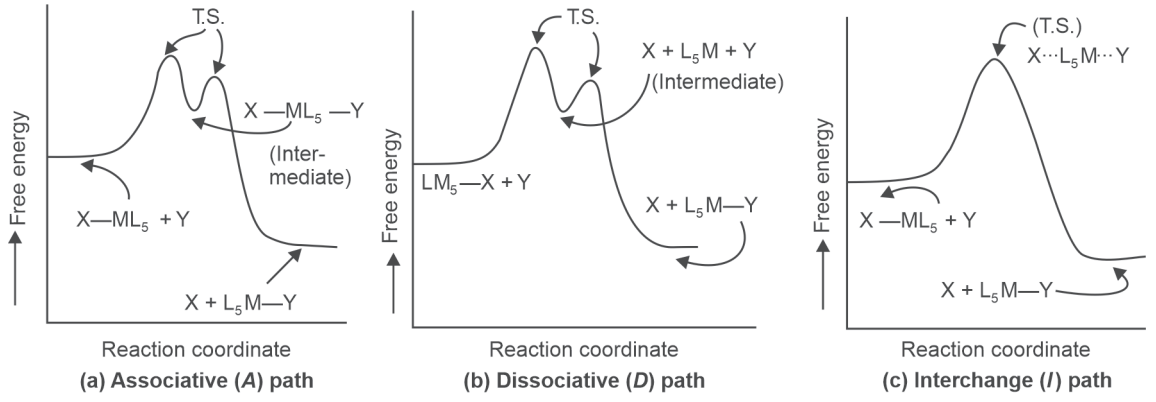


Fig. 5.8.1: Energy-profile (reaction profile) diagrams for the different mechanisms of ligand substitution reactions (see **Fig. 5.30.3.1** for different types of reaction profiles of square planar complexes)

Principle of microscopic reversibility: For a reversible process ($R \rightleftharpoons P$, say), it states that the mechanisms of a reversible reaction in microscopic detail are the same in both directions under the same conditions. According to this principle, the energy profile diagram for the forward reaction (R→P) will be traversed from the right to left for the reverse or backward reaction (P→R). Thus the same energy profile diagram can describe the pathways of both forward and backward reactions.