KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed to be University Established Under Section 3 of UGC Act 1956)

Coimbatore – 641 021.

SYLLABUS

DEPARTMENT OF CHEMISTRY

M.Sc CHEMISTRY **Semester-II**

17CHP203 **PHYSICAL CHEMISTRY- II** **4H 4C**

(CHEMICAL KINETICS AND ELECTROCHEMISTRY)

Instruction Hours/week:L: 4 T:0 P:0 **Marks: Internal:40 External: 60 Total:100**

Scope

Chemical kinetics and electrochemistry frames much of our understanding of the natural world and continues to bring new technologies that are useful to every aspect of human life. Chemical kinetics is an exciting and challenging course, which helps us to understand the various aspects of corrosion and catalysis. Electrochemistry is a part of our daily life. Chemistry interfaces with a myriad of other disciplines and fields. They are fundamental to understand other areas of chemistry, biology and medicine. Due to highly prized nature of chemical kinetics and electrochemistry and its diverse topics, it lays the foundation for extremely productive and exciting career in variety of disciplines as pharmaceutical, agrochemical, mineralogy, molecular biology, biotechnology, nanotechnology, polymer technology, teaching research, scientific publication and so on. The importance of these subjects would not diminish over time, so it will remain a promising career path. It deals with catalysis, corrosion and polarography.

Methodology

Blackboard teaching, Powerpoint presentation and group discussion.

Programme Outcome

1. To enable and impart the knowledge of Chemical kinetics and Electrochemistry.
2. To understand the concept of homogeneous and heterogeneous catalysis

3. To understand the basic concepts of adsorption.
4. To get knowledge about poloragraphy

Programme Learning Outcome

1. The students know the various theories of reaction rates.
2. The students understood theories of double layer

UNIT-I

Theories of reaction rates: Arrhenius theory- hard - sphere collision theory of gas – phase reactions. Activated complex theory or Absolute reaction rate theory (ARRT) for ideal gas reactions (in terms of partition functions).

Reactions in solution: Comparison between gas-phase and solution reactions. The influence of the solvent on the reactions between ions. Influence of ionic strength on rates of reactions in solution - primary salt effect-influence of pressure on rates of reactions in solution -significance of volume and entropy of activations.

Study of fast reactions: Flow methods, pulse methods, relaxation methods, shock-tube method and nuclear magnetic resonance method.

UNIT-II

Homogeneous catalysis: Specific and general acid - base catalysis. Bronsted catalysis law-Hammett acidity functions. Enzyme catalysis (single substrate reaction only). Michaelis Menten law - Influence of pH and temperature on enzyme catalysis.

Surface phenomenon and heterogeneous catalysis: Adsorption and free energy relation at interfaces. Gibb’s adsorption isotherm- physisorption and chemisorptions- Adsorption isotherms (Freundlich & Langmuir). Kinetics of heterogeneous catalysis- Langmuir - Hinshelwood and Langmuir - Rideal - Eley mechanisms.

UNIT-III

Inter ionic attraction theory: Debye – Huckel – Onsager equation - Falkenhagen effect- Wien effect. Activity and activity coefficient- ionic strength- Debye – Huckel limiting law and its applications.

Theories of double layer. Helmholtz – Perrin - Gouy chapmann – Stern theories.

UNIT – IV

Polarography: Current – voltage relationships-the dropping mercury electrode. Diffusion current- half – wave potentials. Applications of polarography- Amperometric titrations.

Fundamental principles of coulometric methods- constant current and controlled potential methods- simple applications.

UNIT – V

Kinetics of corrosion: Importance–graphical presentation of kinetic data-exchange current density- different types of polarization of electrodes. Activation polarization and Tafel plots-mixed potential theory-application of electrode kinetics to experimental observations-faradic impedance and corrosion.

SUGGESTED READINGS:

Text Books:

1. Bahl, A., Bahl, B. S., & Tuli, G. D, (2014). *Essentials of Physical Chemistry* (V Edition). New Delhi: S. Chand & Company.
2. Puri, B. R., Sharma, L.R., & Pathania, M .S. (2015). Elements of Physical Chemistry. Jalandhar: Vishal Publishing House.
3. Atkins, P., & De Paula, J. (2014). *Atkins Physical Chemistry* (X Edition). Oxford: Oxford University Press.

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LECTURE PLAN

DEPARTMENT OF CHEMISTRY

STAFF NAME: H.Revathi

SUBJECT NAME: Chemical kinetics and Electrochemistry

SUB.CODE:17CHP203

CLASS: I M.Sc

SEMESTER: II

S.No	Lecture Duration Period	Topics to be covered	Support Material/Page Nos
		UNIT I	
1	1	Arrhenius theory-hard-sphere collision theory of gas phase reactions	T1:232-234
2	1	Activated complex theory or Absolute reaction rate theory (ARRT) for ideal gas reactions(interms of partition functions)	T1:234-236
3	1	Reactions in solution:comparison between gas-phase and solution reactions.	T2:184-185
4	1	The influence of the solvent on the reactions between ins	T1:246-247
5	1	Influence of ionic strength on rates of reactions in solution	T1:245-246

6	1	Primary salt effect	T2:189-190
7	1	Influence of pressure on rates of reactions in solution	T2:189-190
8	1	Significance of volume and entropy of activations	T2:207-209
9	1	Study of fast reactions:Flow methods, pulse methods	T1:247-249
10	1	Relaxation methods, shock-tube method	T1:249-250
11	1	Nuclear magnetic resonance method	T1:504
12	1	Revision and discussion of question papers	
	Total No of hours planned for Unit I-12		
	UNIT II		
1	1	Specific and general acid-base catalysis.	T1:260-261
2	1	Bronsted catalysis law-Hammett acidity functions.	T1:261
3	1	Enzyme catalysis(Single substrate reaction only)	T1:262-264
4	1	Michaelis Menten law-Influence of p H and temperature on enzyme catalysis	T1:262-264
5	1	Surface phenomenon and heterogeneous catalysis	T1:267-269
6	1	Adsorption and free energy relation at interfaces	T1:267-269
7	1	Gibb's adsorption isotherm-physisorption	T1:817-818
8	1	Chemisorptions	
9	1	Adsorption isotherms (Freundlich and Langmuir)	T1:882-880
10	1	Kinetics of heterogeneous catalysis-Langmuir-Hinshelwood	T1:270-273
11	1	Langmuir-Rideal-Eley mechanisms	T1:270-275
12	1	Revision and discussion of question papers	
	Total No of hours planned for Unit II-12		
	UNIT III		
1	1	Debye-Huckel-Onsager equation	T1:548-550
2	1	Falkenhagen effect	T1:550
3	1	Wien effect	T1:550

4	1	Activity and activity coefficient	T1:572-573
5	1	Ionic strength	T1:871-872
6	1	Debye-Huckel limiting law and its applications	T1:550
7	1	Theories of double layer.Helmholtz	T2:1021-1023
8	1	Perrin theory	T2:1021-1023
9	1	Gouy chapmann theory	T2:1021-1023
10	1	Stern theory	T2:1021-1023
11	1	Revision and discussion of question papers	
	Total No of hours planned for Unit III-11		
	UNIT IV		
1	1	Current-voltage relationships	T1:593-594
2	1	The dropping mercury electrode	T1:596-597
3	1	Diffusion current	T1:596-600
4	1	Half wave potentials	T2:78-79
5	1	Applications of polarography	T1:600-604
6	1	Amperometric titrations	T2:134-137
7	1	Fundamental principles of coulometric methods	T2:134-137
8	1	Constant current	T2:134-137
9	1	Controlled potential methods	T2:139-140
10	1	Simple applications	T2:142-144
11	1	Revision and discussion of question papers	
	Total No of hours planned for Unit IV-11		
	UNIT V		
1	1	Importance –graphical presentation of kinetic data	T1:44-48
2	1	Exchange current density	T1:44-48
3	1	Different types of polarization of electrodes	T1:44-48
4	1	Activation polarization	T1:50-55
5	1	Tafel plots	T1:107-109

6	1	Mixed potential theory	T1:55-59
7	1	Application of electrode	T1:59-61
8	1	Kinetics to experimental observations	T1:59-61
9	1	Faradic impedance	T1:59-61
10	1	corrosion	T1:64-66
11	1	Revision and discussion of question papers	
12	1	ESE question paper discussion	
13	1	ESE question paper discussion	
14	1	ESE question paper discussion	
	Total No of hours planned for Unit V-14		
Total planned hours	60		

SUPPORTING MATERIALS:
Text Books:

T1**:** B.R.Puri, L.R.Sharma, Madan S.Pathania, *Principles of physical chemistry*,(2013) Vishal publishing Co, Jalandhar

T2:Atkins, P.W and Paula, J.D(2011) Physical Chemistry. 9th Edition. Oxford university press.

UNIT I

SYLLABUS

Theories of reaction rates: Arrhenius theory- hard - sphere collision theory of gas – phase reactions.Activated complex theory or Absolute reaction rate theory (ARRT) for ideal gas reactions (in terms of partition functions).
Reactions in solution: Comparison between gas-phase and solution reactions. The influence of the solvent on the reactions between ions. Influence of ionic strength on rates of reactions in solution -primary salt effect-influence of pressure on rates of reactions in solution -significance of volume and entropy of activations.
Study of fast reactions: Flow methods, pulse methods, relaxation methods, shock-tube method and nuclear magnetic resonance method.

Arrhenius theory

The **Arrhenius equation** is a formula for the temperature dependence of reaction rates. The equation was proposed by Svante Arrhenius in 1889, based on the work of Dutch chemist Jacobus Henricus van 't Hoff who had noted in 1884 that Van 't Hoff's equation for the temperature dependence of equilibrium constants suggests such a formula for the rates of both forward and reverse reactions. This equation has a vast and important application in determining rate of chemical reactions and for calculation of energy of activation. Arrhenius provided a physical justification and interpretation for the formula. Currently, it is best seen as an empirical relationship. It can be used to model the temperature variation of diffusion coefficients, population of crystal vacancies, creep rates, and many other thermally-induced processes/reactions. The Eyring equation, developed in 1935, also expresses the relationship between rate and energy.

A historically useful generalization supported by Arrhenius' equation is that, for many common chemical reactions at room temperature, the reaction rate doubles for every 10 degree Celsius increase in temperature.

Dependence of Reaction Rate on Temperature

The dependence of the rate of a reaction on temperature has been studied in much detail. Plots of reaction rate versus temperature can take very many different forms . In the simplest situation, the rate appears to show an exponential increase with temperature. Arrhenius in 1889 proposed an equation for the temperature dependence of reaction rates for simple reactions that is still being used.

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

A is called a 'pre-exponential' , E is the activation energy, T is the system temperature and R is the gas constant.

It is common in practice to represent the rates of non-elementary reactions also with the above formulation. However, in those cases E is not exactly the activation energy in the strict sense. Activation energy has a very specific meaning in the above context, and this matter is worth probing further. Some of the theories for reactions that we consider later should clarify the concept of activation energy.

Clearly, a bit of mathematical manipulation indicates that, if the rate constant of a simple reaction can be measured as a function of temperature, plotting ln(k) vs. 1/T should give a straight line (what can we conclude if it is not a straight line?). The slope of this line gives us -E/R while the intercept gives ln(A). Thus with a few rate measurements, the pre-exponential and the activation energy can be evaluated (provided the order with respect to and the concentration of the reactants is known).

While high school chemistry teaches us some 'rules of thumb' such as the rate of a reaction doubles for every 10^0C raise in temperature, we should be able to see from the expression above that this heuristic is really only valid at some specific activation energy at some specific temperature. In reality, activation energies vary over a large range of values and therefore this is not something particularly useful.

Transition-State Theory

In transition-state theory, the reaction between reactant molecules A & B to form a product C is assumed to occur as follows:

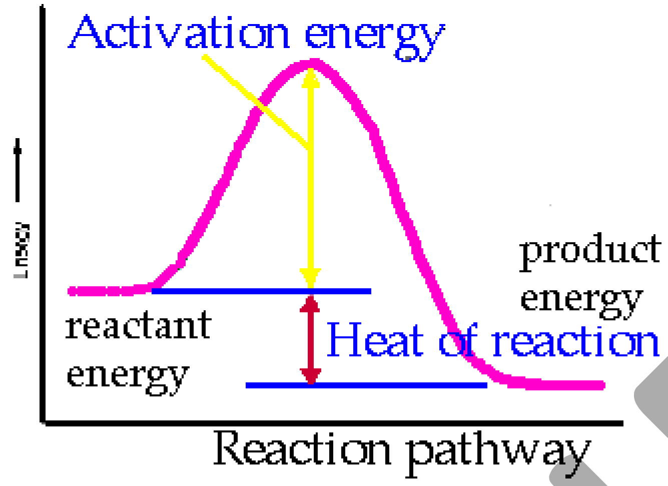
$A+B \leftrightarrow C$

Here AB^* is an activated complex (transition state) formed from the reactants, through a reversible reaction, at equilibrium. The product molecule is formed from the activated complex in a single, irreversible step. Thus, we can formulate, using an equilibrium constant, K^* for the formation of the activated complex, and k, a rate constant for conversion of activated complex to product C,

$[AB^*]=K^*[A][B]$

$Rate=k[AB^*]$

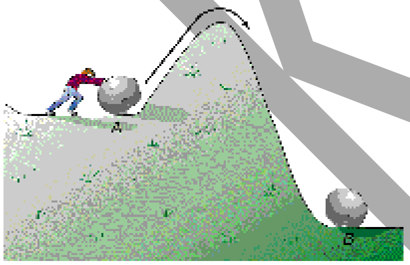
The energy diagram for this process is assumed to look something like this:



where the reactant energy is the energy of A and B, the top of the 'hill' here is the energetic position of AB^*, and product energy is of course the energy of product C. Thus the activation energy is the distance on the energy 'hill' that has to be climbed in going from reactants to the activated complex (or transition-state). From this diagram, the assumption of irreversible conversion of $AB^*$to C is also intuitive. Note that for the reverse reaction, i.e.

$C \leftrightarrow A+B$,

the activation energy is equal to the activation energy for the forward reaction plus the heat of the reaction. Finally, note that this whole reaction can be compared to rolling a boulder up a hill. Once you expend the energy to reach the top of the hill, then you can just let it go, it would roll downhill by itself:



The rate constant for the transition of the activated comples to product can be obtained as the frequency of the critical vibration that decomposes the complex to product, obtained from statistical mechanics.

Activated complex theory or Absolute reaction rate theory(ARRT) for ideal gas reactions

Absolute reaction rate theory

Absolute reaction rate theory is a theory that aims to provide explanations for both the ‘activation energy’ and the pre-exponential factor A (the ‘frequency factor’) in the rate equation from first principles. Its underlying theories are quantum mechanics and statistical mechanics. The success of the theory depends on an accurate calculation of the potential energy surface of the reaction, as well as a detailed consideration of the initial and final states of the molecules.

The theory also introduces a precise concept of a *transition state* which is like a ‘normal’ molecule. The transition state has a definite structure, mass, and so forth. The only exception is that there is one particular direction of motion (the ‘reaction coordinate’) which causes the molecule to ‘break up’ into the end products of the reaction.

The situation is sketched in Figure 1. On the right is a ‘channel’ of reactants which transforms along a ‘reaction coordinate’ into a channel of products. At the height of the energetic barrier between the reactants and the products lies the ‘transition state’, which is thus specified as a particular type of molecule, with the structural property that there is one particular internal coordinate which leads to a decomposition of the molecule.

The further development of absolute reaction rate theory is based on the statistical mechanics of the equilibrium between the reactants and the transition state. Eyring’s introduction of statistical mechanics into the expression of the rate equation is based on the idea that the potential energy surface can be calculated with quantum mechanics, and the motion of the nuclear frame can subsequently be treated classically with statistical mechanics.

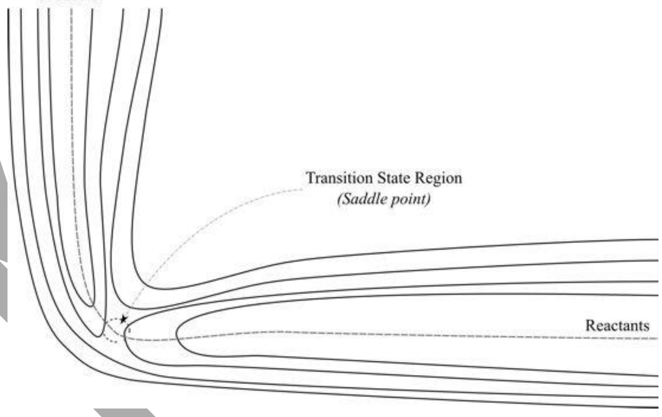


Figure 1: The potential energy surface for a three-atom reaction, indicating the reaction coordinate and the transition state at the saddle point.

It is therefore clear that the absolute theory of reaction rates requires accurate calculations of the potential energy surface for the reaction. Such precise calculations were not possible in the 1930s, and hence Eyring developed a semi-empirical form of quantum mechanics that gives access to the potential energy surface with sufficient precision to allow predictions from the theory.

Eyring's formulation of absolute reaction rate theory uses the following assumptions:

E1. The potential energy surfaces can be calculated with quantum mechanics (or a semi-empirical form of quantum mechanics).
E2. The behavior of the nuclear frame on the potential energy surface (note that this therefore includes the Born-Oppenheimer approximation) can be described with statistical mechanics.
E3. The decomposition of the transition state into the reactants can be described as a translational motion along the reaction coordinate.

Let us reconstruct the remainder of the argument in the form in which it is given in Glasstone *et al*. 1941. The key element of statistical mechanics is the partition function (*Zustandssumme*) *Z*:

$$z = g_i \exp\left(-\frac{e_i}{kT}\right)$$

where g_i is the degeneracy of the state corresponding to energy e_i. The complete partition function for any system is complex to calculate, since it involves all electronic, translational, vibrational and rotational motions of the system with their degeneracies and corresponding energy levels. The rate formula of the absolute theory of reaction rates is given in terms of the partition functions of the reactants and the transition state by

$$k = \frac{kT}{h} \frac{Z^{\ddagger}}{Z_A Z_B Z \ldots} \exp\left(-\frac{E^0_{\ddagger}}{RT}\right)$$

The advantage of this formulation is that the partition functions for all compounds featuring in the reaction (Z_A, Z_B, *etc.*) can be calculated using statistical mechanics for vibrational and rotational motion of mechanical systems. While this is still a difficult problem, a detailed consideration of different reacting systems yields a mechanistic insight in how the reaction occurs on a molecular level. Figure 2 presents a sketch of the situation.

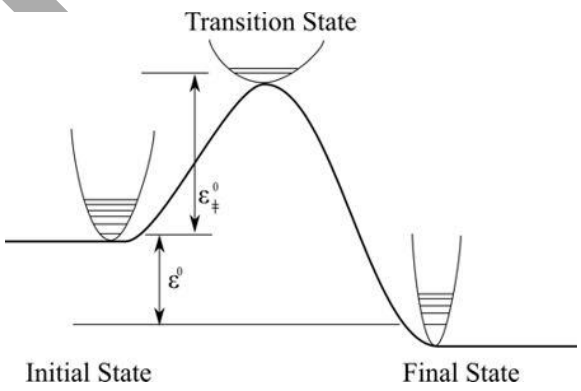
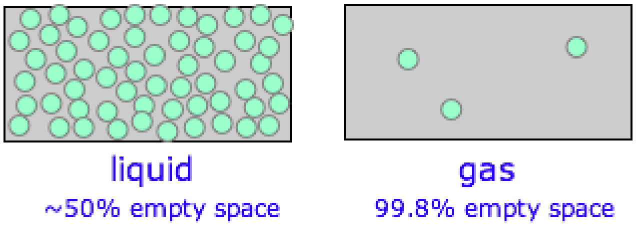


Figure 2: The potential energy surface for reaction seen along the reaction coordinate. The parabolic curves with energetic levels in them should be read as being ‘perpendicular’ to the reaction coordinate.

Reactions in solution

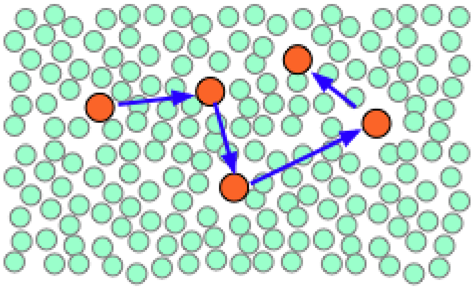
Comparison between gas-phase and solution reactions

Most of the added complications of kinetics and rate processes in liquid solutions arise from the *much higher density* of the liquid phase. In a typical gas at atmospheric pressure, the molecules occupy only about 0.2 per cent of the volume; the other 99.8 percent is empty space. In a liquid, molecules may take up more than half the volume, and the "empty" spaces are irregular and ever-changing as the solvent molecules undergo thermal motions of their own.



Liquid vs. Gases.

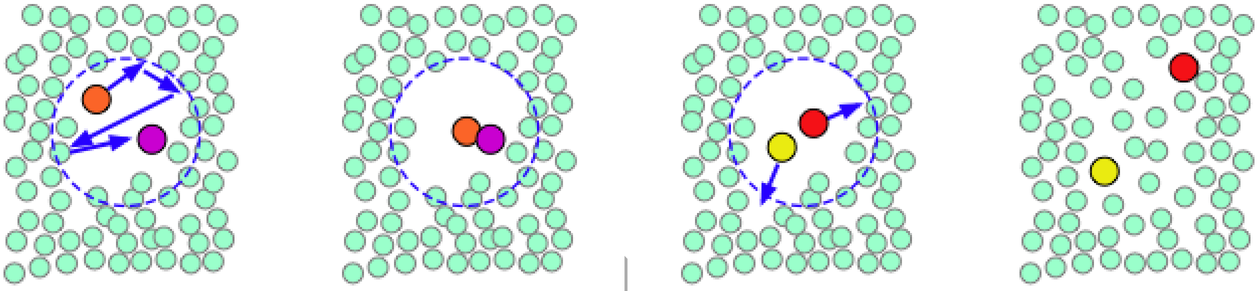
In a typical liquid solution, the solvent molecules massively outnumber the reactant solute molecules, which tend to find themselves momentarily (~10^{-11} sec) confined to a "hole" within the liquid. This trapping becomes especially important when the solvent is strongly hydrogen-bonded as is the case with water or alcohol.



Brownian motion of a particle in solution

When thermal motions occasionally release a solute molecule from this trap, it will jump to a new location. The jumps are very fast (10^{-12} - 10^{-13} sec) and short (usually a few solvent-molecule diameters), and follow an entirely random pattern, very much as in **Brownian motion**. Consider a simple bimolecular process A + B → products. The reactant molecules will generally be jumping from hole to hole in the solvent matrix, only occasionally finding themselves in the same *solvent cage* where thermal motions are likely to bring them into contact.

Solvent cages and encounter pairs



A pair of reactants end up in the same solvent cage, where they bounce around randomly and exchange kinetic energy with the solvent molecules.

Eventually the two reactants form an *encounter pair*. If they fail to react the first time, they have many more opportunities during the lifetime of the cage.

The products form and begin to move away from each other.

Finally, after about 10^{-11}sec, the solvent cage breaks up and the products diffuse away.

The process can be represented as

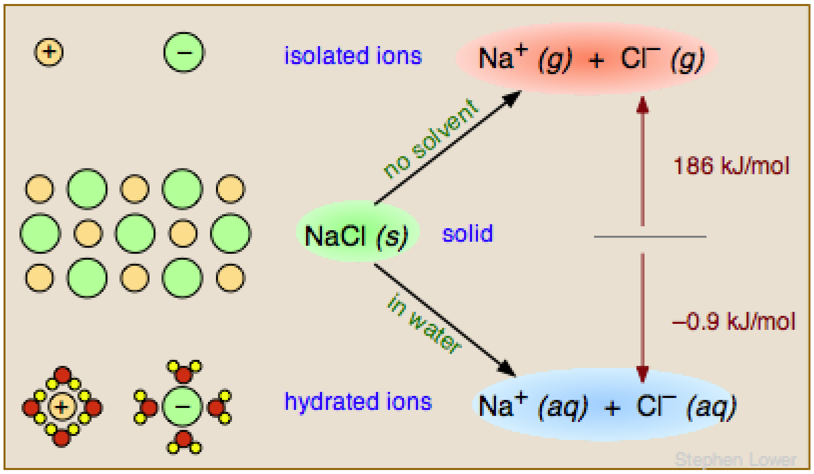
$$A+B \rightarrow \{AB\} \rightarrow \text{products}$$

in which the {AB}{AB} term represents the caged reactants including the *encounter pair* and the activated complex.

Contrast this scenario with a similar reaction taking place in the gas phase; the molecules involved in the reaction will often be the only ones present, so a significant proportion of the collisions will be A-B encounters. However, if the collision should fail to be energetically or geometrically viable, the reactant molecules fly apart and are unlikely to meet again anytime soon. In a liquid, however, the solute molecules are effectively in a constant state of collision — if not with other reactants, then with solvent molecules which can exchange kinetic energy with the reactants. So once an A-B encounter pair forms, the two reactants get multiple whacks at each other, greatly increasing the probability that they will obtain the kinetic energy needed to kick them over the activation hump before the encounter pair disintegrates.

Solvent thermodynamic effect

If the products of the reaction are markedly more or less polar than the reactants, solvent polarity can change the overal thermodynamics (equilibrium constant) of the reaction. Nowhere is this more apparent than when an ionic solid such as salt dissolves in water. The Na^+ and Cl^- ions are bound together in the solid through strong coulombic forces; pulling the solid apart in a vacuum or in a nonpolar solvent is a highly endothermic process. In contrast, dissolution of NaCl in water is slightly exothermic and proceeds spontaneously.

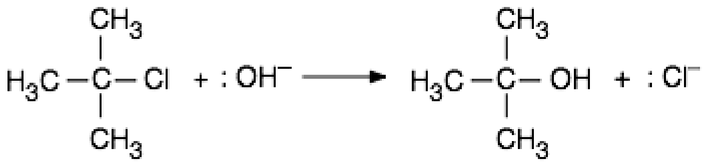


The solvent thermodynamics effect for table salt in water.

The water facilitates this process in two important ways. First, its high dielectric constant of 80 reduces the force between the separated ions to 1/80 of its normal value. Secondly, the water molecules form a *solvation shell* around the ions (lower left), rendering them energetically (thermodynamically) more stable than they were in the NaCl solid.

Solvent kinetic effect

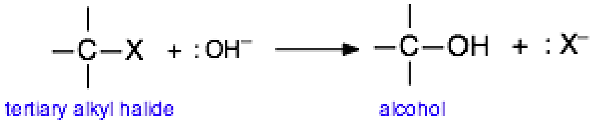
In the same way, a reaction whose mechanism involves the formation of an intermediate or activated complex having a polar or ionic character will have its activation energy, and thus its rate, subject to change as the solvent polarity is altered. As an example we will consider an important class of reactions that you will hear much about if you take a course in organic chemistry. When an aqueous solution of a strong base such as KOH is added to a solution of *tertiary*-butyl chloride in ethanol, the chlorine is replaced by a hydroxyl group, leaving *t*-butyl alcohol as a product:



$$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-Cl + :OH^- \longrightarrow H_3C-\overset{CH_3}{\underset{CH_3}{C}}-OH + :Cl^-$$

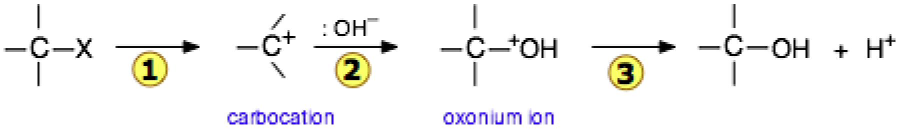
This reaction is one of a large and important class known as *S_N1 nucleophilic substitution processes* that are discussed in most organic chemistry courses. In these reactions, a species that possesses a pair of non-bonding electrons (also called a *nucleophile* or *Lewis base*) uses them to form a new bond with an *electrophile* — a compound in which a carbon atom has a partial positive charge owing to its bonds to electron-withdrawing groups. In the example here, other nucleophiles such as NH_3 or even H_2O would serve as well.

In order to reflect the generality of this process and to focus on the major changes that take place, we will represent this reaction as

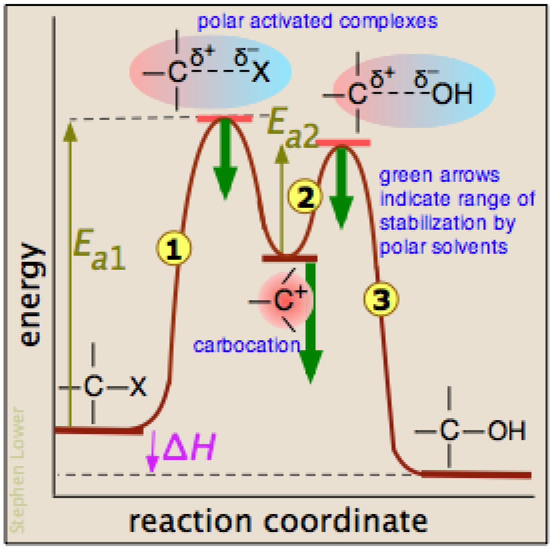


$$-\overset{|}{\underset{|}{C}}-X + :OH^- \longrightarrow -\overset{|}{\underset{|}{C}}-OH + :X^-$$

Extensive studies of this class of reactions in the 1930's revealed that it proceeds in two activation energy-controlled steps, followed by a simple dissociation into the products:



In step ①, which is rate-determining, the chlorine leaves the alkyl chloride which becomes an intermediate known as a *carbocation* ("cat-ion"). These ions, in which the central carbon atom lacks a complete octet, are highly reactive, and in step ② the carbocation is attacked by the hydroxide ion which supplies the missing electron. The immediate product is another cation in which the positive charge is on the oxygen atom. This *oxonium ion* is unstable and rapidly dissociates (③)into the alcohol and a hydrogen ion.



Reaction Coordinate

The reaction coordinate diagram helps us understand the effect of solvent polarity on this reaction. Polar solvent molecules interact most strongly with species in which the electric charge is concentrated in one spot. Thus the carbocation is stabilized to a greater degree than are the activated complexes in which the charge is spread out between the positive and negative ends. As the heavy green arrows indicate, a more polar solvent will stabilize the carbocation more than it will either of the activated complexes; the effect is to materially reduce the activation energy of the rate-determining step, and thus speed up the reaction. Because neither the alkyl chloride nor the alcohol is charged, the change in solvent polarity has no effect on the equilibrium constant of the reaction. This is dramatically illustrated by observing the rate of the reaction in solvents composed of ethanol and water in varying amounts:

Data

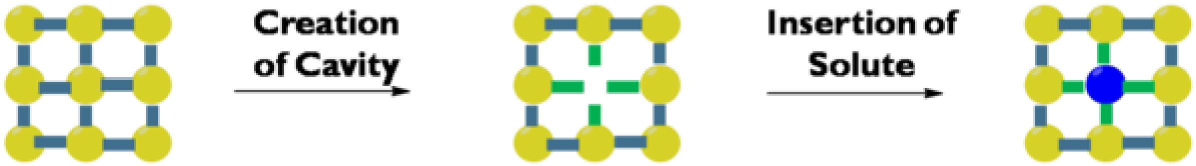
% water	10	20	30	40	50	60
$k1\times10^6$	1.7	9.1	40.3	126	367	1294

The influence of the solvent on the reactions between ions

In chemistry, **solvent effects** are the influence of a solvent on chemical reactivity or molecular associations. Solvents can have an effect on solubility, stability and reaction rates and choosing the appropriate solvent allows for thermodynamic and kinetic control over a chemical reaction.

Effects on solubility

A solute dissolves in a solvent when it forms favorable interactions with the solvent. This dissolving process all depends upon the free energy change of both solute and solvent. The free energy of solvation is a combination of several factors.



First, a cavity must be created in the solvent. The creation of the cavity will be entropically and enthalpicallyunfavorable as the ordered structure of the solvent decreases and there are fewer solvent-solvent interactions. Second, the solute must separate out from the bulk solute. This is enthalpically unfavorable as solute-solute interactions are breaking but is entropically favorable. Third, the solute must occupy the cavity created in the solvent. This results in favorable solute-solvent interactions and is also entropically favorable as the mixture is more disordered than when the solute and solvent are not mixed. Dissolution often occurs when the solute-solvent interactions are similar to the solvent-solvent interactions, signified by the term *like dissolves like*.Hence, polar solutes dissolve in polar solvents, whereas nonpolar solutes dissolve in nonpolar solvents. There is no one measure of solvent polarity and so classification of solvents based on polarity can be carried out using different scales.

Effects on stability

Different solvents can affect the equilibrium constant of a reaction by differential stabilization of the reactant or product. The equilibrium is shifted in the direction of the substance that is preferentially stabilized. Stabilization of the reactant or product can occur through any of the different non-covalent interactions with the solvent such as H-bonding, dipole-dipole interactions, van der waals interactions etc.

Acid-base equilibria

The ionization equilibrium of an acid or a base is affected by a solvent change. The effect of the solvent is not only because of its acidity or basicity but also because of its dielectric constant and its ability to preferentially solvate and thus stabilize certain species in acid-base equilibria. A change in the solvating ability or dielectric constant can thus influence the acidity or basicity.

Solvent properties at 25 °C

Solvent	Dielectric constant
Acetonitrile	37
Dimethylsulfoxide	47
Water	78

In the table above, it can be seen that water is the most polar-solvent, followed by DMSO, and then acetonitrile. Consider the following acid dissociation equilibrium:

$HA \rightleftharpoons A^- + H^+$,

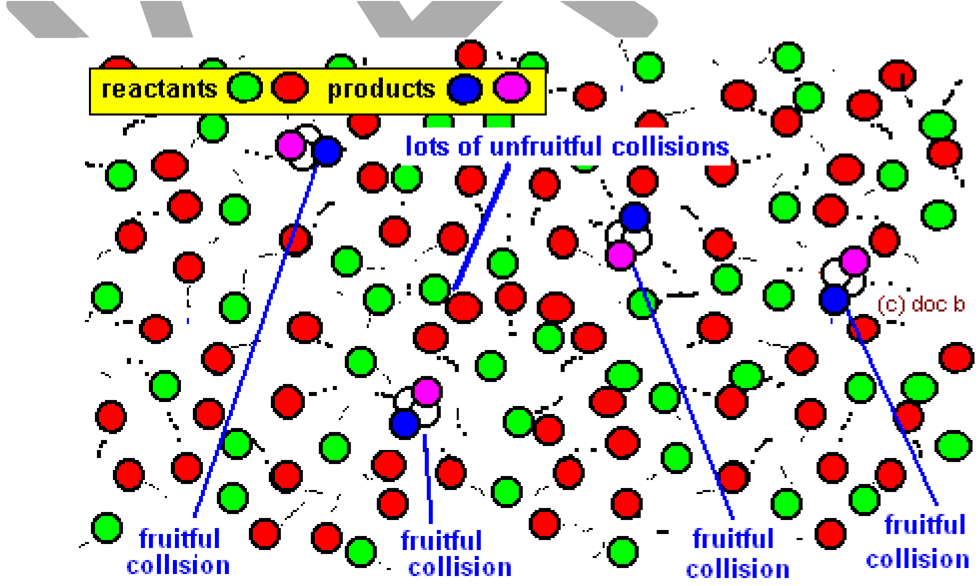
Water, being the most polar-solvent listed above, stabilizes the ionized species to a greater extent than does DMSO or Acetonitrile. Ionization - and, thus, acidity - would be greatest in water and lesser in DMSO and Acetonitrile, as seen in the table below, which shows pK_a values at 25 °C for acetonitrile (ACN) and dimethyl sulfoxide (DMSO) and water.

pK_a values of acids			
$HA \rightleftharpoons A^- + H^+$	**ACN**	**DMSO**	**water**
p-Toluenesulfonic acid	8.5	0.9	strong
2,4-Dinitrophenol	16.66	5.1	3.9
Benzoic acid	21.51	11.1	4.2
Acetic acid	23.51	12.6	4.756

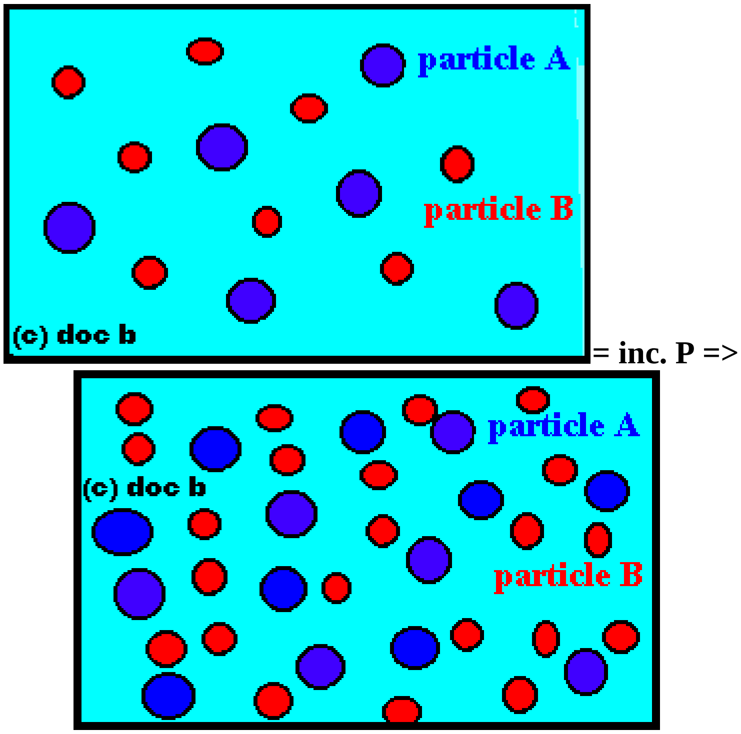
Phenol	29.14	18.0	9.99

Influence of pressure on rates of reactions in solution

- If one or more of the reactants is a gas then increasing pressure will effectively increase the concentration of the reactant molecules and speed up the reaction.
    - So, for gaseous reactants only, pressure is essentially a concentration factor.
    - Increasing pressure has virtually no effect on solids or solutions engaged in a chemical reaction.
- The particles are, therefore on average, closer together and **collisions between the particles will occur more frequently**.
    - The particle diagrams below could represent **lower to higher pressure** situations, resulting in **lesser to greater concentration** and so a **slower to faster reaction**.
    - This all because of the **increased chance of a 'fruitful' collision**, on increasing the total pressure of the reaction system.
    - The arguments based on increased reaction rate with increased pressure to gases reacting freely in the gaseous state (gas phase),
    - OR, gaseous reactants impact on a solid catalyst surface because the increase in pressure increases the collision rate of the reactant molecules with the catalyst surface.
- Increased pressure is used in the Haber Synthesis of Ammonia, not only to increase the yield of ammonia, but to also increase the rate of nitrogen combining with hydrogen to form ammonia.
- Solid reactants and solutions are NOT affected by change in pressure, their concentration is unchanged, so no change in the rate of the reaction.



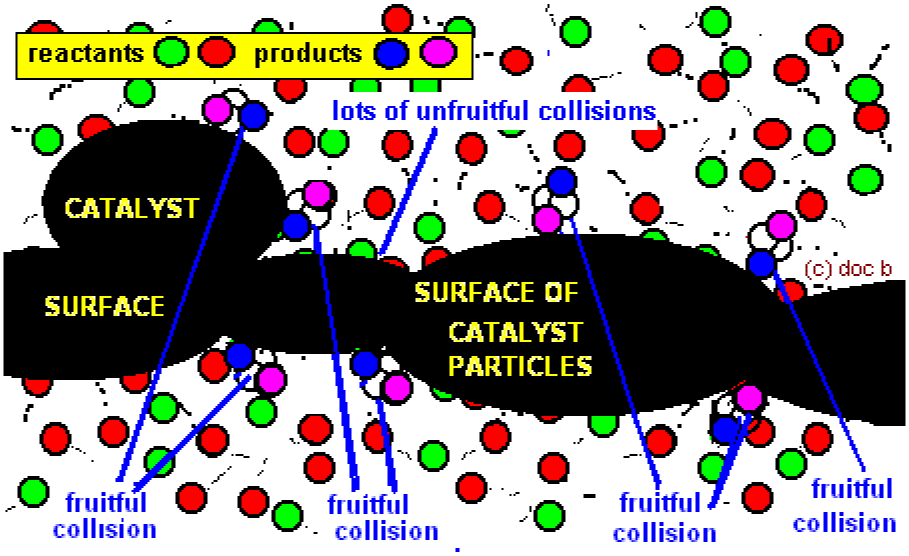
Pictures of a gaseous particles (molecules) undergoing changes in a gaseous chemical reaction



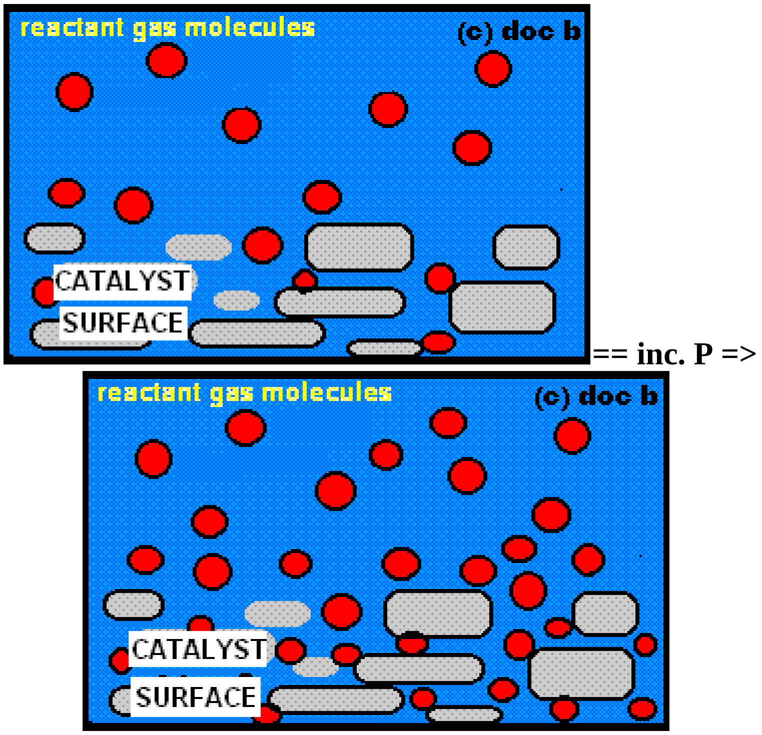
This illustrates a mixture of gases A and B colliding and potentially reacting

The product molecules are not shown, but just imagine how more collisions will occur in the right-hand diagrams!

The diagram at the top of the page gives an idea of how to think about fruitful and unfruitful collisions.



Pictures of a gaseous particles (molecules) undergoing chemical changes on the surface of a catalyst



This illustrates a gas reacting on the surface of a solid catalyst.

again the product molecules are not shown, but just imagine how more collisions will occur in the right-hand diagram on the catalyst surface.

As you increase the pressure, you effectively increase the concentration of the reactants and thereby increase the chance of a fruitful collision.

Significance of volume and entropy of activations

In chemical kinetics, the **entropy of activation** of a reaction is one of the two parameters (along with the *enthalpy of activation*) which are typically obtained from the temperature dependence of a reaction rate constant, when these data are analyzed using the Eyring equation. The standard entropy of activation is symbolized $\Delta S^{\ddagger}$ and equals the change in entropy when the reactants change from their initial state to the activated complex or transition state (Δ = change, S = entropy, ‡ = activation). It determines the preexponential factor A of the Arrhenius equation for temperature dependence of reaction rates. The relationship depends on the molecularity of the reaction: for reactions in solution and unimolecular gas reactions $A = (ek_BT/h) \exp(\Delta S^{\ddagger}/R)$, while for bimolecular gas reactions $A = (e^2k_BT/h) (R'T/p) \exp(\Delta S^{\ddagger}/R)$. In these equations e is the base of natural logarithms, h is the Planck constant, k_B is the Boltzmann constant and T the absolute temperature. R' is the ideal gas constant in units of (bar*L)/(mol*K). The factor is needed because of the pressure dependence of the reaction rate. R' = 8.3145 * 10^-2 (bar*L)/(mol*K).

The value of $\Delta S^{\ddagger}$ provides clues about the molecularity of the rate determining step in a reaction, i.e. whether the reactants are bonded to each other, or not. Positive values suggest that entropy increases upon achieving the transition state, which often indicates a dissociative mechanism in which the activated complex is loosely bound and about to dissociate. Negative values for $\Delta S^{\ddagger}$ indicate that entropy decreases on forming the transition state, which often indicates an associative mechanism in which two reaction partners form a single activated complex.

The pressure dependence of the rate constant for condensed-phase reactions (i.e., when reactants and products are solids or liquid) is usually sufficiently weak in the range of pressures normally encountered in industry that it is neglected in practice.

The pressure dependence of the rate constant is associated with the activation volume. For the reaction proceeding through an activation-state complex:

$$A + B \rightleftharpoons |A\cdots B|^{\ddagger} \rightarrow P$$

the activation volume, $\Delta V^{\ddagger}$, is:

$$, \Delta V^{\ddagger}, = \Delta V^{\ddagger}, - V_A - V_B$$

where $\bar{V}$ denotes the partial molar volume of a species and ‡ indicates the activation-state complex.

For the above reaction, one can expect the change of the reaction rate constant (based either on mole-fraction or on molar-concentration) with pressure at constant temperature to be:

$$\left(\frac{\partial \ln kx}{\partial p}\right)_p = -\frac{\Delta V^{\ddagger}}{RT}$$

In practice, the matter can be complicated because the partial molar volumes and the activation volume can themselves be a function of pressure.

Reactions can increase or decrease their rates with pressure, depending on the value of $\Delta V^{\ddagger}$. As an example of the possible magnitude of the pressure effect, some organic reactions were shown to double the reaction rate when the pressure was increased from atmospheric (0.1 MPa) to 50 MPa (which gives $\Delta V^{\ddagger} = -0.025$ L/mol).

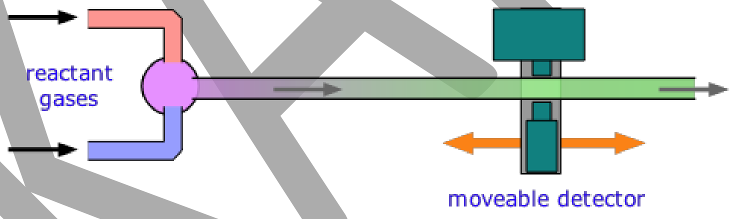
Study of fast reactions.

Flow methods

Flow instruments are a rapid mixing devices used to study the chemical kinetics of fast reactions in solution. There are different flavors that can be implement depending on the nature of the reaction as discussed below.

Continuous Flow Approach

For reactions that take place in milliseconds, the standard approach since the 1950s has been to employ a flow technique of some kind. An early example was used to study fast gas-phase reactions in which one of the reactants is a free radical such as OH that can be produced by an intense microwave discharge acting on a suitable source gas mixture. This gas, along with the other reactant being investigated, is made to flow through a narrow tube at a known velocity.

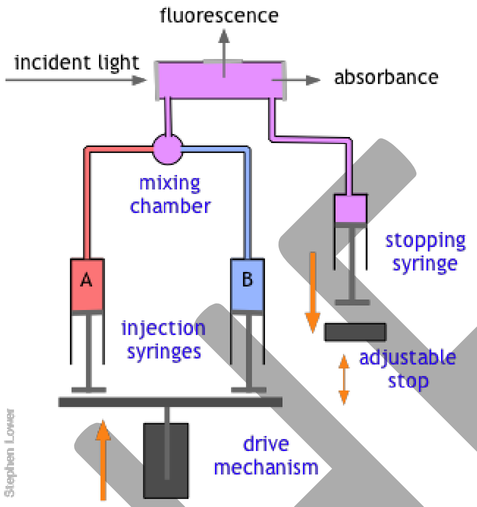


A continuous flow fast kinetic system.

If the distance between the point at which the reaction is initiated and the product detector is known, then the time interval can be found from the flow rate. By varying this distance, the time required to obtain the maximum yield can then be determined. Although this method is very simple in principle, it can be complicated in practice.

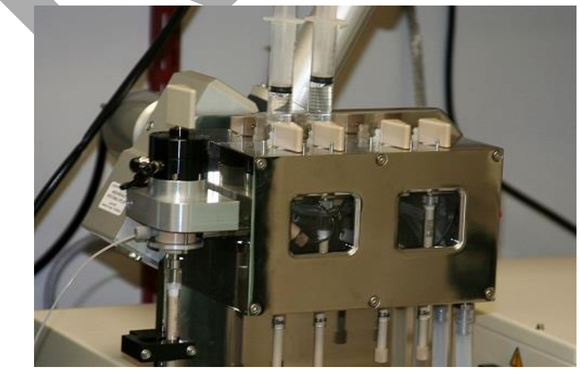
Stopped Flow Approach

Owing to the rather large volumes required, continuous flow method is more practical for the study of gas-phase reactions than for solutions, for which the stopped-flow method described below is generally preferred. These are by far the most common means of studying fast solution-phase reactions over time intervals of down to a fraction of a millisecond. The use of reasonably simple devices is now practical even in student laboratory experiments. These techniques make it possible to follow not only changes in the concentrations of reactants and products, but also the buildup and decay of reaction intermediates.



A stop flow fast kinetic system.

The basic stopped-flow apparatus consists of two or more coupled syringes that rapidly inject the reactants into a small mixing chamber and then through an observation cell that can be coupled to instruments that measure absorption, fluorescence, light scattering, or other optical or electrical properties of the solution. As the solution flows through the cell, it empties into a stopping syringe that, when filled, strikes a backstop that abruptly stops the flow. The volume that the stopping syringe can accept is adjusted so that the mixture in the cell has just become uniform and has reached a steady state; at this point, recording of the cell measurement begins and its change is followed.

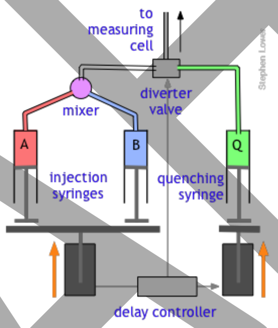


Stop-flow equipment at a biochemistry research laboratory for measuring rapid reactions and properties such as enzyme kinetics. Image used with permission from Wladimir Labeikovsky.

Quenched Flow Approach

In a quenched-flow instrument, the reaction is stopped after a certain amount of time has passed after mixing. The stopping of the reaction is called quenching and it can be achieved by various means, for example by mixing with another solution, which stops the reaction (chemical quenching), quickly lowering the temperature (freeze quenching) or even by exposing the sample to light of a certain wavelength (optical quenching).

Of course, there are many reactions that cannot be followed by changes in light absorption or other physical properties that are conveniently monitored. In such cases, it is often practical to *quench* (stop) the reaction after a desired interval by adding an appropriate quenching agent. For example, an enzyme-catalyzed reaction can be stopped by adding an acid, base, or salt solution that denatures (destroys the activity of) the protein enzyme. Once the reaction has been stopped, the mixture is withdrawn and analyzed in an appropriate manner.



A quench flow fast kinetic system.

The quenched-flow technique works something like the stopped-flow method described above, with a slightly altered plumbing arrangement. The reactants A and B are mixed and fed directly through the diverter valve to the measuring cell, which is not shown in this diagram. After a set interval that can vary from a few milliseconds to 200 sec or more, the controller activates the quenching syringe and diverter valve, flooding the cell with the quenching solution.

Relaxation Methods

To investigate reactions that are complete in less than a millisecond, one can start with a pre-mixed sample in which one of active reactants is generated *in situ*. Alternatively, a rapid change in pressure or temperature can alter the composition of a reaction that has already achieved equilibrium.

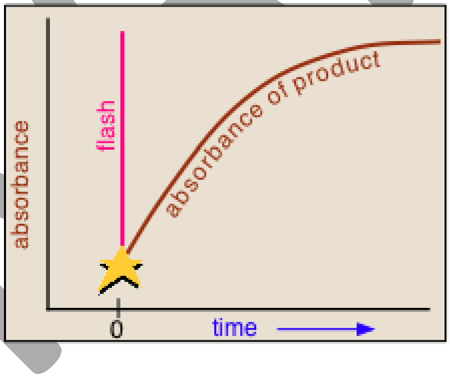
Flash Photolysis

Many reactions are known which do not take place without light of wavelength sufficiently short to supply the activation energy needed to break a bond, often leading to the creation of a highly reactive radical. A good example is the combination of gaseous Cl_2 with H_2, which proceeds explosively when the system is illuminated with visible light. In *flash photolysis*, a short pulse of light is used to initiate a reaction whose progress can be observed by optical or other means.

Photolysis refers to the use of light to decompose a molecule into simpler units, often ions or free radicals. In contrast to *thermolysis* (decomposition induced by high temperature), photolysis is able to inject energy into a molecule almost instantaneously and can be much "cleaner," meaning that there are fewer side reactions that often lead to complex mixtures of products. Photolysis can also be highly *specific*; the wavelength of the light that triggers the reaction can often be adjusted to activate one particular kind of molecule without affecting others that might be present.

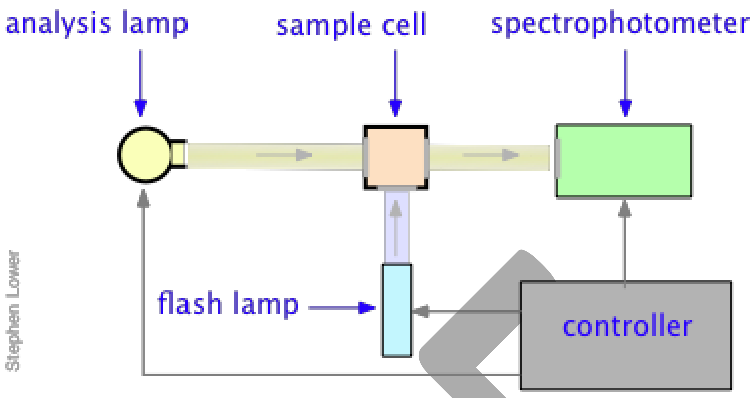
1. All this had been known for a very long time, but until the mid-1940's there was no practical way of studying the kinetics of the reactions involving the highly reactive species produced by photolysis.

In 1945, Ronald Norrish of Cambridge University and his graduate student George Porter conceived the idea of using a short-duration flash lamp to generate gas-phase CH_2 radicals, and then following the progress of the reaction of these radicals with other species by means of absorption spectroscopy.



Basic principle of a flash-photolysis relaxation experiment where an excitation pulse purturbed a system at equilibrium and the subsequent dynamics are resolved in time.

In a flash photolysis experiment, recording of the absorbance of the sample cell contents is timed to follow the flash by an interval that can be varied in order to capture the effects produced by the product or intermediate as it is formed or decays. Norrish and Porter shared the 1967 Nobel Prize in Chemistry for this work.



A flash-photolysis relaxation experiment

Many reactions, especially those that take place in solution, occur too rapidly to follow by flow techniques, and can therefore only be observed when they are already at equilibrium. The classical examples of such reactions are two of the fastest ones ever observed, the dissociation of water

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

and the formation of the triiodide ion in aqueous solution

$$I^-+I_2\rightarrow I^{-3}$$

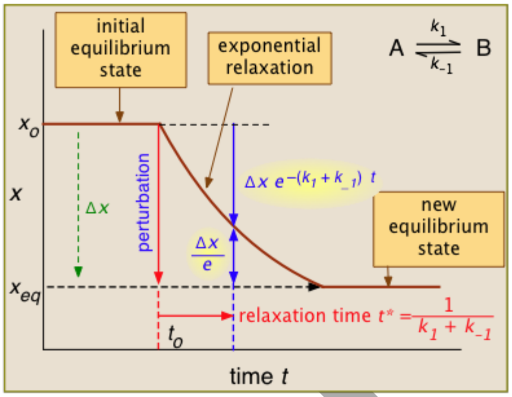
Reactions of these kinds could not be studied until the mid-1950s when techniques were developed to shift the equilibrium by imposing an abrupt physical change on the system.

Temperature Jumps

The rate constants of reversible reactions can be measured using a relaxation method. In this method, the concentrations of reactants and products are allowed to achieve equilibrium at a specific temperature. Once equilibrium has been achieved, the temperature is rapidly changed, and then the time needed to achieve the new equilibrium concentrations of reactants and products is measured. For example, if the reaction

$$A\rightleftharpoons k-1k1B$$

is endothermic, then according to the Le Châtelier principle, subjecting the system to a rapid jump in temperature will shift the equilibrium state to one in which the product B has a higher concentration. The composition of the system will than begin to shift toward the new equilibrium composition at a rate determined by the kinetics of the process.



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Shock tube methods

Shock Tube Investigations of High Temperature Reaction Kinetics

Combustion systems are characterized by a complicated interaction of flow and transport processes and a large number of elementary chemical reactions. The purpose of chemical kinetics is to unravel the underlying complex reaction mechanisms and to investigate the products and rates of selected reactions as function of temperature and pressure. In particular, the formation and the reactions of short-lived reactive intermediates (atoms and radicals) have to be well known. These intermediates maintain the combustion process and determine the end product distribution.

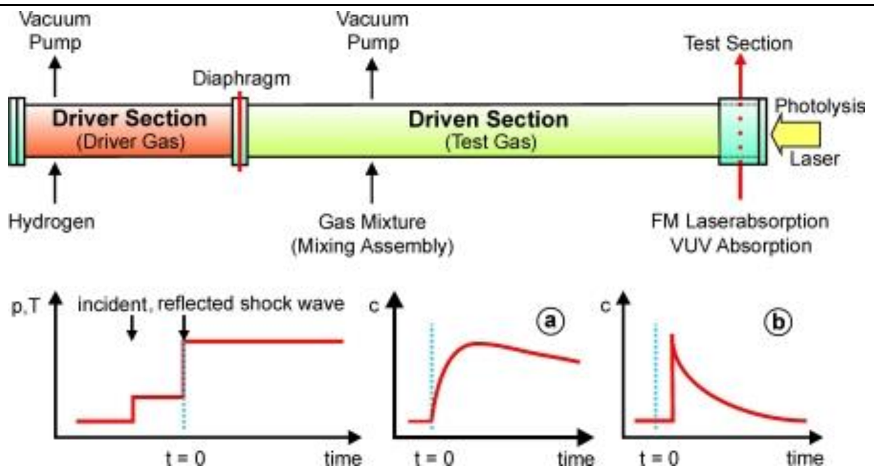


Fig 1:Top: schematic setup of a shock tube. Bottom: pressure/temperature-time profile during a shock tube experiment and typical concentration-time profiles of a) thermal or b) photolytic generation of the detected species.

The shock tube technique has been proven to be a very powerful method for investigating gas phase reactions at high temperatures. With shock tubes, the experimental pressure (0.1-1000 bar) and temperature (500-15000 K) can be easily varied over a wide range. Essentially, a shock tube apparatus (Fig. 1) is just a several meters long tube, which is divided by a diaphragm into a driver (high pressure) and a driven (low pressure) section. The test gas mixture, typically a highly diluted mixture of reactants in argon, is found in the driven section. The driver section is filled with helium or hydrogen until the diaphragm bursts. A shock wave is formed, which propagates downwards the tube at supersonic speed and heats and compresses the test gas within less than 1 µs (incident shock wave). The shock wave is reflected at the end wall and the preheated testgas is heated and compressed again (reflected shock wave). The resulting pressure- and temperature-time-profile is shown in the lower left part of Fig. 1. Typically, the constant conditions behind the reflected wave last for roughly 1 - long enough for studying chemical reactions, which are mostly fast at high temperatures. In many cases, the species of interest are generated thermally by the decomposition of suitable precursor molecules (Fig. 1a), but often a photolytic production is also feasible (Fig. 1b). Finally, real-time detection of the concentration-time-profiles is accomplished through optical windows by means of a variety of sensitive spectroscopic absorption or emission techniques. A recent example is the application of the highly sensitive laser absorption based frequency modulation (FM) spectroscopy for quantitative detection of small radicals behind shock waves. With FM spectroscopy the radicals methylene ($^1CH_2$) and formyl (HCO), which are both of considerable importance in combustion chemistry, could be detected behind shock waves for the first time [1,2]. Both formaldehyde (CH_2O) and formyl radicals (HCO) lie on the main oxidation pathway of hydrocarbons with CH_3 as the chain center. Methane oxidation, for example, proceeds in the following steps:

CH_4 => CH_3 => CH_2O => HCO => CO => CO_2

Under radical-rich conditions, formaldehyde is mainly formed by the reaction of methyl radicals with oxygen atoms. Subsequent abstration reactions of H, OH, O and CH_3 yield formyl radicals. By reactions of HCO with H, O_2 and OH, and also through its unimolecular decomposition, carbon monoxide and eventually carbon dioxide are formed. The high temperature decomposition of CH_2O provides a simple system to investigate some of these reactions. The chain mechanism of the CH_2O decay can be described over a wide range of temperatures and pressures by only five reactions:

CH_2O	+	M	HCO	+	H	+	M	(1a)
CH_2O	+	M	H_2	+	CO	+	M	(1b)
CH_2O	+	H	H_2	+	HCO			(2)
HCO	+	M	H	+	CO	+	M	(3)
HCO	+	H	H_2	+	CO			(4)
HCO	+	HCO	CH_2O	+	CO			(5)

By means of sensitive vacuum-UV-absorption detection of CH_2O at 174 nm and frequency modulation detection of HCO at wavelength around 614 nm, the rate of reaction (2) was directly measured at high temperatures for the first time (CH_2O detection, C_2H_5I as H atom source, T=1510 - 1960 K) and the rate of reaction (3) could be measured at temperatures of 835 - 1230 K (HCO detection, photolysis of CH_2O mixtures) [2, 3]. Furthermore, measurements of reactions (4) and (5) at lower temperatures (HCO detection, photolytic production of HCO) and the detection of CH_2O and HCO profiles during the thermal decomposition of pure formaldehyde mixtures behind shock waves provided additional information about the rates of reactions (1a) and (3) [2,4]. Altogether, sensitive detection methods and extensive experimental data made it possible to separate the strongly coupled reactions and to obtain a consistent set of rate constants.

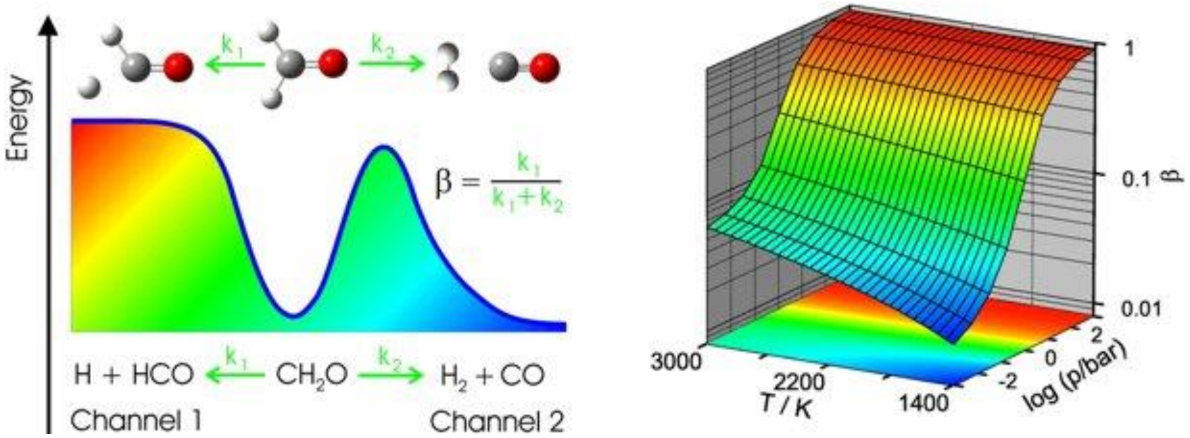


Fig:2Left: schematic potential curve of the thermal decomposition of formaldehyde (CH_2O) with H_2 + CO and H + HCO as reaction products, respectively. Right: calculated branching fraction as function of pressure and temperature; based on two-channel RRKM calculation.

As a final step, the rate of reaction (1b), which becomes more important at low formaldehyde concentrations, and also the branching fraction β of the initiation step (reactions (1a) and (1b)) were calculated using statistical theories of unimolecular reactions. Similar threshold energies and different energy dependencies of the decay rates of the two reaction channels with loose (1a) and tight (1b) transition states, respectively, induce a distinct pressure and temperature dependence of the branching fraction β (Fig. 2). A two-channel RRKM calculation, which takes into account rotational effects and "weak collisions" (master equation analysis) reveals that at temperatures from 1400 to 3000 K and at low pressures (1 mbar) reaction (1b) with H_2 and CO as products is the main channel. However, with increasing pressure, channel (1a) eventually dominates and at very high pressures (1 kbar)

Possible Questions

PART A **(Each Question carries one mark)**

1. The temperature coefficient of a reaction is
(a) The rate constant at a fixed rate constant
(b) The ratio of rate constants at two temperatures
(c)The ratio of rate constants differing by 10° C preferably 25° C and 35° C
(d) The ratio of rate constant at ordinary temperature

2 .A large increase in the rate of reaction for a rise in temperature is due to
(a) Increase in the number of collisions
(b) Increase in the number of activated molecules
(c) Lowering of activation energy
(d) Decrease in the of number of collisions

3. For a reaction, the rate of reaction was found to increase about 1.8 times when the temperature was increased by 10° C, the increase in rate is due to
(a) increase in the number of active molecules
(b) increase in activation energy of reactants
(c) Decrease in activation energy of reactants
(d) Increase in the number of collisions between reacting molecules

4. In a reaction, the threshold energy is equal to
(a) Activation energy + normal energy of reactants
(b) Activation energy - normal energy of reactants
(c) Activation energy
(d) Normal energy of reactants
1.The threshold energy of a chemical reaction depends on
(a)Nature of reacting species (b)Temperature (c)Concentration of species
(d)No of collisions per unit time or collision frequency

5.The minimum energy necessary to permit a reaction to take place is
(a)Threshold energy **(b)Activation energy** **(c)**Free energy (d)Kinetic energy

6.The value of activation energy of a chemical reaction is primarily determined by
(a)Nature of reacting species (b)Temperature (c)concentration of species
(d)No of collisions per unit time or collision frequency

7.As more molecules reach the activation energy of the molecules
(a)Increases (b)Decreases (c)Remains the same (d)varies irregularly

8.Activation energy can be described as the
(a)energy of motion. (b)energy of the activated complex.
(c)energy difference between the reactants and the products.
(d)energy difference between the reactants and the activated complex.

9.The minimum amount of energy required to overcome the energy barrier in a chemical raction is the
(a)heat of reaction. **(b)activation energy.**
(c)KE of the reactants. (d)enthalpy of the products.

10.As reactant particles approach one another, their
(a)kinetic energy increases and their potential energy increases.
(b)kinetic energy increases and their potential energy decreases.
(c)kinetic energy decreases and their potential energy increases.
(d)kinetic energy decreases and their potential energy decreases.

11.In general, a chemical reaction requiring a large activation energy will proceed
(a)at a fast rate **(b)only at slow rate** (c) only at low temperatures
(d)only at low concentrations

12.Efficiency of a catalyst depends on its
(a)particle size (b)Solubility (c)Molecular weight (d)Activation energy

13.Chemical substances speeding up the rate of chemical reaction is called as
(a)Product (b)concentration **(c)catalysts** (d)inhibitors

14.Which statement about a catalyst is incorrect?
(a)The presence of a catalyst speeds up a reaction
(b)The presence of a catalyst changes the rate of a reaction
(c)In some reactions, one of the products acts as a catalyst for the forward reaction
(d)During use, a catalyst may be poisoned

15.An increase in temperature increases the rate of a chemical reaction because
(a)the activation energy is lower.
(b)exothermic reactions are always favoured.
(c)greater fraction of particles have sufficient kinetic energy.
(d)the particles are more likely to have favourable collision geometry.

16.Which of the following changes will increase the average kinetic energy of reactant molecules?
(a)adding a catalyst **(b)increasing the temperature** (c) increasing the surface area
(d)increasing the concentration

17.Among the following methods which is used to determine the rate of fast reactions

(a)pulse method (b)Ostwald's isolation method (c)Graphical method (d)Half change method

18.The activation energy of a reaction in solution
(a)increases with the addition of a catalyst. (b)decreases with a decrease in temperature.
(c)increases if the solution is stirred vigorously. **(d)does not change with an increase in temperature.**

19.To increase the rate of a reaction, there must be
(a)a decrease in the frequency of collisions.
(b)an increase in the frequency of collisions.
(c)a decrease in the frequency of successful collisions.
(d)an increase in the frequency of successful collisions.

20.An increase in temperature increases the rate of a chemical reaction because
(a)the activation energy is lower.
(b)exothermic reactions are always favoured.
(c)a greater fraction of particles have sufficient kinetic energy.
(d) the particles are more likely to have favourable collision geometry.

Part B **(Each question carries 2 marks)**

1.Compare reactions in solution between gas-phase and solution reactions.

2.Explain primary salt effect.

3.Write a note on significance of volume and entropy of activations.

4.Give the principle of flow method.

5.What is the principle involved in shock-tube method.

Part C **(Each question carries 6 marks)**

1. Give a detailed account on ARRT in terms of partition functions with a suitable diagram.

2.Explain in detail Shock - tube method for the study of fast reactions

3.Explain primary salt effect.

4.How will you determine the rate of fast reactions using Flow method?

5. Explain the influence of solvent on the reaction between ions.

6.What are fast reactions? Name the various methods used to study the fast reactions. Explain any one method.

7.Explain the hard sphere collision theory of gas phase reactions.

8.By using relaxation method how will you study the rate of fast reactions.

9.Explain in detail the influence of ionic strength on the rate of reactions.

10. Write notes on nuclear magnetic resonance method.

KARPAGAM ACADEMY OF HIGHER EDUCATION
COIMBATORE-641 021
(For the candidates admitted from 2017 & Onwards)
M.Sc., CHEMISTRY
SECOND SEMESTER

PHYSICAL CHEMISTRY-II (Chemical Kinetics and Electrochemistry) 17CHP203

S.NO	UNIT-I	OPTION 1	OPTION 2	OPTION 3	OPTION 4	ANSWER
1	The temperature coefficient of a reaction is	a)the rate constant at a fixed rate constant	b)the ratio of rate constants at two temperatures	c)The ratio of rate constants differing by 10° C preferably	d)the ratio of rate constant at ordinary temperature	c)The ratio of rate constants differing by 10° C preferably
2	A large increase in the rate of reaction for a rise in temperature is due to	a)Increase in the number of collisions	b)Increase in the number of activated molecules	c)Lowering of activation energy	d)Shortening of activation energy	b)Increase in the number of activated molecules
3	The ratio of the rate constants of a reaction at two temperatures differing by 10 degree celcius is known as	a)presssure coefficient	b)temperature coefficient	c)volume coefficient	d)concentration coefficient	b)temperature coefficient
4	For a reaction, the rate of reaction was found to increase about 1.8 times when the temperature was increased by 10° C, the increase in	a)increase in the number of active molecules	b)increase in activation energy of reactants	c)Decrease in activation energy of reactants	d)Increase in the number of collisions between reacting	a)increase in the number of active molecules
5	On increasing the temperature by 10 k in the case of slow reactions	a)No of collisions get doubled	b)value of rate constant increases	c)Energy of activation increases	d)value of rate constant decreases	b)value of rate constant increases
6	An increase in the rate of a reaction for a rise in temperature is due to	a)Increase in collision frequency	b)Shortening of mean free path	c)Increase in number activated molecules	d)All	d)All
7	If the rate of reaction becomes 2 times for every 10° C rise in temperature, by what factor the rate of reaction increases when	a)16	b)32	c)64	d)128	b)32
8	As the temperature of a gaseous system increases, the number of molecules with a higher kinetic energy	a)Increases	b)decreases	c)Remains same	d)varies irregularly	a)Increases
9	For a slow reaction, the ratio of rate constants at 35° C and 25° C is generally	a)2	b)3	c)1	d)4	a)2
10	In a reaction, the threshold energy is equal to	a)Activation energy + normal energy of reactants	b)Activation energy - normal energy of reactants	c)Activation energy	d)Normal energy of reactants	c)Activation energy
11	Minimum energy required by molecules to enter into chemical reaction is called	a)Kinetic energy	b)Potential energy	c)Threshold energy	d)Activation energy	c)Threshold energy
12	The enzyme catalysed reactions are faster than metal catalysed reactions because their activation energy is	a)Greater	b)smaller	c)same	d)Zero	b)Smaller
13	For a reactionfor which the activation energies of forward and backward reactions are equal	a)$\Delta H = 0$	b)$\Delta S = 0$	c)The order is zero	d)There is no need of catalyst	a)$\Delta H = 0$
14	Activation energy of a reaction is	a)The energy released during the reaction	b)energy involved when activation complex is formed	c)Minimum amount of energy required to overcome the	d)The enrgy needed to form 1 mole of the product	c)Minimum amount of energy required to overcome the
15	Combustion of carbon is exothermic but coal stored in coal depots does not burnt automatically because of	a)High threshold barrier	b)Kinetic stability of coal	c)Higher activation energy required for burning	d)All	d)All
16	The threshold energy of a chemical reaction depends on	a)Nature of reacting species	b)Temperature	c)Concentration of species	d)No of collisions per unit time or collision frequency	a)Nature of reacting species
17	The minimum energy necessary to permit a reaction to take place is	a)Threshold energy	b)Activation energy	c)Free energy	d)Kinetic energy	b)Activation energy
18	The value of activation energy of a chemical reaction is primarily determined by	a)Nature of reacting species	b)Temperature	c)concentration of species	d)No of collisions per unit time or collision frequency	a)Nature of reacting species
19	As more molecules reach the activation energy of the molecules	a)Increases	b)Decreases	c)Remains the same	d)varies irregularly	a)Increases
20	As the energy of activation increases	a)The number of reacting molecules collising decreases	b)The rate of reaction decreases	c)the rate of reaction increases	d)The rate constant increases	b)The rate of reaction decreases
21	The minimum amount of energy required by the reacting molecules at the time of collisions inorder to produce effective collisions is	a)Activation energy	b)Threshold energy	c)Internal energy	d)Potential energy	b)Threshold energy
22	The chemical reactions in which reactants need high amount of activation energy are generally	a)Fast	b)slow	c)very fast	d)spontaneous	b)Slow
23	According to Arrhenius equation a straight line is obtained by ploting the log of the rate constant of a chemical reaction (log k) against	a)T	b)Log T	c)1/T	d)Log 1/T	c)1 / T

24	In arrhenius equation, the fraction of effective collision is given by	a)k = A e-Ea / RT	b)A	c)$e^{-Ea / RT}$	d)E	c)$e^{-Ea / RT}$
25	Which of the following is used to determine the rate of fast reactions	a)Ostwald's isolation method	b)Nuclear magnetic resonance method	c)Graphical method	d)Half change method	b)Nuclear magnetic resonance method
26	The dependance of rate constant K of a reaction on the activation energy E is expressed as	a)k = A e-Ea / RT	b)k = A e-E / RT	c)k = e-E / RT	d)k = E / RT	a)k = A e-Ea / RT
27	According to collision theory of reaction rates	a)Every collision between reactant molecules leads to	b)Rate of reaction is proportional to velocity of	c)All reactions which occur in gaseous phase are zero order	d)Rate of reaction is directly proportional to collision	d)Rate of reaction is directly proportional to collision
28	Kinetic theory of collision is putforward by	a)Max Trautz	b)Arrhenius	c)Lewis	d)Draper	b)Arrhenius
29	Among the following methods which is used to determine the rate of fast reactions	a)Ostwald's isolation method	b)Flash photolysis	c)Graphical method	d)Half change method	b)Flash photolysis
30	Arrhenius plot of log K vs T is a	a)curve	b)parabola	c)Straight line	d)circle	a)Curve
31	The intercept of the line obtained in the Arrhenius	a)Log T	b)Log A	c)Log V	d)Log P	a)Log T
32	High activation energy corresponds to a reaction rate which is	a)sensitive to T	b)sensitive to P	c)sensitive to A	d)sensitive to Ea	a)sensitive to T
33	Which among the following are known as Arrhenius parameters	a)Ea	b)Eb	c)AE	d)E	a)Ea
34	Activation energy of chemical reaction can be determined by	a) Evaluating rate constants at two different temperatures	b)Changing concentrations of reactions	c)Evaluating rate constant at standard temperature	d)Evaluating velocities of reaction at two different	c)Evaluating rate constant at standard temperature
35	What is the activation energy (in kJ) of a reaction whose rate constant increases by a factor of 100 upon increasing the temperature from	a)27	b)35	c)42	d)69	d)69
36	A catalyst	a)actually participates in the reaction	b)changes the equilibrium concentration of the products	c)does not affect a reaction energy path	d)always decreases the rate for a reaction	a)actually participates in the reaction
37	Which statement is false?	a)If a reaction is thermodynamically	b)If a reaction is thermodynamically	c)If a reaction is thermodynamically	d)If a reaction is thermodynamically	d)If a reaction is thermodynamically
38	When the concentration of reactant molecules is increased, the rate of reaction increases. The best explanation is: As the reactant	a)the average kinetic energy of molecules increases.	b)the frequency of molecular collisions increases.	c)the rate constant increases	d)the activation energy increases	b)the frequency of molecular collisions increases.
39	When a catalyst is added to a system at equilibrium, a decrease occurs in the	a)Activation energy	b)heat of reaction	c)Potential energy of the reactants	d)Potential energy of the products	a)Activation energy
40	Which statement explains why the speed of some chemical reactions is increased when the surface area of the reactant is increased?	a)This change increases the density of the reactant	b)This change increases the concentration of the reactant.	c)This change exposes more reactant particles to a possible	d)This change alters the electrical conductivity of the	c)This change exposes more reactant particles to a possible
41	Which conditions will increase the rate of chemical reaction?	a)decreased temperature and decreased concentration of	b)decreased temperature and increased concentration of	c)increased temperature and decreased concentration of	d)increased temperature and increased concentration of	d)increased temperature and increased concentration of
42	Which is a property of a reaction that has reached equilibrium?	a)The amount of products is greater than the amount of	b)The amount of products is equal to the amount of	c)The rate of the forward reaction is greater than the	d)The rate of the forward reaction is equal to than the	d)The rate of the forward reaction is equal to than the
43	Speed of a reaction can be measured through	a)Temperature	b)pressure	c)Concentration	d)a pH change	d)a pH change
44	Factors affecting the speed of reaction include	a)volume of gas	b)change in mass	c)Pressure	d)temperature change	c)pressure
45	The suitable apparatus to measure the volume of gas given off is	a)a tap funnel	b)a conical feeble	c)a graduated cylinder	d)temperature change	d)temperature change
46	At 100 °C, the speed of reaction becomes	a)16 times faster	b)64 times faster	c)128 times faster	d)148 times faster	c)128 times faster
47	Rate of reaction does not depend upon	a)temperature	b)concentration of reactants	c)pressure	d)expanding of gases	d)expanding of gases
48	Chemical substances speeding up the rate of chemical reaction is called as	a)Presuure	b)concentration	c)catalysts	d)inhibitors	c)catalysts
49	Which statement about a catalyst is incorrect?	a)The presence of a catalyst speeds up a reaction	b)The presence of a catalyst changes the rate of a reaction	c)In some reactions, one of the products acts as a catalyst	d)During use, a catalyst may be poisoned	b)The presence of a catalyst changes the rate of a reaction
50	An increase in temperature increases the rate of a chemical reaction because	a)the activation energy is lower.	b)exothermic reactions are always favoured.	c)greater fraction of particles have sufficient kinetic energy.	d)the particles are more likely to have favourable collision	c)greater fraction of particles have sufficient kinetic energy.
51	Which of the following changes will increase the average kinetic energy of reactant molecules?	a)adding a catalyst	b)increasing the temperature	c)increasing the surface area	d)increasing the concentration	b)increasing the temperature

52	An activated complex has	a)low potential energy and is stable.	b)high potential energy and is stable.	c)low potential energy and is unstable.	d)high potential energy and is unstable.	d)high potential energy and is unstable.
53	An activated complex is a chemical species that is	a)stable and has low PE.	b)stable and has high PE.	c)unstable and has low PE.	d)unstable and has high PE.	d)unstable and has high PE.
54	The activation energy of a reaction in solution	a)increases with the addition of a catalyst.	b)decreases with a decrease in temperature.	c)increases if the solution is stirred vigorously.	d)does not change with an increase in temperature.	d)does not change with an increase in temperature.
55	To increase the rate of a reaction, there must be	a)a decrease in the frequency of collisions.	b)an increase in the frequency of collisions.	c)a decrease in the frequency of successful collisions.	d)an increase in the frequency of successful collisions.	d)an increase in the frequency of successful collisions.
56	An increase in temperature increases the rate of a chemical reaction because	a)the activation energy is lower.	b)exothermic reactions are always favoured.	c)a greater fraction of particles have sufficient kinetic energy.	d) the particles are more likely to have favourable collision	c)a greater fraction of particles have sufficient kinetic energy.
57	Which of the following will decrease the number of effective collisions during a chemical reaction?	a)Adding a catalyst.	b)Increasing the surface area.	c)Decreasing the temperature.	d) Increasing reactant concentrations.	c)Decreasing the temperature.
58	When a collision occurs between two reactant species which possess between them the minimum kinetic energy, called activation energy,	a)low temperature.	b)small surface area	c)low concentrations	d)unfavourable geometry	d)unfavourable geometry
59	Activation energy can be described as the	a)energy of motion.	b)energy of the activated complex.	c)energy difference between the reactants and the products.	d)energy difference between the reactants and the activated	d)energy difference between the reactants and the activated
60	The minimum amount of energy required to overcome the energy barrier in a chemical raction is the	a)heat of reaction.	b)activation energy.	c)KE of the reactants.	d)enthalpy of the products.	b)activation energy.
61	As reactant particles approach one another, their	a)kinetic energy increases and their potential energy	b)kinetic energy increases and their potential energy	c)kinetic energy decreases and their potential energy	d)kinetic energy decreases and their potential energy	c)kinetic energy decreases and their potential energy
62	In general, a chemical reaction requiring a large activation energy will proceed	a)at a fast rate	b)only at slow rate	c)only at low temperatures	d)only at low concentrations	b)only at slow rate
63	Which of the following is used to determine the rate of fast reactions	a)Ostwald's isolation method	b)Graphical method	c)Relaxation method	d)Half change method	c)Relaxation method
64	Which of the following is used to determine the rate of fast reactions	a)Shock-tube method	b)Ostwald's isolation method	c)Graphical method	d)Half change method	a)Shock-tube method
65	Among the following methods which is used to determine the rate of fast reactions	a)pulse method	b)Flash photolysis	c)Graphical method	d)Half change method	a)pulse method

UNIT II

SYLLABUS

Homogeneous catalysis: Specific and general acid - base catalysis. Bronsted catalysis law-Hammett acidity functions. Enzyme catalysis (single substrate reaction only). Michaelis Menten law - Influence of pH and temperature on enzyme catalysis.

Surface phenomenon and heterogeneous catalysis: Adsorption and free energy relation at interfaces. Gibb's adsorption isotherm- physisorption and chemisorptions- Adsorption isotherms (Freundlich & Langmuir). Kinetics of heterogeneous catalysis- Langmuir - Hinshelwood and Langmuir - Rideal - Eley mechanisms.

Homogeneous catalysis

Specific and general acid-base catalysis

In **acid catalysis** and **base catalysis** a chemical reaction is catalyzed by an acid or a base. The acid is the proton donor and the base is the proton acceptor, known as Brønsted-Lowry acid and base respectively. Typical reacions catalyzed by proton transfer are esterfications and aldol reactions. In these reactions the conjugate acid of the carbonyl group is a better electrophile than the neutral carbonyl group itself. Catalysis by either acid or base can occur in two different ways: **specific catalysis** and **general catalysis**. Many enzymes operate by acid-catalysis.

Applications and examples

Brønsted acids

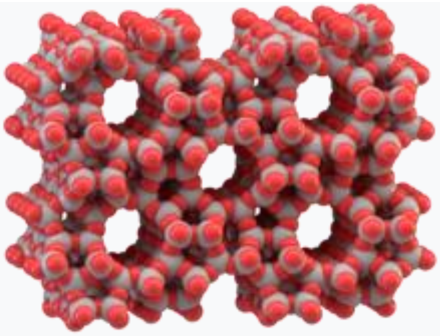
Acid catalysis is mainly used for organic chemical reactions. Many acids can function as sources for the protons. Acid used for acid catalysis include hydrofluoric acid (in the alkylation process), phosphoric acid, toluenesulfonic acid, polystyrene sulfonate, heteropoly acids, zeolites.

Strong acids catalyze the hydrolysis and transesterification of esters, e.g. for processing fats into biodiesel. In terms of mechanism, the carbonyl oxygen is susceptible to protonation, which enhances the electrophilicity at the carbonyl carbon.

Solid acid catalyst

In industrial scale chemistry, many processes are catalysed by "solid acids". As heterogeneous catalysts, solid acids do not dissolve in the reaction medium. Well known examples include these oxides, which function as Lewis acids: silico-aluminates (zeolites, alumina, silico-aluminophosphate), sulfated zirconia, and many transition metal oxides (titania, zirconia, niobia, and more). Such acids are used in cracking. Many solid Brønsted acids are also employed industrially, including sulfonated polystyrene, solid phosphoric acid, niobic acid, and heteropolyoxometallates.

A particularly large scale application is alkylation, e.g., the combination of benzene and ethylene to give ethylbenzene. Another major application is the rearrangement of cyclohexanone oxime to caprolactam. Many alkylamines are prepared by amination of alcohols, catalyzed by solid acids. In this role, the acid converts, OH^-, a poor leaving group, into a good one. Thus acids are used to convert alcohols into other classes of compounds, such as thiols and amines.



Zeolite, ZSM-5 is widely used as a solid acid catalyst.

Mechanism

Two kinds of acid catalysis are recognized, specific acid catalysis and general acid catalysis.[3]

Specific catalysis

In specific acid catalysis, protonated solvent is the catalyst. The reaction rate is proportional to the concentration of the protonated solvent molecules SH^+.[4] The acid catalyst itself (AH) only contributes to the rate acceleration by shifting the chemical equilibrium between solvent S and AH in favor of the SH^+ species. This kind of catalysis is common for strong acids in polar solvents, such as water.

$$S + AH \rightarrow SH^+ + A^-$$

For example, in an aqueous buffer solution the reaction rate for reactants R depends on the pH of the system but not on the concentrations of different acids.

This type of chemical kinetics is observed when reactant $\mathbf{R^1}$ is in a fast equilibrium with its conjugate acid $\mathbf{R^1H^+}$ which proceeds to react slowly with $\mathbf{R^2}$ to the reaction product; for example, in the acid catalysed aldol reaction.

General catalysis

In general acid catalysis all species capable of donating protons contribute to reaction rate acceleration.[5] The strongest acids are most effective. Reactions in which proton transfer is rate-determining exhibit general acid catalysis, for example diazonium coupling reactions.

When keeping the pH at a constant level but changing the buffer concentration a change in rate signals a general acid catalysis. A constant rate is evidence for a specific acid catalyst. When reactions are conducted in nonpolar media, this kind of catalysis is important because the acid is often not ionized.

Enzymes catalyze reactions using general-acid and general-base catalysis.

Bronsted catalysis law

The **Brønsted catalysis equation** or law of correlation, after Johannes Nicolaus Brønsted, gives the relationship between acid strength and catalytic activity in general acid catalysis.

$$\log k=\alpha*\log(k_a)+C$$

A plot of the common logarithm of the reaction rate constant **k** versus the logarithm of the ionization constant $\mathbf{K_a}$ for a series of acids (for example a group of substituted phenols or carboxylic acids) gives a straight line with slope **α** and intercept **C**. The Brønsted equation is a free-energy relationship. The relationship implies that the Gibbs free energy for proton dissociation is proportional to the activation energy for the catalytic step. When the relationship is not linear, the chosen group of catalysts do not operate through the same reaction mechanism.

Specific and general catalysis is also found in base catalysed reactions and base Brønsted equation also exists with constant **β**.

The Brønsted equation gives information about a reaction mechanism. Reactions that have low values for proportionality constants **α** or **β** are considered to have a transition state closely resembling the reactant with little proton transfer. With a high value, proton transfer in the transition state is almost complete. In a study of a group of phenalene compounds it was concluded from Brønsted analysis that phenalene acidity is very different from either indene acidity or phenylene acidity .

Hammett acidity functions

The **Hammett acidity function** (H_0) is a measure of acidity that is used for very concentrated solutions of strong acids, including superacids. It was proposed by the physical organic chemist Louis Plack Hammett[1][2]and is the best-known acidity function used to extend the measure of Brønsted–Lowry acidity beyond the dilute aqueous solutions for which the pH scale is useful.

In highly concentrated solutions, simple approximations such as the Henderson–Hasselbalch equation are no longer valid due to the variations of the activity coefficients. The Hammett acidity function is used in fields such as physical organic chemistry for the study of acid-catalyzed reactions, because some of these reactions use acids in very high concentrations, or even neat (pure).

Definition

The Hammett acidity function, H_0, can replace the pH in concentrated solutions. It is defined using an equation analogous to the Henderson-Hasselbalch equation:

$$H_0 = \mathrm{pk}_{BH+} + \log \frac{B}{BH+}$$

where log(x) is the common logarithm of x, and $\mathrm{p}K_{\mathrm{BH}}{}^{+}$ is −log(K) for the dissociation of BH^+, which is the conjugate acid of a very weak base B, with a very negative $\mathrm{p}K_{\mathrm{BH}}{}^{+}$. In this way, it is rather as if the pH scale has been extended to very negative values. Hammett originally used a series of anilines with electron-withdrawing groups for the bases

Hammett also pointed out the equivalent form

$$H_0 = -\log\left(a\ H^+ \frac{\gamma B}{\gamma BH+}\right)$$

where *a* is the activity, and the γ are thermodynamic activity coefficients. In dilute aqueous solution (pH 0-14) the predominant acid species is H_3O^+ and the activity coefficients are close to unity, so H_0 is approximately equal to the pH. However beyond this pH range, the effective hydrogen-ion activity changes much more rapidly than the concentration. This is often due to changes in the nature of the acid species; for example in concentrated sulfuric acid, the predominant acid species ("H+") is not H_3O^+ but rather $H_3SO_4^+$ which is a much stronger acid. The value $H_0 = -12$ for pure sulfuric acid must not be interpreted as pH = -12 (which would imply an impossibly high H_3O^+ concentration of 10^{+12} mol/L in ideal solution). Instead it means that the acid species present ($H_3SO_4^+$) has a protonating ability equivalent to H_3O^+ at a fictitious (ideal) concentration of 10^{12} mol/L, as measured by its ability to protonate weak bases.

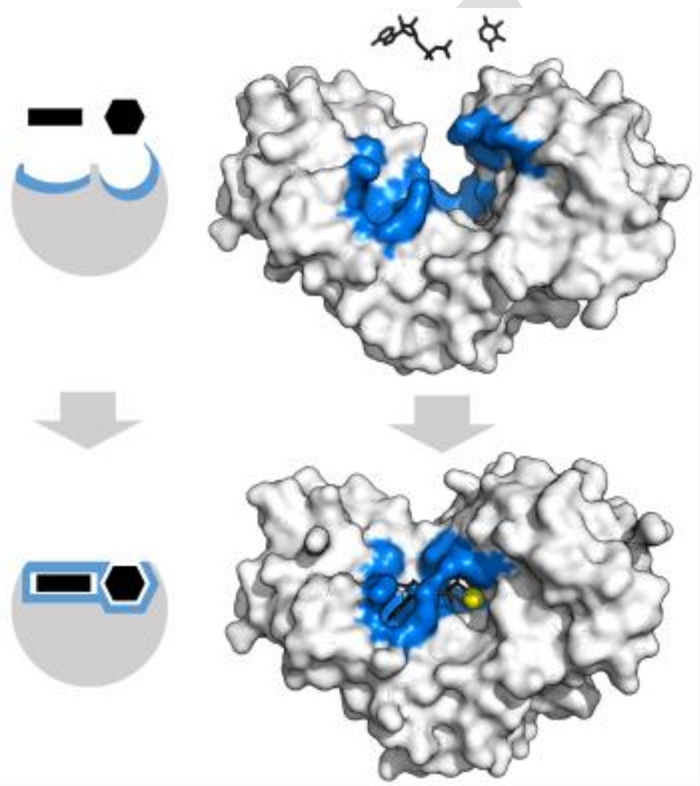
Although the Hammett acidity function is the best known acidity function, other acidity functions have been developed by authors such as Arnett, Cox, Katrizky, Yates, and Stevens.

Enzyme catalysis

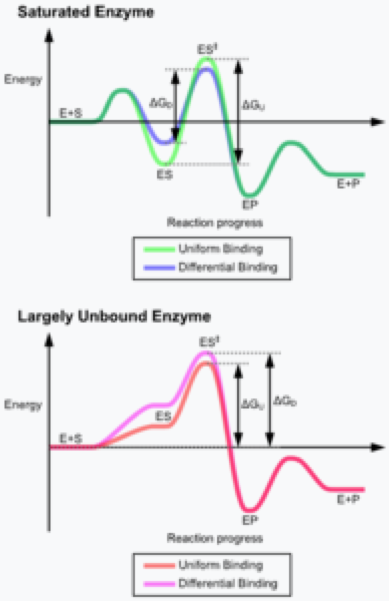
Enzyme catalysis is the increase in the rate of a chemical reaction by the active site of a protein. The protein catalyst (enzyme) may be part of a multi-subunit complex, and/or may transiently or permanently associate with a Cofactor (e.g. adenosine triphosphate). Catalysis of biochemical reactions in the cell is vital due to the very low reaction rates of the uncatalysed reactions at room temperature and pressure. A key driver of protein evolution is the optimization of such catalytic activities via protein dynamics.

The mechanism of enzyme catalysis is similar in principle to other types of chemical catalysis. By providing an alternative reaction route the enzyme reduces the energy required to reach the highest energy transition state of the reaction. The reduction of activation energy (Ea) increases the amount of reactant molecules that achieve a sufficient level of energy, such that they reach the activation energy and form the product. As with other catalysts, the enzyme is not consumed during the reaction (as a substrate is) but is recycled such that a single enzyme performs many rounds of catalysis.

Induced fit



Enzyme changes shape by induced fit upon substrate binding to form enzyme-substrate complex. Hexokinase has a large induced fit motion that closes over the substrates adenosine triphosphate and xylose. Binding sites in blue, substrates in black and Mg^{2+} cofactor in yellow. (PDB: 2E2N, 2E2Q)



The different mechanisms of substrate binding

The favored model for the enzyme-substrate interaction is the induced fit model. This model proposes that the initial interaction between enzyme and substrate is relatively weak, but that these weak interactions rapidly induce conformational changes in the enzyme that strengthen binding.

The advantages of the induced fit mechanism arise due to the stabilizing effect of strong enzyme binding. There are two different mechanisms of substrate binding: uniform binding, which has strong substrate binding, and differential binding, which has strong transition state binding. The stabilizing effect of uniform binding increases both substrate and transition state binding affinity, while differential binding increases only transition state binding affinity. Both are used by enzymes and have been evolutionarily chosen to minimize the activation energy of the reaction. Enzymes that are saturated, that is, have a high affinity substrate binding, require differential binding to reduce the energy of activation, whereas small substrate unbound enzymes may use either differential or uniform binding.

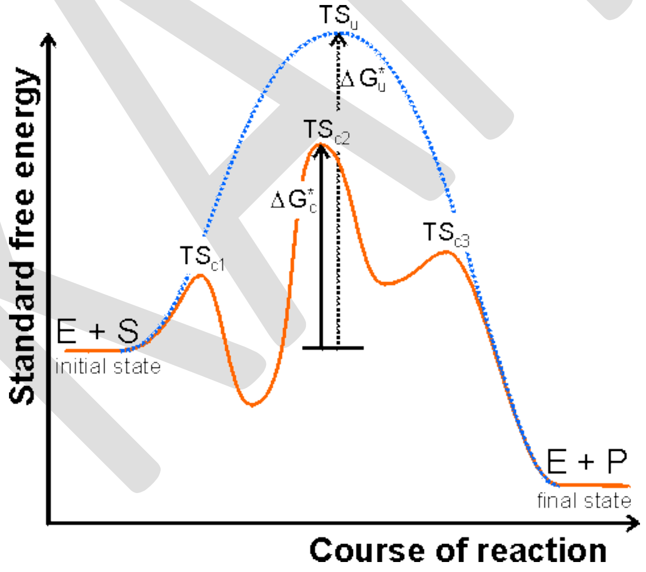
These effects have led to most proteins using the differential binding mechanism to reduce the energy of activation, so most substrates have high affinity for the enzyme while in the transition state. Differential binding is carried out by the induced fit mechanism - the substrate first binds weakly, then the enzyme changes conformation increasing the affinity to the transition state and stabilizing it, so reducing the activation energy to reach it.

It is important to clarify, however, that the induced fit concept cannot be used to rationalize catalysis. That is, the chemical catalysis is defined as the reduction of $Ea^{\ddagger}$ (when the system is already in the $ES^{\ddagger}$) relative to $Ea^{\ddagger}$ in the uncatalyzed reaction in water (without the enzyme). The induced fit only suggests that the barrier is lower in the closed form of the enzyme but does not tell us what the reason for the barrier reduction is.

Induced fit may be beneficial to the fidelity of molecular recognition in the presence of competition and noise via the conformational proofreading mechanism .

The mechanism of enzyme catalysis

In order for a reaction to occur, reactant molecules must contain sufficient energy to cross a potential energy barrier, the **activation energy**. All molecules possess varying amounts of energy depending, for example, on their recent collision history but, generally, only a few have sufficient energy for reaction. The lower the potential energy barrier to reaction, the more reactants have sufficient energy and, hence, the faster the reaction will occur. All catalysts, including enzymes, function by forming a transition state, with the reactants, of lower free energy than would be found in the uncatalysed reaction . Even quite modest reductions in this potential energy barrier may produce large increases in the rate of reaction (e.g. the activation energy for the uncatalysed breakdown of hydrogen peroxide to oxygen and water is 76 kJ M^{-1} whereas, in the presence of the enzyme catalase, this is reduced to 30 kJ M^{-1} and the rate of reaction is increased by a factor of 10^8, sufficient to convert a reaction time measured in years into one measured in seconds).



A schematic diagram showing the free energy profile of the course of an enzyme catalysed reaction involving the formation of enzyme-substrate (ES) and enzyme-product (EP) complexes, i.e.

$$E + S \rightleftharpoons ES \rightleftharpoons EP \rightleftharpoons E + P$$

The catalysed reaction pathway goes through the transition states TS_{c1}, TS_{c2} and TS_{c3}, with standard free energy of activation DG_c^*, whereas the uncatalysed reaction goes through the transition state TS_u with standard free energy of activation DG_u^*. In this example the rate limiting step would be the conversion of ES into EP. Reactions involving several substrates and products, or more intermediates, are even more complicated. The Michaelis-Menten reaction scheme would give a similar profile but without the EP-complex free energy trough. The schematic profile for the uncatalysed reaction is shown as the dashed line. It should be noted that the catalytic effect only concerns the lowering of the standard free energy of activation from DG_u^* to DG_c^* and has no effect on the overall free energy change (i.e. the difference between the initial and final states) or the related equilibrium constant.

There are a number of mechanisms by which this activation energy decrease may be achieved. The most important of these involves the enzyme initially binding the substrate(s), in the correct orientation to react, close to the catalytic groups on the active enzyme complex and any other substrates. In this way the binding energy is used partially in order to reduce the contribution of the considerable activation entropy, due to the loss of the reactants' (and catalytic groups') translational and rotational entropy, towards the total activation energy. Other contributing factors are the introduction of strain into the reactants (allowing more binding energy to be available for the transition state), provision of an alternative reactive pathway and the desolvation of reacting and catalysing ionic groups.

The energies available to enzymes for binding their substrates are determined primarily by the complementarity of structures (i.e. a good 3-dimensional fit plus optimal non-covalent ionic and/or hydrogen bonding forces). The specificity depends upon minimal steric repulsion, the absence of unsolvated or unpaired charges, and the presence of sufficient hydrogen bonds. These binding energies are capable of being quite large. As examples, antibody-antigen dissociation constants are characteristically near 10^{-8} M (free energy of binding is 46 kJ M^{-1}), ATP binds to myosin with a dissociation constant of 10^{-13} M (free energy of binding is 75 kJ M^{-1}) and biotin binds to avidin, a protein found in egg white, with a dissociation constant of 10^{-15} M (free energy of binding is 86 kJ M^{-1}). However, enzymes do not use this potential binding energy simply in order to bind the substrate(s) and form stable long-lasting complexes. If this were to be the case, the formation of the transition state between ES and EP would involve an extremely large free energy change due to the breaking of these strong binding forces, and the rate of formation of products would be very slow. They must use this binding energy for reducing the free energy of the transition state. This is generally achieved by increasing the binding to the transition state rather than the reactants and, in the process, introducing an energetic strain into the system and allowing more favourable interactions between the enzyme's catalytic groups and the reactants.

Michaelis Menten law

After the thermodynamic interpretation, we will now review the fundamental relationships of enzyme kinetics. As we focus on enzymatic reactions, the reactant will be denoted as substrate and will be referred to as “S”. The product will be denoted as P as previously. For simplicity, instead of the previous A + B → P scheme, we will introduce the simplest S → P case.

When the topic of enzyme kinetics first emerged, almost nothing was known about the physical nature of enzymes and the possible mechanisms of rate enhancement.

Let us start with a thought experiment considering the dependence of the rate of a non-catalysed chemical reaction as a function of reactant concentration. In the case of the simplest first-order reaction, the rate of the non-catalysed S→P reaction can be written as $V = d[P]/dt = k[S]$. In other words, the rate of the reaction is linearly proportional to the concentration of the reactant S. In principle, the rate could be increased to “infinity”—the only limit would be set by the solubility of S.

In typical cases, when an enzyme catalyses the same reaction, the rate is enhanced by orders of magnitude. However, very importantly, the plot of the [S]-V function would be principally different in this latter case. At a constant enzyme concentration, [E], and in the range of low [S] values, increasing [S] would result in an almost linear increase of the rate, V. However, as [S] is increased even further, V would not increase to the same extent and it would ultimately approximate a maximal value limit (Figure 1).

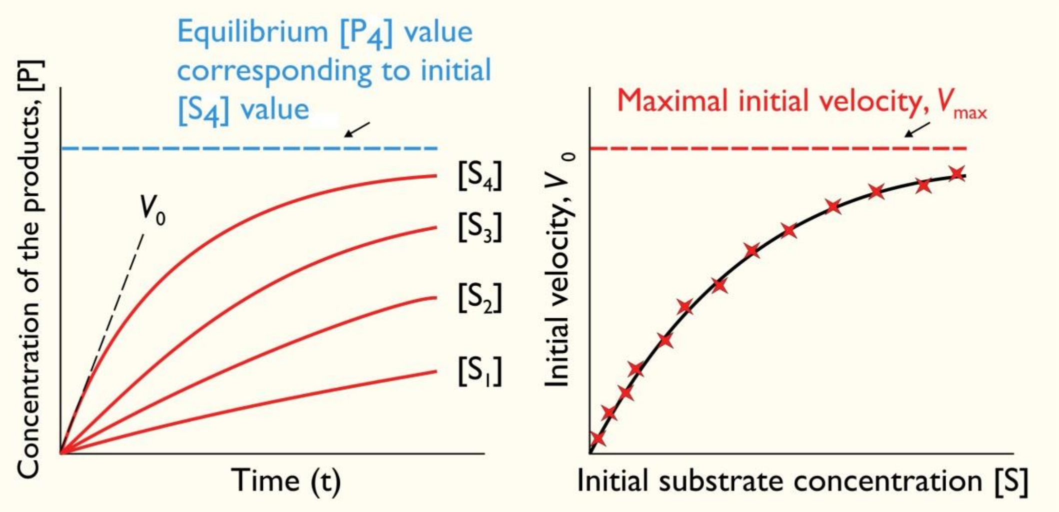


Figure 1. Initial rates (V_0) in enzyme kinetic experiments

The first kinetic model that successfully explained this phenomenon was introduced by Leonor Michaelis and Maud Menten. Their presumption, which nowadays might seem trivial, was revolutionary in their time. They assumed that the enzyme directly interacts with the substrate in a stoichiometric manner, the interaction results in a well-defined intermediate complex, and the interaction leads to thermodynamic equilibrium. This scheme is illustrated by Equation 1 in which ES denotes the complex. As a tribute to this first successful model, ES has been named the Michaelis complex.

$$E + S \overset{K_S}{\leftrightarrows} ES \xrightarrow{k_{cat}} E + P \qquad (1)$$

The above simplest scheme is based on the following assumptions. The interaction between the substrate and the enzymes that generates the ES complex leads to a (quasi-)equilibrium; and the reaction is instantaneous, i.e. so fast that the rate constants corresponding to this step do not restrict the overall rate of the reaction. Accordingly, for this first reaction step, the simple model introduces only an equilibrium constant, K_S, and it is not concerned with the two rate constants that determine K_S. K_S—which, in the case of non-covalent E-S interaction, is a dissociation constant—is defined by Equation 2:

$$K_S = \frac{[E][S]}{[ES]} \qquad (2)$$

According to this model, the catalytic rate constant, k_{cat} that corresponds to the rate of the decomposition of ES towards the product, is much lower than the (non-defined) rate constants corresponding to K_S. Accordingly, the rate of ES decomposition towards the product is so low that (at least in the time frame of the measurement) it does not affect the quasi-equilibrium concentrations of [E], [S] and [ES].

Let us see how the initial rate of the reaction depends on substrate concentration if the starting assumptions apply.

The rate equation corresponding to the scheme introduced in Equation 1 is shown in Equation 3. This equation refers to a first-order reaction in which the rate of the reaction is proportional to the concentration of only a single entity, in this case the ES complex:

$$V_0 = k_{cat}[ES] \qquad (3)$$

The scheme does not consider the opposite reaction, i.e. the one in which the interaction of the enzyme and the product would regenerate the ES complex. This is because the model focuses on the very beginning of the reaction when the concentration of the product is negligible. It is therefore of utmost importance that the rates defined in this model are always initial rates that correspond to the (theoretical) zero time point of the reaction.

The concentration of ES is not pre-set by the experimenter, but it can be determined experimentally once the right model is established. In the following steps, we will transform Equation 3 into a derived one that contains pre-set enzyme and substrate concentration parameters. To do so, we need to express ES concentration as a function of the pre-set enzyme and substrate concentrations. Let us start with Equation 2 that defined the K_S dissociation constant. Then let us consider a self-explanatory relationship shown in Equation 4, between the total enzyme concentration, ($[E]_T$), the free enzyme concentration and ES concentration:

$$[E]=[E]_T-[ES] \tag{4}$$

By combining Equation 4 with Equation 2, we get equation 5:

$$K_S=\frac{[E][S]}{[ES]}=\frac{([E]_T-[ES])[S]}{[ES]}=\frac{[E]_T[S]-[ES][S]}{[ES]} \tag{5}$$

Multiplying both sides by ES concentration yields equation 6:

$$K_S[ES]=[E]_T[S]-[ES][S] \tag{6}$$

In Equation 7, the ES-containing terms are rearranged to be side by side:

$$K_S[ES]+[ES][S]=[E]_T[S] \tag{7}$$

Then, in Equation 8, [ES] is multiplied out from the sum of the products:

$$[ES](K_S+[S])=[E]_T[S] \tag{8}$$

Finally, both sides are divided by the multiplying factor of [ES], which results in Equation 9:

$$[ES]=\frac{[E]_T[S]}{(K_S+[S])} \tag{9}$$

By these algebraic transformations, ES concentration has been expressed as a function of the experimentally pre-set enzyme and substrate concentrations and that of the equilibrium (dissociation) constant.

If the starting conditions are set such that the total substrate concentration exceeds the total enzyme concentration by orders of magnitude, the amount of substrate getting into the ES complex will be negligible compared to the total amount of substrate. Consequently, the free substrate concentration (at the beginning of the reaction) will practically equal the total substrate concentration. This way, both the total enzyme concentration, $[E]_T$, and the free substrate concentration, [S], will be experimentally-set known parameters.

In the next step, based on Equation 3, both sides of Equation 9 are multiplied by the k_{cat} rate constant to yield the initial rate, according to Equation 10:

$$V_0 = k_{cat}[ES] = \frac{k_{cat}[E]_T[S]}{(K_S + [S])} \qquad (10)$$

Note that the highest achievable initial reaction rate, denoted as V_{max}, will be achieved when all enzyme molecules are incorporated into the ES complex. In this case, the substrate saturates the enzyme molecules. Then, and only then, $[ES] = [E]_T$. According to this, the k_{cat} $[E]_T$ product in Equation 10 will be in fact the value of V_{max}. By taking this into account, we can formulate Equation 11, which is the final equation of the simplest enzyme kinetic model:

$$V_0 = \frac{V_{\max}[S]}{(K_S + [S])} \qquad (11)$$

This equation is a so-called rectangular hyperbola function that has the following general description: $Y=P_1X/(P_2+X)$, where X is the independent variable, in our case the substrate concentration, Y is the dependent variable, in our case the initial reaction rate, while P_1 and P_2 are the two parameters of the function, in our case the V_{max} and the K_S, respectively. P_1 is also the horizontal asymptote of the hyperbola, the maximal value of Y that the graph of the function approaches as X tends to infinity. The P_2 parameter is K_S.

Note that this equation is in a perfect accordance with the experimental observations regarding the [S]-V_0 relationship illustrated in Figure 1: when $[S] << K_S$, [S] becomes negligible in the denominator, leading to Equation 12:

$$V_0 = \frac{V_{\max}}{K_S}[S] \qquad (12)$$

In Equation 12, the multiplying factor of the substrate concentration is the quotient of two constants and, as such, it is also a constant. Accordingly, in the [S] range where the substrate concentration is orders of magnitude lower than the value of K_s, the initial reaction rate will be linearly proportional to substrate concentration, exactly as the experiments show. In other words, in this substrate concentration range the reaction is a (pseudo)-first order reaction in respect of the substrate.

In the other extreme case when [S] >> K_S, it is K_S that will be negligible compared to the value of [S] in the denominator of Equation 11. Accordingly, if we consider only this [S] range, we get equation 13:

$$V_0 = \frac{V_{\max}[S]}{[S]} = V_{\max} \qquad (13)$$

In the substrate concentration region where [S] exceeds K_S by orders of magnitude, the substrate saturates the enzyme, i.e. all enzyme molecules will be in the ES complex, and the initial reaction rate reaches a maximal value, i.e. it cannot be further increased by increasing the concentration of the substrate. Accordingly, in this substrate concentration range, the initial reaction rate is practically independent of the substrate concentration, (i.e. it is zero-order in respect of the substrate). This is why the [S]-V_0 plot illustrated in Figure 1 is often referred to as saturation curve.

When the substrate concentration equals the value of K_S, the initial reaction rate is the half of the V_{max} value.

In a simple descriptive way, the deduced Equation 11 appears to be in accordance with the observations. Yet, it leads to serious theoretical contradictions. The more efficient the enzyme, the less rational the initial assumptions of the above model. If the enzyme is highly efficient, the rate of ES conversion into product should be very high. If so, that process should interfere with the presumed quasi-equilibrium between the enzyme, the substrate and the ES complex. Therefore, the assumption of equilibrium for the first step of the reaction renders the model ill-suited for describing the action of genuinely efficient enzymes.

The second—and equally significant—problem is that this first model also contradicts the thermodynamic bases of catalysis. K_S is a dissociation constant and, as such, it defines the affinity, i.e. the strength of the binding interaction. In the first model, K_S describes how strongly the enzyme binds the substrate or, in other words, how stable the ES complex is. The lower the K_S, the more stable the complex. Moreover, based on the model, the lower the K_S, the more effective the enzyme. This is because a low K_S means that the enzyme reaches half-maximal reaction rate at low substrate concentration. But there is a discrepancy here. By increasing the stability of the interaction between the enzyme and the substrate, the reaction rate should decrease because the enzyme would stabilise the substrate in the ground state. Naturally, the enzyme must bind the substrate, but it should not bind it too tightly. Instead, the enzyme should bind tightly the transition state, thereby decreasing the activation free enthalpy of the reaction.

Due to these contradictions, the first kinetic model had to be developed further. The improved model accounts for the two additional kinetic rate constants that were left out from the first model. One of these, denoted as k_1, corresponds to the formation of the ES complex from free enzyme and substrate. The other, denoted as k_{-1}, corresponds to the reverse reaction, the dissociation of the ES complex towards enzyme and substrate. The improved scheme is illustrated in Equation 14:

$$E + S \underset{k_1}{\overset{k_{-1}}{\leftrightarrows}} ES \xrightarrow{k_2} E + P \qquad (14)$$

According to the improved model, when the solutions of the enzyme and the substrate are mixed, instead of a dynamic equilibrium, a steady-state will develop very quickly, almost instantaneously. Depending on the exact initial conditions, the steady-state may last long, i.e. the concentration of the ES complex can remain practically constant for a long period of time (exactly, d[ES]/dt is not zero, but much smaller than either d[P]/dt or d[S]/dt). The steady-state requires equal rates for ES generation and ES decomposition. This is illustrated in Figure 9.4. The reaction is triggered by adding the substrate. (Proportions of the figure are not realistic, as otherwise various parts of the figure could not be shown on the same page. In reality, the steady-state can be reached in milliseconds and it can last for minutes. Moreover, in reality, [S] starts from a much higher level because [S] >> [E].)

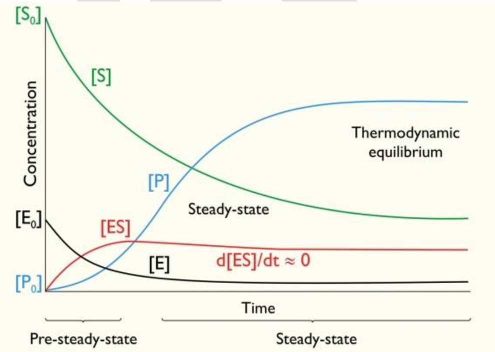


Figure 2. The steady-state

Decomposition of the ES complex can happen on two different routes: it can occur towards product formation with rate constant k_2, and also in the opposite direction towards substrate regeneration with rate constant k_{-1}. The development of the steady-state is illustrated in Figure 2, while the mathematical requirements of steady-state formation are formulated by Equation 15:

$$\frac{d[ES]}{dt} = k_1[E][S] - k_{-1}[ES] - k_2[ES] = 0 \qquad (15)$$

Although the steady-state modification of the model was suggested by George Edward Briggs and John Burdon Sanderson Haldane, the improved model is still being referred to as the kinetic model of Michaelis and Menten and the derived equation as the Michaelis-Menten equation. In this equation, the ES complex forms at a rate $k_1[E][S]$; it decays back towards the substrate at a rate $k_{-1}[ES]$ and decomposes towards the product at a rate $k_2[ES]$. In the steady-state, the rate of ES formation and the sum of the two types of ES decomposition rates are equal in magnitude and, thus, the concentration of the ES complex does not significantly change.

In the next section, Equation 15 will be transformed in several steps in order to yield a final equation containing the experimentally pre-set enzyme concentration and substrate concentration. The improved model has the same initial requirement: the substrate concentration must exceed the enzyme concentration by orders of magnitude. The rate of the reaction can be easily formulated, as shown in Equation 16, which is analogous to Equation 3 of the simpler model:

$$V_0 = k_2[ES] \qquad (16)$$

As the upgraded model contains three rate constants instead of one, the earlier model's k_{cat} is replaced with the k_2 rate constant introduced in the improved scheme. By rearranging Equation 15 we get Equation 17:

$$k_1[E][S] = k_{-1}[ES] + k_2[ES] \qquad (17)$$

Just as it was done in the first model, the free enzyme concentration is expressed as the difference of the total enzyme concentration and the concentration of the ES complex (Equation 18):

$$k_1([E]_T - [ES])[S] = k_{-1}[ES] + k_2[ES] \qquad (18)$$

Simple algebraic transformations result in Equation 19:

$$k_1[E]_T[S] - k_1[ES][S] = (k_{-1} + k_2)[ES] \qquad (19)$$

Then the [ES] term-containing parts are organised to the same side, resulting in Equation 20:

$$k_1[E]_T[S] = (k_{-1} + k_2)[ES] + k_1[ES][S] \qquad (20)$$

By multiplying out the [ES] factor, we get equation 21:

$$k_1[E]_T[S] = (k_{-1} + k_2 + k_1[S])[ES] \qquad (21)$$

In Equation 22, the [ES] term is arranged to the left side:

$$[ES] = \frac{k_1[E]_T[S]}{k_{-1} + k_2 + k_1[S]} \qquad (22)$$

Then, on the right side of the equation, both the numerator and the denominator are divided by the k_1 rate constant, which results in Equation 23:

$$[ES] = \frac{[E]_T[S]}{\frac{(k_{-1} + k_2)}{k_1} + [S]} \qquad (23)$$

In the denominator of Equation 9.40, there is a complex composed of three rate constants. This quotient has been defined as the Michaelis constant, with the abbreviation K_M. Replacing the quotient for K_M yields Equation 24:

$$\frac{(k_{-1} + k_2)}{k_1} \equiv K_M \qquad (24)$$

Note that K_M is defined as the ratio of the two-direction decay rate of the ES complex and the one-direction formation rate of the complex. In other words, it quantifies the instability of the ES complex.

Building Equation 22 into Equation 23 leads to Equation 25:

$$[ES] = \frac{[E]_T[S]}{K_M + [S]} \qquad (25)$$

By combining Equations 9.33 and 9.42, we get Equation 26:

$$V_0 = k_2[ES] = \frac{k_2[E]_T[S]}{(K_M + [S])} \qquad (26)$$

As already mentioned, in the case of Equation 10 of the simpler model, the highest initial rate (at a given total enzyme concentration), V_{max}, is achieved when all enzyme molecules are part of an ES complex, i.e. $[ES] = [E_T]$. Therefore, the $k_2[E]_T$ product in Equation 9.43 is in fact the V_{max}. Taking this into consideration, we get Equation 9.44, which is the final and most commonly used rate equation of the improved Michaelis-Menten model:

$$V_0 = \frac{V_{\max}[S]}{(K_M + [S])} \qquad (27)$$

Note that the mathematical forms of the corresponding final equations of the simple (Equation 11) and the improved (Equation 27) models are identical. Consequently, just like Equation 11, Equation 27 is also consistent with experimental results in terms of the dependence of the initial rate on substrate concentration. In the substrate concentration range where $[S] << K_M$, V_0 is linearly proportional to [S]; while in the range where $[S]>>K_M$, the reaction rate does not depend on the substrate concentration, and it has a maximal value.

When the numerical value of [S] equals that of K_M, the rate of the reaction is exactly half of the maximal one.

In spite of the many formal similarities, there are principal differences in the interpretations of the two models. Note that the K_S constant of the simple model and the K_M constant of the improved model have different meanings. Equation 28 illustrates how the dissociation constant-type K_S is derived from the k_1 and k_{-1} rate constants.

$$K_S = \frac{k_{-1}}{k_1} \qquad (28)$$

As already mentioned, K_S is a kind of affinity descriptor indicating how tightly the enzyme binds the substrate. It is readily apparent from the comparison of Equations 29 and 24 that K_M will equal K_S only if the $k_2 << k_{-1}$ requirement is fulfilled. This requirement would mean that the rate of ES decomposing towards the product would be orders of magnitude lower than the rate of ES decomposing back to substrate. However, for efficient enzymes, the very opposite situation, i.e. $k_2 >> k_{-1}$, may apply. As already mentioned, low values of K_S would—by mathematical formalism—indicate an efficient enzyme. However, from a thermodynamic aspect, the very same characteristics would indicate an inefficient enzyme.

The more efficient the enzyme, the less correct it is to interpret K_M as indicating affinity of the enzyme-substrate interaction.

Clearly, K_M and K_S of the two models are not interchangeable. On the other hand, the k_2 rate constant of the improved model, if the ES complex decays to enzyme and product in a single step, is identical to the k_{cat} rate constant of the simpler model. (If the final product is formed in a complex multi-step process, the k_{cat} rate constant is derived from an equation containing the rate constants of all individual steps.)

Let us examine the meaning of the k_{cat} rate constant based on Equations 29 and 30:

$$V_{\max} = \left(\frac{d[P]}{dt}\right)_{\max} = k_{cat}[E]_T \qquad (29)$$

$$k_{cat} = \frac{\left(\frac{d[P]}{dt}\right)_{\max}}{[E]_T} \qquad (30)$$

As it was shown, the maximal rate is the product of k_{cat} and the total enzyme concentration. Equation 30 is obtained when the rate of product concentration change is divided by the total enzyme concentration. As the product and the enzyme are present in the very same solution having the same volume, the ratio of concentrations is identical to the ratio of the numbers of molecules. Therefore, Equation 30 will provide a value on the number of product molecules generated by a single enzyme molecule in a unit period of time.

Accordingly, the k_{cat} rate constant is also referred to as the turnover number of the enzyme. It has the dimension of reciprocal of time. Naturally, the higher the value of k_{cat}, the more efficient the enzyme as a “chemical” catalyst, working after the ES complex had already been formed. Let us also note that, in cases when in the improved model $k_{cat} = k_2$, this rate constant is present in the nominator of the quotient defining K_M. This means that a high k_{cat} will increase the value of K_M. On the other hand, it is also clear that a lower K_M means that the half-maximal reaction rate is achieved at a lower substrate concentration, which is another measure of being an efficient enzyme. What would then be the best parameter to describe enzyme efficiency?

The most effective enzymes are expected to catalyse the reaction at a high rate even at low substrate concentration and, naturally, their turnover number should also be high. As already explained, at low substrate concentration where $[S] << K_M$, the reaction rate is a linear function of substrate concentration. This is shown in Equation 31:

$$V_0 \cong \frac{k_{cat}}{K_M}[E][S] \qquad (31)$$

The k_{cat}/K_M quotient in the equation is the rate constant of a second-order reaction, as the rate of this reaction depends on the concentration of two compounds. This k_{cat}/K_M quotient illustrates how efficiently the enzyme performs in the most challenging situation when the substrate concentration is very low. Accordingly, the k_{cat}/K_M quotient can be called *catalytic efficiency*, although its commonly used denomination is *specificity constant*.

Let us examine what sets the limit of the catalytic efficiency of enzymes by reviewing the case of the most efficient enzymes. Starting with Equation 31, we can generate Equation 32 by replacing the k_{cat} term with k_2 according to the simple one-step scheme of the reaction, and by replacing K_M (by definition) with the $(k_{-1}+k_2)/k_1$ quotient:

$$V_0 = \frac{k_2}{\frac{(k_{-1}+k_2)}{k_1}}[E][S] = \frac{k_2 k_1}{k_{-1}+k_2}[E][S] \approx k_1[E][S] \qquad (32)$$

In the right side of the resulting equation, and in the special case when $k_2 >> k_{-1}$, the k_{-1} term becomes negligible in the denominator. By ignoring the k_{-1} term, both the numerator and the denominator of the resulting quotient can be divided by the k_2 term. The $k_2 >> k_{-1}$ situation means that the ES complex decays practically exclusively towards the product instead of returning towards the substrate. When this assumption is valid, the k_{cat}/K_M rate constant of the reaction approximates the value of k_1. This means that the limit for the rate of the enzymatic reaction will be set by the rate at which the enzyme and the substrate encounter. Naturally, the steady-state rate of the reaction cannot exceed the rate of ES formation.

At first approximation, the limit for the most effective enzymes is set by the diffusion that limits the speed of the enzyme-substrate encounters. The diffusion rate can be accurately calculated based on the size of the diffusing molecules and the viscosity of the medium. In the case of some extremely efficient enzymes, it turned out that the rate of the enzymatic reaction exceeded the calculated diffusion rate.

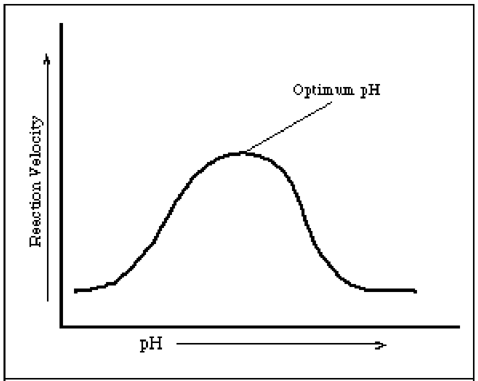
There are at least two situations that can explain this apparent discrepancy. If the substrate carries large number of electric charges of one type and the substrate binding site of the enzyme carries complementary (opposite) electrical charges, then the electrostatic attraction can steer the substrate towards the enzyme. The electrostatic interaction between full charges is a long-range interaction (compared to the size of small molecules). This condition, together with the orienting capacity of the interaction, significantly increases the frequency of enzyme-substrate encounters relative to the simple diffusion-limited case. A second important exception from the simple diffusion limit is related to multi-enzyme complexes. Many "final products" of metabolic or other chemical pathways are formed by a series of consecutive chemical reactions that proceed through many intermediate compounds. This means that the product of a given enzymatic reaction is the substrate of another enzyme catalysing the subsequent reaction. In a simple case, the product of the first reaction must encounter the second enzyme by random diffusion. If, on the other hand, these enzymes are organised in a proper arrangement in multi-enzyme complexes, the intermediate compounds can be "handed" directly from one enzyme to the other. This channelling effect can greatly enhance the overall rates of multi-step pathways.

Influence of p H and temperature on enzyme catalysis

The following has been excerpted from a very popular Worthington publication which was originally published in 1972 as the Manual of Clinical Enzyme Measurements. While some of the presentation may seem somewhat dated, the basic concepts are still helpful for researchers who must use enzymes but who have little background in enzymology.

Effects of pH

Enzymes are affected by changes in pH. The most favorable pH value - the point where the enzyme is most active - is known as the optimum pH. This is graphically illustrated in Figure .



Effect of pH on reaction rate

Extremely high or low pH values generally result in complete loss of activity for most enzymes. pH is also a factor in the stability of enzymes. As with activity, for each enzyme there is also a region of pH optimal stability.

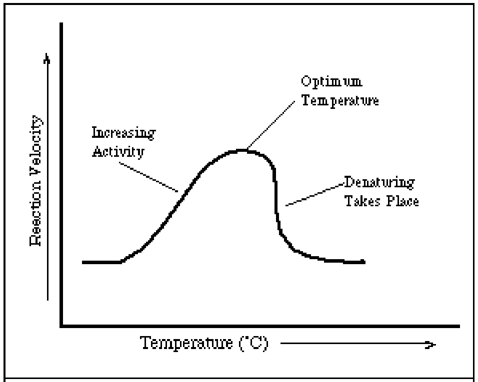
The optimum pH value will vary greatly from one enzyme to another, as Table I shows:

Table I: pH for Optimum Activity

Enzyme	**pH Optimum**
Lipase (pancreas)	8.0
Lipase (stomach)	4.0 - 5.0
Lipase (castor oil)	4.7
Pepsin	1.5 - 1.6
Trypsin	7.8 - 8.7
Urease	7.0
Invertase	4.5
Maltase	6.1 - 6.8
Amylase (pancreas)	6.7 - 7.0
Amylase (malt)	4.6 - 5.2
Catalase	7.0

In addition to temperature and pH there are other factors, such as ionic strength, which can affect the enzymatic reaction. Each of these physical and chemical parameters must be considered and optimized in order for an enzymatic reaction to be accurate and reproducible.

Temperature Effects



Effect of temperature on reaction rate

Like most chemical reactions, the rate of an enzyme-catalyzed reaction increases as the temperature is raised. A ten degree Centigrade rise in temperature will increase the activity of most enzymes by 50 to 100%. Variations in reaction temperature as small as 1 or 2 degrees may introduce changes of 10 to 20% in the results. In the case of enzymatic reactions, this is complicated by the fact that many enzymes are adversely affected by high temperatures. As shown in Figure , the reaction rate increases with temperature to a maximum level, then abruptly declines with further increase of temperature. Because most animal enzymes rapidly become denatured at temperatures above 40°C, most enzyme determinations are carried out somewhat below that temperature.

Over a period of time, enzymes will be deactivated at even moderate temperatures. Storage of enzymes at 5°C or below is generally the most suitable. Some enzymes lose their activity when frozen.

Surface phenomenon and heterogeneous catalysis

Adsorption and free energy relation at interfaces

Gibb's adsorption isotherm

The **Gibbs adsorption isotherm for multicomponent systems** is an equation used to relate the changes in concentration of a component in contact with a surface with changes in the surface tension, which results in a corresponding change in surface energy. For a binary system, the Gibbs adsorption equation in terms of surface excess is:

$$-d\gamma=\Gamma_1 d\mu_1 +\Gamma'_2 d\mu_2$$

where

γ is the surface tension,

Γ_i is the surface excess of component i,

μ_i is the chemical potential of component i.

Adsorption

Different influences at the interface may cause changes in the composition of the near-surface layer Substances may either accumulate near the surface or, conversely, move into the bulk. The movement of the molecules characterizes the phenomena of adsorption. Adsorption influences changes in surface tension and colloid stability. Adsorption layers at the surface of a liquid dispersion medium may affect the interactions of the dispersed particles in the media and consequently these layers may play crucial role in colloid stability. The adsorption of molecules of liquid phase at an interface occurs when this liquid phase is in contact with other immiscible phases that may be gas, liquid, or solid

Conceptual explanation of equation

Surface tension describes how difficult it is to extend the area of a surface (by stretching or distorting it). If surface tension is high, there is a large free energy required to increase the surface area, so the surface will tend to contract and hold together like a rubber sheet.

There are various factors affecting surface tension, one of which is that the *composition* of the surface may be different from the bulk. For example, if water is mixed with a tiny amount of surfactants (for example, hand soap), the bulk water may be 99% water molecules and 1% soap molecules, but the topmost surface of the water may be 50% water molecules and 50% soap molecules. In this case, the soap has a large and positive "surface excess". In other examples, the surface excess may be negative: For example, if water is mixed with an inorganic salt like sodium chloride, the surface of the water is on average *less* salty and more pure than the bulk average.

Consider again the example of water with a bit of soap. Since the water surface needs to have higher concentration of soap than the bulk, whenever the water's surface area is increased, it is necessary to remove soap molecules from the bulk and add them to the new surface. If the concentration of soap is increased a bit, the soap molecules are more readily available (they have higher chemical potential), so it is easier to pull them from the bulk in order to create the new surface. Since it is easier to create new surface, the surface tension is lowered. The general principle is:

When the surface excess of a component is positive, increasing the chemical potential of that component reduces the surface tension.

Next consider the example of water with salt. The water surface is less salty than bulk, so whenever the water's surface area is increased, it is necessary to remove salt molecules from the new surface and push them into bulk. If the concentration of salt is increased a bit (raising the salt's chemical potential), it becomes harder to push away the salt molecules. Since it is now harder to create the new surface, the surface tension is higher. The general principle is:

When the surface excess of a component is negative, increasing the chemical potential of that component increases the surface tension.

The Gibbs isotherm equation gives the exact quantitative relationship for these trends.

Location of surface and defining surface excess

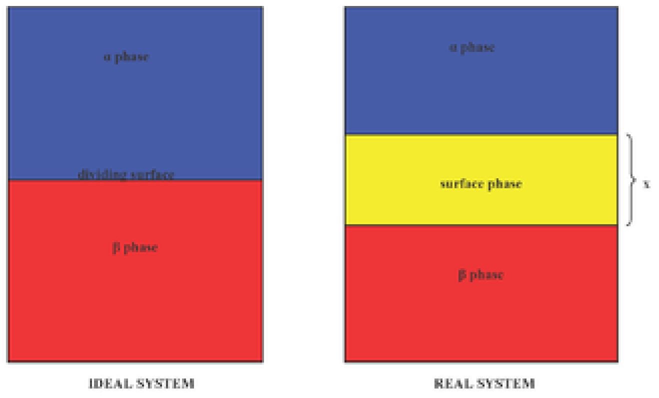


Figure : Comparison between the real and idealized models of the surface

Location of surface

In the presence of two phases (α and β), the surface (surface phase) is located in between the phase α and phase β. Experimentally, it is difficult to determine the exact structure of an inhomogeneous surface phase that is in contact with a bulk liquid phase containing more than one solute. Inhomogeneity of the surface phase is a result of variation of mole ratios. A model proposed by Josiah Willard Gibbs proposed that the surface phase as an idealized model that had zero thickness. In reality, although the bulk regions of α and β phases are constant, the concentrations of components in the interfacial region will gradually vary from the bulk concentration of α to the bulk concentration of β over the distance x. This is in contrast to the idealized Gibbs model where the distance x takes on the value of zero. The diagram to the right illustrates the differences between the real and idealized models.

Physisorption and chemisorption

Chemisorption (or *chemical adsorption*) is adsorption in which the forces involved are valence forces of the same kind as those operating in the formation of chemical compounds. The problem of distinguishing between chemisorption and physisorption (see below) is basically the same as that of distinguishing between chemical and physical interaction in general. No absolutely sharp distinction can be made and intermediate cases exist, for example, adsorption involving strong hydrogen bonds or weak charge transfer.

Some features which are useful in recognizing chemisorption include:

1.The phenomenon is characterized by chemical specificity;

2.Changes in the electronic state may be detectable by suitable physical means (e.g. u.v., infrared or microwave spectroscopy, electrical conductivity, magnetic susceptibility);

3.The chemical nature of the adsorptive(s) may be altered by surface dissociation or reaction in such a way that on desorption the original species cannot be recovered; in this sense chemisorption may not be reversible;

4.The energy of chemisorption is of the same order of magnitude as the energy change in a chemical reaction between a solid and a fluid: thus chemisorption, like chemical reactions in general, may be exothermic or endothermic and the magnitudes of the energy changes may range from very small to very large;

5.The elementary step in chemisorption often involves an activation energy;

6.Where the activation energy for adsorption is large (*activated adsorption*), true equilibrium may be achieved slowly or in practice not at all. For example in the adsorption of gases by solids the observed extent of adsorption, at a constant gas pressure after a fixed time, may in certain ranges of temperature increase with rise in temperature. In addition, where the activation energy for desorption is large, removal of the chemisorbed species from the surface may be possible only under extreme conditions of temperature or high vacuum, or by some suitable chemical treatment of the surface;

7.Since the adsorbed molecules are linked to the surface by valence bonds, they will usually occupy certain *adsorption sites* on the surface and only one layer of chemisorbed molecules is formed .

Physisorption (or *physical adsorption*) is adsorption in which the forces involved are intermolecular forces (van der Waals forces) of the same kind as those responsible for the imperfection of real gases and the condensation of vapours, and which do not involve a significant change in the electronic orbital patterns of the species involved. The term *van der Waals adsorption* is synonymous with physical adsorption, but its use is not recommended.

Some features which are useful in recognizing physisorption include:

1.The phenomenon is a general one and occurs in any solid/fluid system, although certain specific molecular interactions may occur, arising from particular geometrical or electronic properties of the adsorbent and/or adsorptive;

2.Evidence for the perturbation of the electronic states of adsorbent and adsorbate is minimal;

3.The adsorbed species are chemically identical with those in the fluid phase, so that the chemical nature of the fluid is not altered by adsorption and subsequent desorption;

4.The energy of interaction between the molecules of adsorbate and the adsorbent is of the same order of magnitude as, but is usually greater than, the energy of condensation of the adsorptive;

5.The elementary step in physical adsorption from a gas phase does not involve an activation energy. Slow, temperature dependent, equilibration may however result from rate-determining transport processes;

6.In physical adsorption, equilibrium is established between the adsorbate and the fluid phase. In solid/gas systems at not too high pressures the extent of physical adsorption increases with increase in gas pressure and usually decreases with increasing temperature. In the case of systems showing hysteresis the equilibrium may be metastable;

7.Under appropriate conditions of pressure and temperature, molecules from the gas phase can be adsorbed in excess of those in direct contact with the surface (multilayer adsorption or filling of micropores.

Adsorption isotherms

Freundlich adsorption isotherm

(i) Freundlich adsorption isotherm is obeyed by the adsorptions where the adsorbate forms a monomolecular layer on the surface of the adsorbent.

$\frac{x}{m} = kp^{\frac{1}{n}}$ (Freundlich adsorption isotherm) or

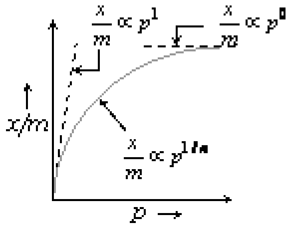
$\log \frac{x}{m} = \log k + \frac{1}{n} \log p$

where x is the weight of the gas adsorbed by m gm of the adsorbent at a pressure p, thus x/m represents the amount of gas adsorbed by the adsorbents per gm (unit mass), k and n are constant at a particular temperature and for a particular adsorbent and adsorbate (gas), n is always greater than one, indicating **that the amount of the gas adsorbed does not increase as rapidly as the pressure.**

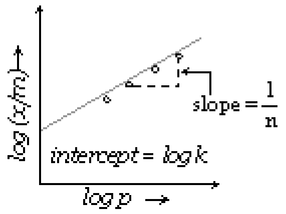
(ii) At low pressure, the extent of adsorption varies linearly with pressure. $\frac{x}{m} \propto p^1$

(iii) At high pressure, it becomes independent of pressure. $\frac{x}{m} \propto p^0$

(iv) At moderate pressure $\frac{x}{m}$ depends upon pressure raised to powers $\frac{x}{m} \propto p^{\frac{1}{n}}$



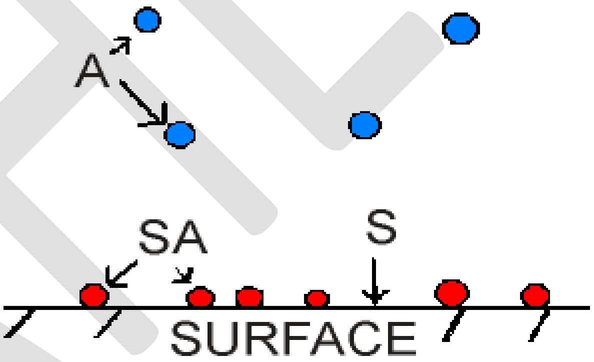
Freundlich adsorption isotherm: plot of x/m against



Plot of log x/m against log p for the adsorption of a gas on a solid

Langmuir adsorption isotherm

For molecules in contact with a solid surface at a fixed temperature, the Langmuir Isotherm, developed by Irving Langmuir in 1916, describes the partitioning between gas phase and adsorbed species as a function of applied pressure.



Thermodynamic Derivation

The adsorption process between gas phase molecules, A, vacant surface sites, S, and occupied surface sites, SA, can be represented by the equation,

$$S + A \rightleftharpoons SA$$

assuming that there are a fixed number of surface sites present on the surface.

An equilibrium constant, K, can be written:

$$K = \frac{[SA]}{[S]\,[A]}$$

q = Fraction of surface sites occupied (0 <q< 1)

Note that

- **[SA]** is proportional to the surface coverage of adsorbed molecules, or proportional to q
- **[S]** is proportional to the number of vacant sites, (1 - q)
- **[A]** is proportional to the pressure of gas, P

Thus it is possible to define the equilibrium constant, b:

$$b = \frac{\theta}{(1-\theta)P}$$

Rearranging gives the expression for surface coverage:

Kinetic Derivation

The rate of adsorption will be proportional to the pressure of the gas and the number of vacant sites for adsorption. If the total number of sites on the surface is N, then the rate of change of the surface coverage due to adsorption is:

$$\frac{d\theta}{dt} = k_a \, p \, N(1 - \theta)$$

The rate of change of the coverage due to the adsorbate leaving the surface (desorption) is proportional to the number of adsorbed species:

$$\frac{d\theta}{dt} = - k_d \, N \, \theta$$

In these equations, k_a and k_d are the rate constants for adsorption and desorption repectively, and p is the pressure of the adsorbate gas. At equilibrium, the coverage is independent of time and thus the adorption and desorption rates are equal. The solution to this condition gives us a relation for q:

where $b = k_a/k_d$.

Dependence of b on external parameters:

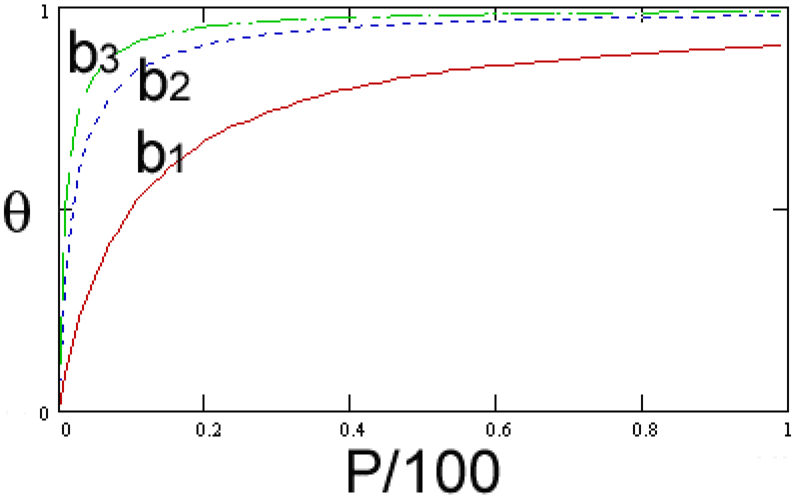
b is only a constant if the enthalpy of adsorption is independent of coverage.

As with all chemical equilibria, the position of equilibrium (determined by the value of b) will depend upon a number of factors:

1. The relative stabilities of the adsorbed and gas phase species involved.
2. The temperature of the system (both the gas and surface, although these are normally the same).
3. The pressure of the gas above the surface.

In general, factors (2) and (3) exert opposite effects on the concentration of adsorbed species - that is to say that the surface coverage may be increased by raising the gas pressure but will be reduced if the surface temperature is raised.

Graphical form of the Langmuir Isotherm



where $b_3 > b_2 > b_1$

Kinetics of heterogeneous catalysis

Langmuir-Hinshelwood mechanism

The rate equation derived from mechanistic model that simulates the actual surface phenomenon during the process is preferred for reactions involving solid catalysts. The Langmuir-Hinshelwood–Hougen-Watson(LHHW) approach is one of the most commonly used way of deriving rate expressions for fluid solid catalytic reactions. The advantages of this method are that:

(1) Rate derived by this method takes into account the adsorption/desorption process occurring over the surface along with the surface reaction.

(2) Rate equation derived can be extrapolated more accurately to concentrations lying beyond the experimentally measured values.

During this method of derivation of rate expression, all the physical transport steps like mass transfer from bulk phase to catalyst surface or diffusion of reactants from pore mouth to interior pore (intraparticle diffusion) are excluded. Thus, it is assumed that the external and internal mass transport processes are very rapid relative to the chemical rate process occurring on or within the catalyst particle. The chemical rate depends on:

(1) chemisorption steps

(2) surface reaction steps

(3) desorption steps

This simple kinetic model assumes isothermal condition about and within catalyst that is temperature gradient is zero.

In LHHW model development, the rate equation is first derived in terms of surface concentration of adsorbed species and vacant sites. Then, these surface concentrations are related to the fluid or bulk concentration that is directly measurable.

For the reaction $A+B \rightleftharpoons C+D$

Let r_a= rates of adsorption ....(g moles/s.gm of catalyst)

r_s = rates of surface reaction................................. ...(g moles/s.gm of catalyst)

r_d =rates of desorption ....(g moles/s.gm of catalyst)

C_{AS}= concentration of adsorbed A on surface ....(g moles/gm of catalyst)

C_{BS}= concentration of adsorbed B on surface ....(g moles/gm of catalyst)

C_{CS}= concentration of adsorbed C on surface ....(g moles/gm of catalyst)

C_{DS}= concentration of adsorbed D on surface.............. (g moles/gm of catalyst)

C_o= total concentration of active sites on surface........ (g moles/gm of catalyst)

C_v= concentration of vacant sites on surface............... (g moles/gm of catalyst)

C_A= concentration of A in bulk gas phase ....(g moles/cm^3)

Similarly C_B,C_C ,C_D are concentration of B,C,D in bulk gas phase respectively.

Let the reaction follows the mechanism given below ;

(1) $A + S \rightleftharpoons A.S$ --- Adsorption of reactant A on surface vacant site S

(2) $B + S \rightleftharpoons BS$ --- Adsorption reactant B on surface vacant site S

(3) $A.S + B.S \rightleftharpoons C.S + D.S$ --- Surface reaction between adsorbed A and B

(4) $CS \rightleftharpoons C + S$ --- Desorption of product C from surface creating a vacant site

(5) $DS \rightleftharpoons D + S$ --- Desorption of product D from surface creating a vacant site

Among the various steps described, the slowest step controls the overall rate of reaction and the other remaining steps are assumed to be at near equilibrium conditions. This approach greatly simplifies the overall rate expression, reducing the number of rate constants and equilibrium constants to be determined from experimental data. Further each step in this method is assumed to be elementary and the number of sites is conserved in each step.

Therefore, the controlling step can be either of the following:

(1) Surface reaction

(2) Adsorption

(3) Desorption

Now total concentration of active sites on surface, C_0, will be the summation concentrations of all sites on which either reactants or products are adsorbed and the concentration of vacant sites.

$$\therefore C_O = C_V + C_{AS} + C_{BS} + C_{CS} + C_{DS}$$

Where C_V is the concentration of vacant sites.

Case 1 : Rate is surface reaction controlling

The surface reaction is the slowest step and is the rate controlling. According to the mechanism, surface reaction occurs between adsorbed A and adsorbed B producing adsorbed C & adsorbed D.

$$AS + BS \rightleftharpoons CS + DS$$

The rate of surface reaction is given as

$$r_S = k_S C_{AS} C_{BS} - k_S^{'} C_{CS} C_{DS}$$

$.k_s$= rate constant for forward surface reaction

$k_S^{'}$ = rate constant for reverse surface reaction

....

$$= k_S \left[C_{AS} C_{BS} - \frac{k_S^{'}}{k_S} C_{CS} C_{DS} \right]$$

$$= k_S \left[C_{AS} C_{BS} - \frac{1}{K_S} C_{CS} C_{DS} \right] \text{----(1)} \qquad K_S = \frac{k_S}{k_S^{'}}$$

..................---

Now, since all the other steps are considered to be in equilibrium, therefore concentration of adsorbed species can be obtained as follows.

For adsorption steps and desorption steps :

From step (1) $K_A = \dfrac{C_{AS}}{C_A C_V}$ from step (4)------ $K_C = \dfrac{C_{CS}}{C_C C_V}$

From step (2) $K_B = \dfrac{C_{BS}}{C_B C_V}$ From step (5)------- $K_D = \dfrac{C_{DS}}{C_D C_V}$

Then the adsorbed phase concentration can be written as

$$C_{AS} = K_A C_A C_V \quad C_{CS} = K_C C_C C_V$$

$$C_{BS} = K_B C_B C_V \quad C_{DS} = K_D C_D C_V$$

Substituting all these value in equation (1)

$$r_S = k_S\left[C_{AS}C_{BS} - \frac{1}{K_S}C_{CS}C_{DS}\right] = k_S\left[K_AC_AC_V.K_BC_BC_V - \frac{K_C}{K_S}C_CC_V.K_DC_DC_V\right]$$

or, $$r_s = k_S\left[K_AK_BC_AC_BC_V^2 - \frac{K_CK_D}{K_S}C_CC_DC_V^2\right]$$

(2)

or $$r_S = k_SK_AK_B\left[C_AC_B - \frac{K_CK_D}{K_SK_AK_B}C_CC_D\right]C_V^2$$

Now, $$C_O = C_{AS} + C_{BS} + C_{CS} + C_{DS} + C_V$$

$$C_O = K_AC_AC_V + K_BC_BC_V + K_CC_CC_V + K_DC_DC_V + C_V$$

$$= C_V\left[1 + K_AC_A + K_BC_B + K_CC_C + K_DC_D\right]$$

$$C_V = \frac{C_O}{1 + K_AC_A + K_BC_B + K_CC_C + K_DC_D} \qquad (3)$$

For the reaction $A+B \rightleftharpoons C+D$, at equilibrium, the overall equilibrium constant is

$$K = \frac{C_CC_D}{C_AC_B}.$$

All concentrations corresponds to the equilibrium conditions in gas phase

$$K = \frac{(C_{CS}/K_CC_V)(C_{DS}/K_DC_V)}{(C_{AS}/K_AC_V)(C_{BS}/K_BC_V)} = \frac{C_{CS}C_{DS}}{C_{AS}C_{BS}}.\frac{K_AK_BC_V^2}{K_CK_DC_V^2}$$

Or, $$K = \frac{K_AK_B}{K_CK_D}.K_S \qquad \because K_S = \frac{C_{CS}C_{DS}}{C_{AS}C_{BS}} \qquad (4)$$

Substituting (3) &(4) in equation (2),

$$r_S = k_S K_A K_B \left[C_A C_B - \frac{1}{K} C_C C_D \right] \frac{C_O^2}{(1 + K_A C_A + K_B C_B + K_C C_C + K_D C_D)^2}$$

$$r_S = k_S K_A K_B C_O^2 \frac{C_A C_B - \frac{1}{K} C_C C_D}{(1 + K_A C_A + K_B C_B + K_C C_C + K_D C_D)^2} \qquad (5)$$

The above rate expression can also be derived in terms of bulk partial pressure.

Case 2: Rate is adsorption control

(a) Adsorption of A controlling

Let adsorption of A be the slowest step so that adsorption of B, surface reaction and desorption of C are at equilibrium.

Adsorption of A is given as

$$A + S \rightleftharpoons AS$$

$$\text{Rate of adsorption} \quad r_a = k_a C_A C_V - k_d C_{AS}$$

$$r_a = k_a \left[C_A C_V - \frac{k_d}{k_a} C_{AS} \right] \qquad (6)$$

$$\text{Or,} \quad r_a = k_a \left[C_A C_V - \frac{1}{K_A} C_{AS} \right] \quad K_A = \frac{k_a}{k_d} \ \text{(adsorption equilibrium constant for A)}$$

$$r_a = k_a C_V \left[C_A - \frac{1}{K_A} \frac{C_{AS}}{C_V} \right]$$

Now as other steps are in equilibrium:

$$K_S = \frac{C_{CS} C_{DS}}{C_{AS} C_{BS}}$$

$$K_B = \frac{C_{BS}}{C_B C_V} \qquad K_C = \frac{C_{CS}}{C_C C_V} \qquad K_D = \frac{C_{DS}}{C_D C_V}$$

$$C_{BS} = K_B C_B C_V \qquad C_{CS} = K_C C_C C_V \qquad C_{DS} = K_D C_D C_V$$

Then ,

$$C_{AS} = \frac{C_{CS} C_{DS}}{K_S C_{BS}} = \frac{K_C C_C C_V . K_D C_D C_V}{K_S K_B C_B C_V} \quad = \frac{K_C K_D}{K_S K_B} \frac{C_C C_D C_V}{C_B}$$

Substituting value in equation (6)

$$r_a = k_a C_V \left[C_A - \frac{1}{K_A C_V} \frac{K_C K_D}{K_S K_B} \frac{C_C C_D C_V}{C_B} \right]$$

$$r_a = k_a C_V \left[C_A - \frac{K_C K_D}{K_S K_A K_B} \frac{C_C C_D}{C_B} \right] \qquad (7)$$

$$r_a = k_a C_V \left[C_A - \frac{1}{K} \frac{C_C C_D}{C_B} \right]$$

$K = \dfrac{K_S K_A K_B}{K_C K_D}$ = Overall equilibrium constant.

Now $C_0 = C_V + C_{AS} + C_{BS} + C_{CS} + C_{DS}$

$$= C_V + \frac{K_C K_D}{K_S K_B} . \frac{C_C C_D C_V}{C_B} + K_B C_B C_V + K_C C_C C_V + K_D C_D C_V$$

$$= C_V \left[1 + \frac{K_C K_D}{K_S K_A} \frac{K_A}{K_B} \left(\frac{C_C C_D}{C_B} \right) + K_B C_B + K_C C_C + K_D C_D \right]$$

$$= C_V \left[1 + \frac{K_A}{K} \frac{C_C C_D}{C_B} + K_B C_B + K_C C_C + K_D C_D \right]$$

$$C_V = \frac{C_O}{1 + \frac{K_A}{K} \frac{C_C C_D}{C_B} + K_B C_B + K_C C_C + K_D C_D} \quad \because K = \frac{K_S K_A K_B}{K_C K_D}$$

Substituting value of C_V in equation (7)

$$r_a = k_a C_0 \frac{C_A - \left[\frac{C_C C_D}{K C_B} \right]}{1 + \frac{K_A C_C C_D}{K C_B} + K_B C_B + K_C C_C + K_D C_D} \qquad (8)$$

For a given catalyst C_0 is constant.

Similarly expression when desorption of product is the rate controlling step can be derived. For desorption of C controlling the whole reaction, the rate expression can be derived as

$$r_d = k_d C_0 K \frac{C_A C_B - \left[\frac{C_C C_D}{K} \right]}{1 + K_A C_A + K_B C_B + K_C K C_A C_B + K_D C_D}$$

Eley Rideal model

Apart from power law and Langmuir-Hinshelwood models, other kinetic models are also used to fit the data. EleyRideal model depicts the reaction mechanism in which one reactant species (say A) is adsorbed while the second reactant species (say B) is not adsorbed on the catalyst surface. The reaction then occurs when the passing gas molecules of B in gas phase directly reacts with the adsorbed species A. The schematic representation is shown in Fig. 1.

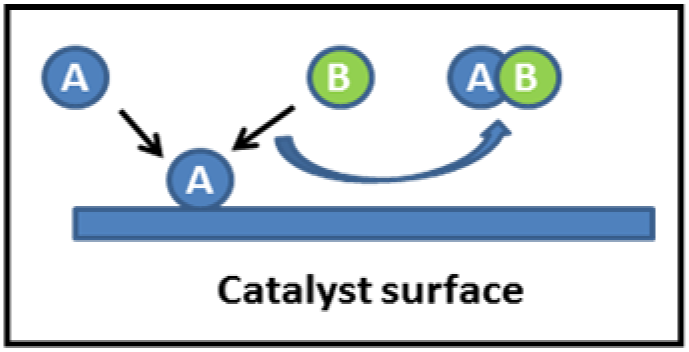


Fig. 1. Eley Rideal mechanism for reaction of adsorbed A with gas phase B producing product AB

$$(1)\ A + S \rightleftharpoons AS$$

$$(2)\ AS + B\ (g) \rightarrow P$$

Assuming that step 2, the reaction between adsorbed A and gas phase B is irreversible and the rate determining step, then the rate of reaction can be written as

$$r = k\ C_{As}\ C_B \tag{9}$$

The concentration of adsorbed A can be given as $C_{AS} = K_A C_A C_V$

Now , $C_O = C_{AS} + C_V = K_A C_A C_V + C_V = C_V(1 + K_A C_A)$

$$C_V = \frac{C_O}{1 + K_A C_A}$$

$$C_{AS} = \frac{K_A C_A C_O}{1 + K_A C_A}$$

Substituting value of C_{AS} in equation (9)

$$r = k\ C_{AS}\ C_B = \frac{kC_O K_A C_A C_B}{1+K_A C_A}$$

If the products are chemisorbed then the reaction may become reversible as shown below.

$$AS + B(g) \underset{k_b}{\overset{k}{\rightleftharpoons}} PS$$

$$PS \rightarrow P + S$$

Then the rate expression can be written as

$$r = k\ C_{AS}\ C_B - k_b C_{PS}$$

The concentration of adsorbed product is $C_{PS} = K_P C_P C_V$

$$C_O = C_{AS} + C_{PS} + C_V = K_A C_A C_V + K_P C_P C_V + C_V = C_V(1+K_A C_A + K_P C_P)$$

$$C_V = \frac{C_O}{1+K_A C_A + K_P C_P}$$

$$C_{AS} = K_A C_A C_V = \frac{K_A C_A C_O}{1+K_A C_A + K_P C_P}$$

$$C_{PS} = K_P C_P C_V = \frac{K_P C_P C_O}{1+K_A C_A + K_P C_P}$$

Substituting C_{AS} and C_{PS} in rate expression,

$$r = k\ C_{As}\ C_B - k_b C_{Ps} = k\left(C_{AS}C_B - \frac{1}{K}C_{PS}\right) \qquad \because K = \frac{k}{k_b}$$

$$r = k\left(\frac{K_A C_A C_O}{(1+K_A C_A + K_P C_P)}C_B - \frac{1}{K}\frac{K_P C_P C_O}{(1+K_A C_A + K_P C_P)}\right)$$

$$r = kC_O \frac{\left(K_A C_A C_B - \frac{K_P}{K}C_P\right)}{1+K_A C_A + K_P C_P}$$

Estimation of model parameters

The various parameters in the kinetic models such as rate constants, reaction orders, and equilibrium constants are derived by fitting the experimental data. The optimal values of the parameters in the rate equation of a heterogeneous reaction are determined traditionally by using gradient or direct search methods. For success of this method, a very good initial estimate of the parameters is required. This proves to be difficult in most cases. If the initial estimates are far from the global optima, then it is likely that the gradient or direct search method will not converge at all or will converge to local optima. Recently genetic algorithm (GA) is increasingly applied in estimation of kinetic parameters. The major advantage of this method is that it is not dependent on the initial estimate of the parameters. GA performs a multi-directional search.

POSSIBLE QUESTIONS

Part A **(Each question carries one marks)**

1.A catalyst increases the rate of reaction by
(a)Decreasing activation energy (b)Decreasing internal energy
(c)Decreasing enthalpy (d)increasing activation energy

2.The ability of catalyst to accelerate the chemical reaction is known as
(a)Selectivity **(b)Activity** (c)Negative catalyst (d)None of these

3.The process which is catalysed one of the product is called
(a)Acid-base catalysis **(b)Auto catalysis** (c)Negative catalyst (d)Positive catalysis

4.When the catalyst is added to the reversible reaction in equlibrium state,the value of equlibrium constant
(a)Increases (b)Decreases (c)Becomes zero **(d)Does not change**

5.Any substance which completely destroys or reduces the activity of the catalyst is called
(a)Catalyst (b)Inhibitor (c)Promotor **(d)Catalyst poison**

6.Which of the following types of materials form effective catalysts
(a)Alkali metals (b)Transition metals
(c)Alkaline earth metals **(d)Radioactive metals**

7.Which of the following statements is universally correct for catalyst
(a)A catalyst remains unchanged at the end of chemical reaction
(b)A catalyst takes part in a chemical reaction
(c)All kinds of catalysts undergo catalytic poisoning
(d)A catalyst physically changes at the end of the reaction

8.Which of the following is not true about heterogeneous catalyst
(a)The catalyst and the reactants are in different states
(b)The catalyst remains unaffected after the completion of the reaction
(c)The catalyst lowers the energy of activation
(d)The catalyst changes the equilibrium constant
5.Efficiency of a catalyst depends on its
(a)particle size (b)Solubility (c)Molecular weight (d)Activation energy

9. Which of the following does not apply to catalytic reactions
(a) Capability to infinite the non feasible reaction

(b)Specificity
(c)Lowering the activation energies of the foreard as well as backward reaction
(d)Constancy in value of delta H

10.Chemical equilibrium is dynamic in nature because,
(a)the equilibrium is mintained in rapidly
(b)the concentration of reactants and products are constant but different
(c)The concentration of reactants and products become same at equilibrium
(d)both forward and backward reactions occur t all times with same speed

11.Physical adsorption
(a)Is reversible (b)Decrease with temperature (c)Is exothermic **(d)All**
5.Which one of the following statements is incorrect regarding physical adsorption
(a)Low heats of adsorption (b)Usually occurs at low temperatures and decreses with an increase an temperature **(c) Forms monomolecular layers** (d)It is reversible

12.An example of an efficient adsorbent is
(a)Glass (b)Diamond **(c)Charcoal** (d)Wood

13.A catalyst is the finely divided form is most effective because
(a)Less surface area is available (b)Most surface area is available
(c)More active centres are formed (d)More energy gets stored in the catalyst

14.The effect of catalyst in a chemical reaction is to change
(a) Heat of reaction (b)Equilibrium constant (c)internal energy of the reactants
(d)Activation energy required for the reaction

15. A substance that increases the reaction rate without itself getting used up is known as a
(a)Catalyst (b) Inhibitor (c) Activated Complex (d) Buffer

16.In a reaction,a positive catalyst will decrease the value of
(a) Δ H **(b) Activation energy** (c) Δ S (d) rate constant

17. In the hydrogenation of vegetable oils, the catalyst commonly used is
(a) Fe_2O_3 (b) Activated charcoal (c) ZnO **(d) Ni**

18 .The catalyst and the reactant are in the same phase Which is called
(a)Heterogenous (b)Activation energy (c) **Homogeneous** (d)rate constant

19.Which one of the following statements is incorrect regarding physical adsorption (a)Low heats of adsorption (b)Usually occurs at low temperatures and decreses with an increase an temperature **(c) Forms monomolecular layers** (d)It is reversible

20.An example of an efficient adsorbent is
(a)Glass (b)Diamond **(c)Charcoal** (d)Wood

Part B **(Each question carries 2 marks)**

1.Give an expression for specific and general acid-base catalysis.

2.Give an expression for Michaelis-Menten equation.

3.Differentiate physisorption and chemisorptions.

4.Define adsorption and absorption.

5.Give an expression for Langmuir-Hinshelwood equation.

Part C **(Each question carries 6 marks)**

1.Write a note on Langmuir – Hinshelwood mechanism.

2.What is enzyme catalysis? Write note on Hammett acidity functions.

3.Write note on Michaelis- Menten law of Enzyme catalysis.

4.State and explain Freundlich adsorption isotherm.

5.Derive an expression for Michaelis-Menten law.

6.What are adsorption Isotherms? Derive Gibbs-Adsorption isotherm

7. Derive Langmuir adsorption isotherm.

8.Write a detailed note on Langmuir –Hinshelwood mechanism
.

9.Explain the effect of temperature and pH on enzyme catalysis?

10. What are the differences between physisorption and chemisorptions? Write a note on Freundlich adsorption isotherm

KARPAGAM ACADEMY OF HIGHER EDUCATION
COIMBATORE-641 021
(For the candidates admitted from 2017 & Onwards)
M.Sc., CHEMISTRY
SECOND SEMESTER
PHYSICAL CHEMISTRY-II (Chemical Kinetics and Electrochemistry) 17CHP203

S.NO	UNIT-II	OPTION 1	OPTION 2	OPTION 3	OPTION 4	ANSWER
1	A substance that increases the reaction rate without itself getting used up is known as a	a)Buffer	b)Catalyst	c)Inhibitor	d)Activated Complex	b)Catalyst
2	In a reaction,a positive catalyst will decrease the value of	a)Delta H	b)Activation energy	c)Delta S	d)rate constant	b)Activation energy
3	In the hydrogenation of vegetable oils,the catalyst commonly used is	a)Fe_2O_3	b)Activated charcoal	c)ZnO	d)Ni	d)Ni
4	The catalyst and the reactant are in the same phase Which is called	a)Heterogenous	b)Activation energy	c)Homogeneous	d)rate constant	c)Homogeneous
5	The catalyst and the reactant are in the different phase Which is called	a)Heterogenous	b)Enzyme	c)Adsorption	d)Activation energy	a)Heterogenous
6	The existence of a substance at a surface in a different concentration compared to the adjoining bulk phase is called	a)Absorption	b)Adsorption	c)Adsorption	d)Phyical adsorption	c)Adsorption
7	The process of removing an adsorbed substance from a surface is called	a)Adsorption	b)Desorption	c)Chemical adsorption	d)Langmuir adsorption	b)Desorption
8	Which one of the following statements is incorrect regarding physical adsorption	a)Low heats of adsorption	b)Usually occurs at low temperatures and decreses with an increase an temperature	c)Forms monomolecular layers	d)It is reversible	c)Forms monomolecular layers
9	An example of an efficient adsorbent is	a)Glass	b)Diamond	c)Charcoal	d)Wood	c)Charcoal
10	A catalyst is the finely divided form is most effective because	a)Less surface area is available	b)Most surface area is available	c)More active centres are formed	d)More energy gets stored in the catalyst	c)More active centres are formed
11	The effect of catalyst in a chemical reaction is to change	a)Heat of reaction	b)Equilibrium constant	c)internal energy of the reactants	d)Activation energy required for the reaction	d)Activation energy required for the reaction
12	When a catalyst is added to a system the	a)Equilibrium concentrations are increased	b)Equilibrium concentrations are unchanged	c)The rate of forward reaction is increased	d)The rate of backward reaction is decreased	b)Equilibrium concentrations are unchanged
13	Efficiency of a catalyst depends on its	a)particle size	b)Solubility	c)Molecular weight	d)Activation energy	a)particle size
14	Which of the following does not a apply to catalytic reactions	a)Capability to infinite the non feasible reaction	b)Specificity	c)Lowering the activation energies of the foreard as well as backward reaction	d)Constancy in value of delta H	a)Capability to infinite the non feasible reaction
15	Chemical equilibrium is dynamic in nature because,	a)the equilibrium is mintained in rapidly	b)the concentration of reactants and products are constant but different	c)The concentration of reactants and products become same at equilibrium	d)both forward and backward reactions occur at all times with same speed	d)both forward and backward reactions occur at all times with same speed
16	Physical adsorption	a)Is reversible	b)Decrease with temperature	c)Is exothermic	d)All	d)All
17	Chemical adsorption	a)Exothermic	b)Irrversible	c)Is unilayer	d)All are correct	d)All are correct
18	which adsorption take place at low temperature	a)Physical adsorption	b)Chemical adsorption	c)both	d)none	a)Physical adsorption
19	Any substance which completely destroys or reduces the activity of the catalyst is called	a)Catalyst	b)Inhibitor	c)Promotor	d)Catalyst poison	d)Catalyst poison
20	Which of the following types of materials form effective catalysts	a)Alkali metals	b)Transition metals	c)Alkaline earth metals	d)Radioactive metals	d)Radioactive metals
21	Which of the following statements is universally correct for catalyst	a)A catalyst remains unchanged at the end of chemical reaction	b)A catalyst takes part in a chemical reaction	c)All kinds of catalysts undergo catalytic poisoning	d)A catalyst physically changes at the end of the reaction	a)A catalyst remains unchanged at the end of chemical reaction
22	Which of the following is not true about heterogeneous catalyst	a)The catalyst and the reactants are in different states	b)The catalyst remains unaffected after the completion of the reaction	c)The catalyst lowers the energy of activation	d)The catalyst changes the equilibrium constant	d)The catalyst changes the equilibrium constant
23	A catalyst is a substance which	a)Alters the equilibrium in a reaction	b)Is always in the same phase as the reactants	c)Participates in the reaction and provides pathway for the same	d)Does not participate in the reaction but speeds it up	d)Does not participate in the reaction but speeds it up
24	Platinised asbestos used as catalyst in the manufacture of H_2SO_4 is an example of	a)Heterogenous catalyst	b)Auto catalyst	c)Homo catalyst	d)Induced catalyst	a)Heterogenous catalyst
25	As a general rule, adding a catalyst to a reacting system	a)Increases the yield of the product	b)Decreases the yield of the product	c)Does not affect the yield of the product	d)Increases and decreases the yield irregularly	c)Does not affect the yield of the product
26	In homogeneous catalytic reactions,the rate of reaction	a)Depends upon the concentration of catalyst	b)Independent upon the concentration of catalyst	c)Depends upon the free energy change	d)Depends upon the physical state of the catalyst	a)Depends upon the concentration of catalyst
27	V_2O_5 has replaced Pt as catalyst in the contact process because	a)It is cheap	b)It is not easily poisoned	c)Both are correct	d)None is correct	c)Both are correct

28	When a catalyst increases the rate of a chemical reaction,the rate constant	a)Increases	b)Decreases	c)Remains constant	d)Becomes infinite	a)Increases
29	A substance which promotes the activity of a catalyst is known as	a)Initiator	b)Catalyst	c)Promotor	d)Autocatalyst	c)Promotor
30	Which is the following is an example of autocatalysis	a)Decomposition of $KClO_3$ + MnO_2 mixt.	b)The decomposition of nitroglycerine	c)Breakdown of $_6C^{14}$	d)Hydrogenation of vegetable oil using Ni catalyst	b)The decomposition of nitroglycerine
31	An auto catalyst is	a)Catalyst for catalyst	b)One which starts a reaction	c)One of the products of the reaction which acts as a catalyst	d)Which retards a chemical reaction	c)One of the products of the reaction which acts as a catalyst
32	Catalytic poison acts by	a)Chemically combining with catalyst	b)Coagualting the catalyst	c)Getting adsorbed on the active centres on the surfaces	d)Chemical combination with anyone of the reactants	c)Getting adsorbed on the active centres on the surfaces
33	In temporary poisoning,catalytic poison acts by	a)Coagualting the catalyst	b)Chemical combination with anyone of the reactants	c)Chemically combining with catalyst	d)Getting adsorbed on the active centres on the catalyst	d)Getting adsorbed on the active centres on the catalyst
34	A substance like CO,As_2O_3,HCN etc,which paralyses the catalytic activity of a catalyst is called	a)A negative catalyst	b)Auto catalyst	c)A Promotor	d)Poison	d)Poison
35	Catalytic poisoners are usually the same as	a)Poison for human body	b)Enzyme for human body	c)Vitamins for human body	d)proteins for human body	a)Poison for human body
36	Negative catalyt is that	a)Which retards the rate of reaction	b)Takes the reaction in the backward direction	c)Promotes the side reaction	d)Coagualting the catalyst	a)Which retards the rate of reaction
37	Which of the following acts as negative catalyst	a)Lead tetraethyl as antiknock compound	b)Glycerol in decomposition of H_2O_2	c)Ethanol in oxidation of chloroform	d)All are correct	d)All are correct
38	The efficiency of an enzyme in catalysing a reaction is due to its capacity	a)To form a strong enzyme substrate molecule	b)To change the shape of the substrate molecule	c)To lower the activation energy of the rection	d)To decrease the bond energy of all substrate molecules	c)To lower the activation energy of the rection
39	enzymes are	a)substance made by chemist to activate washing powder	b)very active vegetable catalysts	c)catalysts found in organisms	d)synthetic catalysts	c)catalysts found in organisms
40	The efficiency of an enzyme in catalysing a reaction is due to its capacity	a)To form a strong enzyme substrate molecule	b)To decrease the bond energies of the substrate molecule	c)To change the shape of the substrate molecule	d)To lower the activation energy of the reaction	d)To lower the activation energy of the reaction
41	enzymes take part in reaction and	a)Decreases the rate of reaction	b)Increases the rate of reaction	c)Both (a) and (b)	d)None	b)Increases the rate of reaction
42	When a catalyst is introduced into a reversible reaction	a)Equilibrium reaction rate increases	b)Backward reaction rate increases	c)Equilibrium is not changed	d)Equilibrium is attained quickly	d)Equilibrium is attained quickly
43	A biological catalyst is essentially	a)An amino acid	b)An enzyme	c)A carbohydrate	d)A nitrogen molecule	b)An enzyme
44	Which of the following is not correct in case of heterogenous catalyst	a)The catalyst decrease the energy of activation	b)The surface of catalyst plays an important role	c)The catalyst actually forms a compound with reactants	d)There is no change in the energy of activation	d)There is no change in the energy of activation
45	Which is true in case of catalyst	a)The catalyst altered during the reaction is regenerated	b)It does not alter the equilibrium	c)It lowers the energy of activation	d)All the above	d)All the above
46	A catalyst in a chemical reaction	a)Does not initiate a reaction	b)Increases the activation energy of the reaction	c)Changes the equilibrium constant of a reaction	d)Does not change the rate of reaction	a)Does not initiate a reaction
47	The enzyme which can catalyze the conversion of glucose to ethanol is	a)Zymase	b)Invertase	c)Maltase	d)Diastate	a)Zymase
48	A catalyst is used	a)Only for increasing the velocity of the reaction	b)For altering the velocity of the reaction	c)Only for decreasing the velocity of the reaction	d)All are correct	b)For altering the velocity of the reaction
49	A catalyst increases the rate of reaction by	a)Decreasing activation energy	b)Decreasing internal energy	c)Decreasing enthalpy	d)increasing activation energy	a)Decreasing activation energy
50	The ability of catalyst to accelerate the chemical reaction is known as	a)Selectivity	b)Activity	c)Negative catalyst	d)None of these	b)Activity
51	The process which is catalysed one of the product is called	a)Acid-base catalysis	b)Auto catalysis	c)Negative catalyst	d)Positive catalysis	b)Auto catalysis
52	When the catalyst is added to the reversible reaction in equlibrium state,the value of equlibrium constant	a)Increases	b)Decreases	c)Becomes zero	d)Does not change	d)Does not change
53	In the case of auto catalysis	a)Solvent catalysis	b)Product catalyses	c)Reactant catalyses	d)Heat produced in the reaction catalyses	b)Product catalyses
54	which of the following is true about the catalyst	a)It initiates reaction	b)It changes equlibrium point	c)It alters the rate of reaction	d)It increase average kinetic energy	c)It alters the rate of reaction
55	Which of the following statements about the active site of an enzyme is correct?	a)The active site of an enzyme binds the substrate of the reaction it catalyses more tightly than it does the transition state intermediate.	b)The active site of an enzyme binds the substrate of the reaction it catalyses less tightly than it does the transition state intermediate.	c)The active site of an enzyme binds the product of the reaction it catalyses more tightly than it does the transition state intermediate.	d)The active site of an enzyme is complementary to the substrate of the reaction it catalyses.	b)The active site of an enzyme binds the substrate of the reaction it catalyses less tightly than it does the transition state intermediate.
56	The substance being adsorbed is called	a)Solvent	b)Solute	c)Adsorbent	d)Adsorbate	d)Adsorbate

57	Which of the following statements about the nature of enzyme catalysis is correct?	a)An enzyme can change the equilibrium position of the reaction it catalyses by lowering the energy of activation of that reaction.	b)An enzyme can lower the energy of activation of the reaction it catalyses by increasing the molecular collisions between the molecules.	c)An enzyme lowers the free energy difference between substrate(s) and product(s) but it cannot change the equilibrium position of the reaction it catalyses.	d)An enzyme cannot change the equilibrium position of the reaction it catalyses but it lowers the energy of activation of that reaction.	d)An enzyme cannot change the equilibrium position of the reaction it catalyses but it lowers the energy of activation of that reaction.
58	Which of the following statements about Michaelis-Menten kinetics is correct?	a)K_m, the Michaelis constant, is defined as the concentration of substrate required for the reaction to reach maximum velocity.	b)K_m, the Michaelis constant, is defined as the dissociation constant of the enzyme-substrate complex.	c)K_m, the Michaelis constant, is expressed in terms of the reaction velocity.	d)K_m, the Michaelis constant, is a measure of the affinity the enzyme has for its substrate.	d)K_m, the Michaelis constant, is a measure of the affinity the enzyme has for its substrate.
59	Which of the following statements about the competitive inhibition of an enzyme-catalyzed reaction is correct?	a)A competitive inhibitor and substrate can bind simultaneously to the enzyme.	b)The V_{max} and K_m (Michaelis constant) for a reaction are unchanged in the presence of a competitive inhibitor.	c)The V_{max} for a reaction remains unchanged in the presence of a competitive inhibitor.	d)The K_m for a reaction remains unchanged in the presence of a competitive inhibitor.	c)The V_{max} for a reaction remains unchanged in the presence of a competitive inhibitor.
60	The Michaelis-Menton equation relates the rate of an enzyme-catalysed reaction to which of the following?	a)Substrate concentration	b)Product concentration	Activation Energy	d)Inhibitor concentration	Substrate concentration
61	Which of the following statements about Michaelis-Menten kinetics are correct? Please select all that apply.	**a)** A high Michaelis constant (K_m) indicates a high affinity of an enzyme for its substrate.	**b)** A low Michaelis constant (K_m) indicates a high affinity of an enzyme for its substrate.	**c)** The Michaelis constant (K_m) of an enzyme increases when the enzyme concentration is increased.	**d)** The Michaelis constant (K_m) of an enzyme is unchanged when the enzyme concentration is increased.	**d)** The Michaelis constant (K_m) of an enzyme is unchanged when the enzyme concentration is increased.

UNIT III

SYLLABUS

Inter ionic attraction theory: Debye – Huckel – Onsager equation - Falkenhagen effect- Wien effect. Activity and activity coefficient- ionic strength- Debye – Huckel limiting law and its applications.

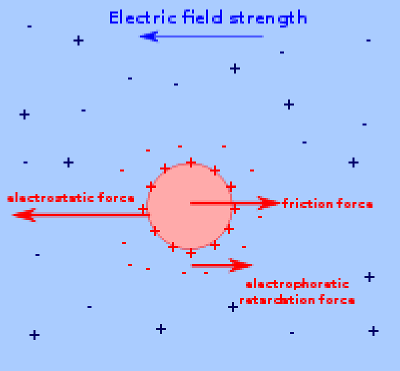
Theories of double layer. Helmholtz – Perrin - Gouy chapmann – Stern theories**.**

Inter ionic attraction theory

Debye-Huckel-Onsager equation

The **Debye–Hückel theory** was proposed by Peter Debye and Erich Hückel as a theoretical explanation for departures from ideality in solutions of electrolytes and plasmas. It is a linearized Poisson–Boltzmann model, which assumes an extremely simplified model of electrolyte solution but nevertheless gave accurate predictions of mean activity coefficients for ions in dilute solution. The Debye–Hückel equation provides a starting point for modern treatments of non-ideality of electrolyte solutions.

Conductivity



Forces affecting a charged ion or cloud moving in an electric field

The treatment given so far is for a system not subject to an external electric field.
When conductivity is measured the system is subject to an oscillating external field due to the application of an AC voltage to electrodes immersed in the solution. Debye and Hückel modified their theory in 1926 and their theory was further modified by Lars Onsager in 1927. All the postulates of the original theory were retained. In addition it was assumed that the electric field causes the charge cloud to be distorted away from spherical symmetry.[17] After taking this into

account, together with the specific requirements of moving ions, such as viscosity and electrophoretic effects, Onsager was able to derive a theoretical expression to account for the empirical relation known as Kohlrausch's Law, for the molar conductivity, Λ_m.

$$\wedge_m=\wedge^0_m-K\sqrt{C}$$

$\wedge^0_m$ is known as the limiting molar conductivity, K is an empirical constant and c is the electrolyte concentration. Limiting here means "at the limit of the infinite dilution"). Onsager's expression is

$$\wedge_m=\wedge^0_m-(A+B\wedge^0_m)\sqrt{C}$$

where A and B are constants that depend only on known quantities such as temperature, the charges on the ions and the dielectric constant and viscosity of the solvent. This is known as the Debye-Hückel-Onsager equation. However, this equation only applies to very dilute solutions and has been largely superseded by other equations due to Fuoss and Onsager, 1932 and 1957 and later.

Debye –Falkenhagen effect

Debye and Falkenhagen examined the conductance behavior of a solution of a strong electrolyte by applying alternating currents of different frequencies. They predicted that if the frequency of alternating current is high so that the time of oscillation is small in comparison with the relaxation time of the ionic atmosphere, the asymmetry effect will be virtually absent. In other words, the ionic atmosphere around the central ion will remain symmetric. The retarding effect due to asymmetry may, therefore be entirely absent and the conductance may be higher. The conductance of a solution, therefore should vary with the frequency of the alternating current used. The higher the frequency, the higher the conductance, evidently. This effect also known as dispersion of conductance, has been verified experimentally.

Wien effect

Speed of an ion in an electric field varies with the applied potential gradient. Thus, under a potential gradient of about 20,000 volt per cm, an ion may have a speed of about 100 cm per sec. the ion, therefore should pass several times through the thickness of the ionic atmosphere during the time of relazation. The moving ion, therefore, will be moving so fast that there will be no time for the ionic atmosphere to be built up. The asymmetry and electrophoretic effects, under these circumstances, may be negligibly small or even absent. Thus, the conductance of a strong electrolyte in aqueous solution increases to a certain limiting value with increase in potential gradient applied.

Activity and activity coefficient

An **activity coefficient** is a factor used in thermodynamics to account for deviations from ideal behaviour in a mixture of chemical substances. In an ideal mixture, the microscopic interactions between each pair of chemical species are the same (or macroscopically equivalent, the enthalpy change of solutionand volume variation in mixing is zero) and, as a result, properties of the mixtures can be expressed directly in terms of simple concentrations or partial pressures of the substances present e.g. Raoult's law. Deviations from ideality are accommodated by modifying the concentration by an *activity coefficient*. Analogously, expressions involving gases can be adjusted for non-ideality by scaling partial pressures by a fugacity coefficient.

The concept of activity coefficient is closely linked to that of activity in chemistry.

As it was already signaled in the introduction, all equilibrium calculations done using concentrations are wrong. Ions are charged so they interact in the solution attracting and repelling each other with coulomb forces. These interactions influence ions behavior and don't allow to treat every ion in the solution independently. Whole phenomenon - although investigated for over 100 years - is still not fully understood and described. To be precise in our equilibrium calculations instead of using concentrations we should use ions activities. Activities are not a theoretical construct - they can be measured for every solution. In fact whenever you put pH electrode into a solution you are measuring not [H^+] but activity of H^+ ions. It is enough to add an inert salt to the solution of a known acid to observe pH change that confirms activity concept (and is in accordance with the results of calculations presented below).

Most popular method used to calculate ions activities is the one proposed by Debye and Hückel in 1923.

First step in calculations is calculation of so called ionic strength, using the following formula:

$$I = \frac{1}{2} \sum C_i z_i^2 \qquad 1$$

where C_i is a molar concentration of i^th^ ion present in the solution and z_i is its charge. Summation is done for all charged molecules present in the solution.

Second step is calculation of activity coefficients given by the formula:

$$\log f_z = \frac{-0.51\, z^2 \sqrt{I}}{1 + \sqrt{I}} \qquad 2$$

An activity coefficient for all ions bearing the same charge is identical (although there exists slightly more precise formula in which activity coefficient is also a function of the ion radius).

And now the most important thing. The activity of any ion (with a charge z) is

$$a_{ion} = f_z C_{ion} \qquad 3$$

where f_z denotes the activity coefficient for z-charged ions.

Equilibrium calculations made using this approach give good results for ionic strength lower than 0.1. There are other theories, that work for higher ionic strengths, but they are based on experimentally determined coefficients that depend on types of ions present in the solution. There are no extensive tables of these coefficients, so their use is rather limited.

In all reaction quotients used throughout all sections we should replace concentrations of all ions with their activities. Mass and charge balances should use analytical concentrations of ions.

What error are we making neglecting ionic strength of the solution? Let's see what will happen if we prepare 0.05M phosphoric buffer pH 7.2 neglecting - and not neglecting - ionic strength of the solution. You can calculate pH of such a buffer using pH calculator - select phosphoric acid and sodium hydroxide from the databases and enter 0.05M as concentration of phosphoric acid and 0.075M as concentration of NaOH. This results in equimolar solution of sodium hydrogen phosphate and sodium dihydrogen phosphate. As pK_{a2} of the phosphoric acid is 7.20 we may expect this solution to have pH=7.20 (see Henderson-Hasselbalch equation - when both concentrations are identical, pH of the solution simply equals pK_a). However, ionic strength of the solution is 0.1 (limit of the Debye-Hückel theory applicability), thus we can't neglect activity coeffcients - to take into account select *calculate I* from the dropdown in the left bottom corner of the calculator window. Now calculated pH is 6.83 - which means that our buffer solution pH (if prepared neglecting ionic strength) will be 0.37 unit off! Note, that 0.1 is a rather low IS value, sea water has ionic strength of about 0.7 and many common lab reagents have much higher ionic strength.

As the activities of ions are function of their concentrations (through ionic strength), calculations have to be done iteratively. In first step you should calculate all concentrations assuming ionic strength of 0 (and all activity coefficients of 1). If some of the reagents obviously dissociated you may already calculate first value of the ionic strength at this stage. After concentrations are known you should use formulas 1 and 2 to find ionic strength and all activity coefficients and repeat calculations using these values. This gives new set of concentrations and whole process should be repeated until results of calculations doesn't change (or the difference between two steps or calculations is small enough). Remember, that ionic strength is calculated as sum of concentrations, not activities of ions.

Debye-Huckel limiting law

Coulombic interactions between ions in solution are relatively strong, long-range forces compared to the other types of intermolecular force in solution. They are thus an important contributor to the non-ideality of ionic solutions, and in the Debye-Hückel theory of such solutions, they are taken to dominate the non-ideality to such an extent that all other contributions may be neglected.
The theory is based around the simple fact that oppositely charged ions attract one another, whilst like-charged ions repel each other.

As a result, the motion of ions in solution is not entirely random; there is a slight tendency for ions of opposite charge to encounter each other more frequently than ions of the same charge.A time-averaged picture of the solution shows that near any given ion, there is an excess of counter-ions.
This time-averaged spherical distribution (in which ions of the same charge as the central ion and counter-ions are both present, though counter-ions predominate) has a net charge equal in magnitude but opposite in sign to the central ion, and is known as its ionic atmosphere. There is a stabilising Coulombic interaction between the central ion and its ionic atmosphere, which has the effect of lowering the energy (and thus the chemical potential) of the central ion.
This model leads to the Debye-Hückel Limiting Law, which applies only at very low concentrations of solute (before other contributions to the non-ideality become important). This law enables calculation of the mean activity coefficient from basic properties of the solution: where z_+ and z_- are the charge number of respectively the cation and the anion concerned. *A* is an empirical parameter, dependant upon the solvent and temperature (eg, for a solution in water at 298K, *A* = 0.509). I is the ionic strength of the solution, defined as
This means for each type of ion ,i, present in solution, take the charge number of the ion (positive for cations, negative for anions), square it, multiply by the molality of the species, and divide by b^o (which has the numerical value 1 mol kg^{-1}). Sum the values for each ion and divide by two to obtain the ionic strength.
Note in the above expression the charge numbers appear as their squares, emphasizing the charge on the ions (and hence the Coulombic interaction between them) as a contributor to non-ideality.

The name 'limiting law' is applied because in the limit of arbitrarily low molalities (ie as the concentration of the solute gets closer and closer to zero), all solutions are expected to behave in a manner consistent with the expression.

However, at more moderate molalities activity coefficients may differ from the values this law predicts. Experimentally, it is found that agreement is good up to a molality of approximately 0.001mol kg^{-1} . At higher solute concentrations, large deviations from the predictions of the model are observed.

Applications

The Debye limiting law has been used to deduce an expression for the electrical work which must be done to build up a polyion from the corresponding single ions in extremely dilute solutions containing various (appreciable) concentrations of 1 — 1 electrolyte. The case of an infinite straight rigid polyion having charges at equal intervals along its length was treated in greater detail, and a corrected expression was obtained for the above-mentioned electrical work, which makes allowance for the finite size of the polyion charges and takes some account of the steric effects due to the remainder of the polyion molecule. The error due to the high electric potential ψ surrounding such a polyion which invalidates the Debye approximation of replacing sinh ($\varepsilon\psi/kT$) by $\varepsilon\psi/kT$ was evaluated by numerical integration of the Poisson-Boltzmann equation. The integration was started at a considerable distance from the polyion on the assumption of cylindrical symmetry and continued at closer distances on the assumption of spherical symmetry surrounding each polyion charge. The results obtained indicated that the error involved in using the simple Debye limiting law formula would seldom be more than a few percent, provided the concentration of the 1 — 1 electrolytewas rather low (not more than about *N*/100)

Theories of double layer

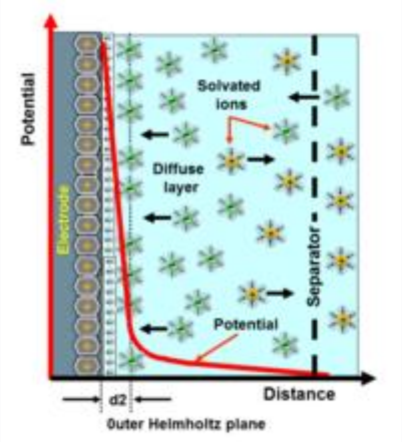
A **double layer** (**DL**, also called an **electrical double layer**, **EDL**) is a structure that appears on the surface of an object when it is exposed to a fluid. The object might be a solid particle, a gas bubble, a liquid droplet, or a porous body. The DL refers to two parallel layers of charge surrounding the object. The first layer, the surface charge (either positive or negative), consists of ions adsorbed onto the object due to chemical interactions. The second layer is composed of ions attracted to the surface charge via the Coulomb force, electrically screening the first layer. This second layer is loosely associated with the object. It is made of free ions that move in the fluid under the influence of electric attraction and thermal motion rather than being firmly anchored. It is thus called the "diffuse layer".

Interfacial DLs are most apparent in systems with a large surface area to volume ratio, such as a colloidor porous bodies with particles or pores (respectively) on the scale of micrometres to nanometres. However, DLs are important to other phenomena, such as the electrochemical behaviour of electrodes.

DLs play a fundamental role in many everyday substances. For instance, homogenized milk exists only because fat droplets are covered with a DL that prevents their coagulation into butter. DLs exist in practically all heterogeneous fluid-based systems, such as blood, paint, ink and ceramic and cement slurry.

The DL is closely related to electrokinetic phenomena and electroacoustic phenomena.

Helmholtz



Simplified illustration of the potential development in the area and in the further course of a Helmholtz double layer.

When an *electronic* conductor is brought in contact with a solid or liquid *ionic* conductor (electrolyte), a common boundary (interface) among the two phases appears. Hermann von Helmholtz was the first to realize that chargedelectrodes immersed in electrolytic solutions repel the co-ions of the charge while attracting counterions to their surfaces. Two layers of opposite polarity form at the interface between electrode and electrolyte. In 1853 he showed that an electrical double layer (DL) is essentially a molecular dielectric and stores charge electrostatically. Below the electrolyte's decomposition voltage the stored charge is linearly dependent on the voltage applied.

This early model predicted a constant differential capacitance independent from the charge density depending on the dielectric constant of the electrolyte solvent and the thickness of the double-layer.

This model, with a good foundation for the description of the interface, does not consider important factors including diffusion/mixing of ions in solution, the possibility of adsorption onto the surface and the interaction between solvent dipole moments and the electrode.

Gouy-Chapman Double Layer

Gouy suggested that interfacial potential at the charged surface could be attributed to the presence of a number of ions of given sign attached to its surface, and to an equal number of ions of opposite charge in the solution. In other words, counter ions are not rigidly held, but tend to diffuse into the liquid phase until the counter potential set up by their departure restricts this tendency. The kinetic energy of the counter ions will, in part, affect the thickness of the resulting diffuse double layer. Gouy and, independently, Chapman developed theories of this so called *diffuse double layer* in which the change in concentration of the counter ions near a charged surface follows the Boltzman distribution

$$n = n_o\exp(-zeY/kT)$$

where n_o = bulk concentration
z = charge on the ion
e = charge on a proton
k = Boltzmann constant

Already, however, we are in error, since derivation of this form of the Boltzman distribution assumes that activity is equal to molar concentration. This may be an OK approximation for the bulk solution, but will not be true near a charged surface.

Now, since we have a diffuse double layer, rather than a rigid double layer, we must concern ourselves with the volume charge density rather than surface charge density when studying the coulombic interactions between charges. The volume charge density, r , of any volume, i, can be expressed as

$$r_i = Sz_ien_i$$

The coulombic interaction between charges can, then, be expressed by the Poisson equation. For plane surfaces, this can be expressed as

$$d^2Y/dx^2 = -4pr/d$$

where Y varies from Y_o at the surface to 0 in bulk solution. Thus, we can relate the charge density at any given point to the potential gradient away from the surface.

Combining the Boltzmann distribution with the Poisson equation and integrating under appropriate limits, yields the electric potential as a function of distance from the surface. The thickness of the diffuse double layer:

$$l_{double} = [e_rkT/(4pe^2Sn_{io}z_i^2)]^{1/2}$$

at room temperature can be simplified as

$$l_{double} = 3.3*10^6e_r/(zc^{1/2})$$

in other words, the double layer thickness decreases with increasing valence and concentration.

The Gouy-Chapman theory describes a rigid charged surface, with a cloud of oppositely charged ions in the solution, the concentration of the oppositely charged ions decreasing with distance from the surface. This is the so-called diffuse double layer.

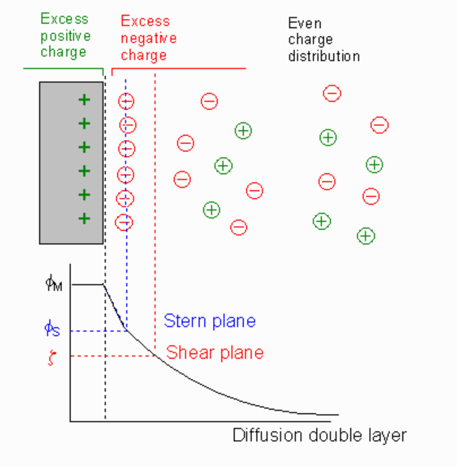
This theory is still not entirely accurate. Experimentally, the double layer thickness is generally found to be somewhat greater than calculated. This may relate to the error incorporated in assuming activity equals molar concentration when using the desired form of the Boltzman distribution. Conceptually, it tends to be a function of the fact that both anions and cations exist in the solution, and with increasing distance away from the surface the probability that ions of the same sign as the surface charge will be found within the double layer increase as well.

Stern Modification of the Diffuse double Layer

The Gouy-Chapman theory provides a better approximation of reality than does the Helmholtz theory, but it still has limited quantitative application. It assumes that ions behave as point charges, which they cannot, and it assumes that there is no physical limits for the ions in their approach to the surface, which is not true. Stern, therefore, modified the Gouy-Chapman diffuse double layer. His theory states that ions do have finite size, so cannot approach the surface closer than a few nm. The first ions of the Gouy-Chapman Diffuse Double Layer are not at the surface, but at some distance d away from the surface. This distance will usually be taken as the radius of the ion. As a result, the potential and concentration of the diffuse part of the layer is low enough to justify treating the ions as point charges.

Stern also assumed that it is possible that some of the ions are specifically adsorbed by the surface in the plane d, and this layer has become known as the Stern Layer. Therefore, the potential will drop by Y_o - Y_d over the "molecular condenser" (i.e., the Helmholtz Plane) and by Y_d over the diffuse layer. Y_d has become known as the zeta (z) potential.

This diagram serves as a visual comparison of the amount of counterions in each the Stern Layer and the Diffuse Layer.



Thus, the double layer is formed in order to neutralize the charged surface and, in turn, causes an electrokinetic potential between the surface and any point in the mass of the suspending liquid. This voltage difference is on the order of millivolts and is referred to as the surface potential. The magnitude of the surface potential is related to the surface charge and the thickness of the double layer. As we leave the surface, the potential drops off roughly linearly in the Stern layer and then exponentially through the diffuse layer, approaching zero at the imaginary boundary of the double layer. The potential curve is useful because it indicates the strength of the electrical force between particles and the distance at which this force comes into play. A charged particle will move with a fixed velocity in a voltage field. This phenomenon is called electrophoresis. The particle's mobility is related to the dielectric constant and viscosity of the suspending liquid and to the electrical potential at the boundary between the moving particle and the liquid. This boundary is called the slip plane and is usually defined as the point where the Stern layer and the diffuse layer meet. The relationship between zeta potential and surface potential depends on the level of ions in the solution.The figure above represents the change in charge density through the diffuse layer. One shows considered to be rigidly attached to the colloid, while the diffuse layer is not. As a result, the electrical potential at this junction is related to the mobility of the particle and is called the zeta potential. Although zeta potential is an intermediate value, it is sometimes considered to be more significant than surface potential as far as electrostatic repusion is concerned.

POSSIBLE QUESTIONS

Part A **(Each question carries one mark)**

1. In Debye Hucklel theory the strong elecrolytes is completely ionised at all----
(a)Dilution (b)High conc (c)low dilution (d)Neutral

2.Which of the following is the strongest reducing agent?
(a)Cu (b)Zn **(c)Mg** (d)Pb

3.In Debye Hucklel theory the anions and cations are---
(a)Not uniform (b)uniform (c)different (d)No change

4.Asymetry effect is also known as
(a)ionic atmosphere (b)Inter ionic (c)Conductance **(d)Relaxation effect**
9.For an ideal solution the activity coefficient is
(a)Zero **(b)Unity** (c)Two (d)Three

5.In Debye Hucklel theory the spherical haze of opposite charge is called
(a)ionic atmosphere (b)Inter ionic (c)Conductance (d)Relaxation effect

6.An oxidising agent is
(a)reduced as it loses electrons **(b)reduced as it gains electrons**
(c)oxidised as it loses electrons (d)oxidised as it gains electrons

7.Referring to the data booklet,which of the following can act as an oxidising agent but not as a reducing agent
(a)Zn (b)Cl^- (c)Sn^{2+} **(d)Fe^{3+}**

8.When 1.0M Na_2SO_4 is electrolyzed, the solution near the anode becomes
(a)basic and bubbles form. **(b) acidic and bubbles form.**
(c)basic and no bubbles form. (d)acidic and no bubbles form.

9.The value of E° for a cell can be used to determine
(a)rate. **(B) spontaneity.** (C) temperature. (d)activation energy.

10.How is the formation of rust on an iron can inhibited by a tin coating?
(a)The tin is a sacrificial anode. (b)The tin cathodically protects the iron.
(c)The tin is a weaker reducing agent than iron. **(d) The tin keeps the oxygen away from the iron.**

11.Which of the following represents the formation of a stronger acid as a result of oxidation?
(a) $H_2SO_3 \rightarrow H_2S$ (b) $HClO_4 \rightarrow HCl$ **(c) $H_2SO_3 \rightarrow H_2SO_4$** (d)$HCO_3 \rightarrow H_2CO_3$

12.Why can an object not be plated with magnesium using 1.0M Mg^{I2}?
(a)Water is a stronger reducing agent than I- (b)Water is a stronger oxidizing agent than I-
(c)Water is a stronger reducing agent than Mg^{2+}
(d) Water is a stronger oxidizing agent than Mg^{2+}

13.How is the formation of rust on an iron can inhibited by a tin coating?
(a)The tin is a sacrificial anode. (b) The tin cathodically protects the iron.
(c) The tin is a weaker reducing agent than iron.
(d) The tin keeps the oxygen away from the iron.

14.Among the following which is the weak reducing agent than iron
(a)Magnesium (b)Calcium **(c)Tin** (d)Lead

15.Which of the following will not react spontaneously with H_2O at standard conditions?
(a)F2 (b)Ca (c)Na **(d)Sn**

16.When 1.0M Na_2SO_4 is electrolyzed, the solution near the anode becomes
(a)basic and bubbles form. **(b) acidic and bubbles form.**
(c) basic and no bubbles form. (d)acidic and no bubbles form.

17.The value of E° for a cell can be used to determine
(a)rate. **(b) spontaneity.** (c) temperature. (d)activation energy.

18.How is the formation of rust on an iron can inhibited by a tin coating?
(a)The tin is a sacrificial anode. (b)The tin cathodically protects the iron.
(c)The tin is a weaker reducing agent than iron.
(d)The tin keeps the oxygen away from the iron.

19.In Debye Hucklel theory the anions and cations are---
(a)Not uniform (b)uniform (c)different (d)No change

20.Asymetry effect is also known as
(a)ionic atmosphere (b)Inter ionic (c)Conductance **(d)Relaxation effect**

PART B **(Each question carries 2 marks)**

1.Write an expression for Debye-Huckel-Onsager equation.

2.What is Falkenhagen effect.

3.What is the principle involved in Wien effect.

4.Define ionic strength.

5.Write a note on Helmholtz model

Part C **(Each question carries 6 marks)**

1.Write a note on Debye- Falkenhagen effect

2.Define electrical double layer theory**.** Explain the Stern model of the electrical double layer theory

.3. Derive the Debye-Huckel Onsager equation.

4. Write a note on Activity and Activity coefficient.

5.Explain Debye-Huckel limiting law.

6. Explain briefly the Gouy chapman model for electrical double layer

7.Write a note on ionic strength of attraction theory.

8.Discuss Helm-Holtz Perrin theory of electrical double layer.

9. Calculate the ionic strength of a solution which is 0.1m in KCl and 0.2 molal in K_2SO_4.

10. Write a note on Wein effect.

KARPAGAM ACADEMY OF HIGHER EDUCATION
COIMBATORE-641 021
(For the candidates admitted from 2017 & Onwards)
M.Sc., CHEMISTRY
SECOND SEMESTER

PHYSICAL CHEMISTRY-II (Chemical Kinetics and Electrochemistry) 17CHP203

S.NO	UNIT-III	OPTION 1	OPTION 2	OPTION 3	OPTION 4	ANSWER
1	In debye huckel theory the strong elecrolytes is completely ionised at all----	a)concentrations	b)Dilution	c)temperatures	d)pressure	b)Dilution
2	Which of the following is the strongest reducing agent?	a)Ni	b)Cu	c)Zn	d)Mg	d)Mg
3	In debye huckel theory the anions and cations are---	a)Not uniform	b)uniform	c)different	d)None of the above	a)Not uniform
4	Assymetry effect is also known as	a)ionic atmosphere	b)Inter ionic	c)Conductance	d)Relaxation effect	d)Relaxation effect
5	This variation of conductance at high frequencies is known as	a)Dispersion of conductance	b)Debye -Falkenhagen effect	c)Both (A)and (B)	d)None of the above	c)Both (A)and (B)
6	Wien effect is observed at high concentrations of electrolytes at ---- valence ions	a)Low	b)High	c)Very low	d)Medium	b)High
7	For an ideal solution the activity coefficient is	a)Zero	b)Unity	c)Two	d)Three	b)Unity
8	In debye hucklel theory the spherical haze of opposite charge is called	a)ionic atmosphere	b)Inter ionic	c)Conductance	d)Relaxation effect	a)ionic atmosphere
9	An oxidising agent is	a)reduced as it loses electrons	b)reduced as it gains electrons	c)oxidised as it loses electrons	d)oxidised as it gains electrons	b)reduced as it gains electrons
10	Referring to the data booklet,which of the following can act as an oxidising agent but not as a reducing agent	a)Zn	b)Cl^-	c)Sn^{2+}	d)Fe^{3+}	d)Fe^{3+}
11	When NO_2 act as a reducing agent,a possible product is	a)NO	b)N_2O	c)N_2O_4	d)N_2O_5	d)N_2O_5
12	The oxidation number of sulphur in $Na_2S_2O_3$	a)-2	b)2	c)1	d)4	c)1
13	In a redox reaction,the species which loses electrons	a)is oxidised	b)is called the cathode	c)Gains mass at the electrode	d)Decreases in oxidation number	a)is oxidised
14	When NO_2 reacts to form N_2O_4 the oxidation number of nitrogen	a)Increased by 2	b)Increased by 4	c)Increased by 8	d)Does not change	d)Does not change
15	The species which gains electrons in a redox reaction	a)loss mass	b)is oxidised	c)is the oxidising agent	d)increase in oxidation number	c)is the oxidising agent
16	In a oxidation half-reaction there is a	a)Gain of protons	b)Gain of electrons	c)loss of protons	d)loss of electrons	d)loss of electrons
17	As a element is oxidised,its oxidation number	a)increases as electrons are lost	b)decreases as electrons are lost	c)increases as electrons are gained	d)decreases as electrons are gained	a)increases as electrons are lost
18	In a electochemical cell, the cathode is	a)is oxidised	b)loss mass	c)is the reducing agent	d)is the site of reduction	d)is the site of reduction
19	The electrons moves from the	a)Zinc to the lead through the wire	b)lead to the zinc through the wire	c)Zinc to the lead through the salt bridge	d)lead to the zinc through the salt bridge	a)Zinc to the lead through the wire
20	The principle function of fuel cell is to	a)Produce fuel	b)electrolyte fuel	c)Produce hydrogen	d)Produce electricity	d)Produce electricity
21	Hydrogen and oxygen react to provide energy in	a)dry cell	b)fuel cell	c)alkaline cell	d)Lead-acid storage cell	b)fuel cell
22	Which of the following should be used to cathodically protect an iron sculpture	a)lead	b)nickel	c)copper	d)magnesium	d)magnesium
23	The process of applying an electric current through a cell to produce a chemical change is called	a)Corrosion	b)ionization	c)hydrolysis	d)electrolysis	d)electrolysis
24	The substance formed at the anode during the electrolysis of 0.1M NaI is	a)Iodine	b)oxygen	c)sodium	d)hydrogen	a)Iodine
25	A chemical process involving the loss of electrons is a definition of	a)oxidation.	b)reduction.	c) galvanization.	d)cathodic protection	a)oxidation.
26	Which of the following is **not** a redox reaction?	a)$2Mg + O_2 \rightarrow 2MgO$	b)$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$	c) $CuS + 2O_2 + C \rightarrow Cu + SO_2 + CO_2$	d)$4Ag + 2H_2S + O_2 \rightarrow 2Ag_2S + 2H_2O$	b)$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$

27	A reducing agent will cause which of the following changes?	a)$ClO_3^- \rightarrow ClO_2$	b)$NO_2^- \rightarrow N_2O_4$	c)$H_3PO_3 \rightarrow H_3PO_4$	d)$HS_2O_4^- \rightarrow H_2SO_3$	a)$ClO_3^- \rightarrow ClO_2$
28	The oxidation number of zinc in a reaction increases by 2. This indicates that	a)zinc is reduced and loses 2 electrons.	b)zinc is reduced and gains 2 electrons.	c)zinc is oxidized and loses 2 electrons.	d) zinc is oxidized and gains 2 electrons.	c)zinc is oxidized and loses 2 electrons.
29	Which metal will react spontaneously with water	a)Ca	b)Ni	c)Pb	d)Hg	a)Ca
30	List the ions $Co^{2+,}$ Cu^{2+} and Zn^{2+} in order from strongest to weakest oxidizing agents.	a)$Zn^{2+} > Co^{2+} > Cu^{2+}$	b)$Co^{2+} > Cu^{2+} > Zn^{2+}$	c)$Cu^{2+} > Zn^{2+} > Co^{2+}$	d)$Cu^{2+} > Co^{2+} > Zn^{2+}$	d)$Cu^{2+} > Co^{2+} > Zn^{2+}$
31	Which two species will not react spontaneously at standard conditions?	a)Co with Cl_2	b)Cu with Ag^+	c)Ag with Zn^{2+}	d) Mg with Cr^{3+}	c)Ag with Zn^{2+}
32	The products of the electrolysis of molten $MgCl_2$ using inert electrodes are	a)hydrogen and oxygen.	b)hydrogen and chlorine.	c)magnesium and oxygen.	d)magnesium and chlorin	d)magnesium and chlorin
33	. When SO_4^{2-} reacts to form $S_2O_6^{2-}$, the sulphur atoms	a)lose electrons and are reduced.	b) gain electrons and are reduced.	c)lose electrons and are oxidized.	d) gain electrons and are oxidized.	b) gain electrons and are reduced.
34	Which of the following is a list of metals in order from strongest to weakest reducing agents?	a)Au > Ni > Rb	b)Ni > Au > Rb	c)Ni > Rb > Au	d)Rb > Ni > Au	d)Rb > Ni > Au
35	Which of the following will **not** react spontaneously with H_2O at standard conditions?	a)F_2	b)Ca	c)Na	d)Sn	d)Sn
36	When 1.0M Na_2SO_4 is electrolyzed, the solution near the anode becomes	a)basic and bubbles form.	b)acidic and bubbles form.	c) basic and no bubbles form.	d)acidic and no bubbles form.	d)acidic and no bubbles form.
37	The value of E° for a cell can be used to determine	a)rate.	b)spontaneity.	c) temperature.	d)activation energy.	b)spontaneity.
38	How is the formation of rust on an iron can inhibited by a tin coating?	a)The tin is a sacrificial anode.	b)The tin cathodically protects the iron.	c)The tin is a weaker reducing agent than iron.	d) The tin keeps the oxygen away from the iron.	d) The tin keeps the oxygen away from the iron.
39	Bromine has an oxidation number of +3 in	a)KBrO	b) $KBrO_2$	c)$KBrO_3$	d)$KBrO_4$	b) $KBrO_2$
40	Which of the following does not affect the cell potential?	a)$[Ni^{2+}]$	b)$[Zn^{2+}]$	c)temperature	d) surface area of the electrodes	d) surface area of the electrodes
41	The electrolysis of 1.0M NaI using inert electrodes will produce	a)sodium and iodine.	b)sodium and oxygen.	c)hydrogen and iodine.	d) hydrogen and oxygen.	c)hydrogen and iodine.
42	In voltaic cells, such as those diagrammed in your text, the salt bridge _______.	a)is not necessary in order for the cell to work	b)acts as a mechanism to allow mechanical mixing of the solutions	c)allows charge balance to be maintained in the cell	d)is tightly plugged with firm agar gel through which ions cannot pass	c)allows charge balance to be maintained in the cell
43	Which of the following represents the formation of a stronger acid as a result of oxidation?	a)$H_2SO_3 \rightarrow H_2S$	b)$HClO_4 \rightarrow HCl$	c) $H_2SO_3 \rightarrow H_2SO_4$	d)$HCO_3^- \rightarrow H_2CO_3$	c) $H_2SO_3 \rightarrow H_2SO_4$
44	Why can an object **not** be plated with magnesium using 1.0M MgI_2?	a)Water is a stronger reducing agent than I^-	b)Water is a stronger oxidizing agent than I^-	c) Water is a stronger reducing agent than Mg^{2+}	d)Water is a stronger oxidizing agent than Mg^{2+}	d)Water is a stronger oxidizing agent than Mg^{2+}
45	How is the formation of rust on an iron can inhibited by a tin coating?	a)The tin is a sacrificial anode.	b)The tin cathodically protects the iron.	c) The tin is a weaker reducing agent than iron.	d) The tin keeps the oxygen away from the iron.	d) The tin keeps the oxygen away from the iron.
46	Among the following which is the weak reducing agengt than iron	a)Magnesium	b)Calcium	c)Tin	d)Lead	c)Tin
47	Debye-Huckel limiting law equation relating the mean ionic activity coefficient to the ---------------------of the solution	a)ionic mobility	b)ionic atmosphere	c)Ionic strength	d)ionic velocity	c)Ionic strength
48	Debye-Huckel limiting law equation can be checked by plotting -log γ+ against	a)$\sqrt{g}$	b)$\sqrt{I}$	c)$\sqrt{F}$	d)$\sqrt{S}$	b)$\sqrt{I}$
49	a is known a	a)activity	b)activity coefficient	c)Activation energy	d)activation	a)activity
50	Activity of a stubstance in any given state is defined as the ratio of the----------of the substance in that state to the fugacity of the same substance in the pure state	a)fugacity	b)volume	c)pressure	d)temperature change	a)fugacity
51	Activity of a gas, lime fugacity, serves as a ---------------------------counterpart of gas pressure	a)pressure	b)pressure coefficient	c)thermodynamic	d)volume	c)thermodynamic
52	For an ideal gas, activity is numerically equal to its ------------------	a)pressure	b)volume	c)concentration	d)temperature	a)pressure
53	γ is known as	a)activity	b)activity coefficient	c)temperature coefficient	d)pressure coefficient	b)activity coefficient
54	a is directly proportional to	a)pressure	b)volume	c)concentration	d)temperature	a)pressure

55	Each substance in a given state has a tendency to escape from that state is known as	a)activiy	b)fugacity	c)activity coefficient	d)temperature coefficient	b)fugacity
56	The drag on the central ion is known as	a)asymmetry	b)asymmetry effect	c)viscosity effect	d)electrophoretic effect	b)asymmetry effect
57	viscous drag of the solvent on the movement of ions is known as	a)asymmetry	b)asymmetry effect	c)viscosity effect	d)electrophoretic effect	c)viscosity effect
58	The value of A for water in Debye-Huckel onsager equation is	a)60.2	b)60.4	c)60.6	d)60.8	a)60.2
59	Conductance under high A.C frequency is given by	a)Debye–Hückel	b)Debye	c)Debye-Falkenhagen	d)Wien	a)60.2
60	Conductance under high potential gradient is given by	a)Debye–Hückel	b)Debye	c)Debye-Falkenhagen	d)Wien	d)Wien

UNIT IV

SYLLABUS

Polarography: Current – voltage relationships-the dropping mercury electrode. Diffusion current-half – wave potentials. Applications of polarography- Amperometric titrations.

Fundamental principles of coulometric methods- constant current and controlled potential methods- simple applications.

POLAROGRAPHY

Current-Voltage relationships

All materials are made up from atoms, and all atoms consist of protons, neutrons and electrons. Protons, have a positive electrical charge. Neutrons have no electrical charge while Electrons, have a negative electrical charge. Atoms are bound together by powerful forces of attraction existing between the atoms nucleus and the electrons in its outer shell.

When these protons, neutrons and electrons are together within the atom they are happy and stable. But if we separate them from each other they want to reform and start to exert a potential of attraction called a potential difference.

Now if we create a closed circuit these loose electrons will start to move and drift back to the protons due to their attraction creating a flow of electrons. This flow of electrons is called an electrical current. The electrons do not flow freely through the circuit as the material they move through creates a restriction to the electron flow. This restriction is called resistance.

Then all basic electrical or electronic circuits consist of three separate but very much related electrical quantities called: Voltage, (v), Current, (i) and Resistance, (Ω).

Electrical Voltage

Voltage, (V) is the potential energy of an electrical supply stored in the form of an electrical charge. Voltage can be thought of as the force that pushes electrons through a conductor and the greater the voltage the greater is its ability to “push” the electrons through a given circuit. As energy has the ability to do work this potential energy can be described as the work required in joules to move electrons in the form of an electrical current around a circuit from one point or node to another.

Then the difference in voltage between any two points, connections or junctions (called nodes) in a circuit is known as the **Potential Difference**, (p.d.) commonly called the **Voltage Drop**.

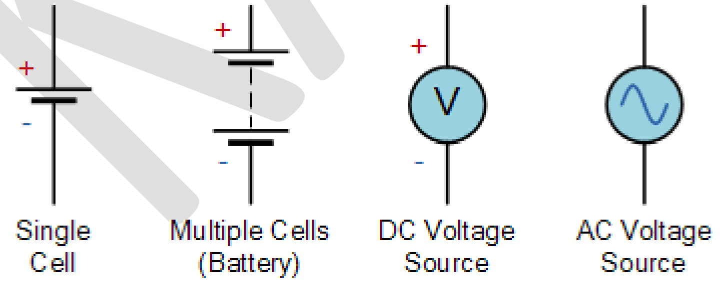
The Potential difference between two points is measured in **Volts** with the circuit symbol V, or lowercase "v", although **Energy**, E lowercase "e" is sometimes used to indicate a generated emf (electromotive force). Then the greater the voltage, the greater is the pressure (or pushing force) and the greater is the capacity to do work.

A constant voltage source is called a **DC Voltage** with a voltage that varies periodically with time is called an **AC voltage**. Voltage is measured in volts, with one volt being defined as the electrical pressure required to force an electrical current of one ampere through a resistance of one Ohm. Voltages are generally expressed in Volts with prefixes used to denote sub-multiples of the voltage such as **microvolts** ($\mu V = 10^{-6}$ V), **millivolts** ($mV = 10^{-3}$ V) or **kilovolts** ($kV = 10^{3}V$). Voltage can be either positive or negative.

Batteries or power supplies are mostly used to produce a steady D.C. (direct current) voltage source such as 5v, 12v, 24v etc in electronic circuits and systems. While A.C. (alternating current) voltage sources are available for domestic house and industrial power and lighting as well as power transmission. The mains voltage supply in the United Kingdom is currently 230 volts a.c. and 110 volts a.c. in the USA.

General electronic circuits operate on low voltage DC battery supplies of between 1.5V and 24V dc The circuit symbol for a constant voltage source usually given as a battery symbol with a positive, + and negative, – sign indicating the direction of the polarity. The circuit symbol for an alternating voltage source is a circle with a sine wave inside.

Voltage Symbols



A simple relationship can be made between a tank of water and a voltage supply. The higher the water tank above the outlet the greater the pressure of the water as more energy is released, the higher the voltage the greater the potential energy as more electrons are released.

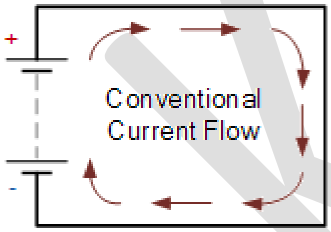
Voltage is always measured as the difference between any two points in a circuit and the voltage between these two points is generally referred to as the “**Voltage drop**“. Note that voltage can exist across a circuit without current, but current cannot exist without voltage and as such any voltage source whether DC or AC likes an open or semi-open circuit condition but hates any short circuit condition as this can destroy it.

Electrical Current

Electrical Current, (I) is the movement or flow of electrical charge and is measured in **Amperes**, symbol **i**, for intensity). It is the continuous and uniform flow (called a drift) of electrons (the negative particles of an atom) around a circuit that are being “pushed” by the voltage source. In reality, electrons flow from the negative (-ve) terminal to the positive (+ve) terminal of the supply and for ease of circuit understanding conventional current flow assumes that the current flows from the positive to the negative terminal.

Generally in circuit diagrams the flow of current through the circuit usually has an arrow associated with the symbol, I, or lowercase i to indicate the actual direction of the current flow. However, this arrow usually indicates the direction of conventional current flow and not necessarily the direction of the actual flow.

Conventional Current Flow

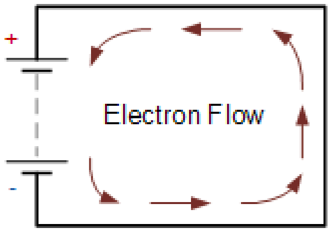


Conventionally this is the flow of positive charge around a circuit, being positive to negative. The diagram at the left shows the movement of the positive charge (holes) around a closed circuit flowing from the positive terminal of the battery, through the circuit and returns to the negative terminal of the battery. This flow of current from positive to negative is generally known as conventional current flow.

This was the convention chosen during the discovery of electricity in which the direction of electric current was thought to flow in a circuit. To continue with this line of thought, in all circuit diagrams and schematics, the arrows shown on symbols for components such as diodes and transistors point in the direction of conventional current flow.

Then **Conventional Current Flow** gives the flow of electrical current from positive to negative and which is the opposite in direction to the actual flow of electrons.

Electron Flow



The flow of electrons around the circuit is opposite to the direction of the conventional current flow being negative to positive.The actual current flowing in an electrical circuit is composed of electrons that flow from the negative pole of the battery (the cathode) and return back to the positive pole (the anode) of the battery.

This is because the charge on an electron is negative by definition and so is attracted to the positive terminal. This flow of electrons is called **Electron Current Flow**. Therefore, electrons actually flow around a circuit from the negative terminal to the positive.

Both conventional current flow and electron flow are used by many textbooks. In fact, it makes no difference which way the current is flowing around the circuit as long as the direction is used consistently. The direction of current flow does not affect what the current does within the circuit. Generally it is much easier to understand the conventional current flow – positive to negative.

In electronic circuits, a current source is a circuit element that provides a specified amount of current for example, 1A, 5A 10 Amps etc, with the circuit symbol for a constant current source given as a circle with an arrow inside indicating its direction.

Current is measured in **Amps** and an amp or ampere is defined as the number of electrons or charge (Q in Coulombs) passing a certain point in the circuit in one second, (t in Seconds).

Electrical current is generally expressed in Amps with prefixes used to denote **micro amps** (μA = 10^{-6}A) or **milliamps** (mA = 10^{-3}A). Note that electrical current can be either positive in value or negative in value depending upon its direction of flow.

Current that flows in a single direction is called **Direct Current**, or **D.C.** and current that alternates back and forth through the circuit is known as **Alternating Current**, or **A.C.**. Whether AC or DC current only flows through a circuit when a voltage source is connected to it with its "flow" being limited to both the resistance of the circuit and the voltage source pushing it.

Also, as alternating currents (and voltages) are periodic and vary with time the "effective" or "RMS", (Root Mean Squared) value given as I_{rms} produces the same average power loss equivalent to a DC current $I_{average}$. Current sources are the opposite to voltage sources in that they like short or closed circuit conditions but hate open circuit conditions as no current will flow.

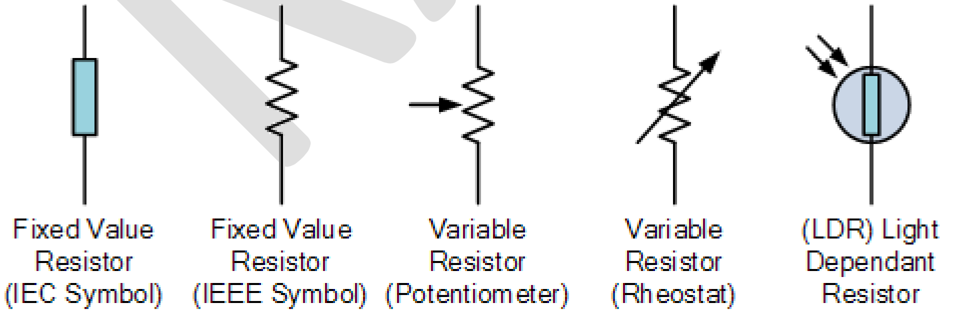
Using the tank of water relationship, current is the equivalent of the flow of water through the pipe with the flow being the same throughout the pipe. The faster the flow of water the greater the current. Note that current cannot exist without voltage so any current source whether DC or AC likes a short or semi-short circuit condition but hates any open circuit condition as this prevents it from flowing.

Resistance

Resistance, (R) is the capacity of a material to resist or prevent the flow of current or, more specifically, the flow of electric charge within a circuit. The circuit element which does this perfectly is called the "Resistor".

Resistance is a circuit element measured in **Ohms**, Greek symbol (**Ω**, Omega) with prefixes used to denote **Kilo-ohms** ($k\Omega = 10^3\Omega$) and **Mega-ohms** ($M\Omega = 10^6\Omega$). Note that resistance cannot be negative in value only positive.

Resistor Symbols



The amount of resistance a resistor has is determined by the relationship of the current through it to the voltage across it which determines whether the circuit element is a “good conductor” – low resistance, or a “bad conductor” – high resistance. Low resistance, for example 1Ω or less implies that the circuit is a good conductor made from materials such as copper, aluminium or carbon while a high resistance, 1MΩ or more implies the circuit is a bad conductor made from insulating materials such as glass, porcelain or plastic.

A “semiconductor” on the other hand such as silicon or germanium, is a material whose resistance is half way between that of a good conductor and a good insulator. Hence the name “semi-conductor”. Semiconductors are used to make **Diodes** and **Transistors** etc.

Resistance can be linear or non-linear in nature. Linear resistance obeys Ohm’s Law as the voltage across the resistor is linearly proportional to the current through it. Non-linear resistance, does not obey Ohm’s Law but has a voltage drop across it that is proportional to some power of the current.

Resistance is pure and is not affected by frequency with the AC impedance of a resistance being equal to its DC resistance and as a result can not be negative. Remember that resistance is always positive, and never negative.

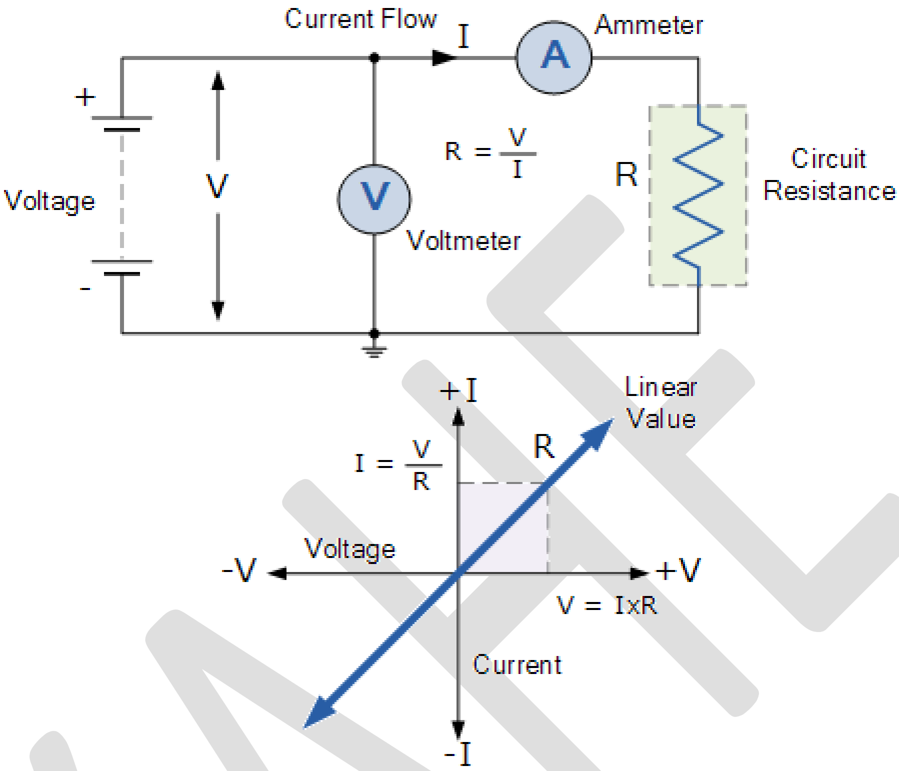
A resistor is classed as a passive circuit element and as such cannot deliver power or store energy. Instead resistors absorbed power that appears as heat and light. Power in a resistance is always positive regardless of voltage polarity and current direction.

For very low values of resistance, for example milli-ohms, (mΩ´s) it is sometimes much easier to use the reciprocal of resistance (1/R) rather than resistance (R) itself. The reciprocal of resistance is called **Conductance**, symbol (**G**) and represents the ability of a conductor or device to conduct electricity.

In other words the ease by which current flows. High values of conductance implies a good conductor such as copper while low values of conductance implies a bad conductor such as wood. The standard unit of measurement given for conductance is the **Siemen**, symbol (**S**).

The unit used for conductance is mho (ohm spelled backward), which is symbolized by an inverted Ohm sign ℧. Power can also be expressed using conductance as: $p = i^2/G = v^2G$.

The relationship between Voltage, (v) and Current, (i) in a circuit of constant Resistance, (R) would produce a straight line i-v relationship with slope equal to the value of the resistance as shown.



Voltage, Current and Resistance Summary

Hopefully by now you should have some idea of how electrical Voltage, Currentand Resistance are closely related together. The relationship between **Voltage**, **Current** and **Resistance** forms the basis of Ohm's law. In a linear circuit of fixed resistance, if we increase the voltage, the current goes up, and similarly, if we decrease the voltage, the current goes down. This means that if the voltage is high the current is high, and if the voltage is low the current is low.

Likewise, if we increase the resistance, the current goes down for a given voltage and if we decrease the resistance the current goes up. Which means that if resistance is high current is low and if resistance is low current is high.

Then we can see that current flow around a circuit is directly proportional (∝) to voltage, (V↑ causes I↑) but inversely proportional (1/∝) to resistance as, (R↑ causes I↓).

A basic summary of the three units is given below.

- Voltage or potential difference is the measure of potential energy between two points in a circuit and is commonly referred to as its " **volt drop** ".
- When a voltage source is connected to a closed loop circuit the voltage will produce a current flowing around the circuit.
- In DC voltage sources the symbols +ve (positive) and -ve (negative) are used to denote the polarity of the voltage supply.
- Voltage is measured in " **Volts** " and has the symbol " V " for voltage or " E " for energy.
- Current flow is a combination of electron flow and hole flow through a circuit.
- Current is the continuous and uniform flow of charge around the circuit and is measured in " **Amperes** " or " **Amps** " and has the symbol " I ".
- Current is Directly Proportional to Voltage ($I \propto V$)
- The effective (rms) value of an alternating current has the same average power loss equivalent to a direct current flowing through a resistive element.
- Resistance is the opposition to current flowing around a circuit.
- Low values of resistance implies a conductor and high values of resistance implies an insulator.
- Current is Inversely Proportional to Resistance ($I\ 1/\propto R$)
- Resistance is measured in " **Ohms** " and has the Greek symbol " Ω " or the letter " R ".

Quantity	Symbol	Unit of Measure	Abbreviation
Voltage	V or E	Volt	V
Current	I	Ampere	A

Resistance	R	Ohms	Ω

In the next tutorial about DC Circuits we will look at **Ohms Law** which is a mathematical equation explaining the relationship between Voltage, Current, and Resistance within electrical circuits and is the foundation of electronics and electrical engineering. **Ohm's Law** is defined as: V = I x R.

The Dropping mercury electrode

The **dropping mercury electrode** (DME) is a working electrode made of mercury and used in polarography. Experiments run with mercury electrodes are referred to as forms of polarography even if the experiments are identical or very similar to a corresponding voltammetry experiment which uses solid working electrodes. Like other working electrodes these electrodes are used in electrochemical studies using three electrode systems when investigating reaction mechanisms related to redox chemistry among other chemical phenomena

Structure

A flow of mercury passes through an insulating capillary producing a droplet which grows from the end of the capillary in a reproducible way. Each droplet grows until it reaches a diameter of about a millimeter and releases. The released droplet is no longer in contact with the working electrode whose contact is above the capillary. As the electrode is used mercury collects in the bottom of the cell. In some cell designs this mercury pool is connected to a lead and used as the cell's auxiliary electrode. Each released drop is immediately followed by the formation of another drop. The drops are generally produced at a rate of about 0.2 Hz.

Considerations

A major advantage of the DME is that each drop has a smooth and uncontaminated surface free from any adsorbed analyte or impurity. The self-renewing electrode does not need to be cleaned or polished like a solid electrode. This advantage comes at the cost of a working electrode with a constantly changing surface area. Since the drops are produced predictably the changing surface area can be accounted for or even used advantageously. In addition the drops' growth causes capacitive current and faradaic current. These changing current effects combined with experiments where the potential is continuously changed can result in noisy traces. In some experiments the traces are continually sampled, showing all the current deviation resulting from the drop growth. Other sampling methods smooth the data by sampling the current at the electrode only once per drop at a specific size. The DME's periodic expansion into the solution and hemispherical shape also affects the way the analyte diffuses to the electrode surface. The DME consists of a fine capillary with a bore size of 20-50 µm.

Diffusion current

Diffusion current is a current in a semiconductor caused by the diffusion of charge carriers (holes and/or electrons). This is the current which is due to the transport of charges occurring because of nonuniform concentration of charged particles in a semiconductor. The drift current, by contrast, is due to the motion of charge carriers due to the force exerted on them by an electric field. Diffusion current can be in the same or opposite direction of a drift current. The diffusion current and drift current together are described by the drift–diffusion equation.[1]

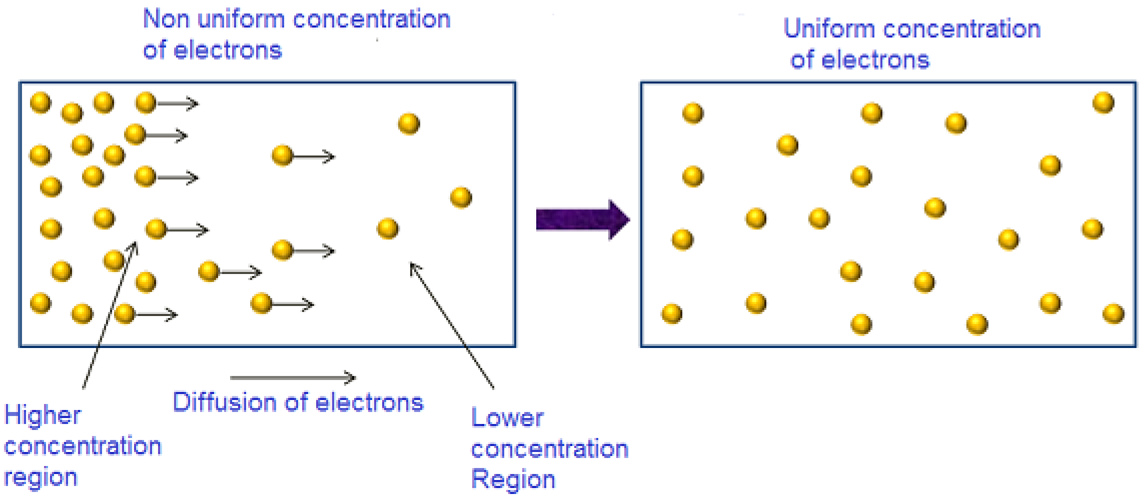
It is necessary to consider the part of diffusion current when describing many semiconductor devices. For example, the current near the depletion region of a p–n junction is dominated by the diffusion current. Inside the depletion region, both diffusion current and drift current are present. At equilibrium in a p–n junction, the forward diffusion current in the depletion region is balanced with a reverse drift current, so that the net current is zero.

The diffusion constant for a doped material can be determined with the Haynes–Shockley experiment. Alternatively, if the carrier mobility is known, the diffusion coefficient may be determined from the Einstein relation on electrical mobility.

The process by which, charge carriers (electrons or holes) in a semiconductor moves from a region of higher concentration to a region of lower concentration is called diffusion.

The region in which more number of electrons is present is called higher concentration region and the region in which less number of electrons is present is called lower concentration region. Current produced due to motion of charge carriers from a region of higher concentration to a region of lower concentration is called diffusion current. Diffusion process occurs in a semiconductor that is non-uniformly doped.

Consider an n-type semiconductor that is non-uniformly doped as shown in below figure. Due to the non-uniform doping, more number of electrons is present at left side whereas lesser number of electrons is present at right side of the semiconductor material. The number of electrons present at left side of semiconductor material is more. So, these electrons will experience a repulsive force from each other.



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The electrons present at left side of the semiconductor material will moves to right side, to reach the uniform concentration of electrons. Thus, the semiconductor material achieves equal concentration of electrons. Electrons that moves from left side to right side will constitute current. This current is called diffusion current. In p-type semiconductor, the diffusion process

occurs in the similar manner.

Both drift and diffusion current occurs in semiconductor devices. Diffusion current occurs without an external voltage or electric field applied. Diffusion current does not occur in a conductor. The direction of diffusion current is same or opposite to that of the drift current.

Concentration gradient

The diffusion current density is directly proportional to the concentration gradient. Concentration gradient is the difference in concentration of electrons or holes in a given area. If the concentration gradient is high, then the diffusion current density is also high. Similarly, if the concentration gradient is low, then the diffusion current density is also low.

The concentration gradient for n-type semiconductor is given by

$$J_n \propto \frac{dn}{dx}$$

The concentration gradient for p-type semiconductor is given by

$$J_p \propto \frac{dp}{dx}$$

Where J_n = diffusion current density due to electrons
J_p = diffusion current density due to holes

Diffusion current density

The diffusion current density due to electrons is given by

$$J_n = +e\,D_n \frac{dn}{dx}$$

Where D_n is the diffusion coefficent of electrons

The diffusion current density due to holes is given by

$$J_p = -e\,D_p \frac{dp}{dx}$$

Where D_p is the diffusion coefficent of holes

The total current density due to electrons is the sum of drift and diffusion currents.

J_n = Drift current + Diffusion current

$$J_n = en\mu_n E + e\,D_n \frac{dn}{dx}$$

The total current density due to holes is the sum of drift and diffusion currents.

$$J_p = \text{Drift current} + \text{Diffusion current}$$

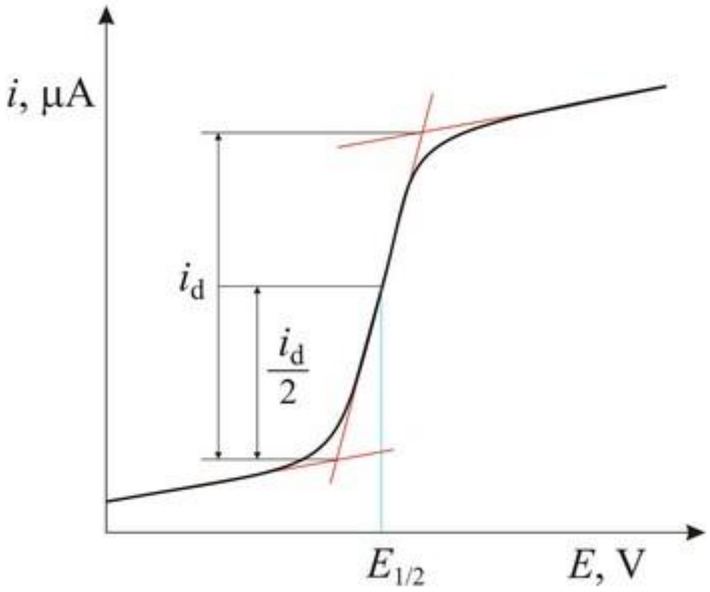
$$J_p = e p \mu_p E - e D_p \frac{dp}{dx}$$

The total current density due to electrons and holes is given by

$$J = J_n + J_p$$

Half-wave potentials

Half-wave potential ($E_{1/2}$) is a potential at which polarographic wave current is equal to one half of diffusion current (i_d). In a given supporting electrolyte, the half-wave potential is unique for each element and its different valence states and chemical forms. Observation of a current peak at a specific half-wave potential therefore identifies the chemical species producing the current.



Application of polarography

APPLICATIONS OF AMPEROMETRIC TITRATIONS

Amperometric titration refers to a class of titrations in which the equivalence point is determined through measurement of the electric current produced by the titration reaction. It is a form of quantitative analysis

Consider a solution containing the analyte, A, in the presence of some conductive buffer. If an electrolytic potential is applied to the solution through a working electrode, then the measured current depends (in part) on the concentration of the analyte. Measurement of this current can be used to determine the concentration of the analyte directly; this is a form of amperometry. However, the difficulty is that the measured current depends on several other variables, and it is not always possible to control all of them adequately. This limits the precision of direct amperometry.

If the potential applied to the working electrode is sufficient to reduce the analyte, then the concentration of analyte close to the working electrode will decrease. More of the analyte will slowly diffuse into the volume of solution close to the working electrode, restoring the concentration. If the potential applied to the working electrode is great enough (an overpotential), then the concentration of analyte next to the working electrode will depend entirely on the rate of diffusion. In such a case, the current is said to be diffusion limited. As the analyte is reduced at the working electrode, the concentration of the analyte in the whole solution will very slowly decrease; this depends on the size of the working electrode compared to the volume of the solution.

What happens if some other species which reacts with the analyte (the titrant) is added? (For instance, chromate ions can be added to oxidize lead ions.) After a small quantity of the titrant (chromate) is added, the concentration of the analyte (lead) has decreased due to the reaction with chromate. The current from the reduction of lead ion at the working electrode will decrease. The addition is repeated, and the current decreases again. A plot of the current against volume of added titrant will be a straight line.

After enough titrant has been added to react completely with the analyte, the excess titrant may itself be reduced at the working electrode. Since this is a different species with different diffusion characteristics (and different half-reaction), the slope of current versus added titrant will have a different slope after the equivalence point. This change in slope marks the equivalence point, in the same way that, for instance, the sudden change in pH marks the equivalence point in an acid-base titration.

The electrode potential may also be chosen such that the titrant is reduced, but the analyte is not. In this case, the presence of excess titrant is easily detected by the increase in current above background (charging) current.

Advantages

The chief advantage over direct amperometry is that the magnitude of the measured current is of interest only as an indicator. Thus, factors that are of critical importance to quantitative amperometry, such as the surface area of the working electrode, completely disappear from amperometric titrations.

The chief advantage over other types of titration is the selectivity offered by the electrode potential, as well as by the choice of titrant. For instance, lead ion is reduced at a potential of -0.60 V (relative to the saturated calomel electrode), while zinc ions are not; this allows the determination of lead in the presence of zinc. Clearly this advantage depends entirely on the other species present in the sample.

.Fundamental principles of coulometric methods

Coulometry is the name given to a group of techniques in analytical chemistry that determine the amount of matter transformed during an electrolysisreaction by measuring the amount of electricity (in coulombs) consumed or produced. It is named after Charles-Augustin de Coulomb.

There are two basic categories of coulometric techniques. Potentiostatic coulometry involves holding the electric potential constant during the reaction using a potentiostat. The other, called coulometric titration or amperostatic coulometry, keeps the current (measured in amperes) constant using an amperostat.

Coulometry is based on an exhaustive electrolysis of the analyte. By exhaustive we mean that the analyte is completely oxidized or reduced at the working electrode or that it reacts completely with a reagent generated at the working electrode. There are two forms of coulometry: **controlled-potential coulometry**, in which we apply a constant potential to the electrochemical cell, and **controlled-current coulometry**, in which we pass a constant current through the electrochemical cell.

During an electrolysis, the total charge, QQ, in coulombs, passing through the electrochemical cell is proportional to the absolute amount of analyte by **Faraday's law**

$$Q=nFNA$$

where n is the number of electrons per mole of analyte, F is Faraday's constant (96487 C mol^{-1}), and N_A is the moles of analyte. A coulomb is equivalent to an A·sec; thus, when passing a constant current, i, the total charge is

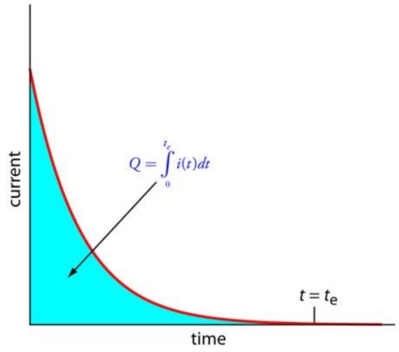
$$Q=ite$$

where t_e is the electrolysis time. If the current varies with time, as it does in controlled-potential coulometry, then the total charge is

$$Q=\int teoi(t)dt$$

Controlled-Potential Coulometry

The easiest way to ensure 100% current efficiency is to hold the working electrode at a constant potential, chosen so that the analyte reacts completely without simultaneously oxidizing or reducing an interfering species. As electrolysis progresses the analyte's concentration decreases, as does the current. The resulting current-versus-time profile for controlled-potential coulometry is shown in Figure. Integrating the area under the curve from $t = 0$ to $t = t_e$gives the total charge. In this section we consider the experimental parameters and instrumentation needed to develop a controlled-potential coulometric method of analysis.



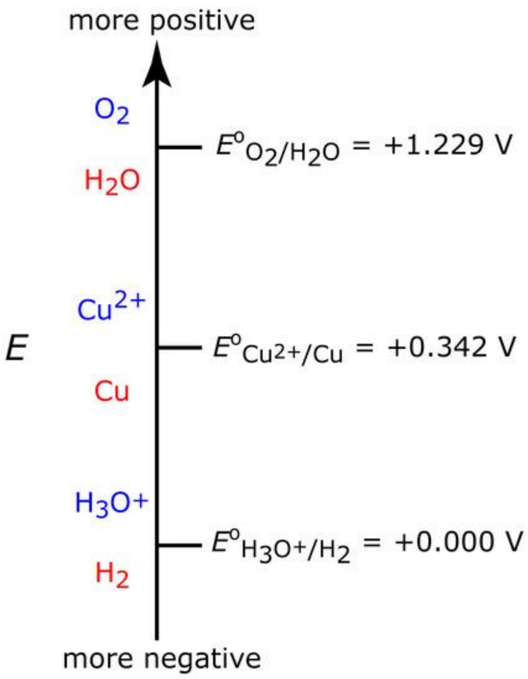
Current versus time for a controlled-potential coulometric analysis. The measured current is shown by the red curve. The integrated area under the curve, shown in blue, is the total charge.

Selecting a Constant Potential

To see how an appropriate potential for the working electrode is selected, let's develop a constant-potential coulometric method for Cu^{2+} based on its reduction to copper metal at a Pt working electrode.

$$Cu^{2+(}aq)+2e^{-}\leftrightharpoons Cu(s)$$

The below Figure shows a ladder diagram for an aqueous solution of Cu^{2+}. From the ladder diagram we know that reaction 11.28 is favored when the working electrode's potential is more negative than +0.342 V versus the standard hydrogen electrode. To ensure a 100% current efficiency, however, the potential must be sufficiently more positive than +0.000 V so that the reduction of H_3O^+ to H_2 does not contribute significantly to the total current flowing through the electrochemical cell.



Ladder diagram for an aqueous solution of Cu^{2+} showing steps for the reductions of O_2 to H_2O, of Cu^{2+} to Cu, and of H_3O^+ to H_2. For each step, the oxidized species is in blue and the reduced species is in red.

Instrumentation

A three-electrode potentiostat is used to set the potential in controlled-potential coulometry. The working electrodes is usually one of two types: a cylindrical Pt electrode manufactured from platinum-gauze, or a Hg pool electrode. The large overpotential for the reduction of H_3O^+ at Hg makes it the electrode of choice for an analyte requiring a negative potential. For example, a potential more negative than –1 V versus the SHE is feasible at a Hg electrode—but not at a Pt electrode—even in a very acidic solution. Because mercury is easily oxidized, it is less useful if we need to maintain a potential that is positive with respect to the SHE. Platinum is the working electrode of choice when we need to apply a positive potential.

The auxiliary electrode, which is often a Pt wire, is separated by a salt bridge from the analytical solution. This is necessary to prevent the electrolysis products generated at the auxiliary electrode from reacting with the analyte and interfering in the analysis. A saturated calomel or Ag/AgCl electrode serves as the reference electrode.

The other essential instrumental need for controlled-potential coulometry is a means for determining the total charge. One method is to monitor the current as a function of time and determine the area under the curve, as shown in Figure 11.27. Modern instruments use electronic integration to monitor charge as a function of time. The total charge at the end of the electrolysis is read directly from a digital readout.

The majority of controlled-potential coulometric analyses involve the determination of inorganic cations and anions, including trace metals and halides ions. Below Table summarizes several of these methods.

Representative Controlled-Potential Coulometric Analyses for Inorganic Ions

analyte	electrolytic reaction[a]	electrode
antimony	$Sb(III) + 3e^- \leftrightharpoons Sb$	Pt
arsenic	$As(III) \leftrightharpoons As(V) + 2e^-$	Pt

Representative Controlled-Potential Coulometric Analyses for Inorganic Ions

analyte	electrolytic reaction[a]	electrode
cadmium	$Cd(II) + 2e^{-} \leftrightharpoons Cd$	Pt or Hg
cobalt	$Co(II) + 2e^{-} \leftrightharpoons Co$	Pt or Hg
copper	$Cu(II) + 2e^{-} \leftrightharpoons Cu$	Pt or Hg
halides (X^{-})	$Ag + X^{-} \leftrightharpoons AgX + e^{-}$	Ag
iron	$Fe(II) \leftrightharpoons Fe(III) + e^{-}$	Pt
lead	$Pb(II) + 2e^{-} \leftrightharpoons Pb$	Pt or Hg
nickel	$Ni(II) + 2e^{-} \leftrightharpoons Ni$	Pt or Hg
plutonium	$Pu(III) \leftrightharpoons Pu(IV) + e^{-}$	Pt

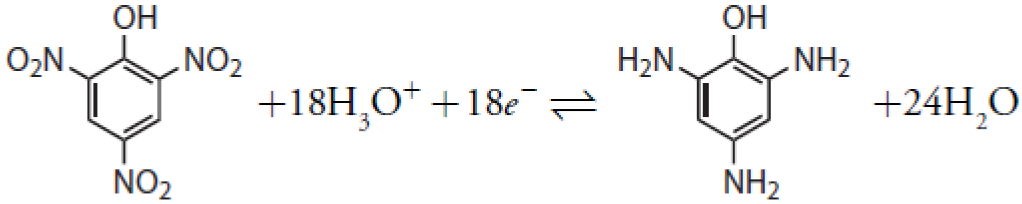
Representative Controlled-Potential Coulometric Analyses for Inorganic Ions

analyte	electrolytic reaction[a]	electrode
silver	$\text{Ag(I)} + e^- \leftrightharpoons \text{Ag}$	Pt
tin	$\text{Sn(II)} + 2e^- \leftrightharpoons \text{Sn}$	Pt
uranium	$\text{U(VI)} + 2e^- \leftrightharpoons \text{U(IV)}$	Pt or Hg
zinc	$\text{Zn(II)} + 2e^- \leftrightharpoons \text{Zn}$	Pt or Hg

The ability to control selectivity by carefully adjusting the working electrode's potential makes controlled-potential coulometry particularly useful for the analysis of alloys. For example, we can determine the composition of an alloy containing Ag, Bi, Cd, and Sb by dissolving the sample and placing it in a matrix of 0.2 M H_2SO_4 along with a Pt working electrode and a Pt counter electrode. If we apply a constant potential of +0.40 V versus the SCE, Ag(I) deposits on the electrode as Ag and the other metal ions remain in solution. When electrolysis is complete, we use the total charge to determine the amount of silver in the alloy. By shifting the working electrode's potential to –0.08 V versus the SCE, we deposit Bi on the working electrode. When the coulometric analysis for bismuth is complete, we determine antimony by shifting the working electrode's potential to –0.33 V versus the SCE, depositing Sb. Finally, we determine cadmium following its electrodeposition on the working electrode at a potential of –0.80 V versus the SCE.

We also can use controlled-potential coulometry for the quantitative analysis of organic compounds, although the number of applications is significantly less than that for inorganic analytes. One example is the six-electron reduction of a nitro group, $–NO_2$, to a primary amine, –

NH_2, at a mercury electrode. Solutions of picric acid—also known as 2,4,6-trinitrophenol, or TNP, a close relative of TNT—can be analyzed by reducing it to triaminophenol.

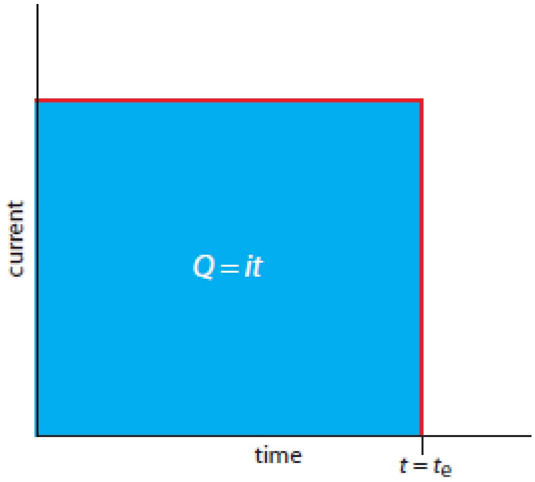


Another example is the successive reduction of trichloroacetate to dichloroacetate, and of dichloroacetate to monochloroacetate

We can analyze a mixture of trichloroacetate and dichloroacetate by selecting an initial potential at which only the more easily reduced trichloroacetate reacts. When its electrolysis is complete, we can reduce dichloroacetate by adjusting the potential to a more negative potential. The total charge for the first electrolysis gives the amount of trichloroacetate, and the difference in total charge between the first electrolysis and the second electrolysis gives the amount of dichloroacetate.

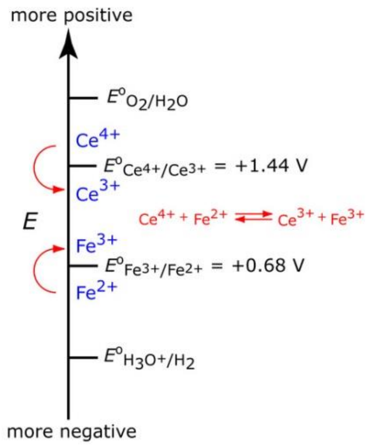
Controlled-Current Coulometry

A second approach to coulometry is to use a constant current in place of a constant potential, which produces the current-versus-time profile shown in Figure 11.30. Controlled-current coulometry has two advantages over controlled-potential coulometry. First, the analysis time is shorter because the current does not decrease over time. A typical analysis time for controlled-current coulometry is less than 10 min, compared to approximately 30–60 min for controlled-potential coulometry. Second, because the total charge is simply the product of current and time (equation 11.26), there is no need to integrate the current-time curve in Figure 11.30.



Current versus time for a controlled-current coulometric analysis. The measured current is shown by the red curve. The integrated area under the curve, shown in blue, is the total charge.

Using a constant current presents us with two important experimental problems. First, during electrolysis the analyte's concentration—and, therefore, the current due to the its oxidation or reduction—continuously decreases . To maintain a constant current we must allow the potential to change until another oxidation reaction or reduction reaction occurs at the working electrode. Unless we design the system carefully, this secondary reaction decreases the current efficiency to less than 100%. The second problem is that we need a method for determining when the analyte's electrolysis is complete. As shown in Figure 11.27, in a controlled-potential coulometric analysis we know that electrolysis is complete when the current reaches zero, or when it reaches a constant background or residual current. In a controlled-current coulometric analysis, however, current continues to flow even when the analyte's electrolysis is complete. A suitable method for determining the reaction's endpoint, t_e, is needed.



Ladder diagram for the constant-current coulometric analysis of Fe^{2+} in the presence of a Ce^{3+} mediator. As the potential drifts to more positive values, we eventually reach a potential where Ce^{3+} undergoes oxidation. Because Ce^{4+}, the product of the oxidation of Ce^{3+}, reacts with Fe^{2+}, we maintain current efficiency.

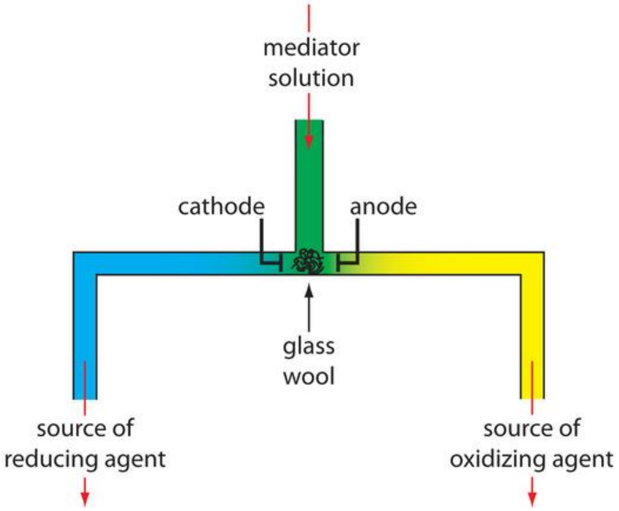
Endpoint Determination

Adding a mediator solves the problem of maintaining 100% current efficiency, but it does not solve the problem of determining when the analyte's electrolysis is complete. Using our same example, when the oxidation of Fe^{2+} is complete current continues to flow from the oxidation of Ce^{3+}, and, eventually, the oxidation of H_2O. What we need is a signal that tells us when there is no more Fe^{2+} in solution.

For our purposes, it is convenient to treat a controlled-current coulometric analysis as a reaction between the analyte, Fe^{2+}, and the mediator, Ce^{3+}. This reaction is identical to a redox titration; thus, we can use the end points for a redox titration—visual indicators and potentiometric or conductometric measurements—to signal the end of a controlled-current coulometric analysis. For example, ferroin provides a useful visual endpoint for the Ce^{3+}mediated coulometric analysis for Fe^{2+}, changing color from red to blue when the electrolysis of Fe^{2+} is complete.

Instrumentation

Controlled-current coulometry normally is carried out using a two-electrode galvanostat, consisting of a working electrode and a counter electrode. The working electrode—often a simple Pt electrode—is also called the generator electrode since it is where the mediator reacts to generate the species that reacts with the analyte. If necessary, the counter electrode is isolated from the analytical solution by a salt bridge or porous frit to prevent its electrolysis products from reacting with the analyte. Alternatively, we can generate the oxidizing agent or the reducing agent externally, and allow it to flow into the analytical solution. Figure 11.33 shows one simple method for accomplishing this. A solution containing the mediator flows into a small-volume electrochemical cell, with the products exiting through separate tubes. Depending upon the analyte, the oxidizing agent or the reducing reagent is selectively delivered to the analytical solution. For example, we can generate Ce^{4+}using an aqueous solution of Ce^{3+}, directing the Ce^{4+} that forms at the anode into our sample.



One example of a device for the external generation of oxidizing agents and reducing agents for controlled-current coulometry. A solution containing the mediator flows into a small-volume electrochemical cell. The resulting oxidation products, which form at the anode, flow to the right and may serve as an oxidizing agent. Reduction at the cathode generates a reducing agent.

There are two other crucial needs for controlled-current coulometry: an accurate clock for measuring the electrolysis time, t_e, and a switch for starting and stopping the electrolysis. An analog clock can record time to the nearest ±0.01 s, but the need to frequently stop and start the electrolysis as we approach the endpoint may result in an overall uncertainty of ±0.1 s. A digital clock allows for a more accurate measurement of time, with an overall uncertainty of ±1 ms being possible. The switch must control both the current and the clock, so that we can make an accurate determination of the electrolysis time.

POSSIBLE QUESTIONS

Part A **(Each question carries 1 mark)**

1.In which year the polarography method was developed?
(a)1933 **(b)1922** (c)1943 (d)1956

2.Polarography is used to determine the
(a)Organic functional groups (b)Ketone group (c)Amine group (d)Ester groups

3.In polarography the small current flows which is known as
(a)Diffusion current (b)Limiting current **(c)Residual current** (d)None of the above

4. In polarography the current corresponding to the CD which is known as
(a)Diffusion current **(b)Limiting current** (c)Residual current (d)None of the above

5.Battery is a type of _________ cell
(a)Electrolytic (b)**Electrochemical**
(c)Chemo electric (d)Thermal

6.During a cathodic protection, the sacrificial anode
(a)accepts electrons from the protected metal.
(b)reacts spontaneously with the protected metal.
(c) oxidizes more readily than the protected metal.
(d)causes the protected metal to become an anode.

7.In the electrolysis of 1.0M Na_2SO_4, what is formed at the cathode?
(a)$S_2O_8^{2-}$ (b)O **(c)H_2** (d)H_2SO_3

8.During the electrolysis of an aqueous solution of KI, what substance is formed at the cathode?
(a)iodine (b)oxygen **(c)hydrogen** (d)potassium

9. $Zn^{2+} + 2e^- \rightarrow Zn$ Manganese has an oxidation number of +4 in
(a)MnO **(b) MnO_2** (c) Mn_2O_3 (d)Mn_2O_7

10.In which reaction is nitrogen is reduced?
(a)$2NO + O_2 \rightarrow 2NO_2$ (b) $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$
(c) $Cu^{2+} + 2NO_2 + 2H_2O \rightarrow Cu + 4H^+ + 2NO_3^-$
(d)$4Zn + 10H^+ + NO_3 \rightarrow 4Zn^{2+} + NH_4^+ + 3H_2O$

11.In Lithium batteries, electrolytes can't acts as aqueous solution because,
(a)High reactivity of Li with H_2O (b) Low density of Li w. r. t. H_2O
(c) High electro positivity of Li+ (d)None of above

12.A fresh dry cell has potential ______V
(a)1 **(b)1.5** (c)2 (d)3.5

13. <u>The mean activity coefficient is proportional to the</u>
(a)square root of the ionic strength. (b)Ionic strength
(c)Trible the strength (d)Double of the ionic strength

14.as the amount of inter-ionic interaction increases as the concentration of the electrolyte
(a)increases b)Decreases (c)no change (d)no effect

15.By increasing the concentration of the electrolyte, the amount of inter-ionic interaction
(a)increases (b)Decreases (c)no change (d)no effect

16.Debye -Huckle theory is used to calculate the
(a)Activity coefficient (b)Activation energy (c)Ionic strength (d)Atomic size
13.In which of the following 1.0M solutions will both ions react spontaneously with tin?
(a) Ag^+ and Cu^{2+} (b) Ni^{2+} and Cu^{2+} (c) Zn^{2+} and Ni^{2+} (d)Mg^{2+} and Zn^{2+}

17.In amperometric titration the indicator electrode is known as
(a)Saturated calomel electrode **(b)Rotating platinum electrode** (c)platinum electrode
(d)calomel electrode

18.In amperometric titration the reference electrode is known as
(a)Saturated calomel electrode (b)Rotating platinum electrode
(c)platinum electrode (d)calomel electrode

19.The reference electrode is
(a)Saturated calomel electrode (b)Rotating platinum electrode (c) platinum electrode

(d)calomel electrode

20. In polarography the current corresponding to the CD which is known as
(a)Diffusion current **(b)Limiting current** (c)Residual current (d)None of the above

Part B **(Each question carries 2 marks)**

1.Write a note on current-voltage relationships.

2.Mention few applications of amperometric titrations.

3.What is constant current methods.

4.What is controlled potential methods.

5.Mention few applications of coulometric methods.

Part C **(Each question carries 6 marks)**

1.Give a detailed account on the principle and applications of coulometric method.

2.Write a note on dropping mercury electrode.

.3. What is diffusion current? Mention the factors which affect diffusion current.

4.Give a brief note an constant current.

.5. Write short notes on Amperometric titrations.

6.Explain in detail about Half –Wave potentials

7.What are the current-voltage relationships and their applications.

8. Give a detailed account on the application of polarography

9.Explain the principle and working of polarography.

10.Write a note on Limiting current and the factors which affect it.

KARPAGAM ACADEMY OF HIGHER EDUCATION
COIMBATORE-641 021
(For the candidates admitted from 2017 & Onwards)
M.Sc., CHEMISTRY
SECOND SEMESTER
PHYSICAL CHEMISTRY-II (Chemical Kinetics and Electrochemistry) 17CHP203

UNIT-IV	OPTION 1	OPTION 2	OPTION 3	OPTION 4	ANSWER
In which year the polarography method was developed?	a)1933	b)1922	c)1943	d)1956	b)1922
Polarography is used to determine the	a)Organic functional groups	b)Ketone groups	c)Amine groups	d)Ester groups	a)Organic functional groups
In polarography the small current flows which is known as	a)Diffusion current	b)Limiting current	c)Residual current	d)residual and limiting current	c)Residual current
In polarography the current corresponding to the CD which is known as	a)Diffusion current	b)Limiting current	c)Residual current	d)residual and limiting current	b)Limiting current
Half wave potential is characteristic of the	a)Electro active material	b)Electrical	c) Electrochemical	d) Chemo electric	a)Electro active material
Organic electrode reactions are comparatively ----	a)Fast	b)Slow	c)Very slow	d)Very fast	b)Slow
The difference between limiting current and diffusion current is known as	a)Diffusion current	b)Limiting current	c)Residual current	d)None of the above	a)Diffusion current
P^{OH} of pure water at 25^0 C is ______________.	a)7	b)0	c)11	d)None of above	a)7
In amperometric titration the indicator electrode is known as	a)Saturated calomel electrode	b)Rotating platinum electrode	c)platinum electrode	d)calomel electrode	b)Rotating platinum electrode
In amperometric titration the reference electrode is known as	a)Saturated calomel electrode	b)Rotating platinum electrode	c)platinum electrode	d)calomel electrode	a)Saturated calomel electrode
In polarography, the rate-determining step in the discharge of ions is essentially	a)Diffusion	b)voltage	c)Conductance	d)emf	a)Diffusion
The phenomenon of the departure of the electrode potential from the reversible value as a result of the change of concentration in the vicinity of the electrode, is known as	a)polarisation	b)concentration polarisation	c)diffusion polarisation	d)limiting current	b)concentration polarisation
The current-voltage curve is called	a)polarogram	b)polarography	c)diffusion	d)limiting current	a)polarogram
The rate-determining step in the discharge of ions is essentially	a)polarogram	b)polarography	c)diffusion	d)limiting current	c)diffusion
The current density at which the rapid increase of potential takes place is known as the ------------------current density	a)upper	b)lower	c)limiting	d)controlled	c)limiting
The potential at the centre of the rising part of the wave, referred to as the -------------potential	a)half	b)half-wave	c)diffusion	d)limiting	b)half-wave
Mercury forms amalgam with many metals therby lowering their--------potential	a)oxidation.	b)limiting	c)diffusion	d)Reduction	d)Reduction
By using DME, the surface poisoning effects are--------------	a)slightly Increased	b)minimized	c)Not affected	d)severly affected	b)minimized
The overvoltage of hydrogen gas on mercury is -------------	a)minimum	b)very high	c)zero value	d)infinity	b)very high
If the bulk concentration decreases the limiting diffusion current obtained at a constant potential --------------------proportionately	a)increases	b)no effect	c)decreases	d)decreases and then increases	c)decreases
In amperometric titrations volume of titrant added is plotted against	a)diffusion current	b)Limiting current	c)voltage	d)conductance	a)diffusion current
Polarographic technique was developed by the ------------chemist, Jaroslav Heyrovsky	a)Czech	b)swedish	c)russian	d)american	a)Czech
An electrode whose potential does not change from its reversible value-------	a)platinum	b)glass	c)zinc	d)calomel	d)calomel
An electrode whose potential changes from its reversible value	a)platinum	b)DME	c)zinc	d)calomel	b)DME
Polarizable microelectrode is ---------	a)platinum	b)DME	c)zinc	d)calomel	b)DME
Non-polarizable current-carrying electrode is	a)platinum	b)glass	c)zinc	d)calomel	d)calomel
Owing to slow diffusion there will be a ----------of centration of ions in the immediate vicinity of the electrode	a)raise	b)fall	c)no effect	d)raise and fall	b)fall
If the solution is kept unstirred ----------is eliminated	a)convection	b)Limiting current	c)diffusion current	d)concentration coefficient	a)convection
If the solution is kept unstirred---------------will be present	a)convection	b)Limiting current	c)diffusion current	d)transference	d)transference

If the electrolysis is carried out in the presence of an excess of an indifferent electrolyte whose ions are not discharged at the applied potential, then almost the entire amount of current will be carried by the ions of the indifferent electrolyte. Such electrolytes are known as -------------electrolytes	a)supporting	b)liming	c)concentration	d)diffusion	a)supporting
The ion which is being discharged is known as ------------ion	a)supporting	b)key	c)cation	d)anion	b)key
In polarographic cell assembly ------------electrode serves as the anode	a)calomel	b)glass	c)platinum	c)copper	a)calomel
In DME ------------acts as cathode	a)calomel	b)glass	c)mercury	d)copper	c)mercury
The current strength is measured by means of a sensitive ---------------	a)voltmeter	b)galvanometer	c)ammeter	d)potentiometer	b)galvanometer
The potential of the cathode is easily determined by subtracting from the applied------------	a)emf	b)voltage	c)potential	d)energy	a)emf
The half-wave potential, designated as ----------	a)H 1/2	b)E1/2	c)G 1/2	d)F 1/2	b)E1/2
The limiting current which is given by the height of the wave, corresponds to the ---------------of the electroactive species	a)concentration	b)temperature	b)pressure	d)volume	a)concentration
The surface area un DME is-------------	a)not reproducible	b)reproducible	c)no effect	d)no effect for sometime and becomes reproducible	b)reproducible
DME furnishes ideal conditions for obtaining a completely diffsion controlled--------------current	a)diffusion	b)limiting	c)polarogram	d)voltage	b)limiting
Oscillation is observed in DME, when -------falls	a)voltage	b)potential	c)current	d)concentration	c)current
Oscillation is so uniform that it is easy to observe the --------------current	a)limiting	b)average	c)diffusion	d)concentration	b)average
The average current becomes reproducible soon after the ---------voltage is changed	a)applied	b)average	c)limiting	d)diffusion	a)applied
Half wave potential is characteristic of the --------------------material	a)electroactive	b)electro	c)electric	d)potentio	a)electroactive
Zero subscripts in the nernst equation of half-wave potential indicates that the -----------------------apply only to the film surrounding the DME which acts as cathode	a)concentration	b)temperature	c)presure	d)volume	a)concentration
Polarographic technique has been successfully applied for estimating a large variety of electroactive materials, both inorganic and organic, using the-------------electrode	a)glass	b)DME	c)calomel	d)mercury	b)DME
Atmospheric oxygen dissolved in an aqueous solution shows two distinct cathodic waves called---------------waves	a)hydrogen and oxygen.	b)nitrogen	c)carbon	d)oxygen	d)oxygen
Diffusion coefficients can be determined by-------------	a)polarography	b)conductometry	c)potentiometry	d)p H metry	a)polarography
-------------- is based on an exhaustive electrolysis of the analyte	a)polarography	b)conductometry	c)potentiometry	d)coulometry	d)coulometry
--------------------- in which we apply a constant potential to the electrochemical cell,	a)controlled potential coulometry	b)conductometry	c)potentiometry	d)coulometry	a)controlled potential coulometry
--------------------- in which we pass a constant current through the electrochemical cell.	a)controlled potential coulometry	b)controlled-current coulometry	c)potentiometry	d)coulometry	b)controlled-current coulometry
In coulometry, we monitor current as a function of ----------	a)concentration	b)time	c)pressure	d)temperature	b)time
coulometry requires -----------% current efficiency or an accurately measured current efficiency established using a standard a factor that we must be consider when designing a coulometric method of analysis.	a)0	b)1	c)100	d)98.5	c)100
------------- is the percentage of current that actually leads to the analyte's oxidation or reduction.	a)voltage efficiency	b)current efficiency	c)potential efficiency	d)concentration efficiency	b)current efficiency
In controlled potential coulometry,as electrolysis progresses the analyte's concentration -------------, as does the current.	a)increases	b)increases and decreases	c)decreases and increases	d)decreases	d)decreases
In controlled potential coulometry the ----------- decreases over time.	a)current	b)concentration	c)temperature	d)pressure	a)current
A ---------------electrode potentiostat is used to set the potential in controlled-potential coulometry	a)two	b)four	c)three	d)five	c)three

----------------can be used to determine n-values of the organic compounds.	a)coulometry	b)potentiometry	c)conductometry	d)p H metry	a)coulometry
----------------can be use determine the environment pollutants.	a)coulometry	b)potentiometry	c)conductometry	d)p H metry	a)coulometry
------------------is used to separate of the nickel and cobalt	a)coulometry	b)potentiometry	c)conductometry	d)p H metry	a)coulometry
-------------------can be used to determined total carbon in ferrous and non-ferrous metals.	a)coulometry	b)potentiometry	c)conductometry	d)p H metry	a)coulometry

UNIT V

SYLLABUS

Kinetics of corrosion: Importance–graphical presentation of kinetic data-exchange current density- different types of polarization of electrodes. Activation polarization and Tafel plots-mixed potential theory-application of electrode kinetics to experimental observations-faradic impedance and corrosion.

KINETICS OF CORROSION

Importance-graphical presentation of kinetic data-Exchange Current Density

In electrochemistry, **exchange current density** is a parameter used in the Tafel equation, Butler-Volmer equation and other expressions. The Tafel equation describes the dependence of current for an electrolytic process to overpotential.

The exchange current density is the current in the absence of net electrolysis and at zero overpotential. The exchange current can be thought of as a background current to which the net current observed at various overpotentials is normalized. For a redox reaction written as a reduction at the equilibrium potential, electron transfer processes continue at electrode/solution interface in both directions. The cathodic current is balanced by the anodic current. This ongoing current in both directions is called the exchange current density. When the potential is set more negative than the formal potential, the cathodic current is greater than the anodic current. Written as a reduction, cathodic current is positive. The net current density is the difference between the cathodic and anodic current density.

Exchange current densities reflect intrinsic rates of electron transfer between an analyte and the electrode. Such rates provide insights into the structure and bonding in the analyte and the electrode. For example, the exchange current densities for platinum and mercury electrodes for reduction of protons differ by a factor of 10^{10}, indicative of the excellent catalytic properties of platinum. Owing to this difference, mercury is preferred electrode material at reducing (cathodic) potentials in aqueous solution.

Parameters affecting exchange current density

The exchange current density depends critically on the nature of the electrode, not only its structure, but also physical parameters such as surface roughness. Of course, factors that change the composition of the electrode, including passivating oxides and adsorbed species on the surface, also influences the electron transfer. The nature of the electroactive species (the analyte) in the solution also critically affects the exchange current densities, both the reduced and oxidized form.

Less important but still relevant are the environment of the solution including the solvent, nature of other electrolyte, and temperature. For the concentration dependence of the exchange current density, the following expression is given for a one-electron reaction

Example values

Comparison of exchange current density for proton reduction reaction in 1 mol/kg H_2SO_4

Electrode material	**Exchange current density -$\log_{10}$(A/cm^2)**
Palladium	3.0
Platinum	3.1
Rhodium	3.6
Iridium	3.7
Nickel	5.2
Gold	5.4
Tungsten	5.9
Niobium	6.8
Titanium	8.2

Comparison of exchange current density for proton reduction reaction in 1 mol/kg H_2SO_4

Electrode material	Exchange current density $-\log_{10}(A/cm^2)$
Cadmium	10.8
Manganese	10.9
Lead	12.0
Mercury	12.3

Different types of polarization of electrodes

Polarization is a mechanism that typically results in a change in the potential of an electrode during electrolysis, when the anode's potential becomes nobler than that of the cathode. It has the effect (based on conditions) of decreasing the output voltage of batteries, and increasing the voltage required for electrolysis cells or lowering currents.

Polarization can also be described as a kinetic deviation from equilibrium due to an electric current passing through a galvanic cell. Polarization may occur at the cathode (cathodic polarization) or at the anode (anodic polarization). Cathodic polarization is more common.

Polarization

Polarization as an electrochemical phenomenon is of importance in the corrosion process. For all metals and alloys in any aqueous environment, cathodic polarization always reduces the corrosion rate. Cathodic protection refers to the application of a cathodic polarization to a corroding system.

Polarization can occur in three ways:

- Concentration polarization
- Resistance polarization
- Activation polarization

Concentration polarization of an electrode is the result of the formation of a diffusion layer adjacent to the surface of the electrode where there is a gradient of ion concentration. Diffusion of the ions through the layers controls the electrochemical reaction and is important for processes such as electroplating and corrosion. Concentration polarization may be reduced by increasing agitation or raising the temperature of the electrolyte.

Resistance polarization describes the potential drop due to the high resistivity of the electrolyte surrounding the electrode. It may also be a result of the insulation effect of the film on the electrode surface formed by the reaction products. Resistance polarization is expressed by the Ohm's law.

Activation polarization occurs when the electrochemical reaction proceeds through several successive steps. The speed of the overall reaction is determined by the slowest step (known as the rate-determining step) of the process. For example, in a hydrogen reduction reaction, the reaction may proceed as follows:

1. Hydrogen ions are absorbed from the solution onto the anode surface.
2. Electron transfer occurs from the anode to the hydrogen ions to form hydrogen.
3. The hydrogen atoms form hydrogen gas molecules.
4. Hydrogen gas bubbles are formed.

Tafel plots

The **Tafel equation** is an equation in electrochemical kinetics relating the rate of an electrochemical reaction to the overpotential.[1] The Tafel equation was first deduced experimentally and was later shown to have a theoretical justification. The equation is named after Swiss chemist Julius Tafel.

On a single electrode the Tafel equation can be stated as

where

- is the overpotential

- is the so-called "Tafel slope", V
- is the current density, A/m^2 and
- is the so-called "exchange current density", A/m^2.

he exchange current is the current at equilibrium, i.e. the rate at which oxidized and reduced species transfer electrons with the electrode. In other words, the exchange current density is the rate of reaction at the reversible potential (when the overpotential is zero by definition). At the reversible potential, the reaction is in equilibrium meaning that the forward and reverse reactions progress at the same rates. This rate is the exchange current density.

The Tafel slope is measured experimentally. It can, however, be shown theoretically that when the dominant reaction mechanism involves the transfer of a single electron that

where A is defined as

where

- is Boltzmann's constant,
- is the absolute temperature,
- is the elementary charge, and
- is the "charge transfer coefficient", the value of which must be between 0 and 1.

An alternative form

The Tafel equation can be also written as:

where

- the plus sign under the exponent refers to an anodic reaction, and a minus sign to a cathodic reaction,
- k is the rate constant for the electrode reaction,
- R is the universal gas constant,
- F is the Faraday constant.

Applicability

Where an electrochemical reaction occurs in two half reactions on separate electrodes, the Tafel equation is applied to each electrode separately.

The Tafel equation assumes that the reverse reaction rate is negligible compared to the forward reaction rate.

The Tafel equation is applicable to the region where the values of polarization are high. At low values of polarization, the dependence of current on polarization is usually linear (not logarithmic):

.

This linear region is called *polarization resistance* due to its formal similarity to the Ohm's law.

Mixed potential theory

Mixed potential theory is a theory used in electrochemistry that relates the potentials and currents from differing constituents to come up with a 'weighted' potential at zero net current. In other words, it is an electrode potential resulting from a simultaneous action of more than a single redox couple, while the net electrode current is zero.

Mixed potential is the effective potential of the metal surface in contact with an electrolyte that is driving electrochemical corrosion. Mixed potential theory explains metal corrosion as a reaction of two or more electrodes working simulatneously at the interface of the given metal surface and electrolyte.

The study of mixed potential is important because:

- It helps explain cathodic protection, which is an effective method of protecting burried pipelines, storage tanks, structures and marine equipment
- It is useful for fine tuning and calibration of measuring as well as monitoring devices used for corrosion protection systems, and useful for different environmental conditions
- It is useful in the design of corrosion protection systems and the selection of required components

Mixed Potential

Corrosion involves two partial reactions: oxidation and reduction. It occurs only when the total rate of oxidation equals the total rate of reduction.

Mixed potential is based on mixed potential theory, which considers a metal surface dipped in electrolyte as being made up of two or more electrodes.

Electrochemical corrosion is caused by these mixed electrodes formed on the metal surface, with oxidation directly coupled to the reduction reaction of the depolarizer. The resulting potential of the electrodes is the mixed potential, driving corrosion that needs to be controlled for the elimination of the corrosive reaction. By cathodically polarizing the cathode, the corrosion current density can be reduced to reduce and eliminate corrosion.

The value of mixed-potential, being a result of both anodic as well as the cathodic polarization on the metal surface, is affected by ambient temperature, the electrolyte's concentration and anode-to-cathode surface area ratio.

Faradic impedance

In electrochemistry, **faradaic impedance** is the resistance and capacitance acting jointly at the surface of an electrode of an electrochemical cell. The cell may be operating as either a galvanic cell generating an electric current or inversely as an electrolytic cell using an electric current to drive a chemical reaction. In the simplest nontrivial case faradaic impedance is modeled as a single resistor and single capacitor connected in parallel, as opposed say to in series or as a transmission line with multiple resistors and capacitors.

Mechanism

The resistance arises from the prevailing limitations on availability (local concentration) and mobility of the ions whose motion between the electrolyte and the electrode constitutes the faradaic current. The capacitance is that of the capacitor formed by the electrolyte and the electrode, separated by the Debye screening length and giving rise to the double-layer capacitance at the electrolyte-electrode interface. When the supply of ions does not meet the demand created by the potential the resistance increases, the effect being that of a constant current source or sink, and the cell is then said to be polarized at that electrode. The extent of polarization, and hence the faradaic impedance, can be controlled by varying the concentration of electrolyte ions and the temperature, by stirring the electrolyte, etc. The chemistry of the electrolyte-electrode interface is also a crucial factor.

Electrodes constructed as smooth planar sheets of metal have the least surface area. The area can be increased by using a woven mesh or porous or sintered metals. In this case faradaic impedance may be more appropriately modeled as a transmission line consisting of resistors in series coupled by capacitors in parallel.

Dielectric spectroscopy

Over the past two decades faradaic impedance has emerged as the basis for an important technique in a form of spectral analysis applicable to a wide variety of materials. This technique depends on the capacitive component of faradaic impedance. Whereas the resistive component is independent of frequency and can be measured with DC, the impedance of the capacitive component is infinite at DC (zero admittance) and decreases inversely with frequency of an applied AC signal. Varying this frequency while monitoring the faradaic impedance provides a method of spectral analysis of the composition of the materials at the electrode-electrolyte interface, in particular their electric dipole moment in the role of dielectric of a capacitor. The technique yields insights into battery design, the performance of novel fuel cell designs, biomolecular interactions, etc.

Faradic corrosion

Assume an electrolytic dissolution reaction involving a chemical species, S:

$S \rightarrow S^{n+} + ne^{-}$

You can relate current flow to mass via Faraday's Law.

$Q_S = n F M_S$

where

Q_S is the charge in coulombs resulting from the reaction of species S,

n is the number of electrons transferred per molecule or atom of S,

F is Faraday's constant = 96 485.34 coulombs/mole,

M_S is the number of moles of species S reacting.

A more useful form of Faraday's Law requires the idea of *equivalent weight*. The equivalent weight (EW_S) is the mass of species S that will react with one faraday of charge. For an atomic species, EW = AW/n (where AW is the atomic weight of the species). For a complex alloy that undergoes uniform dissolution, the equivalent weight is a weighted average of the equivalent weights of the alloy components. Mole fraction, not mass fraction, is used as the weighting factor. If the dissolution is not uniform, you may have to measure the corrosion products to calculate EW.

Substituting into Faraday's Law we get:

$W_S = EW_S\, Q_S / F$

where

W_S is the mass of species S that has reacted.

In cases where the corrosion occurs uniformly across a metal's surface, you can calculate the corrosion rate in units of distance per year. Be careful: this calculation underestimates the problem when localized corrosion occurs!

Conversion from a weight loss to a corrosion rate (CR) is straightforward. We need to know the density, d, and the sample area, A. Charge is given by $Q = I\, t$, where $t$is the time in seconds and I is a current. We can substitute in the value of Faraday's constant. Modifying the previous equation,

$$CR = I_{corr}\, K\, EW / d\, A$$

CR	The corrosion rate. Its units are given by the choice of K
I_{corr}	The corrosion current in amperes.
K	A constant that defines the units for the corrosion rate.
EW	The equivalent weight in grams/equivalent
d	Density in grams/cm^3
A	Area of the sample in cm^2

The following table shows the value of K used in the corrosion rate equation for corrosion rates in the units of your choice.

Corrosion Rate Constants

Units for Corrosion Rate	K
mm/year	3272
µm/year	3.272×10^6
mils/year (Gamry default)	1.288×10^5

POSSIBLE QUESTIONS

Part A **(Each question carries 1 mark)**

1 . In an **electrolytic** cell the electrode at which the electrons enter the solution is called
(a)Anode (b)redox **(C)cathode** (d)Anode and redox

2. The chemical change that occurs at this electrode is called
(a)Redox **(b)reduction** (c)oxidation (d)no reaction

3.In voltaic cells, such as those diagrammed in your text, the salt bridge
(a)is not necessary in order for the cell to work
(b)acts as a mechanism to allow mechanical mixing of the solutions
(c) allows charge balance to be maintained in the cell
(d)is tightly plugged with firm agar gel through which ions cannot pass

4.In the standard notation for a voltaic cell, the double vertical line "||" represents:
(a)a phase boundary (b)gas electrode (c)a wire (metal) connection **(d)a salt bridge**

5.In the standard notation for a voltaic cell, the double vertical line "||" represents:
(a)a phase boundary (b)gas electrode (c) a wire (metal) connection
(d)a salt bridge

6.Volatile oxidation corrosion product of a metal is,
(a)Fe_2O_3 **(b)MoO_3** (c)Fe_3O_4 (d)FeO

7.Lower is P^H, corrosion is,
(a)Greater (b)Lower (c)Constant (d)No change

8.Electrochemical corrosion takes place on,
(a)Anodic area (b)Cathodic area c)Near cathode (d)Near anode

9.Principles cannot be used to predict corrosion currents or corrosion rates
(a) Thermodynamic (b)Electrochemical (c)Electrolytic (D)Electrical

10.In which of the following 1.0M solutions will both ions react spontaneously with tin?
(a) **Ag^+ and Cu^{2+}** (b)Ni^{2+} and Cu^{2+} (c) Zn^{2+} and Ni^{2+} (d)Mg^{2+} and Zn^{2+}

11.In amperometric titration the indicator electrode is known as
(a)Saturated calomel electrode **(b)Rotating platinum electrode** (c)platinum electrode
(d)calomel electrode

12.polarization diagrams can be quite useful for describing or explaining many ------- phenomena.
(a) Thermodynamic (b)Electrochemical **(c)Corrosion** (d)electrolytic

13. Which can be obtained by dividing the anodic current by the surface area of the specimen
(a)Corrosion current density (b)Current density (c)corrosion (d)Overpotential

14.Salting of roads during the winter increases the corrosion of cars.This is because the salt
(a)reacts with the iron. **(b)provides an electrolyte.** (c)acts as a reducing agent.
(d)acts as an oxidizing agent.

15.Which of the following will inhibit the corrosion of iron?
(a) high [O_2(aq)] (b)wet conditions **(c)coating with zinc** (d) increasing the temperature

16.Among the following which one is known as reference electrode
(a)Saturated calomel electrode (b)Rotating platinum electrode (c)platinum electrode
(d)calomel electrode

17.Standard electrode potential of hydrogen is,
(a)1.00 V **(b)0.001 V** (c)0.01 V (d) 0.001 V

18.Standard electrode potential of Al / Al^{3+} is,
(a)+ 0.66V (b) - 0.66 V **(c) - 1.66 V** (d) + 1.66 V

19.Which of the following metal does not resists the corrosion process?
(a)Ni (b)Cu (c)Pb **(d)Fe**

20.In the standard notation for a voltaic cell, the double vertical line "||" represents:
(a)a phase boundary (b)gas electrode (c)a wire (metal) connection **(d)a salt bridge**

Part B **(Each question carries 2 marks)**

1.Give graphical presentation of kinetic data.

2.What is exchange current density.

3.Mention different types of polarization of electrodes.

4.What is activation polarization.

5.What is faradic impedance.

Part C **(Each question carries 6 marks)**

1.By using Tafel plots, how will you explain the current density.

2.Give a detiled account on exchange current density.

3.Explain the applications of electrode kinetics to experimental observations.

4.What are the different types of polarization of electrodes. Explain any one of it.

5.Discuss the Mixed potential theory.

6.Explain briefly the Faradic impedance.

7.Explain in detail the importance of Kinetics of corrosion.

8.Give a detailed account on Activation polarization.

9. Explain the Graphical presentation of kinetic data for kinetics of corrosion.

10. Explain Applications of electrode kinetics to corrosion.

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PHYSICAL CHEMISTRY-II (Chemical Kinetics and Electrochemistry) 17CHP203

UNIT-I	OPTION 1	OPTION 2	OPTION 3	OPTION 4	ANSWER
In an **electrolytic** cell the electrode at which the electrons enter the solution is called	a)Anode	b)redox	c)cathode	d)Both (a)and (b)	c)cathode
The chemical change that occurs at this electrode is called	a)Redox	b)reduction	c)oxidation	d)none	b)reduction
In voltaic cells, such as those diagrammed in your text, the salt bridge	a)is not necessary in order for the cell to work	b) acts as a mechanism to allow mechanical mixing of the solutions	c)allows charge balance to be maintained in the cell	d) is tightly plugged with firm agar gel through which ions cannot pass	c)allows charge balance to be maintained in the cell
In the standard notation for a voltaic cell, the double vertical line "‖" represents:	a)a phase boundary	b)gas electrode	c)a wire (metal) connection	d)a salt bridge	d)a salt bridge
Volatile oxidation corrosion product of a metal is,	a)Fe_2O_3	b)MoO_3	c) Fe_3O_4	d)FeO	b)MoO_3
Lower is PH, corrosion is,	a)Greater	b) Lower	c)Constant	d)greater first and remains constant	a)Greater
Electrochemical corrosion takes place on,	a)Anodic area	b)Cathodic area	c) Near cathode	d) Near anode	a)Anodic area
Smaller the grain size, corrosion is,	a)Greater	b) Lower	c)Constant	d)Doesn't affected	a)Greater
Process of corrosion enhanced by,	a)Air & Moisture	b)Electrolytes in water	c)Gases like CO_2 & SO_2	d)All of above.	d)All of above.
Standard electrode potential of hydrogen is,	a)1.00 V	b)0.00 V	c)0.01 V	d) 0.001 V	b)0.00 V
Standard electrode potential of Al / Al^{3+} is,	a)+ 0.66V	b)- 0.66 V	c) - 1.66 V	d) + 1.66 V	c) - 1.66 V
Which of the following metal does not resists the corrosion process?	a)Ni	b)Cu	c)Pb	d)Fe	d)Fe
To prevent corrosion phenomenon, combination of ___________ is used	a)Phosphorous or Antimony	b)Phosphorous or Chlorine	c) Phosphorous or Nitrogen	d)Antimony or Sodium	a)Phosphorous or Antimony
In differential aeration corrosion, poor oxygenated parts are	a)Anodic	b)Cathodic	c)anodic and cathodic	d)cathodic and anodic	a)Anodic
Pitting corrosion is a __________ accelerated attack.	a)Non- localized	b) Localized	c)None of above	d) Diverse	b) Localized
Paints which are used to restrict corrosion are known as,	a)Anticorrosion paints	b)Antifouling paints	c)Special paints	d)Marine paints	b)Antifouling paints
In galvanic series, a metal high in series is more _________.	a)Anodic	b)Cathodic	c)acidic	d)basic	a)Anodic
Acidic media are more corrosive than _________ and neutral media.	a)Less acidic	b) Alkaline	c)Inert	d)Non reactive	b) Alkaline
Reduction in over voltage of corroding metal / alloy accelerates the _________.	a)Reactivity	b)Inertness	c)Corrosion	d)Reduction	c)Corrosion
In waterline corrosion highly oxygenated parts acts as	a)Anodic	b)Cathodic	c)Corrode	d)catalyst poison	b)Cathodic
Evolution of hydrogen type corrosion occurs in _______ environment.	a)Acidic	b)Neutral	c)Basic	d) Alkaline	a)Acidic
Corrosion is a process reverse of ______ of metal	a)Destruction	b)Extraction	c)Rusting	d)Galvanizing	b)Extraction
Corrosion process is nothing but ________.	a)Reduction	b)Oxidation	c)Protection	d)photolysis	b)Oxidation
Standard electrode potential of Zn^{2+}/ Zn is,	a)+ 0.76 V	b)- 0.76 V	c)- 2.76 V	d) + 2.76 V	b)- 0.76 V
Dry cell is an example of _________cell.	a)Primary	b)Secondary	c)Electrochemical	d) Electrolytic	a)Primary
_______ is acts as anode in dry / laclanche cell	a)Carbon rod	b)Mn	c)Zn	d)Fe	c)Zn
Standard electrode potential of Fe^{2+}/Fe is,	a)+ 0.44 V	b)- 0.44 V	c) + 1.44 V	d) - 1.44 V	b)- 0.44 V
Caustic embrittlement, a type of stress corrosion contains deposition of corrosion products,	a)Na_2FeO_2	b)$NaFeO_2$	c)K_2FeO_2	d) Fe_3O_4	b)$NaFeO_2$
Coating of Zn, Al and Cd on steel are _________ , because their electrode potentials are lower.	a)Anodic	b)Cathodic	c)Not affected	d)affected	a)Anodic
On anode ______ reaction occurs.	a)Reduction	b)Oxidation	c)Redox	d)nuclear	b)Oxidation

Mathematically equivalent conductance is given as,	a)□eq = (1000 □ / N)	b) □eq = (1000 □ / N)	c) □eq = (1000 □ □ / N)	d) □eq = (1000□ / 2N)	b) □eq = (1000 □ / N)
Fuel cells are _______ cells	a)Primary	b)Secondary	c)Galvanic	d)None of above	c)Galvanic
Cell potential of Ni - Metal hydride battery is,	a)1.25 to 1.35 V	b)0.25 to 1.3 V	c)0.25 to 0.35 V	d)0.025 to 1.35 V	a)1.25 to 1.35 V
In fuel cell net energy profit is _______ %.	a)20	b)30	c)40	d)45	c)40
Aqueous ____ solution is used as electrolytic solution in H_2-O_2 fuel cell.	a)NaOH	b)KOH	c)NH_4OH	d)Mg $(OH)_2$	b)KOH
Practically emf of fuel cell is ____ V.	a)0.8 to 1.0	b) 0.8 to 0.1	c) 0.5 to 1.0	d)0.7 to 1.7	a)0.8 to 1.0
In H_2 - O_2 fuel cell O_2 gas acts as _____.	a)Anode	b) Cathode	c)Reductant	d)Oxidant	d)Oxidant
In Lithium batteries, electrolytes can't acts as aqueous solution because,	a)High reactivity of Li with H_2O	b) Low density of Li w. r. t. H2O	c) High electro positivity of Li+	d)High electro positivity of Pt	a)High reactivity of Li with H_2O
A fresh dry cell has potential ______V	a)1	b)1.5	c)2	d)3.5	b)1.5
Cell constant can be defined as ______	a)(Specific / Observed) Conductance	b)(Observed / Specific) Conductance	c) (1 / Specific) Conductance	d)(1 / Observed) Conductance	a)(Specific / Observed) Conductance
Principles cannot be used to predict corrosion currents or corrosion rates	a)Thermodynamic	b)Electrochemical	c) Electrolytic	d)Electrical	a)Thermodynamic
The difference between the resultant potential and each individual reaction equlibrium potential is called	a)Polarography	b)polarization	c)Overpotential	d)Corrosion	c)Overpotential
When the anodic processes on the electrode are accelerated by changing the specimen potential in the	a)Positive direction	b)Negative direction	c)horizontal direction	d)vertical direction	a)Positive direction
How many distinct types of polarization are there?	a)Four	b)Three	c)Two	d)One	b)Three
Activation polarization is usually the controlling factor during corrosion in ------	a)Strong acid	b)Strong base	c)Weak acid	d)Weak base	a)Strong acid
-------is surely the single most important variable that explains the large differences in the rate of hydrogen on metallic surfaces	a)exchange current density	b)Current density	c)polarization	d)Overpotential	a)exchange current density
When the cathodic processes are accelerated by moving the potential in the	a)Positive direction	b)Negative direction	c)horizontal direction	d)vertical direction	b)Negative direction
Concentration polarization usually predominates when the concentration of the active species is	a)low	b)high	c)very high	d)very low	a)low
If a corrosion reaction is activation controlled then stirring or agitation will have ------ on the corrosion rate.	a)high effect	b)low effect	c)very high effect	d)No effect	d)No effect
polarization diagrams can be quite useful for describing or explaining many -------phenomena.	a)Thermodynamic	b)Electrochemical	c)Corrosion	d)electrolytic	c)Corrosion
-----can be obtained by dividing the anodic current by the surface area of the specimen	a)Corrosion current density	b)Current density	c)corrosion	d)Overpotential	a)Corrosion current density
Salting of roads during the winter increases the corrosion of cars.This is because the salt	a)reacts with the iron.	b)provides an electrolyte.	c)acts as a reducing agent.	d)acts as an oxidizing agent.	b)provides an electrolyte.
Which of the following will inhibit the corrosion of iron?	a)high [$O_{2(aq)}$]	b)wet conditions	c) coating with zinc	d) increasing the temperature	c) coating with zinc
The corrosion rate of ----------- is greater than that of pure zinc exposed to identical concentrations of HCl	a)copper	b)iron	c)platinum	d)nickel	b)iron
There is ----------------exchange current density for hydrogen evolution reaction on zinc surface as compared to iron surface	a)high	b)low	c)medium	d)low and high	b)low
Emf series predicts that Al will be ---------------to Zn	a)cathodic	b)lower	c)lower and cathodic	d)anodic	d)anodic
Any electrochemical reaction can be divided into two or more partial oxidation and reduction reactions is known as	a)mixed potential theory	b)mixed theory	c)potential theory	d)corrosion theory	a)mixed potential theory

According to ----------------------there can be no net accumulation of electrical charge during an electrochemical reaction	a)mixed potential theory	b)mixed theory	c)potential theory	d)corrosion theory	a)mixed potential theory
The anode potential is displaced in a ------------------------- direction by anodic polarization	a)Positive direction	b)Negative direction	c)horizontal direction	d)vertical direction	a)Positive direction
The cathode potential is displaced in a --------------------------- direction by the cathode polarization	a)Positive direction	b)Negative direction	c)horizontal direction	d)vertical direction	b)Negative direction

[17CHP203]

Reg. No...................

KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed to beUniversity Established Under Section 3 of UGC Act 1956)

PG DEGREE EXAMINATION, JANUARY 2018

(For the candidates admitted from 2017 onwards)

DEPARTMENT OF CHEMISTRY
EVEN SEMESTER

I M.Sc., CHEMISTRY
INTERNAL EXAM-I
PHYSICAL CHEMISTRY-II (Chemical Kinetics and Electrochemistry)

Time: 2 hours
Date : 31-1-2018

Maximum: 50 marks

PART- A
Answer All the Questions (20 × 1=20 Marks)

1.Among the following methods which is used to determine the rate of fast reactions
(a)pulse method (b)Ostwald's Dilution method (c) Ostwald isolation method (d)Half change method

2 To increase the rate of a reaction, there must be
(a) a decrease in the frequency of collisions (b) an increase in the frequency of collisions
(c) a decrease in the frequency of successful collisions (d) an increase in the frequency of successful collisions

3. An increaee in temperature increases the rate of a chemical reaction because
(a)the activation energy is lower (b)exothermic reactions are always favoured
(c)a greater fraction of particles have sufficient kinetic energy (d)the particles are more likely to have favourable collision geometry

4. In a reaction, the threshold energy is equal to
(a) Activation energy + normal energy of reactants (b) Activation energy - normal energy of reactants (c) Activation energy (d) Normal energy of reactants

5.The threshold energy of a chemical reaction depends on
(a)Nature of reacting species (b)Temperature (c)Concentration of species
(d)No of collisions per unit time or collision frequency

6.The minimum energy necessary to permit a reaction to take place is
(a)Threshold energy (b)Activation energy (c)Free energy (d)Kinetic energy

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7.The value of activation energy of a chemical reaction is primarily determined by
(a)Nature of reacting species (b)Temperature (c)concentration of species
(d)No of collisions per unit time or collision frequency

8.When the catalyst is added to the reversible reaction in equilibrium state the value of equilibrium constant
(a)Increases (b)Decreases (c)Becomes zero (d)Does not change

9.Activation energy can be described as the
(a)energy of motion. (b)energy of the activated complex.
(c)energy difference between the reactants and the products. (d)energy difference between the reactants and the activated complex.

10.Which of the following types of materials form effective catalysts
(a)Alkali metals (b)Transition metals (c)Alkaline earth metals (d)Radioactive metals

11.As reactant particles approach one another, their
(a)kinetic energy increases and their potential energy increases.
(b)kinetic energy increases and their potential energy decreases.
(c)kinetic energy decreases and their potential energy increases.
(d)kinetic energy decreases and their potential energy decreases.

12.In general, a chemical reaction requiring a large activation energy will proceed
(a)at a fast rate (b)only at slow rate (c) only at low temperatures
(d)only at low concentrations

13. A substance that increases the reaction rate without itself getting used up is known as a
(a)Catalyst (b) Inhibitor (c) Activated Complex (d) Buffer

14.In a reaction,a positive catalyst will decrease the value of
(a) Δ H (b) Activation energy (c) Δ S (d) rate constant

15. In the hydrogenation of vegetable oils, the catalyst commonly used is
(a) Fe_2O_3 (b) Activated charcoal (c) ZnO (d) Ni

16 .The catalyst and the reactant are in the same phase Which is called
(a)Heterogenous (b)Activation energy (c) Homogeneous (d)rate constant

17.Which one of the following statements is incorrect regarding physical adsorption
(a)Low heats of adsorption (b)Usually occurs at low temperatures and decreses with an increase an temperature (c) Forms monomolecular layers (d)It is reversible

18.An example of an efficient adsorbent is
(a)Glass (b)Diamond (c)Charcoal (d)Wood

19.Physisorption is
(a)reversible (b)irreversible (c)specific (d)irreversible and specific

20.The effect of catalyst in a chemical reaction is to change
(a) Heat of reaction (b)Equilibrium constant (c)internal energy of the reactants
(d)Activation energy required for the reaction

PART- B (3 × 2=6 Marks)

Answer All the Questions

21.Write a note on entropy of activation in reactions in solution.

22.Write an expression for Hammett acidity function.

23.Differentiate physisorption and chemisorptions.

PART- C (3 × 8=24 Marks)

Answer All the Questions

24. a) Give a detailed account on ARRT in terms of partition functions with a suitable diagram.

(OR)

b)Explain in detail Shock - tube method for the study of fast reactions.

25. a)Derive Langmuir adsorption isotherm.

(OR)

b)Write a detailed note on Langmuir –Hinshelwood mechanism

26.a)Explain the hard sphere collision theory of gas phase reactions.

(OR)

b) Derive the Debye-Huckel Onsager equation.

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PG DEGREE EXAMINATION, FEBRUARY 2018
(For the candidates admitted from 2016 onwards)

DEPARTMENT OF CHEMISTRY
EVEN SEMESTER

I M.Sc., CHEMISTRY
INTERNAL EXAM-I
Answer Key
PHYSICAL CHEMISTRY-II (Chemical Kinetics and Electrochemistry)

PART- A

1.a)Pulse method

2.d)an increase in the frequency of successful collisions

3.c)a greater fraction of particles have sufficient kinetic energy

4.c)Activation energy

5.a)Nature of reacting species

6.b)Activation energy

7.a)Nature of reacting species

8.d)Does not change

9.d)energy difference between the reactants and the activated complex

10.d)Radioactive metals

11.c)Kinetic energy decreases and their potential energy increases

12.b)only at slow rate

13.a)catalyst

14.b)Activation energy

15.d)Ni

16.c)Homogeneous

17.c)Forms monomolecular layers

18.c)Charcoal

19.a)Reversible

20.d)Activation energy required for the reaction

PART B

21. In chemical kinetics, the **entropy of activation** of a reaction is one of the two parameters (along with the *enthalpy of activation*) which are typically obtained from the temperature dependence of a reaction rate constant, when these data are analyzed using the Eyring equation. The standard entropy of activation is symbolized $\Delta S^{\ddagger}$ and equals the change in entropy when the reactants change from their initial state to the activated complex or transition state (Δ = change, S = entropy, ‡ = activation). It determines the preexponential factor A of the Arrhenius equation for temperature dependence of reaction rates

22. The Hammett acidity function, H_0, can replace the pH in concentrated solutions. It is defined using an equation analogous to the Henderson-Hasselbalch equation:

$$H_0 = pk_{BH+} + \log \frac{B}{BH+}$$

where log(x) is the common logarithm of x, and $pK_{BH}{}^{+}$ is −log(K) for the dissociation of BH^+, which is the conjugate acid of a very weak base B, with a very negative $pK_{BH}{}^{+}$. In this way, it is rather as if the pH scale has been extended to very negative values. Hammett originally used a series of anilines with electron-withdrawing groups for the bases

Hammett also pointed out the equivalent form

$$H_0 = -\log(a\ H^+ \frac{\gamma B}{\gamma BH+})$$

23.Physisorption is a surface phenomena where the adsorbate adsorbs only on the surface.

Chemisorption is a bulk phenomena where the adsorbate penetrates deep into the solution.

PART C

24.a) Absolute reaction rate theory is a theory that aims to provide explanations for both the ‘activation energy’ and the pre-exponential factor A (the ‘frequency factor’) in the rate equation from first principles. Its underlying theories are quantum mechanics and statistical mechanics. The success of the theory depends on an accurate calculation of the potential energy surface of the reaction, as well as a detailed consideration of the initial and final states of the molecules.

The theory also introduces a precise concept of a *transition state* which is like a ‘normal’ molecule. The transition state has a definite structure, mass, and so forth. The only exception is that there is one particular direction of motion (the ‘reaction coordinate’) which causes the molecule to ‘break up’ into the end products of the reaction.

The situation is sketched in Figure 1. On the right is a ‘channel’ of reactants which transforms along a ‘reaction coordinate’ into a channel of products. At the height of the energetic barrier between the reactants and the products lies the ‘transition state’, which is thus specified as a particular type of molecule, with the structural property that there is one particular internal coordinate which leads to a decomposition of the molecule.

The further development of absolute reaction rate theory is based on the statistical mechanics of the equilibrium between the reactants and the transition state. Eyring’s introduction of statistical mechanics into the expression of the rate equation is based on the idea that the potential energy surface can be calculated with quantum mechanics, and the motion of the nuclear frame can subsequently be treated classically with statistical mechanics.

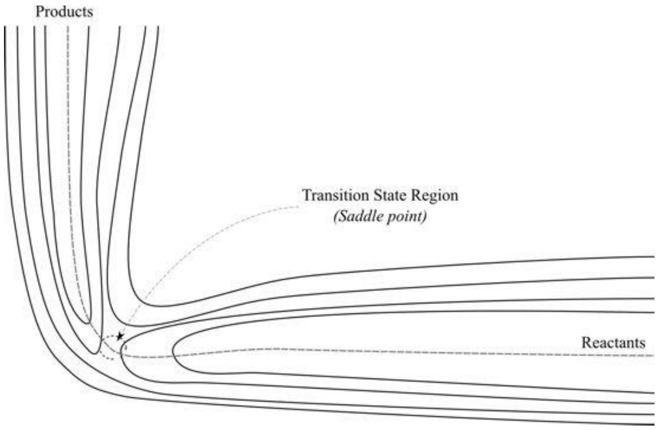


Figure 1: The potential energy surface for a three-atom reaction, indicating the reaction coordinate and the transition state at the saddle point.

It is therefore clear that the absolute theory of reaction rates requires accurate calculations of the potential energy surface for the reaction. Such precise calculations were not possible in the 1930s, and hence Eyring developed a semi-empirical form of quantum mechanics that gives access to the potential energy surface with sufficient precision to allow predictions from the theory.

Eyring’s formulation of absolute reaction rate theory uses the following assumptions:

E1. The potential energy surfaces can be calculated with quantum mechanics (or a semi-empirical form of quantum mechanics).
E2. The behavior of the nuclear frame on the potential energy surface (note that this therefore includes the Born-Oppenheimer approximation) can be described with statistical mechanics.
E3. The decomposition of the transition state into the reactants can be described as a translational motion along the reaction coordinate.

Let us reconstruct the remainder of the argument in the form in which it is given in Glasstone *et al*. 1941. The key element of statistical mechanics is the partition function (*Zustandssumme*) *Z*:

$$z = g_i \exp\left(\frac{-e_i}{kT}\right)$$

where g_i is the degeneracy of the state corresponding to energy e_i. The complete partition function for any system is complex to calculate, since it involves all electronic, translational, vibrational and rotational motions of the system with their degeneracies and corresponding energy levels. The rate formula of the absolute theory of reaction rates is given in terms of the partition functions of the reactants and the transition state by

$$k = \frac{kT}{h}\frac{Z^{\ddagger}}{Z_A Z_B Z \ldots}\exp\left(\frac{-E^0_{\ddagger}}{RT}\right)$$

The advantage of this formulation is that the partition functions for all compounds featuring in the reaction (Z_A, Z_B, *etc.*) can be calculated using statistical mechanics for vibrational and rotational motion of mechanical systems. While this is still a difficult problem, a detailed consideration of different reacting systems yields a mechanistic insight in how the reaction occurs on a molecular level. Figure 2 presents a sketch of the situation.

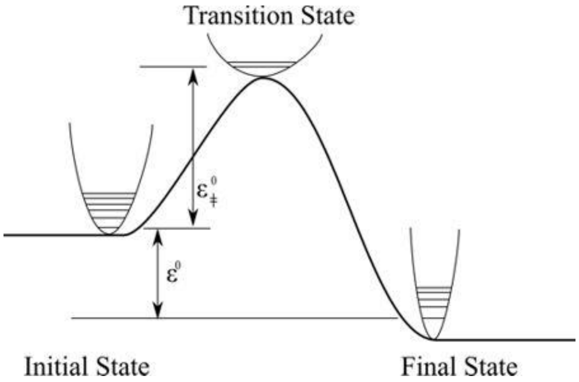


Figure 2: The potential energy surface for reaction seen along the reaction coordinate. The parabolic curves with energetic levels in them should be read as being ‘perpendicular’ to the reaction coordinate.

b) **Shock tube methods**

Shock Tube Investigations of High Temperature Reaction Kinetics

Combustion systems are characterized by a complicated interaction of flow and transport processes and a large number of elementary chemical reactions. The purpose of chemical kinetics is to unravel the underlying complex reaction mechanisms and to investigate the products and rates of selected reactions as function of temperature and pressure. In particular, the formation and the reactions of short-lived reactive intermediates (atoms and radicals) have to be well known. These intermediates maintain the combustion process and determine the end product distribution.

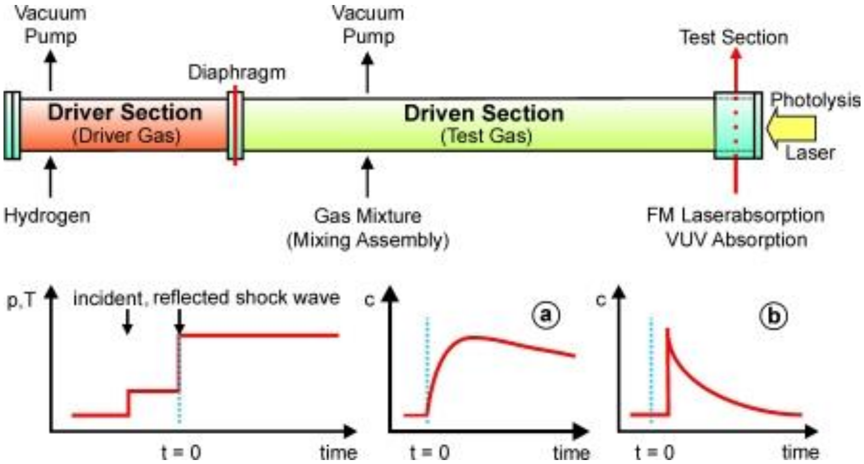


Fig 1:Top: schematic setup of a shock tube. Bottom: pressure/temperature-time profile during a shock tube experiment and typical concentration-time profiles of a) thermal or b) photolytic generation of the detected species.

The shock tube technique has been proven to be a very powerful method for investigating gas phase reactions at high temperatures. With shock tubes, the experimental pressure (0.1-1000 bar) and temperature (500-15000 K) can be easily varied over a wide range. Essentially, a shock tube apparatus (Fig. 1) is just a several meters long tube, which is divided by a diaphragm into a driver (high pressure) and a driven (low pressure) section. The test gas mixture, typically a highly diluted mixture of reactants in argon, is found in the driven section. The driver section is filled with helium or hydrogen until the diaphragm bursts. A shock wave is formed, which propagates downwards the tube at supersonic speed and heats and compresses the test gas within less than 1 µs (incident shock wave). The shock wave is reflected at the end wall and the preheated testgas is heated and compressed again (reflected shock wave). The resulting pressure- and temperature-time-profile is shown in the lower left part of Fig. 1. Typically, the constant conditions behind the reflected wave last for roughly 1 - long enough for studying chemical reactions, which are mostly fast at high temperatures. In many cases, the species of interest are generated thermally by the decomposition of suitable precursor molecules (Fig. 1a), but often a photolytic production is also feasible (Fig. 1b). Finally, real-time detection of the concentration-time-profiles is accomplished through optical windows by means of a variety of sensitive spectroscopic absorption or emission techniques. A recent example is the application of the highly sensitive laser absorption based frequency modulation (FM) spectroscopy for quantitative detection of small radicals behind shock waves. With FM spectroscopy the radicals methylene ($^1CH_2$) and formyl (HCO), which are both of considerable importance in combustion chemistry, could be detected behind shock waves for the first time [1,2]. Both formaldehyde (CH_2O) and formyl radicals (HCO) lie on the main oxidation pathway of hydrocarbons with CH_3 as the chain center. Methane oxidation, for example, proceeds in the following steps:

CH_4 => CH_3 => CH_2O => HCO => CO => CO_2

Under radical-rich conditions, formaldehyde is mainly formed by the reaction of methyl radicals with oxygen atoms. Subsequent abstration reactions of H, OH, O and CH_3 yield formyl radicals. By reactions of HCO with H, O_2 and OH, and also through its unimolecular decomposition, carbon monoxide and eventually carbon dioxide are formed. The high temperature decomposition of CH_2O provides a simple system to investigate some of these reactions. The chain mechanism of the CH_2O decay can be described over a wide range of temperatures and pressures by only five reactions:

CH_2O	+	M	HCO	+	H	+	M	(1a)
CH_2O	+	M	H_2	+	CO	+	M	(1b)
CH_2O	+	H	H_2	+	HCO			(2)
HCO	+	M	H	+	CO	+	M	(3)
HCO	+	H	H_2	+	CO			(4)
HCO	+	HCO	CH_2O	+	CO			(5)

By means of sensitive vacuum-UV-absorption detection of CH_2O at 174 nm and frequency modulation detection of HCO at wavelength around 614 nm, the rate of reaction (2) was directly measured at high temperatures for the first time (CH_2O detection, C_2H_5I as H atom source, T=1510 - 1960 K) and the rate of reaction (3) could be measured at temperatures of 835 - 1230 K (HCO detection, photolysis of CH_2O mixtures) [2, 3]. Furthermore, measurements of reactions (4) and (5) at lower temperatures (HCO detection, photolytic production of HCO) and the detection of CH_2O and HCO profiles during the thermal decomposition of pure formaldehyde mixtures behind shock waves provided additional information about the rates of reactions (1a) and (3) [2,4]. Altogether, sensitive detection methods and extensive experimental data made it possible to separate the strongly coupled reactions and to obtain a consistent set of rate constants.

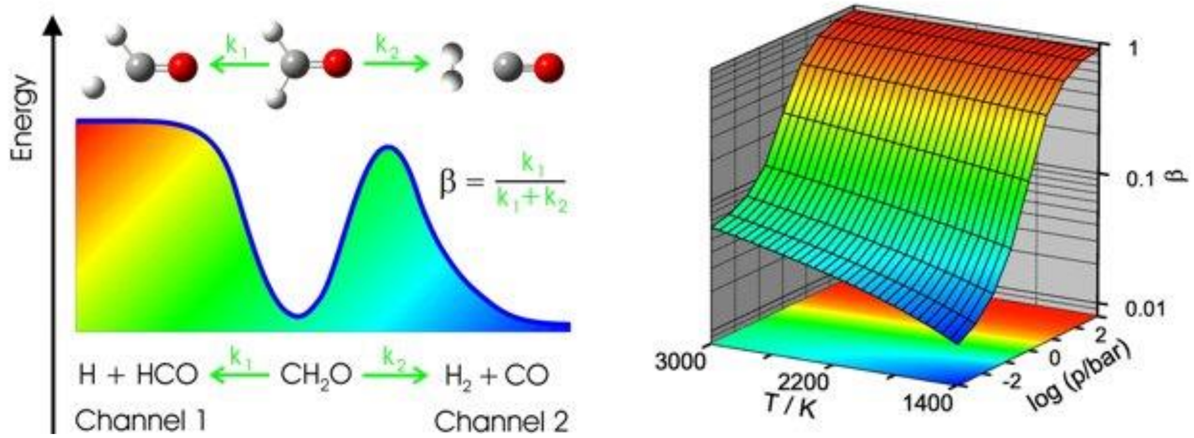
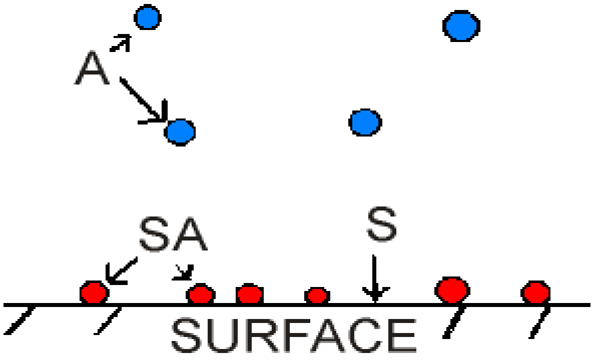


Fig:2Left: schematic potential curve of the thermal decomposition of formaldehyde (CH_2O) with H_2 + CO and H + HCO as reaction products, respectively. Right: calculated branching fraction as function of pressure and temperature; based on two-channel RRKM calculation.

As a final step, the rate of reaction (1b), which becomes more important at low formaldehyde concentrations, and also the branching fraction β of the initiation step (reactions (1a) and (1b)) were calculated using statistical theories of unimolecular reactions. Similar threshold energies and different energy dependencies of the decay rates of the two reaction channels with loose (1a) and tight (1b) transition states, respectively, induce a distinct pressure and temperature dependence of the branching fraction β (Fig. 2). A two-channel RRKM calculation, which takes into account rotational effects and "weak collisions" (master equation analysis) reveals that at temperatures from 1400 to 3000 K and at low pressures (1 mbar) reaction (1b) with H_2 and CO as products is the main channel. However, with increasing pressure, channel (1a) eventually dominates and at very high pressures (1 kbar)

25.a)

For molecules in contact with a solid suface at a fixed temperature, the Langmuir Isotherm, developed by Irving Langmuir in 1916, describes the partitioning between gas phase and adsorbed species as a function of applied pressure.



Thermodynamic Derivation

The adsorption process between gas phase molecules, A, vacant surface sites, S, and occupied surface sites, SA, can be represented by the equation,

$$S + A \rightleftharpoons SA$$

assuming that there are a fixed number of surface sites present on the surface.

An equilibrium constant, K, can be written:

$$K = \frac{[SA]}{[S]\,[A]}$$

q = Fraction of surface sites occupied (0 <q< 1)

Note that

- **[SA]** is proportional to the surface coverage of adsorbed molecules, or proportional to q
- **[S]** is proportional to the number of vacant sites, (1 - q)
- **[A]** is proportional to the pressure of gas, P

Thus it is possible to define the equilibrium constant, b:

$$b = \frac{\theta}{(1-\theta)P}$$

Rearranging gives the expression for surface coverage:

Kinetic Derivation

The rate of adsorption will be proportional to the pressure of the gas and the number of vacant sites for adsorption. If the total number of sites on the surface is N, then the rate of change of the surface coverage due to adsorption is:

$$\frac{d\theta}{dt} = k_a \, p \, N(1 - \theta)$$

The rate of change of the coverage due to the adsorbate leaving the surface (desorption) is proportional to the number of adsorbed species:

$$\frac{d\theta}{dt} = - k_d \, N \theta$$

In these equations, k_a and k_d are the rate constants for adsorption and desorption repectively, and p is the pressure of the adsorbate gas. At equilibrium, the coverage is independent of time and thus the adorption and desorption rates are equal. The solution to this condition gives us a relation for q:

where $b = k_a/k_d$.

Dependence of b on external parameters:

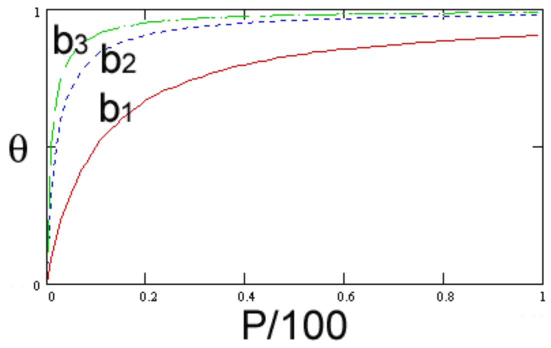
b is only a constant if the enthalpy of adsorption is independent of coverage.

As with all chemical equilibria, the position of equilibrium (determined by the value of b) will depend upon a number of factors:

1. The relative stabilities of the adsorbed and gas phase species involved.
2. The temperature of the system (both the gas and surface, although these are normally the same).
3. The pressure of the gas above the surface.

In general, factors (2) and (3) exert opposite effects on the concentration of adsorbed species - that is to say that the surface coverage may be increased by raising the gas pressure but will be reduced if the surface temperature is raised.

Graphical form of the Langmuir Isotherm



where $b_3 > b_2 > b_1$

b) **Langmuir-Hinshelwood mechanism**

The rate equation derived from mechanistic model that simulates the actual surface phenomenon during the process is preferred for reactions involving solid catalysts. The Langmuir-Hinshelwood–Hougen-Watson(LHHW) approach is one of the most commonly used way of deriving rate expressions for fluid solid catalytic reactions. The advantages of this method are that:

(1) Rate derived by this method takes into account the adsorption/desorption process occurring over the surface along with the surface reaction.

(2) Rate equation derived can be extrapolated more accurately to concentrations lying beyond the experimentally measured values.

During this method of derivation of rate expression, all the physical transport steps like mass transfer from bulk phase to catalyst surface or diffusion of reactants from pore mouth to interior pore (intraparticle diffusion) are excluded. Thus, it is assumed that the external and internal mass transport processes are very rapid relative to the chemical rate process occurring on or within the catalyst particle. The chemical rate depends on:

(1) chemisorption steps

(2) surface reaction steps

(3) desorption steps

This simple kinetic model assumes isothermal condition about and within catalyst that is temperature gradient is zero.

In LHHW model development, the rate equation is first derived in terms of surface concentration of adsorbed species and vacant sites. Then, these surface concentrations are related to the fluid or bulk concentration that is directly measurable.

For the reaction $A+B \rightleftharpoons C+D$

Let r_a= rates of adsorption ....(g moles/s.gm of catalyst)

r_s = rates of surface reaction.................................. ...(g moles/s.gm of catalyst)

r_d =rates of desorption ....(g moles/s.gm of catalyst)

C_{AS}= concentration of adsorbed A on surface ....(g moles/gm of catalyst)

C_{BS}= concentration of adsorbed B on surface ....(g moles/gm of catalyst)

C_{CS}= concentration of adsorbed C on surface ....(g moles/gm of catalyst)

C_{DS}= concentration of adsorbed D on surface.............. (g moles/gm of catalyst)

C_o= total concentration of active sites on surface........ (g moles/gm of catalyst)

C_v= concentration of vacant sites on surface............... (g moles/gm of catalyst)

C_A= concentration of A in bulk gas phase ....(g moles/cm^3)

Similarly C_B,C_C ,C_D are concentration of B,C,D in bulk gas phase respectively.

Let the reaction follows the mechanism given below ;

(1) $A + S \rightleftharpoons A.S$ --- Adsorption of reactant A on surface vacant site S

(2) $B + S \rightleftharpoons BS$ --- Adsorption reactant B on surface vacant site S

(3) $A.S + B.S \rightleftharpoons C.S + D.S$ --- Surface reaction between adsorbed A and B

(4) $C.S \rightleftharpoons C + S$ --- Desorption of product C from surface creating a vacant site

(5) $DS \rightleftharpoons D + S$ --- Desorption of product D from surface creating a vacant site

Among the various steps described, the slowest step controls the overall rate of reaction and the other remaining steps are assumed to be at near equilibrium conditions. This approach greatly simplifies the overall rate expression, reducing the number of rate constants and equilibrium constants to be determined from experimental data. Further each step in this method is assumed to be elementary and the number of sites is conserved in each step.

Therefore, the controlling step can be either of the following:

(1) Surface reaction

(2) Adsorption

(3) Desorption

Now total concentration of active sites on surface, C_0, will be the summation concentrations of all sites on which either reactants or products are adsorbed and the concentration of vacant sites.

$$\therefore C_0 = C_V + C_{AS} + C_{BS} + C_{CS} + C_{DS}$$

Where C_V is the concentration of vacant sites.

Case 1 : Rate is surface reaction controlling

The surface reaction is the slowest step and is the rate controlling. According to the mechanism, surface reaction occurs between adsorbed A and adsorbed B producing adsorbed C & adsorbed D.

$$AS + BS \rightleftharpoons CS + DS$$

The rate of surface reaction is given as

$$r_S = k_S C_{AS} C_{BS} - k_S^{'} C_{CS} C_{DS}$$

.k_s= rate constant for forward surface reaction

$k_S^{'}$ = rate constant for reverse surface reaction

....

$$= k_S \left[C_{AS} C_{BS} - \frac{k_S^{'}}{k_S} C_{CS} C_{DS} \right]$$

$$= k_S \left[C_{AS} C_{BS} - \frac{1}{K_S} C_{CS} C_{DS} \right] \text{----(1)} \qquad K_S = \frac{k_S}{k_S^{'}}$$

.................---

Now, since all the other steps are considered to be in equilibrium, therefore concentration of adsorbed species can be obtained as follows.

For adsorption steps and desorption steps :

From step (1) $K_A = \frac{C_{AS}}{C_{A.} C_V}$ from step (4)------ $K_C = \frac{C_{CS}}{C_{C.} C_V}$

From step (2) $K_B = \frac{C_{BS}}{C_{B.}C_V}$ From step (5)------- $K_D = \frac{C_{DS}}{C_{D.}C_V}$

Then the adsorbed phase concentration can be written as

$$C_{AS} = K_A C_A C_V \;\; C_{CS} = K_C C_C C_V$$

$$C_{BS} = K_B C_B C_V \;\; C_{DS} = K_D C_D C_V$$

Substituting all these value in equation (1)

$$r_S = k_S\left[C_{AS}C_{BS} - \frac{1}{K_S}C_{CS}C_{DS}\right] = k_S\left[K_A C_A C_V . K_B C_B C_V - \frac{K_C}{K_S}C_C C_V . K_D C_D C_V\right]$$

$$\text{or,}\quad r_s = k_S\left[K_A K_B C_A C_B C_V^2 - \frac{K_C K_D}{K_S}C_C C_D C_V^2\right]$$

(2)

$$\text{or } r_S = k_S K_A K_B\left[C_A C_B - \frac{K_C K_D}{K_S K_A K_B}C_C C_D\right]C_V^2$$

$$\text{Now , } C_O = C_{AS} + C_{BS} + C_{CS} + C_{DS} + C_V$$

$$C_O = K_A C_A C_V + K_B C_B C_V + K_C C_C C_V + K_D C_D C_V + C_V$$

$$= C_V\,[1 + K_A C_A + K_B C_B + K_C C_C + K_D C_D \;\;]$$

$$C_V = \frac{C_O}{1 + K_A C_A + K_B C_B + K_C C_C + K_D C_D} \qquad (3)$$

For the reaction A+B $\rightleftharpoons$ C+D, at equilibrium, the overall equilibrium constant is

$$K = \frac{C_C C_D}{C_A C_B}.$$

All concentrations corresponds to the equilibrium conditions in gas phase

$$K = \frac{(C_{CS}/K_C C_V)(C_{DS}/K_D C_V)}{(C_{AS}/K_A C_V)(C_{BS}/K_B C_V)} = \frac{C_{CS}C_{DS}}{C_{AS}C_{BS}} \cdot \frac{K_A K_B C_V^2}{K_C K_D C_V^2}$$

$$\text{Or}, K = \frac{K_A K_B}{K_C K_D} . K_S \qquad \because K_S = \frac{C_{CS}C_{DS}}{C_{AS}C_{BS}} \tag{4}$$

Substituting (3) &(4) in equation (2),

$$r_S = k_S K_A K_B \left[C_A C_B - \frac{1}{K} C_C C_D \right] \frac{C_O^2}{(1 + K_A C_A + K_B C_B + K_C C_C + K_D C_D)^2}$$

$$r_S = k_S K_A K_B C_O^2 \frac{C_A C_B - \frac{1}{K} C_C C_D}{(1 + K_A C_A + K_B C_B + K_C C_C + K_D C_D)^2} \tag{5}$$

The above rate expression can also be derived in terms of bulk partial pressure.

Case 2: Rate is adsorption control

(a) Adsorption of A controlling

Let adsorption of A be the slowest step so that adsorption of B, surface reaction and desorption of C are at equilibrium.

Adsorption of A is given as

$$A + S \rightleftharpoons AS$$

Rate of adsorption $r_a = k_a C_A C_V - k_d C_{AS}$

$$r_a = k_a \left[C_A C_V - \frac{k_d}{k_a} C_{AS} \right] \qquad (6)$$

Or, $r_a = k_a \left[C_A C_V - \frac{1}{K_A} C_{AS} \right]$ $K_A = \frac{k_a}{k_d}$ (adsorption equilibrium constant for A)

$$r_a = k_a C_V \left[C_A - \frac{1}{K_A} \frac{C_{AS}}{C_V} \right]$$

Now as other steps are in equilibrium:

$$K_S = \frac{C_{CS} C_{DS}}{C_{AS} C_{BS}}$$

$$K_B = \frac{C_{BS}}{C_B C_V} \qquad K_C = \frac{C_{CS}}{C_C C_V} \qquad K_D = \frac{C_{DS}}{C_D C_V}$$

$$C_{BS} = K_B C_B C_V \qquad C_{CS} = K_C C_C C_V \qquad C_{DS} = K_D C_D C_V$$

Then ,

$$C_{AS} = \frac{C_{CS} C_{DS}}{K_S C_{BS}} = \frac{K_C C_C C_V . K_D C_D C_V}{K_S K_B C_B C_V} = \frac{K_C K_D}{K_S K_B} \frac{C_C C_D C_V}{C_B}$$

Substituting value in equation (6)

$$r_a = k_a C_V \left[C_A - \frac{1}{K_A C_V} \frac{K_C K_D}{K_S K_B} \frac{C_C C_D C_V}{C_B} \right]$$

$$r_a = k_a C_V \left[C_A - \frac{K_C K_D}{K_S K_A K_B} \frac{C_C C_D}{C_B} \right] \qquad (7)$$

$$r_a = k_a C_V \left[C_A - \frac{1}{K} \frac{C_C C_D}{C_B} \right]$$

$K = \frac{K_S K_A K_B}{K_C K_D}$ = Overall equilibrium constant.

Now $C_0 = C_V + C_{AS} + C_{BS} + C_{CS} + C_{DS}$

$$= C_V + \frac{K_C K_D}{K_S K_B} . \frac{C_C C_D C_V}{C_B} + K_B C_B C_V + K_C C_C C_V + K_D C_D C_V$$

$$= C_V \left[1 + \frac{K_C K_D}{K_S K_A} \frac{K_A}{K_B} \left(\frac{C_C C_D}{C_B} \right) + K_B C_B + K_C C_C + K_D C_D \right]$$

$$= C_V \left[1 + \frac{K_A}{K} \frac{C_C C_D}{C_B} + K_B C_B + K_C C_C + K_D C_D \right]$$

$$C_V = \frac{C_O}{1 + \frac{K_A}{K} \frac{C_C C_D}{C_B} + K_B C_B + K_C C_C + K_D C_D} \quad \because K = \frac{K_S K_A K_B}{K_C K_D}$$

Substituting value of C_V in equation (7)

$$r_a = k_a C_0 \frac{C_A - \left[\frac{C_C C_D}{K C_B} \right]}{1 + \frac{K_A C_C C_D}{K C_B} + K_B C_B + K_C C_C + K_D C_D} \qquad (8)$$

For a given catalyst C_0 is constant.

Similarly expression when desorption of product is the rate controlling step can be derived. For desorption of C controlling the whole reaction, the rate expression can be derived as

$$r_d = k_d C_0 K \frac{C_A C_B - \left[\frac{C_C C_D}{K} \right]}{1 + K_A C_A + K_B C_B + K_C K C_A C_B + K_D C_D}$$

26.a) **Collision theory** is a theory proposed independently by Max Trautz in 1916[1] and William Lewis in 1918, that qualitatively explains how chemical reactions occur and why reaction rates differ for different reactions.[2] The collision theory states that when suitable particles of the reactant hit each other, only a certain percentage of the collisions cause any noticeable or significant chemical change; these successful changes are called successful collisions. The successful collisions have enough energy, also known as activation energy, at the moment of impact to break the preexisting bonds and form all new bonds. This results in the products of the reaction. Increasing the concentration of the reactant particles or raising the temperature, thus bringing about more collisions and therefore many more successful collisions, increases the rate of reaction.

When a catalyst is involved in the collision between the reactant molecules, less energy is required for the chemical change to take place, and hence more collisions have sufficient energy for reaction to occur. The reaction rate therefore increases.

Collision theory is closely related to chemical kinetics.

Derivation of the rate law through the Collision theory:

With the reaction profile in mind, the collision theory predics that the rate law for a reaction:

$$\mathbf{A} + \mathbf{B} \rightarrow \mathbf{P}$$

is proportional to:
(a) The encounter rate;
(b) The minimum energy requirement;
(c) The steric factor.
where:

(a) The encounter rate:

The rate of collisions between species A and B is proportional to both their concentrations: if the concentration of B is doubled, then the rate at which A molecules collide with B molecules is doubled, and, if the concentration of A is doubled, then the rate at which B molecules collide with A molecules is also doubled. The kinetic theory of gasses goes even a step further and allows us to write:

$$v \propto \sigma \left(\frac{8 k_B T}{\pi \mu} \right)^{1/2} N_A^2 [\mathrm{A}][\mathrm{B}]$$

where N_A is Avogadro's constant, k_B is Boltzmann's constant, T is the temperature, s is the collision cross-section (see fig. 3), and m is the reduced mass given by:

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

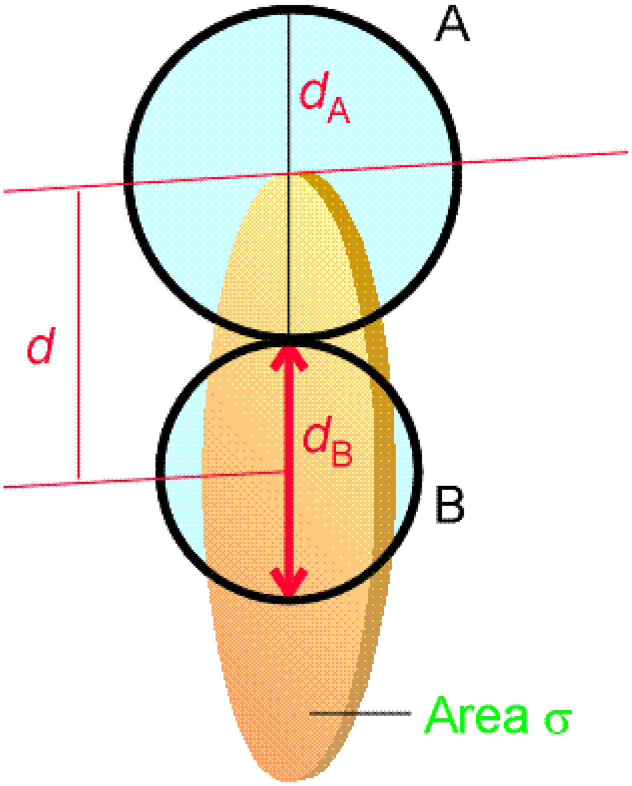
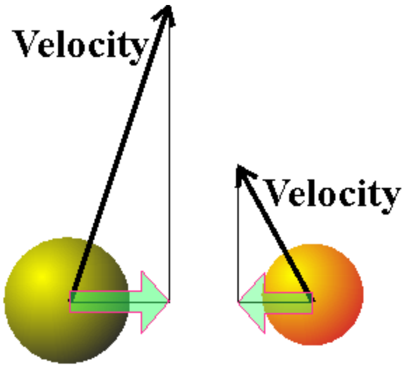


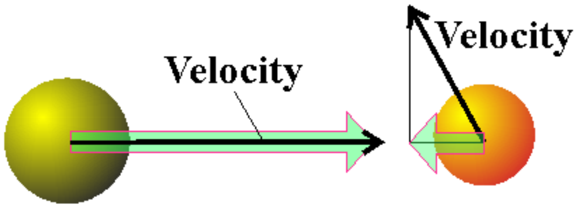
Fig. 3: The collision cross-section for two molecules can be regarded to be the area within which the centre of the projectile molecule (A) must enter around the target molecule (B) in order for a collision to occur. If the diameters of the two molecules are d_A and d_B, the radius of the target area is $d = 1/2\ (d_A + d_B)$ and the cross-section is pd^2.

(b) The minimum energy requirement:

Next, we need to multiply the collision rate by a factor *f* that represents the fraction of collisions that occur with at least a kinetic energy E_a along the line of approach (Fig 4), for only these collisions will lead to the formation of products. Molecules that approach with less than a kinetic energy E_a will behave like a ball that rolls toward the activation barrier, fails to surmount it, and rolls back.



(a) Low kinetic energy of approach



(b) High kinetic energy of approach

Fig. 4: The criterion for a successful collision is that the two reactant species should collide with a kinetic energy along their line of approach that exceeds a certain minimum value E_a that is characteristic of the reaction. The two molecules might also have components of velocity (and an associated kinetic energy) in other directions (for example, the two molecules depicted here might be moving up the page as well as towards each other): but only the energy associated with their mutual approach can be used to overcome the activation energy.

It follows from very general arguments concerning the probability that a molecule has a specified energy that the fraction of collisions that occur with at least a kinetic energy E_a is (from the kinetic theory of gasses):

$$f = \mathbf{exp}\left(-\frac{E_a}{RT}\right)$$

i.e. at this stage we can conclude that the rate of reaction, which is proportional to the rate of collision multiplied by the fraction of successful collisions, is:

$$v \propto \sigma\left(\frac{8k_BT}{\pi\mu}\right)^{1/2} N_A^2 \exp\left(-\frac{E_a}{RT}\right)[\mathrm{A}][\mathrm{B}]$$

Note that this equation now has the Arrehenius form, i.e.:

$$v = k[\mathrm{A}][\mathrm{B}] \qquad k = A\exp\left(-\frac{E_a}{RT}\right)$$

This means that at this stage we can already conclude that The *activation energy*, E_a, is the minimum kinetic energy required for a collision to result in reaction.

(c) The steric factor

However, it is often found that the experimental value of *A* is smaller than that calculated from the kinetic theory so far, i.e.:

$$\sigma\left(\frac{8k_BT}{\pi\mu}\right)^{1/2} N_A^2$$

One possible explanation is that, not only must the molecules collide with sufficient kinetic energy, but they must also come together in a specific relative orientation (Fig 5).

It follows that the reaction rate is proportional to the probability that the encounter occurs in the correct relative orientation. The pre-exponential factor *A* should therefore include a **steric factor,***P*, which usually lies between 0 (no relative orientations lead to reaction) and 1 (all relative orientations lead to reaction).

E.g. 1: The reactive collision in which two NOCl molecules collide and break apart into two NO molecules and a Cl_2 molecule:

$$\mathbf{NOCl + NOCl \rightarrow NO + NO + Cl_2} \qquad P \approx \mathbf{0.16}$$

E.g. 2: For the hydrogen addition reaction in which a hydrogen molecule attaches directly to an ethene molecule to form an ethane molecule:

$$H_2 + H_2C = CH_2 \rightarrow H_3C - CH_3 \qquad P = 1.7 \times 10^{-6}$$

This very low value of *P* which suggests that the reaction has very stringent orientational requirements.

Some reactions have $P > 1$. Such a value may seem absurd, because it appears to suggest that the reaction occurs more often than the molecules meet! An example of a reaction of this kind is the reaction in which a K atom plucks a Br atom out of a Br_2 molecule:

$$\mathbf{K + Br_2 \rightarrow KBr + Br} \qquad P = \mathbf{4.10}$$

In this reaction, the distance of approach at which reaction can occur seems to be considerably larger than the distance needed for deflection of the path of the approaching molecules in a non-reactive collision! To explain this surprising conclusion, it has been proposed that the reaction proceeds by a 'harpoon mechanism'.

ASIDE: The harpoon mechanism is based on a model of the reaction that pictures the K atom as approaching the Br_2 molecules, and when the two are close enough an electron (the harpoon) flips across to the Br_2 molecule. In place of two neutral particles there are now two ions, and so there is a Coulombic attraction between them: this attraction is the line on the harpoon. Under its influence the ions move together (the line is wound in), the reaction takes place, and KBr and Br emerge. The harpoon extends the cross-section for the reactive encounter and we would greatly underestimate the reaction rate if we used for the collision cross-section the value for simple mechanical contact between K and Br_2.

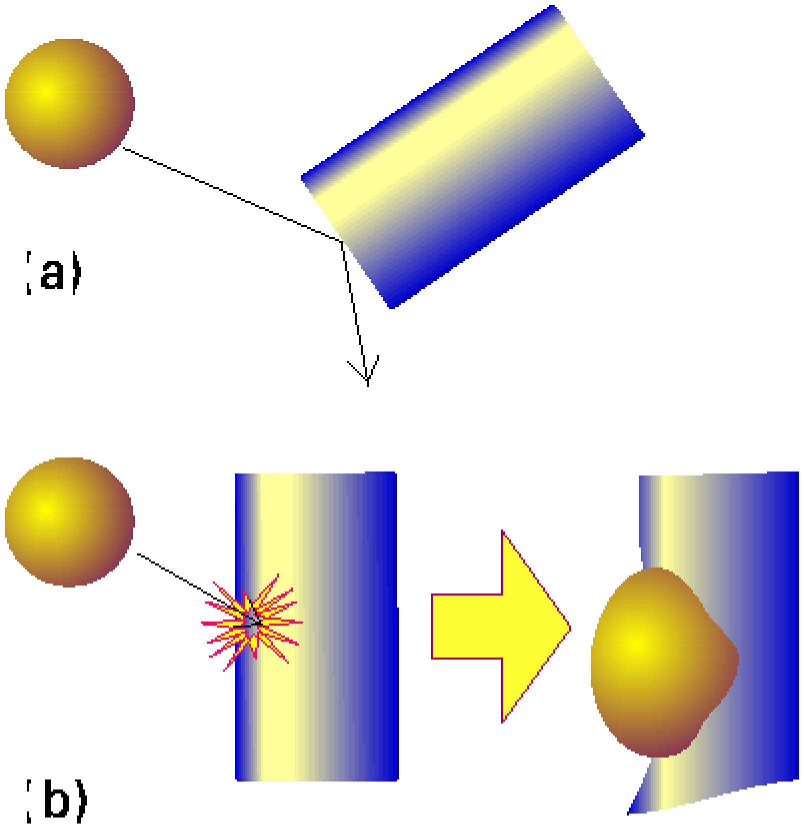
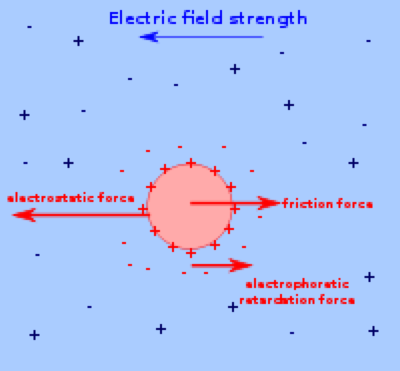


Fig. 5: Energy is not the only criterion of a successful reactive encounter, for relative orientation may also play a role. (a) In this collision, the reactants approach in an inappropriate relative orientation, and no reaction occurs even though their energy is sufficient, (b) In this encounter, both the energy and the orientation are suitable for reaction.

b) Debye-Huckel-Onsager equation

The **Debye–Hückel theory** was proposed by Peter Debye and Erich Hückel as a theoretical explanation for departures from ideality in solutions of electrolytes and plasmas. It is a linearized Poisson–Boltzmann model, which assumes an extremely simplified model of electrolyte solution but nevertheless gave accurate predictions of mean activity coefficients for ions in dilute solution. The Debye–Hückel equation provides a starting point for modern treatments of non-ideality of electrolyte solutions.

Conductivity



Forces affecting a charged ion or cloud moving in an electric field

The treatment given so far is for a system not subject to an external electric field. When conductivity is measured the system is subject to an oscillating external field due to the application of an AC voltage to electrodes immersed in the solution. Debye and Hückel modified their theory in 1926 and their theory was further modified by Lars Onsager in 1927. All the postulates of the original theory were retained. In addition it was assumed that the electric field causes the charge cloud to be distorted away from spherical symmetry.[17] After taking this into account, together with the specific requirements of moving ions, such as viscosity and electrophoretic effects, Onsager was able to derive a theoretical expression to account for the empirical relation known as Kohlrausch's Law, for the molar conductivity, Λ_m.

$$\wedge_m=\wedge^0_m-K\sqrt{C}$$

$\wedge^0_m$ is known as the limiting molar conductivity, K is an empirical constant and c is the electrolyte concentration. Limiting here means "at the limit of the infinite dilution"). Onsager's expression is

$$\wedge_m=\wedge^0_m-(A+B\wedge^0_m)\sqrt{C}$$

where A and B are constants that depend only on known quantities such as temperature, the charges on the ions and the dielectric constant and viscosity of the solvent. This is known as the Debye-Hückel-Onsager equation. However, this equation only applies to very dilute solutions and has been largely superseded by other equations due to Fuoss and Onsager, 1932 and 1957 and later.