

Kinetics and mechanisms of inorganic reactions in solution



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Kinetics and reaction mechanisms in inorganic chemistry

Despite extensive study, inorganic chemistry has yet to achieve the understanding of reaction mechanisms enjoyed by organic chemistry; this situation can be attributed to the inherent difficulties involved in trying to systematize the reactions of more than one hundred elements. Even attempts to predict from one element to another in the same group are not always successful.

Ideally, chemists hope to understand a number of reaction mechanisms well enough that predictions about a diverse assortment of complexes involving different metals ligands, and reaction conditions can be made. To understand the kinetics of reaction mechanism the knowledge of kinetics terms is necessary.

Basic Terminology

As with most fields, the study of reaction kinetics has some terminology with which one must be familiar in order to understand advanced books and research papers in the area. The following is a summary of some of these basics terms and definitions. Many of these may be known from previous studies in the introductory and physical chemistry and further background can be obtained from text books devoted to the physical chemistry aspects of reaction kinetics.

Rate of a reaction:

The rate of change of concentration of reactants or products with time is called rate of reaction.

According to the reaction,

$$\frac{dx}{dt} = -kx \quad (\text{With respect to reactants})$$

$$\frac{dx}{dt} = kx \quad (\text{With respect to products})$$

Rate Law:

The rate law is the experimentally dependence of the reaction rate on reagent concentrations. It has the following general form. $Rate = k[A]^m[B]^n$. Where order of reaction is $m + n$ and k is proportionality constant called the rate constant. The exponent m and n are determined experimentally from the kinetic study and have **no necessary relationship to the stoichiometric coefficient** in the balanced chemical reaction. The rate law may contain species that do not appear in the balanced reaction and may be the sum of several terms for different reaction pathways. The rate law is an essential piece of mechanistic information because it contains the

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concentrations of species necessary to get from the reactant to the product by the lowest energy pathway. A fundamental requirement of an acceptable mechanism is that it must predict a rate law consistent with the experimental law.

Order of the rate law:

The order of the rate law is the sum of the exponents in the rate law. For example, if $m = 1$ and $n = -2$, then according to the above equations, the rate law has an overall order of -1 . However, except in the simplest cases, it is best to describe the order with respect to individual reagents. The order of a reaction is from $-ive$ to $+3$.

Rate constant:

The rate constant, k , is the proportionality constant that relates the rate to the reagent concentrations (or activities, or pressure, for example), as shown in the above equation. The units of k depend on the rate law and must give the right-hand side of the above equation, the same units as the left-hand side.

Half-time:

The half-time, $t_{1/2}$, is the time required for a reactant concentration to change by half of its total change. This term is used to convey a qualitative idea of the time scale for the reaction and has a quantitative relationship to the rate constant in simple cases. In complex system, the half-time may be different and one should specify the reagent to which the $t_{1/2}$ refers.

Lifetime: The life, for particular specie is the concentration of that species divided by its rate of disappearance. This term is commonly used in so-called lifetime method, such as NMR, and in relaxation method, such as temperature jump.

Analysis of Rate Data

In general, a kinetic study begins with the collection of data of concentration versus time of a reactant or product. As will be seen later, this can also be accompanied by determining the time dependence of some variable that is proportional to concentration, such as absorbance or NMR peak intensity. The next step is to fit the concentration-time data to some model that will allow one to determine the rate constant if the data fits the model. For this some integrated rates law must be encounter in inorganic kinetics.

So the main approach to the mechanism is the kinetic one, emphasis is placed on the rate measurements and their interpretations (Benson).

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Theories of reaction rates

According to the theory of absolute reaction rates, the reactants in a chemical reaction are in equilibrium with an energetic species known as the **activated complex**. The thermal energy required to make such a complex is called the **activation energy**. The activated complex occupies an energy level called the **transition state** which occurs at the point of higher energy on the path from one stable configuration to another as in fig-1(Benson). The full rate law will involve all species necessary to form the transition state. An intermediate is the species present at any valley on a reaction coordinate diagram. When a valley is shallow, it can be ambiguous whether or not an intermediate really is formed. In chemistry, an intermediate is expected to have a lifetime longer than a few vibrational lifetimes ($>10^{-3}$ s) and the valley should be deeper than the thermal energy ($RT = 2.5\text{kJ mol}^{-1}$ at 25°C).

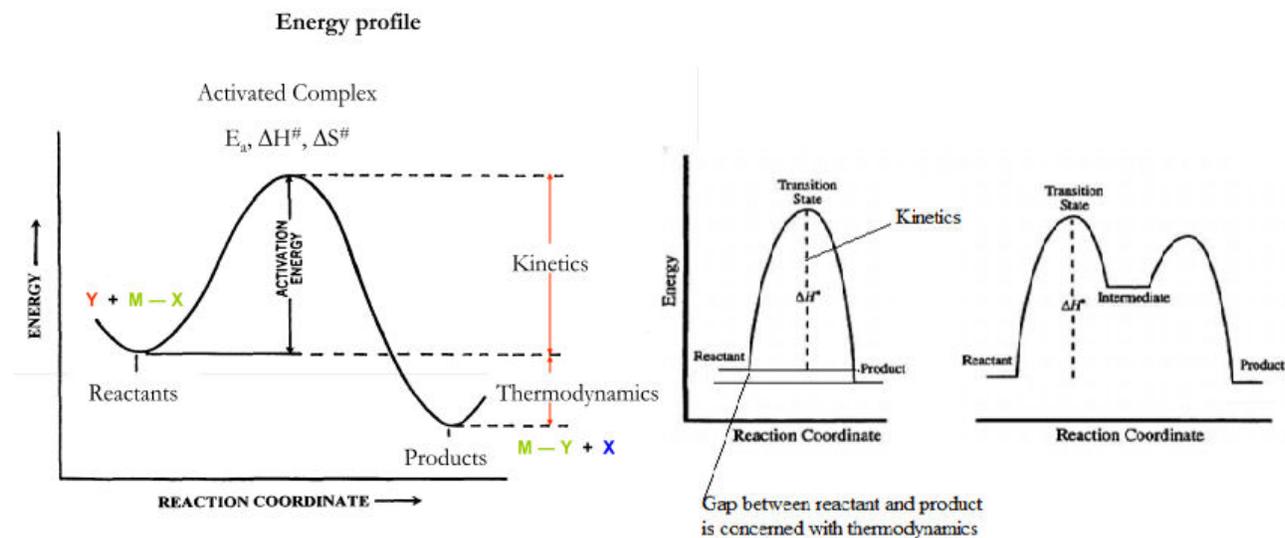


Figure 1 Reaction profile showing position of transition and intermediate state.

There are two paths of this diagram

1. Thermodynamic path.

Energy gap between reactant and product is concerned with thermodynamics. It deals with stability of product and possibility of reaction.

1. Kinetic path

Reaction gap between reactants and activated complex. Kinetics is supported by thermodynamics. If a reaction is feasible than what is the rate of the reaction? Here in this course we will be concerned with kinetics and not thermodynamics but thermodynamics act as a pioneer for kinetics. If the height of the transition state is greater than activation energy will also be high. It

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means the kinetics of the reaction is smaller (rate) and if the height of the energy profile diagram is smaller the rate of reaction is high. So kinetics tell us about rate and factors affecting rate of a reaction.

Rate of reaction on the basis of thermodynamic approach

Rate of reaction

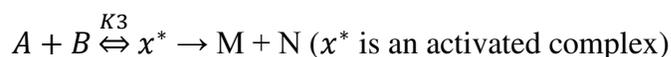
Rate of reaction is defined as rate of change of reactants or products per unit time.

Mathematically it can be represented as,

$$\frac{dx}{dt} = -\frac{d[R]}{d[t]} = \frac{d[P]}{d[t]}$$

Where x is small change in the concentration of reactants or products.

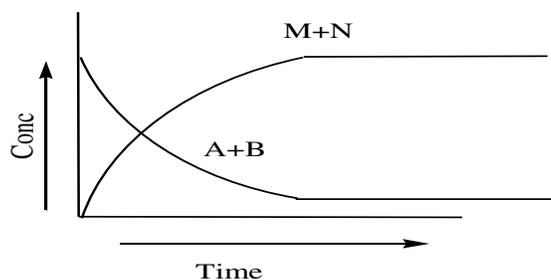
Let suppose a reaction given below as,



$$\frac{dx}{dt} (\text{rate}) = -k [A][B] \quad (\text{Rate of disappearance of reactants})$$

$$\frac{dx}{dt} = k[M][N] \quad (\text{Rate of appearance of product})$$

The above equations can be represented schematically as



Keeping in view the kinetics of a reaction there are two types of reactions

1. Fast reactions: those reactions



2. Slow reactions: Rusting of iron

3. Extremely slow reactions: decomposition of H_2O

Quantitatively the rate of passage from one stable state to the next can be derived from a thermodynamic approach.

Consider a simple reaction



$$\text{At equilibrium } [X^\#] = K^\# [A][B] \text{ or } [K^\#] = [X^\#]/[A][B] \quad (1)$$

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and we know that the rate of formation of product is

$$\frac{d[M]}{dt} = \frac{kt}{h} [X^\ddagger] \quad (2) \quad \text{Putting eq (1) in eq (2)} = \frac{d[M]}{dt} = \frac{kt}{h} [K^\ddagger][A][B] \quad \text{eq (3)}$$

$$\text{as } K_2 = \frac{k^\ddagger kt}{h} \text{ so eq (3) can be written as } \frac{d[M]}{dt} = K_2[A][B] \quad (4)$$

($K_2 =$ if the reaction is bimolecular from), in eq (4) A and B are concentrations but for very dilute solution we take activity (as in a reaction all molecules do not take part, these are only the active masses which are involved in a reaction).

Activity is directly related with concentration but activity is not equal to concentration

$a \propto C$ and $a = \gamma C$ where γ is called activity coefficient and can also be represented as f .

By replacing concentration eq (1) can be represented as $K^\ddagger_a = a_{X^\ddagger}/a_{A.a_B}$ eq (5a) and by putting

activity coefficient in eq (1) can also be written as $K^\ddagger_a = \gamma_{X^\ddagger}[X^\ddagger]/\gamma_A[A] \cdot \gamma_B[B]$ and also

$[X^\ddagger]/[A][B] = K^\ddagger_a / \gamma_{X^\ddagger} / \gamma_A \cdot \gamma_B = K^\ddagger_a \cdot \gamma_A \cdot \gamma_B / \gamma_{X^\ddagger}$ eq (5b). Now comparing eq (5b) with (1) we get

$$[K^\ddagger] = K^\ddagger_a \cdot \gamma_A \cdot \gamma_B / \gamma_{X^\ddagger} \quad \text{eq (6) now put the eq (6) in eq (3) to get eq (7) as}$$

$$\frac{d[M]}{dt} = \frac{kt}{h} = K^\ddagger_a \cdot \frac{\gamma_A \cdot \gamma_B}{\gamma_{X^\ddagger}} [A][B] = K_2^\ddagger \frac{\gamma_A \cdot \gamma_B}{\gamma_{X^\ddagger}} [A][B] \quad \text{eq (8) (as } K_2^\ddagger = \frac{kt}{h} K^\ddagger_a)$$

Equation (4) is in term of concentration where as eq (8) is in term of activity.

Now again starting from eq (3) we know that $\frac{d[M]}{dt} = \frac{kt}{h} [K^\ddagger][A][B] = K_2[A][B] = K_2 =$

$$\frac{\frac{kt}{h} [K^\ddagger][A][B]}{[A][B]} = \frac{kt}{h} [K^\ddagger] \quad \text{eq (9) Now putting the value of } [K^\ddagger] \text{ from eq (5a) into eq (9) we obtained}$$

$$K_2 = \frac{kt}{h} [a_{X^\ddagger}/a_{A.a_B}] \quad \text{eq (10). As } a = \gamma C \text{ so rearrange eq10 as } K_2 = \frac{kt}{h} \frac{[X^\ddagger]}{[A][B]} \cdot \frac{\gamma_{X^\ddagger}}{\gamma_A \cdot \gamma_B} \quad \text{eq (11). Putting}$$

$$\text{the value of } X^\ddagger \text{ from eq (1) we get } K_2 = \frac{kt}{h} \frac{[K^\ddagger]}{\gamma_A \cdot \gamma_B} \quad \text{eq (12)}$$

At infinite dilution the activity coefficient value become equal to 1. Eq (12) becomes as $K_2 = K_0$.

T. As K_0 is constant so K_2 is directly proportional to temperature which indicate that rate constant or rate of reaction depends on temperature. The factors of activity can be calculated by

Deby-Huckel equation

$-\log \gamma_i = Z_i^2 \beta \mu^{1/2} / 1 + \alpha \mu^{1/2}$. Here α and β are constants and its value is 0.51 at 25°C (in aqueous solution)

As a reaction is incomplete without thermodynamic parameters so applying thermodynamic

parameters $\frac{d[M]}{dt} = \frac{kt}{h} [K^\ddagger][A][B]$ as given below.

In term of Gibbs free energy of the activated complex (kinetic approach)

Gibbs free energy is the energy associated with a chemical reaction that can be used to do some useful work (it tell us about the spontaneity of a reaction). Under conditions of constant temperature and pressure, chemical change will tend to occur in whatever direction leads to a decrease in the value of the *Gibbs free energy*. This means, of course that if the total free energy G of a mixture of reactants and products goes through a minimum value as the composition changes, then all net change will cease the reaction system will be in a state of *chemical equilibrium*.

The free energy (available energy) G is a quantity that becomes more negative during the course of any natural process. Thus as a chemical reaction takes place, G only falls and will never become more positive. Eventually a point is reached where any further transformation of reactants into products would cause G to increase. At this point G is at a minimum (see the plot below), and no further net change can take place; the reaction is at equilibrium. Look in a molecule of glucose inside a human body. The entropy is minimum; the enthalpy is maximum and what about the free energy (available energy). When respiration takes place then glucose molecule is break down into CO_2 and H_2O so enthalpy decreases and entropy increases with the release of energy (called available energy) so Gibbs free energy also decreases (goes to negative). The energy released is used for useful work of human body.

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

If $\Delta G < 0$ reaction is spontaneous (farward direction), if $\Delta G > 0$ reaction is non spontaneous (backward direction) and if $\Delta G = 0$ reaction is at equilibrium.

$$\frac{d[M]}{dt} = \frac{kt}{h} e^{\left(-\frac{\Delta G^\ddagger}{Rt}\right)} [A][B] \quad (\text{In trem of Ginbbs free energy.})$$

In term of enthalpy and entropy of the activated complex (thermodynamic approach).

$$\frac{d[M]}{dt} = \frac{kt}{h} e^{\left(-\frac{\Delta S^\ddagger}{R}\right)} \frac{\Delta H^\ddagger}{Rt} [A][B]$$

It is noteworthy that kinetics and thermodynamics depends upon the media of the reaction. As we can see that for solid the equation $E = \Delta H + RT$ assume the form $E = \Delta H$ ($RT = 0$), as there are minimum motions (rotational etc) of the molecules within a crystal and for solution $E = \Delta H + RT$. The difference is very minor. $E = 10\text{-}20\text{kcal/mol}$ and $RT = 0.6\text{ Kcal/mol}$. It mean rate of reaction

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is affected by activation energy to a greater extent and not by ΔH^\ddagger . In the same way ΔG^\ddagger may be negative or positive depending upon the charges of the reactants at transition state and solvation.

Effect of entropy of activated complex (ΔS^\ddagger)/How to determine the entropy of activated complex with respect to reactants, solvent and product.

As during a reaction in solution charges play its role. ΔS^\ddagger is called entropy of activation, which is defined as the total entropy change of the reactants and solvent. Entropy may be positive or negative, it depends whether entropy of activation is increased or decreased. The entropy of activation is positive when entropy of activation of the activated complex is greater than reactants and entropy of activation is negative when entropy of activation of the activated complex is smaller than the reactants.

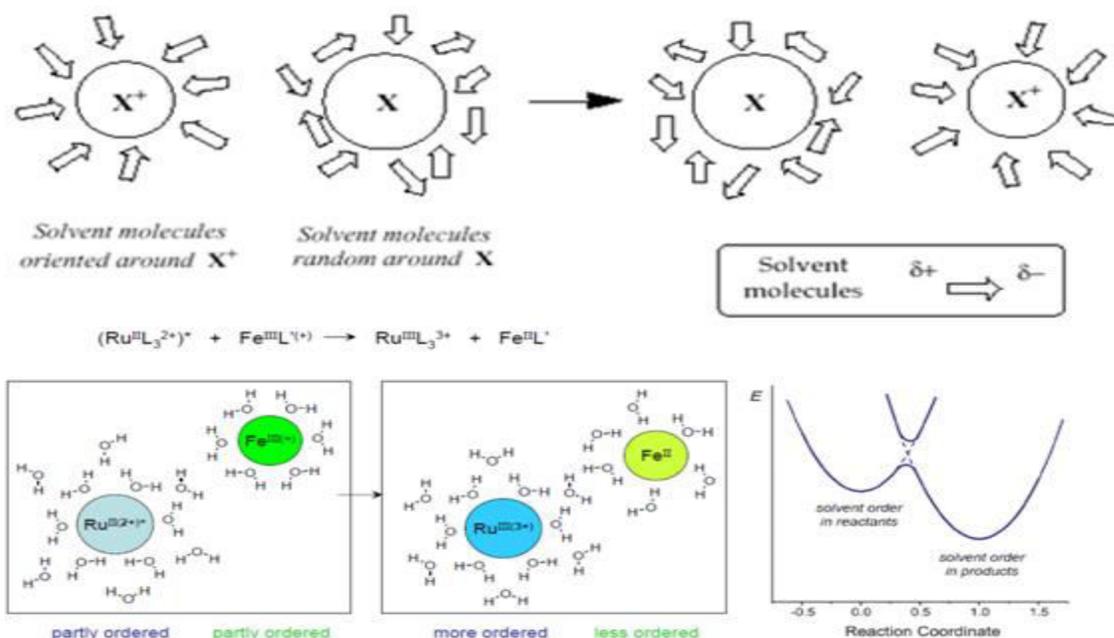


Figure 2: solvation process during a reaction

It can be determined from the charges on the reactants and solvent. If the charges on the reactants are opposite then the charges on the activated complex is less and hence less solvation and entropy of activated complex will be greater. The entropy of activation of the activated complex (ΔS^\ddagger) will be positive as less solvation would occur around the activated complex and the activated complex will be in order as compared to the reactants. If the reactants are of same

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charge then entropy of activated complex will be negative because less solvation would occur (Fig.2).

Differences between transition state and intermediate

Transition state

The highest energy level where activated complex reside in the energy profile diagram.

Activated complex

The chemical species in a chemical reaction that are always in equilibrium with the reactants but not with the product. Energy of the activated complex is higher than the reactants and dissociate to the product. It tells us about the rate of a reaction. Activated complex can reside anywhere on the energy profile diagram Fig (1).

Intermediate

A specie that is present at energy minima at the energy profile diagram (Fig 1). An intermediate can be isolated (organic chemistry) to elucidate the structure and mechanism of reaction can be suggested but as the intermediate in inorganic reactions are shortly lived and cannot be isolated (inorganic chemistry) so mechanism cannot be determined. Determination of intermediate is necessary to suggest reaction mechanism; therefore, different techniques are used. i.e spectroscopy, these techniques are useful up to some extent but for complete characterization some kinetics rules are incorporated.

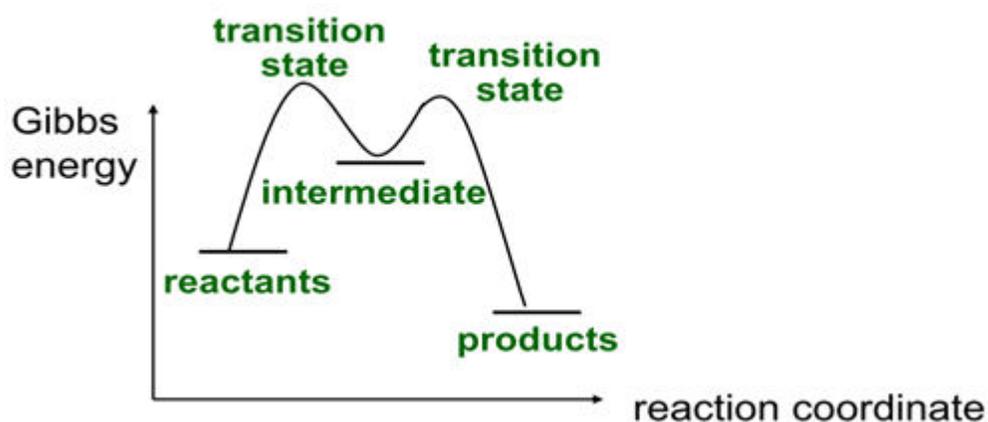


Figure 3: Intermediate and transition state: Reaction profile diagram for dissociative and associative reactions mechanism

How structure of intermediate or activated complex can be determined

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The structure of an intermediate can be determined by the entropy. If entropy of the reaction is equal to entropy of the activated complex ($\Delta S_{\text{reaction}} = \Delta S^{\#}_{\text{activated complex}}$). The structure of the intermediate will be more similar to the structure of the product. Activated complex can be determined by using Arrhenius equation which tells us about the activation energy. Once activation energy has been calculated, it means we are very close to the activated complex.

$$k = Ae^{-Ea/RT}$$

Where A is called Arrhenius constant.

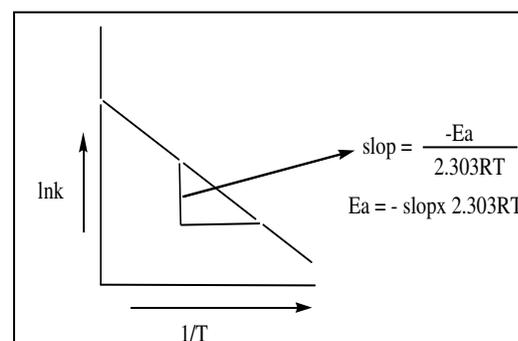
$$\ln k = \ln A + \frac{-Ea}{Rt} \quad \ln e = \ln k = \ln A - \frac{Ea}{R} \frac{1}{T}$$

Where K = rate constant

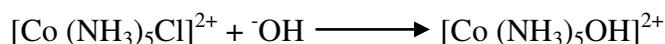
A = Arrhenius constant

Ea = activation energy

T = absolute temperature



But the problem is that only energy of activated complex has been determined and no structural information is available from this activation energy. For determination of structure entropy can be used. If $\Delta S_{\text{reaction}} = \Delta S^{\#}_{\text{activated complex}}$ then structure of the activated complex would be like the product but if $\Delta S_{\text{reaction}} \neq \Delta S^{\#}_{\text{activated complex}}$ then structure of the activated complex would be like that of reactants. eg. If entropy is not same.



$$\Delta S_{\text{reaction}} = -1.0 \text{ cal/deg.mol} \text{ and } \Delta S^{\#}_{\text{activated complex}} = +37 \text{ cal/deg.mol}$$

In this case structure is almost unknown and difficult to determine. This reaction is not simple bimolecular reaction but it is very much complicated due to

- i. The role of solvent

As we do not know about the nature of the solvent so very difficult to determine this reaction.

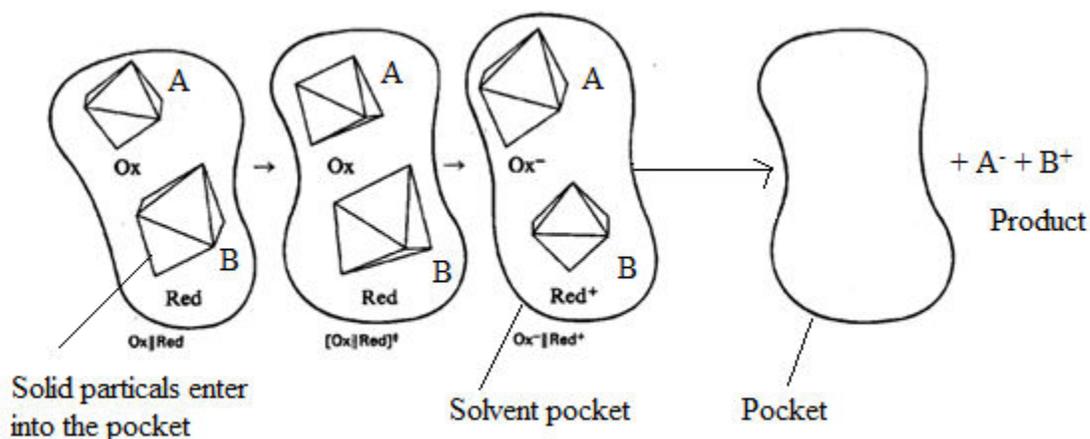
- ii. Role of stoichiometry

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If stoichiometry and rate law are not reinforcing each other this means reaction is not simple so it will mean that stoichiometry and rate law are not according to our theory.

How equilibrium is set up between reactants and products in gas phase reaction

In gas phase reaction the equilibrium is set up between reactants and products. In gas phase reaction there is 99.8% empty space but in solution the equilibrium is between reactants and activated complex. In solution there is 50% empty space, the remaining space is occupied by the solvent pocket. When reactants A and B come for collision in the reaction medium these are hindered by the solid particles of the reactants and solvent as well. If accidentally A (ox) and B (red) comes in these solvent particles collision takes place which lead to the reaction. It remains for 10^{-12} sec in the solvent pocket. As the energy of A and B are higher and when it come close in the solvent pocket then the thermal energy is increased to the extent to cross the barrier of energy; collision occurs and product is formed. Reaction speed depends on the activated complex.



Rate law and mechanism

Mechanism is defined as an actual pathway through which a reaction proceeds. Or a pathway in which we study all the stages between reactants and products. Mechanism depends upon kinetics. On the basis of mechanism inorganic reactions are divided into two types

1. Simple reactions

A reaction in which only one transition state is involved.

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1. Complex reaction

A reaction in which more than one transition stages are involved.

Rate law

The rate law is the experimentally determined dependence of the reaction rate on reagent concentration. It has the following general form



$$dx/dt \text{ (rate)} = k [A]^a [B]^b$$

Where k is proportionality constant called the rate constant. The exponents' m and n are determined experimentally from the kinetic study and have no necessary relationship to the stoichiometric coefficients in the balanced chemical reaction. The rate law may contain species that do not appear in the balanced reaction and may be the sum of several terms for different reaction pathways.

Order of rate law

The order of the rate law is the sum of the exponents in the rate law. Here $a+b$ is called order of reaction it ranges from -ive to 3. For example if $a=1$ and $b=-2$ in above equation, the rate law has an overall order of -1. If $a=2$ and $b=1$ then the overall order would be 3. However, except in the simplest cases, it is best to describe the order with respect to individual reagents. As we know that rate depends upon the concentration of solvent and stoichiometry, when rate (kinetics) of reaction changes then structure of intermediate also changes and when stoichiometry changes then rate law is also affected which effects rate of reaction. Depending upon the speed of various steps involved in a chemical reactions, reaction may be classified as

1. Simple reaction

If the speed of different steps in a chemical reaction is same than it is called simple complicated reaction.

2. Complicated reaction

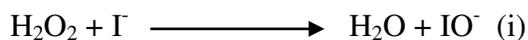
If the speed of different steps in a reaction is different than the reaction is called complicated reaction. As we know that in a reaction each step is different, so rate law depends on the slowest step and sometime rate law is determined by more than one step. To evaluate the rate determining step and eliminate the unnecessary steps steady state approximation is used.



Experimental rate law.

$$\frac{-dx}{dt} [\text{H}_2\text{O}_2] = \frac{dx}{dt} [\text{I}_3^-] = k_1 [\text{H}_2\text{O}_2] [\text{I}^-]$$

H^+ has no role because the reaction is complexed as the mechanism consists of more than one step.



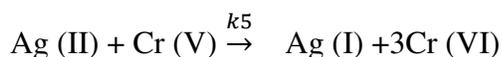
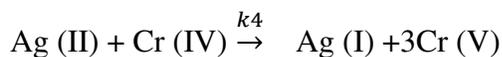
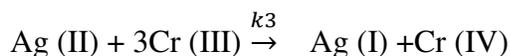
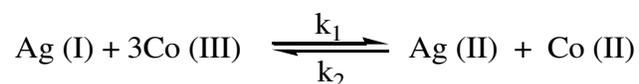
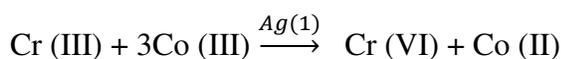
It is a complicated reaction and each step is different so rate law depends upon the slowest step (i) which is determined from the mechanism and it is very difficult in inorganic reaction. It is almost impossible experimentally but theoretically it can be found by the assumption of Bodestien for rate law determination in case a reaction consists of more than one step. This approximation is called steady state approximation. This approximation is then compared with the experimental calculations if the steady state approximation agree with the experimental rate law the mechanism is true otherwise false. For a complex reaction more than one reactions takes place for a single product formation so more than one constant are possible and 1st step rate constant is very slow than the 2nd and so on ($k_1 \ll k_2$). This law is applicable to reaction where intermediate are unstable so in the last equation there must not be an intermediate. The main theme of steady state approximation is:

1. It is applicable to those reactions where intermediate is unstable

- Rate of intermediate is kept constant/negligible (means intermediate is considered stationary/steady that is why it is called steady state approximation)
- 1st step is the slowest step ($k_1 \ll k_2$)
- Product of 1st step (K_1 will be reactants for the 2nd reaction (step with k_2) and so on.
- At the end of the steady state approximation there must not be any intermediate in the equation.

Steady state approximation

Reaction:



According to steady state approximation

Rate of formation of a substance = rate of disappearance of a substance.

As we know that the only stable states of chromium are Cr (III) and Cr (VI), rest of the state of chromium is intermediates. Likewise the stable state of silver is Ag (I), Ag (II) is an intermediate so it should not be present in the end result. As far as cobalt is concerned it is stable in Co (II) and Co (III) states and rests of its states are unstable.

The main approximation is:

Rate of formation of Cr (VI) = Rate of disappearance of Cr (V)

$$\frac{dx}{dt} [\text{Cr(VI)}] = K_5 [\text{Cr(V)}] [\text{Ag (II)}] = \frac{dx}{dt} [\text{Cr(V)}] = K_5 [\text{Cr(V)}] [\text{Ag (II)}]$$

$$\frac{dx}{dt} [\text{Cr(VI)}] = \frac{dx}{dt} [\text{Cr(V)}] = K_5 [\text{Cr(V)}] [\text{Ag (II)}] \quad (1)$$

As rate of formation of Cr (V) consist of different steps that give us Cr (VI) and Cr (V) is also an intermediate and must be eliminated also so in this case

Rate of formation of Cr (V) = Rate of disappearance of Cr (V)

$$\frac{dx}{dt} [\text{Cr(V)}] = K_4 [\text{Cr(IV)}] [\text{Ag (II)}] = \frac{dx}{dt} [\text{Cr(V)}] = K_5 [\text{Cr(V)}] [\text{Ag (II)}]$$

OR

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Rate of formation of Cr (V) = Rate of formation of Cr (V) - Rate of disappearance of Cr (V) = 0

$$\frac{dx}{dt} [Cr(V)] = K_4 [Cr(IV)][Ag(II)] - K_5 [Cr(V)][Ag(II)] = 0$$

$$\text{So } \frac{dx}{dt} [Cr(V)] = K_4 [Cr(IV)][Ag(II)] = K_5 [Cr(V)][Ag(II)] \quad (2)$$

Simplification of Eq (2) we get the following result

$$K_4 [Cr(IV)][Ag(II)] = K_5 [Cr(V)][Ag(II)]$$

$$\frac{dx}{dt} [Cr(V)] = Cr(V) = \frac{k_4 (Cr(IV))}{k_5} \quad (2a)$$

So Cr (V) has been eliminated (evaluated)

Apply the same procedure to eliminate Cr (IV) intermediate

Rate of formation of Cr (IV) = Rate of disappearance of Cr (IV) OR

Rate of formation of Cr (IV) = Rate of formation of Cr (IV) - Rate of disappearance of Cr (IV) = 0

$$\frac{dx}{dt} [Cr(IV)] = K_3 [Cr(III)][Ag(II)] - K_4 [Cr(IV)][Ag(II)] = 0 \quad (3)$$

$$\frac{dx}{dt} [Cr(IV)] = K_3 [Cr(III)][Ag(II)] = K_4 [Cr(IV)][Ag(II)]$$

$$\frac{dx}{dt} [Cr(IV)] = Cr(IV) = \frac{k_3 (Cr(III))}{k_4} \quad (3a)$$

To eliminate Cr (IV) put eq (3a) in eq (2a).

$$\frac{dx}{dt} [Cr(V)] = Cr(V) = \frac{k_4 k_3 (Cr(III))}{k_4 \times k_5} = \frac{k_3 (Cr(III))}{k_5} \quad (4)$$

Now we got the value of Cr (V). put the value of Cr (V) into eq (1)

$$\frac{dx}{dt} [Cr(VI)] = K_5 [Cr(V)][Ag(II)] = \frac{dx}{dt} [Cr(VI)] = K_5 \left[\frac{k_4 k_3 (Cr(III))}{k_4 \times k_5} \right] [Ag(II)]$$

$$\frac{dx}{dt} [Cr(VI)] = k_3 [Cr(III)][Ag(II)] \quad (5)$$

Now it is the turn of the Intermediate Ag (II)

Rate of formation of Ag (II) = Rate of formation of Ag (II) - Rate of disappearance of Ag (II) = 0

$$\frac{dx}{dt}[Ag(II)] = K_1[Co(III)][Ag(I)] - K_2[Co(II)][Ag(II)] - K_3[Cr(III)][Ag(II)] - K_4[Cr(VI)][Ag(II)] - K_5[Cr(V)][Ag(II)] = 0$$

(6)

From eq (2) we know that $K_4[Cr(IV)][Ag(II)] = K_5[Cr(V)][Ag(II)]$

And also from eq (3) $K_3[Cr(III)][Ag(II)] = K_4[Cr(IV)][Ag(II)]$

So $K_3[Cr(III)][Ag(II)] = K_4[Cr(IV)][Ag(II)] = K_5[Cr(V)][Ag(II)]$

By putting the value $K_3[Cr(III)][Ag(II)]$ in eq (6) instead of K_4 and K_5 we get the following equation:

$$\frac{dx}{dt}[Ag(II)] = K_1[Co(III)][Ag(I)] - K_2[Co(II)][Ag(II)] - K_3[Cr(III)][Ag(II)] - K_3[Cr(III)][Ag(II)] - K_3[Cr(III)][Ag(II)] = 0$$

$$\frac{dx}{dt}[Ag(II)] = K_1[Co(III)][Ag(I)] - K_2[Co(II)][Ag(II)] - 3 K_3[Cr(III)][Ag(II)]$$

$$\frac{dx}{dt}[Ag(II)] = K_1[Co(III)][Ag(I)] = K_2[Co(II)][Ag(II)] + 3 K_3[Cr(III)][Ag(II)]$$

$$\frac{dx}{dt}[Ag(II)] = K_1[Co(III)][Ag(I)] = [Ag(II)][K_2[Co(II)] + 3 K_3[Cr(III)]]$$

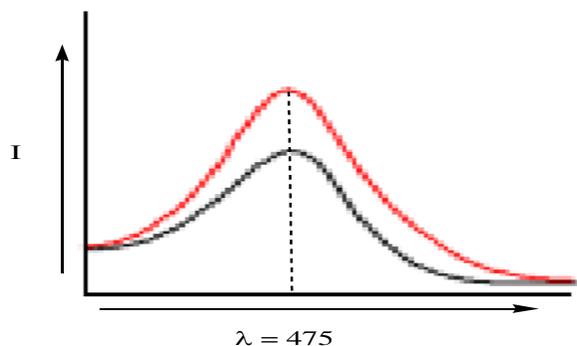
$$[Ag(II)] = \frac{K_1[Co(III)][Ag(I)]}{[K_2[Co(II)] + 3 K_3[Cr(III)]]} \quad (7)$$

Now by putting the value of eq (7) into eq (5) we get the final equation without intermediate.

$$\frac{dx}{dt}[Cr(VI)] = k_3[Cr(III)] \left[\frac{K_1[Co(III)][Ag(I)]}{[K_2[Co(II)] + 3 K_3[Cr(III)]]} \right]$$

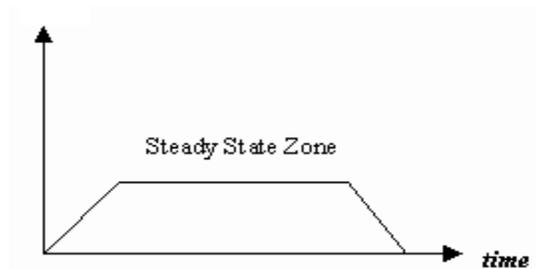
Hence the final result do not contains any intermediate.

If we plot a graph between intensity and wavelength we see that by increasing the concentration of Cr (VI) the intensity also increases at an optimized wavelength of 478nm. At this wavelength Ag (I) which act as a catalyst also absorb but are negligible.



Assignment: steady state approximation on $S_2O_8^{2-}$ (Peroxodisulphate)

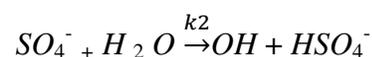
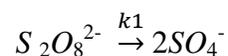
When a reaction involves one or more intermediates, the concentration of one of the intermediates remains constant at some stage of the reaction. Thus, the system has reached a **steady-state**, hence the name of the technique is called **steady state approximation**.



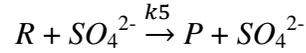
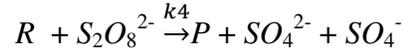
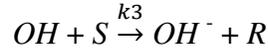
Example-2

Oxidation by peroxodisulphate ($S_2O_8^{2-}$) provides an example of Steady State Approximation in handling complicated chain mechanism. Uncatalyzed reaction by peroxodisulphate commonly described by rate law showing a first order dependence on ($S_2O_8^{2-}$) but zero order dependence on reducing agent. The aqueous decomposition of peroxodisulphate is first order. A proposed mechanism must account of this. The following scheme has been proposed in which S represent an oxidizable substrate, R is a radical derived from S, and p is a product of reaction. In this reaction S and $S_2O_8^{2-}$ are used.

The main theme of this reaction is the decomposition of $S_2O_8^{2-}$. So all the intermediate species must not be present in the end rate expression.



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The rate of decomposition of $(S_2O_8^{2-})$ and substrate are given by

$$-d[S_2O_8^{2-}]/dt = k_1[S_2O_8^{2-}] + k_4[R][S_2O_8^{2-}] \quad (1)$$

$$-d[S]/dt = k_3[OH][S] \quad (2)$$

Rate of formation of radicals SO_4^- , R and OH are given by

$$d[SO_4^-]/dt = 2k_1[S_2O_8^{2-}] - k_2[SO_4^-] + k_4[R][S_2O_8^{2-}] - k_5[R][SO_4^-] \quad (3)$$

$$d[R]/dt = k_3[OH][S] - k_4[R][S_2O_8^{2-}] - k_5[R][SO_4^-] \quad (4)$$

$$d[OH]/dt = k_2[SO_4^-] - k_3[OH][S] \quad (5)$$

By the steady state approximation the concentrations of these radicals are constants.

$$d[SO_4^-]/dt = d[R]/dt = d[OH]/dt = 0 \quad (6)$$

Elimination of [OH]

equation 5 in the light of eq 6 can be written as

$$d[OH]/dt = k_2[SO_4^-] - k_3[OH][S]$$

$$0 = k_2[SO_4^-] - k_3[OH][S] \quad (\text{when } d[OH]/dt = 0)$$

$$k_2[SO_4^-] = k_3[OH][S]$$

$$[S] = \frac{k_2}{k_3} \frac{SO_4^-}{OH} \quad (7)$$

Elimination of [S]

By putting the value of [S] from equation 7 to equation 2

$$-d[S]/dt = k_2 \cdot k_3 [SO_4^-][OH] / k_3 [OH]$$

$$-d[S]/dt = k_2 [SO_4^-] \quad (8)$$

Or from eq 7 into eq 4 to give $k_2[SO_4^-]$. As $k_2[SO_4^-] = k_3[OH][S]$, so replacing $k_3[OH][S]$ in eq 4 with $k_2[SO_4^-]$.

$$d[R]/dt = k_2[SO_4^-] - k_4[R][S_2O_8^{2-}] - k_5[R][SO_4^-] = 0 \quad (9)$$

Addition of equation 3 and 9

$$2k_1[S_2O_8^{2-}] - k_2[SO_4^-] + k_4[R][S_2O_8^{2-}] - k_5[R][SO_4^-] + K_2[SO_4^{2-}] - k_4[R][S_2O_8^{2-}] - K_5[R][SO_4^{2-}] = 0$$

$$2k_1[S_2O_8^{2-}] - 2k_5[R][SO_4^-] = 0$$

$$k_1[S_2O_8^{2-}] = k_5[R][SO_4^-] \quad (10)$$

Similarly by subtracting 9 from 3

$$2k_1[S_2O_8^{2-}] - k_2[SO_4^-] + k_4[R][S_2O_8^{2-}] - k_5[R][SO_4^-] - K_2[SO_4^{2-}] - k_4[R][S_2O_8^{2-}] - K_5[R][SO_4^{2-}] = 0$$

$$2k_1[S_2O_8^{2-}] - 2k_2[SO_4^-] - 2k_4[R][S_2O_8^{2-}] = 0$$

$$2k_2[SO_4^-] = 2[k_1[S_2O_8^{2-}] + k_4[R][S_2O_8^{2-}]]$$

$$k_2[SO_4^-] = k_1[S_2O_8^{2-}] + k_4[R][S_2O_8^{2-}] \quad (11)$$

By comparing equation 8 and 11

$$d[S]/dt = k_1[S_2O_8^{2-}] - k_4[R][S_2O_8^{2-}] \quad (12)$$

By comparing equation 12 and 1

$$-d[S]/dt = -d[S_2O_8^{2-}]/dt \quad (12a)$$

From equation 10

$$[SO_4^-] = k_1[S_2O_8^{2-}]/k_5[R] \quad (12b)$$

Elimination of $[SO_4^-]$ from equation 11

By putting eq (12 b) into 11 we can get an equation as

$$k_2[SO_4^-] = k_1[S_2O_8^{2-}] - k_4[R][S_2O_8^{2-}] = k_2 \cdot k_1[S_2O_8^{2-}]/k_5[R] = k_1[S_2O_8^{2-}] - k_4[R][S_2O_8^{2-}]$$

$$k_1 \cdot k_2/k_5[R] = k_1 + k_4[R] \quad (13)$$

rearranging eq 13

$$k_1 \cdot k_2/k_5 = [k_1[R] + k_4[R]^2]$$

$$k_4 [R]^2 + [k_1[R] - k_1 \cdot k_2/k_5] = 0$$

Elimination of [R]

[R] is obtained by solving quadratic equation.

$$a = k_4, b = k_1, c = -k_1 \cdot k_2/k_5$$

$$R = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-k_1 \pm \sqrt{(k_1)^2 - 4k_4(-)k_1 \cdot \frac{k_2}{k_5}}}{2(k_4)}$$

$$[R] = -k_1 \frac{(k_1^2 + 4k_1 \cdot k_2 k_4/k_5)^{1/2}}{2k_4} \quad (13)$$

Putting the value of [R] into equation 1

$$-d[S_2O_8^{-2}]/dt = k_1[S_2O_8^{-2}] + k_4[R][S_2O_8^{-2}]$$

$$-d[S_2O_8^{-2}]/dt = k_1[S_2O_8^{-2}] + k_4 \left[-k_1 \frac{(k_1^2 + 4k_1 \cdot k_2 k_4/k_5)^{1/2}}{2k_4} [S_2O_8^{-2}] \right]$$

$$-d[S_2O_8^{-2}]/dt = k_1[S_2O_8^{-2}] + \left[-k_1 \frac{(k_1^2 + 4k_1 \cdot k_2 k_4/k_5)^{1/2}}{2} [S_2O_8^{-2}] \right]$$

$$= [S_2O_8^{-2}] \left[k_1 + \left[\frac{(-k_1^2 + 4k_1 \cdot k_2 k_4/k_5)}{2} \right]^{1/2} \right]$$

$$= [S_2O_8^{-2}] \left[\frac{2k_1 - k_1 \pm (-k_1^2 + 4k_1 \cdot k_2 k_4/k_5)}{2} \right]^{1/2}$$

$$= 1/2 [S_2O_8^{-2}] \left[\frac{2k_1 - k_1 \pm (k_1^2 + 4k_1 \cdot k_2 k_4)}{k_5} \right]^{1/2}$$

$$\text{If } k_1 = 0 \text{ then } = 1/2 [S_2O_8^{-2}] \left[\frac{4k_1 k_2 k_4}{k_5} \right]^{1/2}$$

$$[S_2O_8^{-2}]/dt = [S_2O_8^{-2}] [k_1 \cdot k_2 k_4]$$

As observed rate is independent of the concentration of substrate but it is first order in $S_2O_8^{2-}$ concentration.

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Factors effecting rate of inorganic reactions

1. Effect of solvent and solvation of ions on the rate of inorganic reactions

Inorganic reactions are mostly carried out in water (polar solvent) because it is universal solvent, easily available, dielectric constant is compatible with inorganic substances, in case it is not compatible than reactants will not be soluble in the solvent. As most of the coordinated complexes proceed through substitution reaction in which water is mostly used as a solvent but instead of our desired product. There are 100 % chances of aquo complexes which is a major problem. now question arise how to decide whether the reaction in such type of situation is SN^1 , SN^2 or SN^1_{CB} . To solve this dilemma, let's consider a general substitution reaction of octahedral complex.



When H_2O is used along with Y^- then there are 100% chances of the formation of aquo complexes.



$$\text{Rate} \propto [[CoA_5X]^{2+}][H_2O]$$

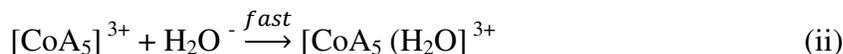
The end product in both reactions are same then why H_2O is problematic, it is because of the fact that in the rate equation (kinetic study) water is involved which means rate of reaction depends on water and complex specie but independent as far as the concentration of desired ligand Y^- is concerned which is a major problem related with the synthesis of complex in aquos medium.

Influences of water in a chemical reaction through different ways/or evaluation of the rate is a problem)/or Evaluation of H_2O

Evaluation of the rate of aquo complexes is very difficult. we are not certain whether reaction are SN^1 , SN^1_{CB} or SN^2 (in inorganic chemistry the reaction is not perfectly SN^1 like in organic chemistry but SN^1 type).

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In case it is SN^1 then the product will follow the following route.



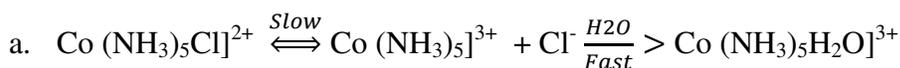
In case the reaction proceeds through SN^2 mechanism



Rate $\propto [CoA_5X]^{2+} [H_2O]$

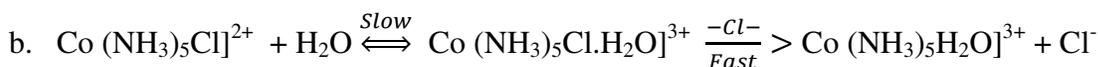
Now consider a specific example

i. SN^1



$$Rate = K_a [Co(NH_3)_5Cl]^{2+}$$

ii. SN^2



$$Rate = K_b [Co(NH_3)_5Cl.H_2O]^{3+}$$

iii. SN^1CB (Acid base reaction as a problem)



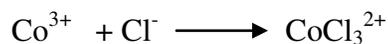
$$Rate = k [Co(NH_3)_5Cl]^{2+} \quad \text{as } H_2O \text{ is conc is constant so } K_b \cdot k = k'$$

So different mechanism is followed by this particular reaction in the presence of H_2O . Here H_2O inside the coordination sphere act as an acid and outside the coordination sphere as a reactant act as a base. We can also say that hydrolysis of H_2O takes place ($H_2O \leftrightarrow ^-OH + H_3O^+$).

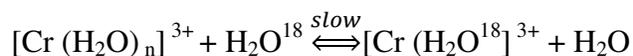
During a reaction metal ions and its counter reacting ion must be free so that it may easily react with each other. There must not be solvation of these ions as solvation hinders the reaction

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between ions (Co^{3+} and Cl^-). So 3rd interfering species must be avoided for smooth and easy reaction to take place (here H_2O is a 3rd interfering species). If a direct reaction between the ions takes place then it would be as follow



But as we know that ions are not bare in aquos medium and the complex is an aquo complex, during substitution water molecule is replaced from the coordination sphere by the entering ligand (Cl^- in this case). Now the problem for such type of reactions is the uncertainty of the number of water molecules (extent of hydration), though know in some cases ($n=6$ for octahedral type complexes). It is solved by isotopic hydration method in which oxygen of water molecule labeled as O^{18} . On mixing solution of Cr^{3+} aquo complex with H_2O^{18} , a slow isotopic exchange takes place.



Which can be followed either the decrease in the amount of isotopically labeled H_2O^{18} concentration or increase in concentration of isotopically labeled in the complex by sampling the complex at various times by distillation procedure. The isotopic exchange has a half life of about 40hrs at 25°C . For a given solution of Cr^{3+} the number of unbound water molecules can be calculated from the isotopic dilution which results within a short time of mixing with O^{18} containing solvent. The number of bound water molecules is the difference between this value and the total number present. Let the total number of water molecules are bound to the metal ions are unknown. At mixing of the isotopic water, say 20 molecules and performing distillation, we get 6 molecules of unlabeled water which was exchanged by the labeled water. The difference between $20-6 = 14$ (O^{18}). Hence it can be confirmed either by calculating the number of isotopic water molecules left or by the unlabeled water (O^{16}) removed by exchanging with O^{18} . Ions of Cr^{3+} to molecules of bound water were found to be in the proportion of 1 to 6. The number of water molecules comprising the primary coordination shell of metal ion has rarely been so exactly defined for the case of Cr^{3+} . The determination becomes more difficult as the exchange rate increases. However by employing a flow technique, a value of 6 for the hydration number can be obtained (as obtained for Al^{3+}).

How to avoid/ evaluate the problem of H₂O entering into a chemical reaction/ what is the possible solution of the interference of H₂O in inorganic reactions.

To tackle the problem of H₂O that has unwanted interference in substitution reactions in octahedral complexes discussed above. We should use the following solvents.

1. Polar solvent
2. Non-polar solvent

These solvents could be used but the 1st problem is the dielectric constant which affects the solubility. If dielectric constant is small as of organic solvent then metal ion will aggregate or associate more easily, which is not demanded in complex formation reactions as interpretation of data is difficult. So it is probably true that kinetic study of the reactions of metal ions in such media (non aqueous) is worthless and can be used for non kinetic study. Keeping in view this entire factor of using non aqueous medium and also the shortcoming of H₂O but still we prefer water as a solvent because it is cheap, easily available and has high dielectric constant.