KARPAGAM ACADEMY OF HIGHER EDUCATION
(Deemed to be University)
(Established Under Section of UGC Act 1956)
Coimbatore-641 021
For the Candidates admitted from 2016 Onwards
DEPARTMENT OF CHEMISTRY

SUBJECT :**PHYSICAL CHEMISTRY III(Phase equilibria and chemical kinetics)**
SEMESTER :**III**
SUBJECT CODE :**17CHU301** **CLASS** : **II B.Sc Chemistry**

Scope
To give the students a knowledge on advanced electrochemistry with emphasis on modern electrochemical techniques. The course helps the student to understand the nature of the electrochemical reactions and the peculiarities of electrochemical kinetics. The course also gives knowledge of surface chemistry.

Programme Outcome
The course enables the students to
1. Explain the nature of the electrochemical terms and concepts
2. Understand the nature of electrochemical reactions
3. Understand the phase equilibrium.
4. Understand different electrochemical cells and EMF measurements.
5. Understand the fundamentals of surface chemistry

Programme learning Outcome
The course enabled the students
1. The student know the electrochemical terms and concepts
2. The student understood different electrochemical reactions
3. The student learnt the phase equilibrium.
4. The student learnt different electrochemical cells and EMF measurements.
5. The student learnt fundamentals of surface chemistry

UNIT I
Phase Equilibria: Concept of phases, components and degrees of freedom, derivation of Gibbs Phase Rule for nonreactive and reactive systems; Clausius-Clapeyron equation and its applications to solid-liquid, liquid-vapour and solid-vapour equilibria, phase diagram for one component systems (H_2O and S), with applications. Phase diagrams for systems of solid-liquid equilibria involving eutectic, congruent and incongruent melting points.

UNIT II

Three component systems: triangular plots, water-chloroform-acetic acid system. Binary solutions: Gibbs-Duhem-Margules equation, its derivation and applications to fractional distillation of binary miscible liquids (ideal and non ideal), azeotropes, lever rule, partial miscibility of liquids, CST, miscible pairs, steam distillation. Nernst distribution law: its derivation and applications.

UNIT III

Electrochemical Cells: Rules of oxidation/reduction of ions based on half-cell potentials, applications of electrolysis in metallurgy and industry. Chemical cells, reversible and irreversible cells with examples. Electromotive force of a cell and its measurement, Nernst equation; Standard electrode (reduction) potential and its application to different kinds of half-cells.

UNIT IV

Application of EMF measurements in determining (i) free energy, enthalpy and entropy of a cell reaction, (ii) equilibrium constants, and (iii) pH values, using hydrogen, quinone-hydroquinone, glass and SbO/Sb_2O_3 electrodes. Concentration cells with and without transference, liquid junction potential; determination of activity coefficients and transference numbers. Qualitative discussion of potentiometric titrations (acid-base, redox, precipitation).

UNIT V

Surface chemistry: Physical adsorption, chemisorption, adsorption isotherms (Langmuir and Freundlich). nature of adsorbed state. Qualitative discussion of BET.

Suggested Readings:

Text Books:

1. B.R.Puri, L.R.Sharma, Madan S.Pathania, *Principles of physical chemistry*,(2013) Vishal publishing Co, Jalandhar
2. Madan, R.L. (2015). *Chemistry for Degree Students.* New Delhi: S. Chand and Company Pvt, Ltd.

Reference Books

1. Assael, M. J., Goodwin, A. R. H., Stamatoudis, M., Wakeham, W. A. & Will, S. (2011). *Commonly Asked Questions in Thermodynamics*. NY : CRC Press.
2. Zundhal, S.S. (2011). *Chemistry concepts and applications*. Cengage India • Ball, D. W. (2012). *Physical Chemistry*. Cengage India.
3. Levine, I. N. (2011). *Physical Chemistry*. 6th Ed. Tata McGraw-Hill.

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LECTURE PLAN

DEPARTMENT OF CHEMISTRY

S.No	Lecture Duration Period	Topics to be covered	Support Material/Page Nos
		UNIT I	
1	1	Phase equilibria:concept of phases, components and degrees of freedom	T1:797-799
2	1	Derivation of Gibbs phase rule for non reactive and reactive systems	T1:801-802
3	1	Clausius-clapeyron equation and its applications to solid-liquid, liquid-vapour and solid-vapour equilibria	T1:573-575
4	1	Phase diagram for water system	T1:803-805
5	1	Phase diagram for sulphur system	T1:809-810
6	1	Phase diagrams for systems of solid-liquid equilibria involving eutectic points	T1:816-817
7	1	Lead silver system	T1:816-817
8	1	Congruent melting point	T1:822-823
9	1	Incongruent melting points	T1:825-826

10	1	Revision and discussion of question papers	
	Total No of hours planned for Unit I-10		
	UNIT-II		
1	1	Three component systems-Traingular plots	T1:830-831
2	1	Water-chloroform-acetic acid system	T1:830-831
3	1	Binary solutions: Gibbs-Duhem-Margules equation, its derivation and applications to fractional distillation of binary miscible liquids	T2:753-755
4	1	Azeotropes	T1:762
5	1	Lever rule, partial miscibility of liquids	T1:764-765
6	1	CST, miscible pairs	T1:766-769
7	1	Steam distillation	T1:765-766
8	1	Nernst distribution law: its derivation	T1:834-836
9	1	Application of Nernst distribution law	T1:834-840
10	1	Revision and discussion of question papers	
	Total No of hours planned for Unit II-10		
	UNIT-III		
1	1	Electrochemical cells:Rules of oxidation/reduction of ions based on half-cell potentials	T1:925-926
2	1	Applications of electrolysis in metallurgy and industry	T1:925-927
3	1	Chemical cells	T1:926-927
4	1	Reversible and irreversible cells with examples	T1:930-931
5	1	Electromotive force of a cell and its measurement	T1:954-957
6	1	Nernst equation	T1:934-936
7	1	Standard electrode potential	T1:937-938

8	1	Application to different kinds of half-cells	T1:938-940
9	1	Application to different kinds of half-cells	T1:938-940
10	1	Revision and discussion of question papers	
	Total No of hours planned for Unit III-10		
	UNIT-IV		
1	1	Application of EMF measurements in determining free energy, enthalpy and entropy of a cell reaction	T1:930-932
2	1	Equilibrium constants	T1:933
3	1	P H values using hydrogen electrode	T1:959
4	1	Quinone-hydorquinone electrode	T1:959-960
5	1	SbO/Sb_2O_3 electrodes	T1:960-961
6	1	Concentration cells with and without transference	T1:943-950
7	1	Liquid junction potential, determination of activity coefficients and transference numbers	T1:950-951
8	1	Qualitative discussion of potentiometric titrations 9acid-base, redox, precipitation)	T1:962-969
9	1	Revision and discussion of question papers	
	Total No of hours planned for Unit IV-9		
	UNIT-V		
1	1	Surface chemistry:Physical adsorption, chemisorption	T1:1010-1011
2	1	Adsorption isotherms-Freundlich isotherm	T1:1013
3	1	Langmuir adsorption isotherm	T1:1015-1018
4	1	Nature of adsorbed state	T1:1012-1013
5	1	Qualitative discussion of BET	T1:1018-1020
6	1	Revision and discussion of question papers	
7	1	ESE question paper discussion	
8	1	ESE question paper discussion	

9	1	ESE question paper discussion	
	Total No of hours planned for Unit V-9		
Total planned hours	48		

SUPPORTING MATERIALS:
Text Books:

T1:B.R.Puri, L.R.Sharma and Madan. S Pathania,(2015), *Principles of Physical Chemistry*, Vishal Publishing Co, Jalandhar.

UNIT I

SYLLABUS

Phase Equilibria: Concept of phases, components and degrees of freedom, derivation of Gibbs phase Rule for nonreactive and reactive systems:Clausius-Claypeyron equation and its applications to solid-liquid, liquid-vapour and solid-vapour equilibria, Phase diagram for one component systems(H_2O and S),with applications. Phase diagrams for systems of solid-liquid equilibria involving eutectic,congruent and incongruent melting points.

PHASE EQUILIBRIA

Gibbs' phase rule was proposed by Josiah Willard Gibbs in his landmark paper titled On the Equilibrium of Heterogeneous Substances, published from 1875 to 1878. The rule applies to non-reactive multi-component heterogeneous systems in thermodynamic equilibrium and is given by the equality

$$F=C-P+1$$

where F is the number of degrees of freedom, C is the number of components and P is the number of phases in thermodynamic equilibrium with each other.

The number of degrees of freedom is the number of independent intensive variables, i.e. the largest number of thermodynamic parameters such as temperature or pressure that can be varied simultaneously and arbitrarily without affecting one another. An example of one-component system is a system involving one pure chemical, while two-component systems, such as mixtures of water and ethanol, have two chemically independent components, and so on. Typical phases are solids, liquids and gases.

Phase:It is defined as any homogeneous, physically distinct and mechanically separable portion of a system, which is separated from other such parts of the system by definite boundary surfaces in a system.

Component- It is defined as the smallest number of independently variable constituents taking part in the state of equilibrium by means of which the composition of each phase can be expressed directly or in the form of chemical equation.

Degree of freedom- It is defined as the minimum number of the independently variable factors such as the temperature, pressure and composition of the phases which must be arbitrarily specified in order to represent perfectly the condition of a system.

A phase is a form of matter that is homogeneous in chemical composition and physical state. Typical phases are solid, liquid and gas. Two immiscible liquids (or liquid mixtures with different compositions) separated by a distinct boundary are counted as two different phases, as are two immiscible solids.

The number of components (C) is the number of chemically independent constituents of the system, i.e. the minimum number of independent species necessary to define the composition of all phases of the system.[2] For examples see component (thermodynamics).

The number of degrees of freedom (F) in this context is the number of intensive variables which are independent of each other.

The basis for the rule (Atkins and de Paula,[2] justification 6.1) is that equilibrium between phases places a constraint on the intensive variables. More rigorously, since the phases are in thermodynamic equilibrium with each other, the chemical potentials of the phases must be equal. The number of equality relationships determines the number of degrees of freedom. For example, if the chemical potentials of a liquid and of its vapour depend on temperature (T) and pressure (p), the equality of chemical potentials will mean that each of those variables will be dependent on the other. Mathematically, the equation $\mu_{liq}(T, p) = \mu_{vap}(T, p)$, where μ = chemical potential, defines temperature as a function of pressure or vice versa. (Caution: do not confuse p = pressure with P = number of phases.)

To be more specific, the composition of each phase is determined by C − 1 intensive variables (such as mole fractions) in each phase. The total number of variables is (C − 1)P + 2, where the extra two are temperature T and pressure p. The number of constraints is C(P − 1), since the chemical potential of each component must be equal in all phases. Subtract the number of constraints from the number of variables to obtain the number of degrees of freedom as

$$F = (C - 1)P + 2 - C(P - 1) = C - P + 2.$$

The rule is valid provided the equilibrium between phases is not influenced by gravitational, electrical or magnetic forces, or by surface area, and only by temperature, pressure, and concentration.

CLAUSIUS CLAPEYRON EQUATION

The vaporization curves of most liquids have similar shape. The vapour pressure steadily increase as the temperature increases. A good approach is to find a mathematical model for the pressure increase as a function of temperature. Experiments showed that the pressure P, enthalpy of vaporization, ΔH_{vap}, and temperature T are related,

$$P = A \exp(- \Delta H_{vap} / R\,T)$$

where R (= 8.3145 J mol^{-1} K^{-1}) and A are the gas constant and unknown constant. This is known as the Clausius- Clapeyron equation. If P_1 and P_2 are the pressures at two temperatures T_1 and T_2, the equation has the form:

$$\text{In}\,\frac{P1}{P2} = \frac{\Delta H\ vap}{R}\,\frac{1}{T2} - \frac{1}{T1}$$

The Clausius-Clapeyron equation allows us to estimate the vapor pressure at another temperature, if the vapor pressure is known at some temperature, and if the enthalpy of vaporization is known.

Phase diagram for water

Water is a unique substance in many ways. One of these special properties is the fact that solid water (ice) is less dense than liquid water just above the freezing point. The phase diagram for water is shown in the Figure below .

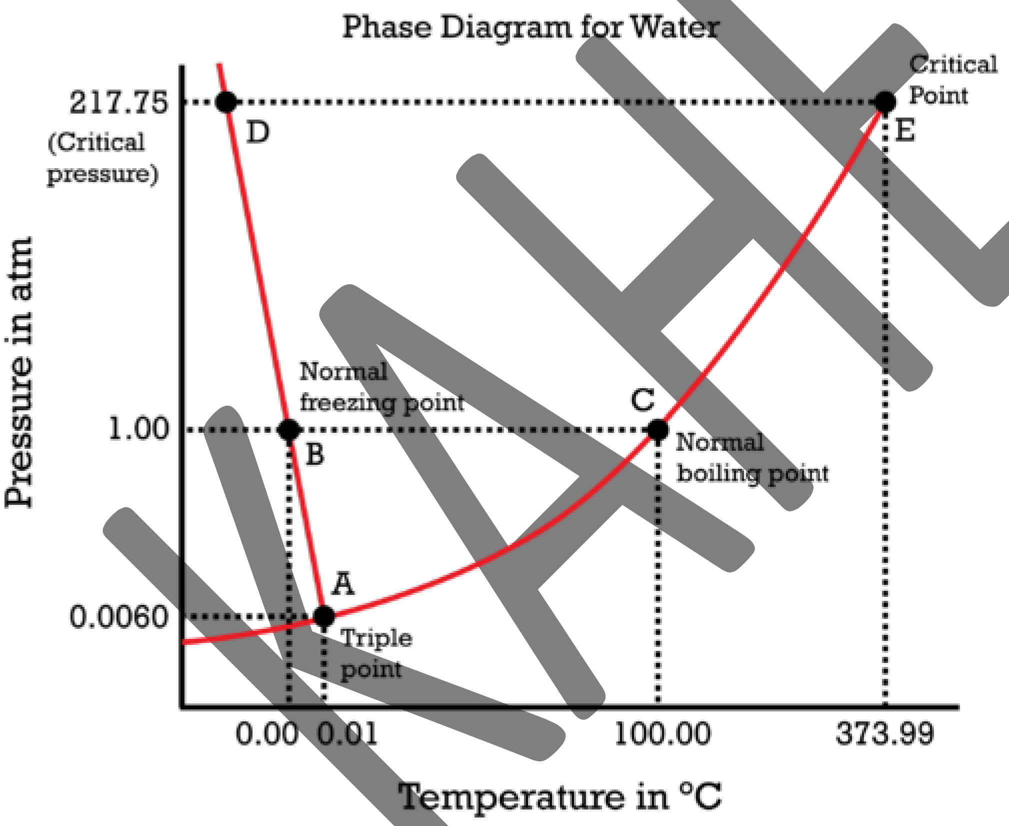


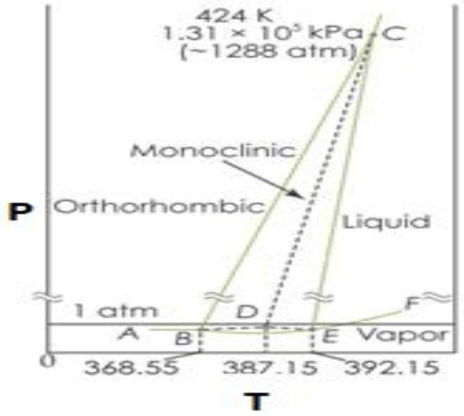
Figure 1

Notice one key difference between the general phase diagram and the phase diagram for water. In water's diagram, the slope of the line between the solid and liquid states is negative rather than positive. The reason is that water is an unusual substance in that its solid state is less dense than the liquid state. Ice floats in liquid water. Therefore, a pressure change has the opposite effect on those two phases. If ice is relatively near its melting point, it can be changed into liquid water by the application of pressure. The water molecules are actually closer together in the liquid phase than they are in the solid phase.

The point E in the above phase diagram labeled the critical point . At 373.99°C, particles of water in the gas phase are moving very, very rapidly. At any temperature higher than that, the gas phase cannot be made to liquefy, no matter how much pressure is applied to the gas.
The critical pressure (P_c) is the pressure that must be applied to the gas at the critical temperature in order to turn it into a liquid. For water, the critical pressure is very high, 217.75 atm. The critical point is the intersection point of the critical temperature and the critical pressure.

PHASE DIAGRAM OF SULPHUR

Phase Diagram of Sulphur In the following example, we will use the phase diagram of sulphur in the form of overhead projector (OHPI transparencies to illustrate such overlapping. Fig.6.1 shows the phase diagram of sulphur pressure . Except that a different presentation of the lines (eg. the dotted lines, the continuous lines and a solid dark line) is used to show the three fundamental parts of this phase diagram.



The curves AB, BC, CD, BE, CE, EG divide the diagram into four areas. Curve AB, the Vapour Pressure curve of SR. It shows the vapour pressure of solid rhombic sulphur (SR) at different temperatures. Along this curve the two phases SR and sulphur vapour (SV) are in equilibrium. The system SR/SV has one degree of freedom, F = C – P + 2 = 1 – 2 + 2 = 1 i.e., it is monovariant.

Curve BC, the Vapour Pressure curve of SM. It shows variation of the vapour pressure of monoclinic sulphur (SM) with temperature. SM and SV coexist in equilibrium along this curve. The system SM/SV is monovariant. Curve CD, the Vapour Pressure curve of SL. It depicts the variation of the vapour pressure of liquid sulphur (SL) with temperature. SL and SV are in equilibrium along CD. The two phase system SL/SV is monovariant. One atmosphere line meets this curve at a temperature (444.6ºC) which is the boiling point of sulphur. Curve BE, the Transition curve. It shows the effect of pressure on the transition temperature for SR and SM. As two solid phases are in equilibrium along the curve, the system SR/SM is monovariant. The transformation of SR and SM is accompanied by increase of volume (density of SR = 2.04; SM = 1.9) and absorption of heat i.e., SR + Q (heat energy) YZZ ZZX SM Thus the increase of pressure will shift the equilibrium to the left (Le Chatelier's Principle) and the transition temperature will, therefore, be raised. This is why the line BE slopes away from the pressure axis showing thereby that the transition temperature is raised with increase of pressure. Curve CE, the Fusion curve of SM. It represents the effect of pressure on the melting point of SM. The two phases in equilibrium along this curve are SM and SL. The system SM/SL is monovariant. As the melting or fusion of SM is accompanied by a slight increase of volume, the melting point will rise by increase of pressure (Le Chatelier's principle). Thus the curve CE slopes slightly away from the pressure axis. The curve ends at E because SM ceases to exist beyond this point. Curve EG, the Fusion curve for SR. Here the two phases in equilibrium are SR and SL. The number of phases being two, the system SR/SL is monovariant.

The Triple points B, C, E Triple point B. This is the meeting point of the three curves AB, BC and BE. Three phases, solid SR, solid SM and SV are in equilibrium at the point B. There being three phases and one component, the system SR/SM/SL is nonvariant. F = C – P + 2 = 1 – 3 + 2 = 0 At B, SR is changed to SM and the process is reversible. Thus the temperature corresponding to B is the transition temperature (95.6ºC). Triple point C. The curves BC, CD, CE meet at this point. The three phases in equilibrium are SM, SL and SV. There being three phases and one component, the system SM/SL/SV is nonvariant. The temperature corresponding to C as indicated on the phase diagram is 120ºC. This is the melting point of SM. Triple point E. The two lines CE and BE, having different inclinations away from the pressure axis, meet at E where a third line EG also joins. The three phases SR, SM and SL are in equilibrium and the system at the point E is nonvariant. This point gives the conditions of existence of the system SR/SM/SL at 155ºC and 1290 atmospheres pressure. (3) The Areas The phase diagram of the sulphur system has four areas or regions. These are labelled as rhombic sulphur, monoclinic sulphur, liquid sulphur and vapour. These represent single phase systems which have two degrees of freedom, F = C – P + 2 = 1 – 1 + 2 = 2 That is, each of the systems SR, SM, SL, and SV are bivariant.

Metastable Equilibria The change of SR to SM takes place very slowly. If enough time for the change is not allowed and SR is heated rapidly, it is possible to pass well above the transition point without getting SM. In that case, there being three phases (SR, SL, SV) only and one component, the phase diagram, like that of water system, will consist of three curves, one triple point and three areas. The dashed curve BF, the Vapour Pressure curve of metastable SR. This is a continuation of the vapour pressure curve AB of stable SR. The metastable phases SR and SV are in equilibrium along this curve. It is a monovariant system. The dashed curve CF, the Vapour Pressure curve of supercooled SL. On supercooling liquid sulphur, the dashed curve CF is obtained. It is, in fact, the back prolongation of DC. The curve CF represents the metastable equilibrium between supercooled SL and SV. Thus it may be designated as the vapour pressure curve of supercooled SL. It meets the dashed curve BF at F. The dashed curve FE, the Fusion curve of metastable SR. The two metastable phases SR and SL are in equilibrium along this curve and the system is monovariant. This shows that the melting point of metastable SR is increased with pressure. Beyond E, this curve depicts the conditions for the stable equilibrium

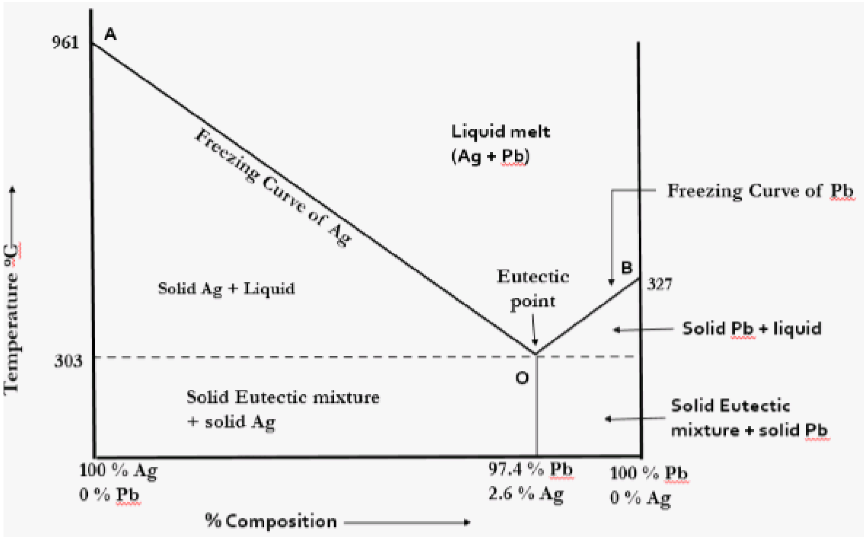
SR/SL as the metastable SR disappears. The metastable Triple point F. At this point, three metastable phases SR, SL and SV are in equilibrium. The system is a metastable triple point with no degree of freedom. The corresponding temperature is the melting point of metastable SR (114°C)

Phase diagrams for systems of solid liquid equilibria involving eutectic points.

Lead-Silver system

TWO–COMPONENT SYSTEMS When a single phase is present in a two-component system, the degree of freedom is three, F = 2 – 1 + 2 = 3 This means that three variables must be specified in order to describe the condition of the phase.

Phase diagram of Ag-Pb system



In two component systems there are four possible phases solid Ag, solid Pb, solution of Ag, + Pb and vapour. Since the pressure has no effect on equilibrium so the system can be represented by temperature concentration diagram at constant atmospheric pressure. As pressure is neglected the phase rule is called condensed phase rule.

1) Curve AO. It is a freezing point curve of Ag. Ag Co exists as solid and liquid. Melting point of Ag falls gradually on adding Pb till the lowest point is reached. The solution gets saturated with respective to lead.

2) Curve BO. It is a freezing point curve of Pb. At this curve the melting point gradually falls on the addition of Ag till lowest point it reach.

3) Point O. It is eutectic point. Here 3 phases co-exists and point O represents a fixed composition and system is in variant.

Below the temperature line of eutectic temperature, we have two regions.

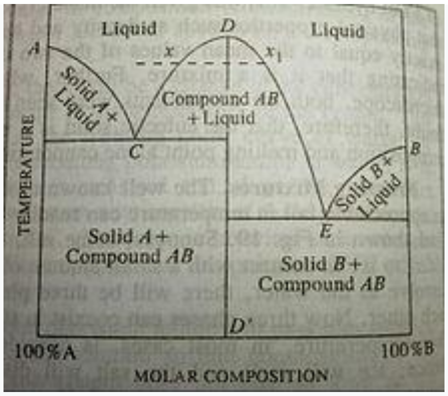
a) The region marked eutectic plus solid Ag in which crystalline silver and solid eutectic are stable.

b) The region marked eutectic plus solid Pb in which crystalline lead and solid eutectic are stable.

4) Area AOB. It represents solution of Pb Ag. On lowering temperature the lead begins to separate out till the point O is reached.

Phase diagrams for systems of congruent melting point

Congruent melting occurs during melting of a compound when the composition of the liquid that forms is the same as the composition of the solid. It can be contrasted with incongruent melting. This generally happens in two- component systems. To take a general case, let A and B be the two components and AB a stable solid compound formed by their chemical combination. If we draw a phase diagram for the system, we notice that there are three solid phases, namely A, B and compound AB. Accordingly, there will be three fusion or freezing point curves AC, BE and CDE for the three solid phases. In the phase diagram, we can notice that the top point D of the phase diagram is the congruent melting point of the compound AB because the solid and liquid phases now have the same composition. Evidently, at this temperature, the two-component system has become a one-component system because both solid and liquid phases contains only the compound AB.



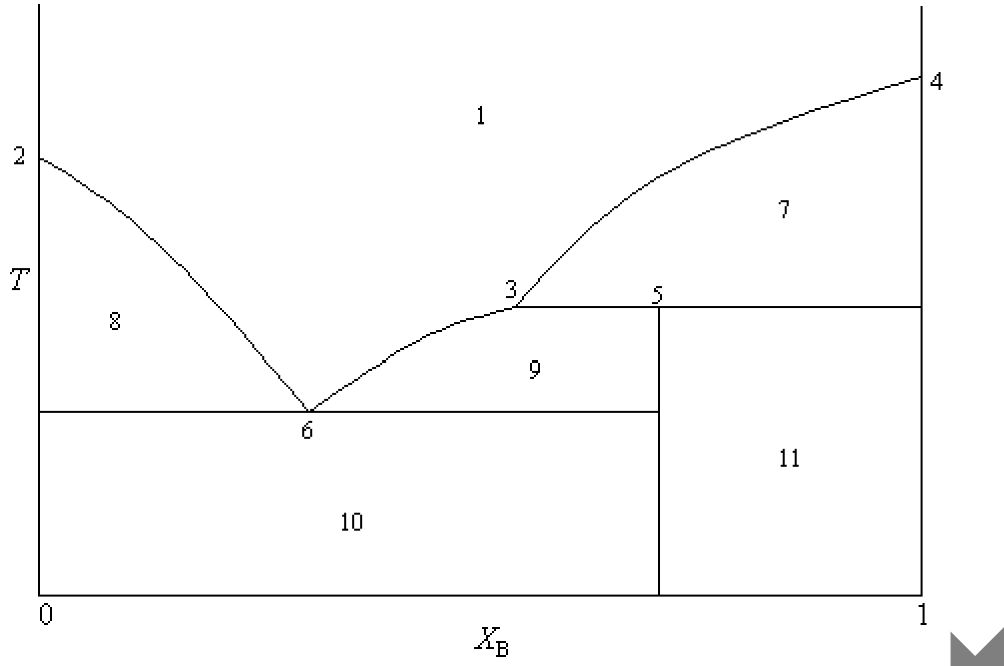
Phase Diagram for the Formation of a compound with congruent Melting Point

Congruent melting point represents a definite temperature just like the melting points of pure components. In the phase diagram, the congruent melting point D of compound AB lies above the melting points of pure components A and B. But it is not necessarily true. There are different types of systems known in which the congruent melting point is observed to be less than melting points of pure components.

This happens for inter-metallic compounds. For example, MgSi

Phase diagram for system of incongruent melting point

Incongruent Melting Point (melting with decomposition)



This phase diagram shows an incongruent melting point. The vertical line at point 5 represents formation of a compound. It looks like the composition of the compound is $X_B = 2/3$, from which we conclude using the previous arguments,

$$X_B = \frac{2}{3} = \frac{n_B}{n_A + n_B} = \frac{2}{1+2},$$

so that the compound is AB_2. Point 5 is the melting point of AB_2, but notice that melting AB_2 does not give liquid of the same composition. Rather, melting of AB_2gives liquid with the composition at point 3 and pure B(s). So the compound, AB_2 , melts and decomposes at the same time. An analysis of the points and regions is:

1 = liquid

2 = MP of A

3 = the peritectic point (we don't get a eutectic of AB_2 and B)

4 = MP of B

5 = the incongruent melting point of AB_2

6 = eutectic of A and AB_2

7 = liquid + B(s)

8 = A(s) and liquid

9 = liquid and AB_2(s)

10 = A(s) + AB_2(s)

11 = AB_2(s) + B(s)

POSSIBLE QUESTIONS

UNIT I

Part -A(20 MARKS)

(Q.NO 1 TO 20 Online Examinations)

Part-B(2 MARKS)

1.Define Phase.

2.Define Component.

3.Define Degree of freedom.

4.State reduced phase rule.

5.What is meant by triple point?

6.What is meant by eutectic point?

7.What is meant by congruent melting point?

8.What is meant by incongruent melting point?

Part- C(6 MARKS)

1.What is phase rule. Define the terms phase, component and degrees of freedom with suitable examples.

2.Explain the phase diagram of water system.

3.Derive Clausius-clapeyron equation and apply to solid-liquid, liquid-vapour and solid-vapour equilibria.

4.Explain simple eutectic system by taking lead-silver as an example

5.Explain incongruent melting point by taking sodium-potassium system.

6.Explain congruent melting point by taking Zn-Mg alloy system.

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(For the Canditates admitted from 2017 & onwards)

II B.Sc Chemistry

PHYSICAL CHEMISTRY III(Phase equilibria and chemical kinetics)

Unit I (PHASE EQUILIBRIA)

S.No	Question	Option1	Option 2	Option 3	Option 4	Answer
1	J.W.Gibbs enunciated the phase rule in	1876	1875	1874	1873	1876
2	A gas mixture constitutes	single phase	two phase	three phase	four phase	single phase
3	CCl4 and water forms	three phase	two phase	four phase	single phase	two phase
4	Benzene and alcohol constitutes	single phase	two phase	three phase	four phase	single phase
5	Calcium component is an example for	one component	two component	three component	four component	two component
6	Sulphur exist in	three phase	one phase	two phase	four phase	four phase
7	Sugar and water is and example for	two component	one component	three component	four component	two component
8	In a chemically reactive system, the number of components is given by	C=N-m-N-R	C=n-M-N-r	C=N-m-n-R	C=R-N-n-m	C=N-m-n-R
9	If F=0, the system is called	bivariant	univariant	invariant	trivariant	invariant
10	If F=1, the system is called	bivariant	univariant	invariant	trivariant	univariant
11	If F=2, the system is called	bivariant	univariant	invariant	trivariant	bivariant
12	The greater the number of components in a system,the ------------- is the number of degrees of freedom for a given number of phase	greater	lower	greater and lower	constant	greater
13	The greater the number of phases in a system,the ------------- is the number of degrees of freedom for a given number of phase	greater	smaller	greater and smaller	constant	smaller
14	For a given number of components, the number of phases is --------- when the number of degrees of	maximum	minimum	constant	maximum and minimum	maximum

	freedom is zero					
15	All the phases must be at the ------------temperature otherwise there will be flow of heat from one phase to another	greater	same	lower	same or lower	same
16	All the phases must be at the ------------pressure otherwise the volume of one phase will increase at the expense of another	greater	same	lower	same or lower	same
17	Gibbs phase rule equation for one component system is	F=C-P+2	F=C-P+1	F=C-P	F=P-C+2	F=C-P+2
18	Gibbs phase rule equation for two component system is	F=C-P+2	F=C-P+1	F=C-P	F=P-C+2	F=C-P+1
19	Water is an example for	three component	two component	one component	four component	one component
20	Sulphur is an example for	four component	two component	three component	one component	one component
21	The temperature at which all the three phases will be equilibrium is known as	eutectic point	congruent melting point	incongruent melting point	triple point	triple point
22	The temperature at which two solid and one liquid phase are in equilibrium is known as	incongruent melting point	congruent melting point	triple point	eutectic point	eutectic point
23	Carbon di-oxide is an example for	three component	two component	one component	four component	one component
24	Reduced phase rule is otherwise known as	condensed phase rule	phase rule equation	Gibbs phase rule equation	expanded phase rule	condensed phase rule
25	Lead-Silver is an example for	three component	two component	one component	four component	two component
26	A compound which melts sharply at a constant temperature into a liquid of the same composition as the solid is said to possess a	incongruent melting point	congruent melting point	d)triple point	eutectic point	congruent melting point
27	Ferric chloride -water is an example for	congruent melting point	triple point	incongruent melting point	eutectic point	congruent melting point
28	The compounds formed by the combination of two components, instead of melting congrently, decompose when heated giving a new solid phase and	incongruent melting point	congruent melting point	d)triple point	eutectic point	incongruent melting point

	a solution with a composition different from that of the solid phase. Such a compound is said to possess a					
29	Transition temperature is otherwise known as	peritectic temperature	melting temperature	sublimation temperature	vapour pressure temperature	peritectic temperature
30	Phase rule becomes -----------------for a three component system	F=5-P	F=4-P	F=3-P	F=2-P	F=5-P
31	Isothermal critical point is otherwise known as	plait point	melting point	sublimation point	plait and melting point	plait point
32	Acetic acid-chloroform and water is an example for	three component	two component	one component	four component	three component
33	An equation of fundamental importance which finds extensive application in one-component, two phase systems was derived independently by	Clausius	Einstein	Gibbs	Henry	Clausius
34	By supplying heat infinitesimally slowly to the system, it is possible to change any desired amount of the substance from the---------------------at the same temperature and pressure	liquid to solid	solid to vapour	liquid to vapour	solid to liquid	liquid to vapour
35	G is known as	enthalpy	entropy	free energy	work	free energy
36	Clapeyron equatiion gives change in pressure d P which accompany the change in-----------	temperature	volume	composition	temperature and composition	temperature
37	ΔHv is known as	molar heat of sublimation	molar heat of vaporisation	molar heat of fusion	molar heat of enthalpy	molar heat of vaporisation
38	ΔHf is known as	molar heat of sublimation	molar heat of vaporisation	molar heat of fusion	molar heat of enthalpy	molar heat of fusion
39	ΔS is known as	change in free energy	change in entropy	change in enthalpy	change in energy	change in entropy
40	Lewis introduce the concept of	fugacity	volume	pressure	temperature	fugacity
41	Calculate F in water↔vapour equilibria	1	2	3	4	1
42	Calculate F in solid↔liquid	2	1	3	4	1

	equilibria					
43	Calculate F in solid↔vapour equilibria	3	5	4	1	1
44	calculate F in ice↔liquid↔vapour equilibria	0	1	2	4	0
45	Pressure-temperature axis is drawn for-------------------	two component	one component	three component	one and two component	one component
46	Temperature-composition axis is drawn for	two component	one component	three component	one and two component	two component
47	The simplest three component systems are those in which a liquid system breaks down into ---------- phases	one	two	three	four	two
48	Application of the phase rule to a systme corresponding to a point in the two phase region gives F=	3	2	1	b)0	3
49	Tie lines are drawn in	one component	two component	three component	four component	three component
50	A system of two salts and water furnishes an example of a	two component	three component	one component	four component	three component
51	Bismuth-cadmium is an example for	incongruent melting point	congruent melting point	eutectic system	triple point	eutectic system
52	Potassium iodide-water is an example for	eutectic system	one component	b)three component	four component	eutectic system
53	The well known observation that the addition of salt to ice produces an appreciable fall in ------------------------------	temperature	pressure	pressure and temperature	composition	temperature
54	On adding increasing amounts of ferric chloride in ferric chloride -water system there will be fall in---------------	pressure	temperature	composition	temperature and composition	temperature
55	S1↔S2+-----------------	solution	S3	S2	S1+S2	solution
56	Number of phases in water↔solid is	1	2	3	4	2
57	Number of phases in water↔vapour is	1	2	3	4	2
58	Number of phases in solid ↔vapour is	2	3	1	0	1
59	Number of component in NaCl and water is	1	2	3	4	2

60	Number of component in alcohol and water is	2	1	3	4	2

UNIT II

SYLLABUS

Three Component Systems:Triangular plots, water-chloroform-acetic acid system. Binary solutions:Gibbs-Duhem-Margules equation, its derivation and applications to fractional distillation of binary miscible liquids(ideal and non ideal),azeotropes, lever rule, partial miscibility of liquids, CST, misicible pairs, steam distillation, Nernst distribution law:its derivation and applications

Three component systems

The system acetic acid - chloroform - water is one of the classical examples of partial miscibility in a ternary system, first studied by Wright, Thompson, and Leon in 1891 (1). Thanks to the subsequent workers Brancker, Hunter, and Nash (2), the equilibrium relations at 25" are very well known, as far as the compositions of equilibrium liquid layers are concerned. Nothing, however, is known about: (a) the solid-liquid equilibria at low temperatures; (b) equilibrium liquid compositions at temperatures other than 25"; (c) the critical phenomena, L1-V (L1 = chloroform layer) and L2-V (Lz = aqueous layer). So far no study has been made of critical phenomena in any system exhibiting partial miscibility in the liquid state and the results arrived at in this paper have general applicability to all systems of this kind. A previous paper (3) has dealt with the thermodynamics of this system, as exemplified by the vapor pressures and densities

Because of the chemical natures of the substances named in the title, formation of compounds or of solid solutions is inherently improbable and therefore the study of the freezing point curves was expected to yield little of interest. The study was, however, carried out for the binary systems chloroform - acetic acid and chloroform - water, and for the ternary system, using a double-junction copper-constantan thermocouple, a Brown Elektronik recorder, and liquid nitrogen as a coolant. The system acetic acid -water was previously studied by various workers (4) and the eutectic found to lie at 58.1% acetic acid and -28.5 to -27.0'. The eutectic of the chloroform - acetic acid system was found to lie at 91.8% CHCl3 by weight, and -67.5" (Fig. 1). In the system chloroform-water, the eutectic lies at O.lyo Hz0 and -64.0". The ternary eutectic was found to lie at -70" and 90.7% chloroform, 8.3% acetic acid, and 1.0% water. The eutectic trough leading from the acetic acid -water eutectic to the acetic acid -chloroform eutectic was determined experimentally.

Gibbs-Duhem –Margules equation

The Gibbs free energy can be defined in two different ways once by subtracting off combinations of entropy S, enthalpy H and temperature T and other as a sum of chemical potentials and amounts of species. The fact that they are equal gives a new relation known as "Gibbs-Duhem Relation." The Gibbs-Duhem relation helps us to calculate relationships between quantities as a system which remains in equilibrium. One example is the Clausius-Clapeyron equation which states that two phases at equilibrium with each other having equaled amount of a given substance must have exactly the same free energy i.e. it relates equilibrium changes in pressure to changes in temperature as a function of material parameters.

Deriving the Gibbs-Duhem equation from thermodynamics state equations is very easy. The Gibbs free energy G in equilibrium can be expressed in terms of thermodynamics as:

$dG=\mu_1\, dn_1 + n_1\, d\mu_1 + \mu_2\, dn_2 + n_2\, d\mu_2 \ldots\ldots\ldots\ldots \mu_j\, dn_j + n_j\, d\mu_j$

$= (\mu_1\, dn_1 + \mu_2\, dn_2 + \ldots\ldots\ldots\, \mu_j\, dn_j) + (n_1\, d\mu_1 + n_2\, d\mu_2 + \ldots\ldots\ldots\ldots\, n_j\, d\mu_j)$

At constant temperature and pressure, the above equation can be written as:

$\mathbf{n_1\, d\mu_1 + n_2\, d\mu_2 + \ldots\ldots\ldots\ldots n_j\, d\mu_j = 0}$

$\mathbf{\sum n_i\, d\mu_i = 0}$ ……………………..(1)

Because at constant temperature and pressure, $(\mu_1\, dn_1 + \mu_2\, dn_2 + \ldots\ldots\ldots\, \mu_j\, dn_j) = dG$

The equation (1) is known as the Gibbs-Duhem equation.

ApplicationsofGibbs-Duhemequation:

(i) Gibbs-duhem equation is helpful in calculating partial molar quantity of a binary mixture by measuring the composition of the mixture which depends on the total molar quantity.

(ii) Gibbs-duhem equation is helpful in calculating the partial vapor pressures by calculating the total vapor pressure. All these calculations require a curve-fitting procedure. Using tabulated experimental data the accuracy of the calculated quantities was found to be comparable to the accuracy of the original experimental data.

Lever rule

The **lever rule** is a tool used to determine weight percentages of each phase of a binary equilibrium phase diagram. It is used to determine the percent weight of liquid and solid phases for a given binary composition and temperature that is between the liquidus and solidus line.

In an alloy with two phases, α and β, which themselves contain two elements, A and B, the lever rule states that the weight percentage of the α phase is

$$X_\alpha = \frac{c-b}{a-b}$$

where

- a is the weight percentage of element B in the α phase
- b is the weight percentage of element B in the β phase
- c is the weight percentage of element B in the entire alloy

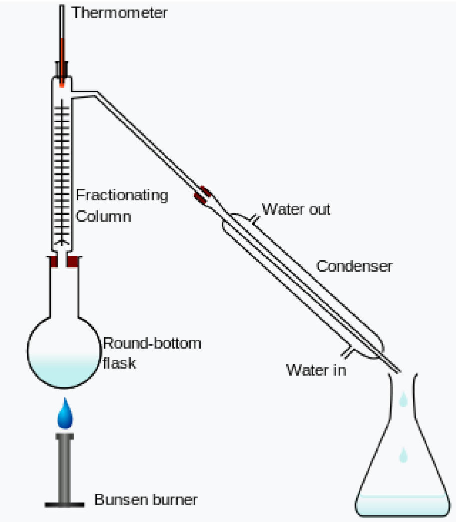
all at some fixed temperature.

Fractional distillation of binary miscible liquids

Fractional distillation is the separation of a mixture into its component parts, or fractions. Chemical compounds are separated by heating them to a temperature at which one or more fractions of the compound will vaporize. It uses distillation to fractionate. Generally the component parts have boiling points that differ by less than 25 °C from each other under a pressure of one atmosphere. If the difference in boiling points is greater than 25 °C, a simple distillation is typically used.

Fractional distillation in a laboratory makes use of common laboratory glassware and apparatuses, typically including a Bunsen burner, a round-bottomed flask and a condenser, as well as the single-purpose fractionating column.

Apparatus



Fractional distillation

An Erlenmeyer flask is used as a receiving flask. Here the distillation head and fractionating column are combined in one piece.[1]

- heat source, such as a hot plate with a bath, and ideally with a magnetic stirrer.
- distilling flask, typically a round-bottom flask
- receiving flask, often also a round-bottom flask
- fractionating column
- distillation head
- thermometer and adapter if needed
- condenser, such as a Liebig condenser or Allihn condenser
- vacuum adapter (not used in image to the right)
- boiling chips, also known as anti-bumping granules
- Standard laboratory glassware with ground glass joints, e.g. quickfit apparatus.

As an example consider the distillation of a mixture of water and ethanol. Ethanol boils at 78.4 °C while water boils at 100 °C. So, by heating the mixture, the most volatile component (ethanol) will concentrate to a greater degree in the vapor leaving the liquid. Some mixtures form azeotropes, where the mixture boils at a lower temperature than either component. In this example, a mixture of 96% ethanol and 4% water boils at 78.2 °C; the mixture is more volatile than pure ethanol. For this reason, ethanol cannot be completely purified by direct fractional distillation of ethanol-water mixtures.

The apparatus is assembled as in the diagram. (The diagram represents a batch apparatus as opposed to a continuous apparatus.) The mixture is put into the round bottomed flask along with a few anti-bumping granules (or a Teflon coated magnetic stirrer bar if using magnetic stirring), and the fractionating column is fitted into the top. The fractional distillation column is set up with the heat source at the bottom on the still pot. As the distance from the stillpot increases, a temperature gradient is formed in the column; it is coolest at the top and hottest at the bottom. As the mixed vapor ascends the temperature gradient, some of the vapor condenses and revaporizes along the temperature gradient. Each time the vapor condenses and vaporizes, the composition of the more volatile component in the vapor increases. This distills the vapor along the length of the column, and eventually the vapor is composed solely of the more volatile component (or an azeotrope). The vapor condenses on the glass platforms, known as trays, inside the column, and runs back down into the liquid below, refluxing distillate. The efficiency in terms of the amount of heating and time required to get fractionation can be improved by insulating the outside of the column in an insulator such as wool, aluminium foil or preferably a vacuum jacket. The hottest tray is at the bottom and the coolest is at the top. At steady state conditions, the vapor and liquid on each tray are at *equilibrium*. The most volatile component of the mixture exits as a gas at the top of the column. The vapor at the top of the column then passes into the condenser, which cools it down until it liquefies. The separation is more pure with the addition of more trays (to a practical limitation of heat, flow, etc.) Initially, the condensate will be close to the azeotropic composition, but when much of the ethanol has been drawn off, the condensate becomes gradually richer in water. The process continues until all the ethanol boils out of the mixture. This point can be recognized by the sharp rise in temperature shown on the thermometer.

The above explanation reflects the theoretical way fractionation works. Normal laboratory fractionation columns will be simple glass tubes (often vacuum-jacketed, and sometimes internally silvered) filled with a packing, often small glass helices of 4 to 7 mm diameter. Such a column can be calibrated by the distillation of a known mixture system to quantify the column in terms of number of theoretical trays. To improve fractionation the apparatus is set up to return condensate to the column by the use of some sort of reflux splitter (reflux wire, gago, Magnetic swinging bucket, etc.) - a typical careful fractionation would employ a reflux ratio of around 4:1 (4 parts returned condensate to 1 part condensate take off).

In laboratory distillation, several types of condensers are commonly found. The Liebig condenser is simply a straight tube within a water jacket, and is the simplest (and relatively least expensive) form of condenser. The Graham condenser is a spiral tube within a water jacket, and the Allihn condenser has a series of large and small constrictions on the inside tube, each increasing the surface area upon which the vapor constituents may condense.

Alternate set-ups may use a multi–outlet distillation receiver flask (referred to as a "cow" or "pig") to connect three or four receiving flasks to the condenser. By turning the cow or pig, the distillates can be channeled into any chosen receiver. Because the receiver does not have to be removed and replaced during the distillation process, this type of apparatus is useful when distilling under an inert atmosphere for air-sensitive chemicals or at reduced pressure. A Perkin triangle is an alternative apparatus often used in these situations because it allows isolation of the receiver from the rest of the system, but does require removing and reattaching a single receiver for each fraction.

Vacuum distillation systems operate at reduced pressure, thereby lowering the boiling points of the materials. Anti-bumping granules, however, become ineffective at reduced pressures.

Nernst distribution law

At constant temperature, a solute distributes itself between two immiscible solvents only in a particular ratio"This statement is a Nernst Distribution Law – i.e. the law that determines the relative distribution of a component that is soluble in two liquids, these liquids being immiscible or miscible to a limited extent. This law is one of the laws applying to ideal dilute solutions. It was discovered by W. Nernst in 1890. The Nernst distribution law states that, at equilibrium, the ratio of the concentrations of a third component in two liquid phases is constant. The law may be expressed in the form

$$c_1/c_2 = k$$

where c_1 and c_2 are the molar equilibrium concentrations of the third component in the first and second phase, respectively; the constant k is the distribution coefficient, which is temperature dependent.

The Nernst distribution law permits us to determine the most favorable conditions for the extraction of substances from solutions. If the dissolved compound in one of the solvents can associate:

$$nA \Leftrightarrow A_n \text{ nA}$$

than the ration c_1/c_2 is **not** stable at constant temperature

Partial miscibility of liquids

Only pairs of liquids that are completely miscible have been considered so far. Many pairs of liquids, however, are only partially miscible in one another, the degree of miscibility often depending strongly on temperature. In most cases, rising temperature produces enhanced solubility, but this is not always so. For example, at 50° C the solubility (weight percent) of *n*-butyl alcohol in water is 6.5 percent, whereas that of water in *n*-butyl alcohol is 22.4 percent. At 127° C, the upper consolute temperature, complete miscibility is attained: above 127° C the two liquids mix in all proportions, but below 127° C they show a miscibility gap. Thus, if *n*-butyl alcohol is added to water at 50° C, there is only one liquid phase until 6.5 weight percent of the mixture is alcohol; when more alcohol is added, a second liquid phase appears the composition of which is 22.4 weight percent water. When sufficient alcohol is present to make the overall composition 77.6 weight percent alcohol, the first phase disappears, and only one liquid phase remains. A qualitatively different example is the system water-triethylamine, which has a lower consolute temperature at 17° C. Below 17° C the two liquids are completely miscible, but at higher temperatures they are only partially miscible. Finally, it is possible, although rare, for a binary system to exhibit both upper and lower consolute temperatures. Above 128° C and below 49° C butyl glycol and water are completely miscible, but between these temperatures they do not mix in all proportions.

Colligative properties

Colligative properties depend only on the concentration of the solute, not on the identity of the solute molecules. The concept of an ideal solution, as expressed by Raoult's law, was already well-known during the last quarter of the 19th century, and it provided the early physical chemists with a powerful technique for measuring molecular weights. (Reliable measurements of molecular weights, in turn, provided important evidence for the modern atomic and molecular theory of matter.)

Rise in boiling point

It was observed that, whenever one component in a binary solution is present in large excess, the partial pressure of that component is correctly predicted by Raoult's law, even though the solution may exhibit departures from ideal behaviour in other respects. When Raoult's law is applied to the solvent of a very dilute solution containing a nonvolatile solute, it is possible to calculate the mole fraction of the solute from an experimental determination of the rise in boiling point that results when the solute is dissolved in the solvent. Since the separate weights of solute and solvent are readily measured, the procedure provides a simple experimental method for the determination of molecular weight. If a weighed amount of a nonvolatile substance, w_2, is dissolved in a weighed amount of a solvent, w_1, at constant pressure, the increase in the boiling temperature, ΔTb_1, the gas constant, R (derived from the gas laws), the heat of vaporization of the pure solvent per unit weight, l_1^{vap}, and the boiling temperature of pure solvent, Tb_1, are related in a simple product of ratios equal to the molecular weight of the solute, M_2.

Azeotropes

An **azeotrope** or a **constant boiling mixture** is a mixture of two or more liquids whose proportions cannot be altered by simple distillation.[1] This happens because when an azeotrope is boiled, the vapour has the same proportions of constituents as the unboiled mixture.

Because their composition is unchanged by distillation, azeotropes are also called (especially in older texts) **constant boiling mixtures**. The word azeotrope is derived from the Greek words (boil) and τρόπος (turning) combined with the prefix α- (no) to give the overall meaning, "no change on boiling". The term "azeotrope" was coined in 1911 by English chemist John Wade (1864–1912) and Richard William Merriman.

Many azeotropic mixtures of pairs of compounds are known,[4] and many azeotropes of three or more compounds are also known.[5] In such a case it is not possible to separate the components by fractional distillation. There are two types of azeotropes: minimum boiling azeotrope and maximum boiling azeotrope. A solution that shows greater positive deviation from Raoult's law forms a minimum boiling azeotrope at a specific composition. For example, an ethanol-water mixture (obtained by fermentation of sugars)

Steam distillation

Steam distillation is a special type of distillation (a separation process) for temperature sensitive materials like natural aromatic compounds. It once was a popular laboratory method for purification of organic compounds, but has become obsolete by vacuum distillation. Steam distillation remains important in certain industrial sectors.[1]

Many organic compounds tend to decompose at high sustained temperatures. Separation by distillation at the normal (1 atmosphere) boiling points is not an option, so water or steam is introduced into the distillation apparatus. The water vapor carries small amounts of the vaporized compounds to the condensation flask, where the condensed liquid phase separates, allowing for easy collection. This process effectively allows for distillation at lower temperatures, reducing the deterioration of the desired products. If the substances to be distilled are very sensitive to heat, steam distillation may be applied under reduced pressure, thereby reducing the operating temperature further.

After distillation the vapors are condensed. Usually the immediate product is a two-phase system of water and the organic distillate, allowing for separation of the components by decantation, partitioning or other suitable methods.

Applications

A boiling water distiller. Boiling tank on top and holding tank on the bottom.

Steam distillation is employed in the isolation of essential oils, for use in perfumes, for example. In this method, steam is passed through the plant material containing the desired oils. Eucalyptus oil and orange oil are obtained by this method on an industrial scale. Steam distillation is also sometimes used to separate intermediate or final products during the synthesis of complex organic compounds.

Steam distillation is also widely used in petroleum refineries and petrochemical plants where it is commonly referred to as "steam stripping".

Steam distillation also is an important means of separating fatty acids from mixtures and for treating crude products such as tall oils to extract and separate fatty acids, soaps and other commercially valuable organic compounds.

Miscible pairs

Miscibility is the property of substances to mix in all proportions (that is, to fully dissolve in each other at any concentration), forming a homogeneous solution. The term is most often applied to liquids, but applies also to solids and gases. Water and ethanol, for example, are miscible because they mix in all proportions.

By contrast, substances are said to be immiscible if a significant proportion does not form a solution. Otherwise, the substances are considered miscible. For example, butanone is significantly soluble in water, but these two solvents are not miscible because they are not soluble in all proportions.

Determination

Miscibility of two materials is often determined optically. When the two miscible liquids are combined, the resulting liquid is clear. If the mixture is cloudy the two materials are immiscible. Care must be taken with this determination. If the indices of refraction of the two materials are similar, an immiscible mixture may be clear and give an incorrect determination that the two liquids are miscible.

POSSIBLE QUESTIONS

UNIT II

Part-A(20 MARKS)

(Q.NO 1 TO 20 Online Examination)

Part-B(2 MARKS)

1.What is known as CST?

2.What is known as UCST?

3.What is known as LCST?

4.State Nernst distribution law.

5.Mention few examples for three component system.

6.Mention the applications of Nernst distribution law.

7.What are miscible pairs.

Part-C(6 MARKS)

1.Derive Gibbs- Duhem-Margules equation and mention its applications.

2.Derive Nernst distribution law and mention its important applications

3.Derive Gibbs-Duhem Margules equation.

4.Explain fractional distillation in detail

5.write notes on
(i)Fractional distillation
(ii)Steam distillation

6.What is triangular plot. Apply phase rule to water-chloroform-acetic acid system.

7.Analyse type I, type II and type III fractional distillation

KARPAGAM ACADEMY OF HIGHER EDUCATION

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

COIMBATORE-641 021

(For the Canditates admitted from 2017 & onwards)

II B.Sc Chemistry

PHYSICAL CHEMISTRY III(Phase equilibria and chemical kinetics)

Unit II (THREE COMPONENT SYSTEMS)

S.No	Question	Option1	Option 2	Option 3	Option 4	Answer
1	For a three component system, the phase rule becomes	F=4-P	F=5-P	F=3-P	F=2-P	F=5-P
2	The simplest three component systems are those in which a liquid system breaks down into	two phases	three phases	four phases	five phases	two phases
3	Isothermal critical point is otherwise known as	eutectic point	triple point	plait point	melting point	plait point
4	Application of the phase rule to a system corresponding to a point in the two phase region gives	F=2	F=3	F=1	F=0	F=3
5	Tie lines are represented in	two component sytem	one component system	three component system	four component system	three component system
6	A system of two salts and water furnishes an example of a ---------------------	three component	two component	one component	four component	three component

	--- system involving solids and liquids					
7	An ------------------ solution is defined as the one in which the activity of each component is equal to its mole fraction under all conditions of temperature, pressure and concentration	ideal	real	ideal and real	non-ideal	ideal
8	A binary solution of components A and B in equilibrium with their vapours, at constant temperature and pressure is given by	Gibbs equation	Margules equation	Gibbs-Duhem-Margules equation	Duhem equation	Gibbs-Duhem-Margules equation
9	nA and n B are the numbers of moles of components A and B	Gibbs equation	Margules equation	Gibbs-Duhem-Margules equation	Duhem equation	Gibbs-Duhem-Margules equation
10	In Gibbs-Duhem-Margules equation, if the vapour behaves as an ideal gas,the fugacity can be replaced by	temperature	pressure	concentration	vapour pressure	vapour pressure
11	The process of separating	steam distillation	fractional distillation	distillation	condensation	fractional distillation

	mixtures by repeated distillation and condensation is known as					
12	In type I of fractional distillation	possible to isolate both the pure consituents from each other	not possible to isolate both the pure consituents from each other	possible as well as not possible to isolate both the pure constituents from each other	possible to isolate one constituent	possible to isolate both the pure consituents from each other
13	In type II of fractional distillation	possible to isolate both the pure consituents from each other	not possible to isolate both the pure consituents from each other	possible as well as not possible to isolate both the pure constituents from each other	possible to isolate one constituent	possible to isolate one constituent
14	In type III of fractional distillation	possible to isolate both the pure consituents from each other	not possible to isolate both the pure consituents from each other	possible as well as not possible to isolate both the pure constituents from each other	possible to isolate one constituent	possible to isolate one constituent
15	In type II constant boiling mixture obtained as	residue	distillate	residue and distillate	vapour	distillate
16	In type II Pure A or Pure B obtained as	residue	distillate	residue and distillate	vapour	residue
17	In type III constant boiling mixture obtained as	residue	distillate	residue and distillate	vapour	residue
18	In type III pure A or pure B obtained as	residue	distillate	residue and distillate	vapour	distillate

19	The constant boiling point in type II is	minimum	maximum	increases and then decreases	decreases and then increases	minimum
20	The constant boiling point in type III is	minimum	maximum	increases and then decreases	decreases and then increases	maximum
21	Pure water boils at	100 degree celsius	50 degree celsius	120 degree celsius	d0110 degree celsius	100 degree celsius
22	pure hydrogen chloride boils at	65 degree celsius	100 degree celsius	-85 degree celsius	85 degree celsius	-85 degree celsius
23	In water-ethanol system, the constant boiling mixture correspoding to the point has a composition of	100% ethanol	95.6%ethanol	93%ethanol	94%ethanol	95.6%ethanol
24	Ethanol in type II fractional distillation is obtained as	residue	distillate	residue and distillate	vapour	distillate
25	pure water is obtained as	residue	distillate	residue and distillate	vapour	residue
26	Ethanol boils at----------------------- under a presuure of 1 atmosphere	78.13 degree celsius	80 degree celsius	100 degree celsius	20 degree celsius	78.13 degree celsius
27	Water-ethanol system is an example for	type I	type II	type III	type IV	type II
28	Mixture of acetone and chloroform is an example for	type I	type II	type III	type IV	type III
29	Mixture of water and	type I	type II	type III	type IV	type III

	hydrogen chloride are example for					
30	Mixture of water and nitric acid are example for	type I	type II	type III	type IV	type III
31	Mixture like a pure chemical compound boils at a constant temperature and distils over completely at the same temperature without change in composition is called	azeotropic mixture	liquid mixture	solid mixture	gaseous mixture	azeotropic mixture
32	azeotropic mixture is otherwise known as	constant boiling mixture	liquid mixture	gaseous mixture	solid mixture	constant boiling mixture
33	maximum boling point is said to be	high volatile	least volatile	no volatile	volatility increases and then decreases	least volatile
34	minimum boiling point is said to be	high volatile	least volatile	no volatile	volatility increases and then decreases	high volatile
35	------------------------ are used in fractional distillation	fractionating column	distillation column	condensation column	fractionating and distillation column	fractionating column
36	compostion of liquid and vapour phases can be determined with the help of	phase rule	lever's rule	gibbs rule	charles rule	lever's rule
37	The masses of the liquids in	fractional distillation	steam distillation	fractional and steam	column distillation	steam distillation

	the distillate will be in the ratio of their vapour pressures and molar masses			distillation		
38	Any mixture of two immiscible liquids will boil at a temperature ---------------------than that at which any pure constituent of the misture boils	lower	higher	lower and higher	constant	lower
39	The boiling point of aniline is	180 degree celsius	100 degree celsius	120 degree celsius	85 degree celsius	180 degree celsius
40	A compound immisicible or nearly so in water is	benzene	aniline	phenol	amide	aniline
41	partial miscibility increases on increasing the temperature	phenol-water	water-nicotine			phenol-water
42	partial miscibility increases on lowering the temperature	phenol-water	$(C_2H_5)_2$ NH-H_2O	water-picotine	ether-water system	$(C_2H_5)_2$ NH-H_2O
43	parital misicibility increases on both rasing as well as lowering the temperature	water-nicotine	phenol-water	water-benzene	ether-water system	water-nicotine
44	complete miscibility temperature cannot be	water-benzene	phenol-water	ether-water	water-nicotine	ether-water

	obtained					
45	The temperature above which a pair of partially miscible liquids become miscible in all proportions is called	lower critical solution temperatue	higher critical solution tmeperature	critical solution temperature	critical temperature	critical solution temperature
46	critical solution temperature is otherwise known as	consolute temperture	solubility temperature	misicibility temperature	melting temperature	consolute temperture
47	Liquid pairs attain complete misicibility above a certain temperature in which case they are said to have the	LCST	UCST	b)CST	ST	UCST
48	Liquid pairs show complete miscibility below a certain temperature when they are said to have	LCST	UCST	b)CST	ST	LCST
49	The composition points of the conjugate phases are joined by	tie lines	conjugate lines	upper lines	lower lines	tie lines
50	The two phases having dissimilar composition in equilibrium	conjugate phase	non-conjugate phase	tie phase	gibbs phase	conjugate phase

	with each other at a given temperature constitute a pair of					
51	Solutions of different composition coexisting with one another are termed as	conjugate solutions	non-conjugate solutions	mixed solutions	non-mixed solutions	conjugate solutions
52	aniline-hexane is an example for	partial miscibility increases on increasing the temperature	partial miscibility increases on lowering the temperature	parital misicibility increases on both rasing as well as lowering the temperature	complete miscibility temperature cannot be obtained	partial miscibility increases on increasing the temperature
53	triethylamine-water system is an example for	partial miscibility increases on increasing the temperature	partial miscibility increases on lowering the temperature	parital misicibility increases on both rasing as well as lowering the temperature	complete miscibility temperature cannot be obtained	partial miscibility increases on lowering the temperature
54	partition coefficient is otherwise known as	distribution coefficient	diffusion coefficient	viscosity coefficient	freezing coefficient	distribution coefficient
55	The Nernst distribution law is calid only for ---------------------of single molecules in the two phases	concentrations	pressure	b)volume	temperature	concentrations
56	benzene-water	mutually insoluble	mutually soluble	insoluble	completely soluble	mutually insoluble
57	The mutual solubility is not altered by the presence of the solute	aniline-water	benzene-water	amide-water	chloroform-water	benzene-water

	in					
58	complex ions are studied in	nernst distribution law	gibbs distribution law	einstein distribution law	albert distribution law	nernst distribution law
59	One of the important validity in Nernst distribution law is	constant temperature	constant pressure	constant volume	constant composition	constant temperature
60	Existence of similar molecular species in the two phases in----------- with other	contact	no contact	contact and no contact	bonded	contact

UNIT III

SYLLABUS

Electrochemical Cells:Rules of oxidation/reduction of ions based on half-cell potentials, applications of electrolysis in metallurgy and industry. Chemical cells, reversible and irreversible cells with examples. Electromotive force of a cell and its measurement. Nernst equation; Standard electrode(reduction)potential and its application to different kinds of half cells.

ELECTROCHEMICAL CELLS

Rules of oxidation/reduction of ions based on half-cell potentials

A **half-cell** is a structure that contains a conductive electrode and a surrounding conductive electrolyte separated by a naturally occurring Helmholtz double layer. Chemical reactions within this layer momentarily pump electric charges between the electrode and the electrolyte, resulting in a potential difference between the electrode and the electrolyte. The typical anode reaction involves a metal atom in the electrode dissolved and transported as a positive ion across the double layer, causing the electrolyte to acquire a net positive charge while the electrode acquires a net negative charge. The growing potential difference creates an intense electric field within the double layer, and the potential rises in value until the field halts the net charge-pumping reactions. This self-limiting action occurs almost instantly in an isolated half-cell; in applications two dissimilar half-cells are appropriately connected to constitute a Galvanic cell.

A standard half-cell, used in electrochemistry, consists of a metal electrode in a 1 molar (1 mol/L) aqueous solution of the metal's salt, at 298 kelvin (25 °C).[1] The electrochemical series, which consists of standard electrode potentials and is closely related to the reactivity series, was generated by measuring the difference in potential between the metal half-cell in a circuit with a standard hydrogen half-cell, connected by a salt bridge.

The standard hydrogen half-cell:

$2H^+(aq) + 2e^- \rightarrow H_2(g)$

The half-cells of a Daniell cell:

Original equation

$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

Half-cell (anode) of Zn

$Zn \rightarrow Zn^{2+} + 2e^-$

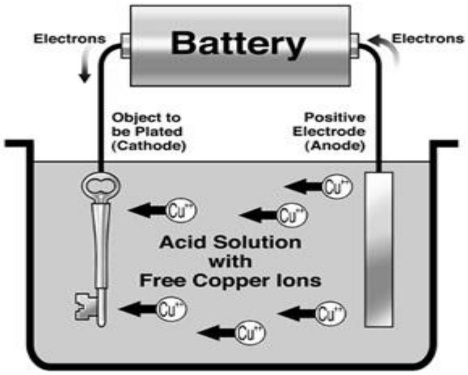
Half-cell (cathode) of Cu

$Cu^{2+} + 2e^- \rightarrow Cu$

Applications of electrolysis in metallurgy and industry

Electroplating is used to coat one metal with another metal by using electrolysis. Electroplating is usually done to improve the appearance of the metal or prevent the corrosion of the metal.

Chromium plating is used to prevent iron from rusting.



The cathode is the object to be plated, while anode is the desired metal to coat the object. The electrolyte solution must contain ions of the same metal for plating. During electrolysis, the anode will dissolve into the solution. The ions produced will migrate to the cathode where they are discharged and deposited as a layer on the cathode.

It is important to ensure that the cathode is electrically conductive. (If not, the electrolysis does not work.)

Example:Silver Plating

Electrodes: Silver anode, Cathode is object to be plated with silver

Electrolyte: Solution of soluble silver salt. (E.g. Silver nitrate, $AgNO_3(aq)AgNO_3(aq)$)

$$AgNO_3(aq)\leftrightarrow Ag^{+}(aq)+NO^{-3}(aq)$$

$$H_2O(l)\leftrightarrow H^{+}(aq)+OH^{-}(aq)$$

Ions present in solution: $Ag^{+}Ag^{+}$, $H^{+}H^{+}$, $NO^{-3}NO^{-3}$, $OH^{-}OH^{-}$

Reaction at CATHODE:

- Ag^{+} and $H^{+}$is attracted to the cathode.
- Ag^{+} is preferentially discharged.
- Silver metal is deposited on the cathode.
- $Ag^{+}(aq)+e- \longrightarrow Ag(s)$

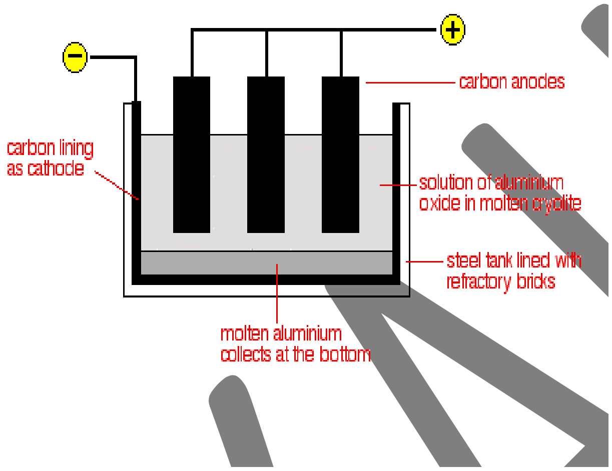
Reaction at ANODE:

- $NO^{-3}$and OH^{-} is attracted to the anode.
- Neither NO^{-3} nor OH^{-} is discharged.
- Each silver atom loses one electron to form one Ag^{+} ion.
- The silver anode dissolves into the solution.

- $Ag(s) \rightarrow Ag^{+}(aq) + e^{-}$

Extraction Of Reactive Metals

Reactive metals are the metals that occupy the top positions in the electrochemical series. Metals that are higher than zinc in the electrochemical series are extracted using electrolysis. These very reactive metals cannot be extracted by other metals such as reduction with carbon. The reactive metals are obtained by electrolyzing a molten ionic compound of metal.



Example:Extraction Of Aluminium

Aluminium is extracted from aluminium oxide (Al_2O_3) or known as bauxite.

The electrolytic cell is an iron tank lined with carbon, which acts as the cathode. The anodes are blocks of carbon dipped into the electrolyte. The electrolyte is a solution of molten aluminum oxide in molten cryolite. Cryolite acts as a solvent to dissolve aluminium oxide and as an impurity to lower the melting point of aluminium oxide. The electrolytic cell is maintained at around 900 ^{0}C

Electrodes: Carbon

Ions present in electrolyte: Al^{+3}, O^{2-}

Reaction at cathode: $Al^{+3}(l) + 3e^{-} \longrightarrow Al(l)$

Reaction at anode: $2O^{2-}(l) \rightarrow O_2(g) + 4e^{-}$

Aluminium ions are discharged at the cathode, forming a pool of molten aluminium at the bottom of the tank.

At high temperature, oxygen reacts with the carbon anode to form carbon dioxide gas. Hence, the anodes are slowly burnt away as carbon dioxide gas and needs to be replaced frequently.

Chemical cells

An **electrochemical cell** is a device capable of either generating electrical energy from chemical reactions or facilitating chemical reactions through the introduction of electrical energy. A common example of an electrochemical cell is a standard 1.5 - volt cell meant for consumer use. This type of device is known as a single galvanic cell. A battery consists of one or more cells, connected in either parallel or series pattern.

Equilibrium reaction

Each half-cell has a characteristic voltage. Various choices of substances for each half-cell give different potential differences. Each reaction is undergoing an equilibrium reaction between different oxidation states of the ions: When equilibrium is reached, the cell cannot provide further voltage. In the half-cell that is undergoing oxidation, the closer the equilibrium lies to the ion/atom with the more positive oxidation state the more potential this reaction will provide. Likewise, in the reduction reaction, the closer the equilibrium lies to the ion/atom with the more negative oxidation state the higher the potential.

Cell potential

The cell potential can be predicted through the use of electrode potentials (the voltages of each half-cell). These half-cell potentials are defined relative to the assignment of 0 volts to the standard hydrogen electrode (SHE). (See table of standard electrode potentials). The difference in voltage between electrode potentials gives a prediction for the potential measured. When calculating the difference in voltage, one must first rewrite the half-cell reaction equations to obtain a balanced oxidation-reduction equation.

1. Reverse the reduction reaction with the smallest potential (to create an oxidation reaction/ overall positive cell potential)
2. Half-reactions must be multiplied by integers to achieve electron balance.

Note that the cell potential does not change when the reaction is multiplied by a constant.

Cell potentials have a possible range of roughly zero to 6 volts. Cells using water-based electrolytes are usually limited to cell potentials less than about 2.5 volts, because the very powerful oxidizing and reducing agents that would be required to produce a higher cell potential tend to react with the water. Higher cell potentials are possible with cells using other solvents instead of water. For instance, lithium cells with a voltage of 3 volts are commonly available.

The cell potential depends on the concentration of the reactants, as well as their type. As the cell is discharged, the concentration of the reactants decreases and the cell potential also decreases

Reversible and irreversible cells with examples

A cell is said to be reversible if the following two conditions are fulfilled

(i) The chemical reaction of the cell stops when an exactly equal external emf is applied.

(ii) The chemical reaction of the cell is reversed and the current flows in opposite direction when the external emf is slightly higher than that of the cell. Any other cell, which does not obey the above two conditions, is termed as irreversible. Daniell cell is reversible but $Zn| H_2SO_4 | Ag$ cell is irreversible in nature

(5) **Types of electrochemical cells:** Two main types of electrochemical cells have been reported, these are,

(i) **Chemical cells:** The cells in which electrical energy is produced from the energy change accompanying a chemical reaction or a physical process are known as chemical cells. Chemical cells are of two types,

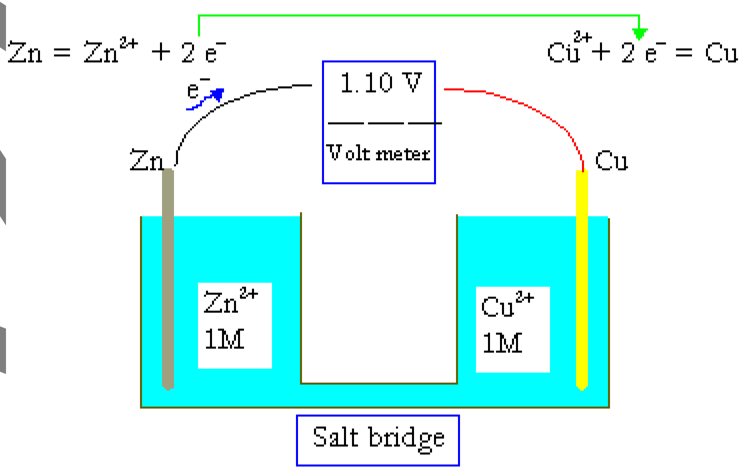
(a) **Chemical cells without transference:** In this type of chemical cells, the liquid junction potential is neglected or the transference number is not taken into consideration. In these cells, one electrode is reversible to cations while the other is reversible to the anions of the electrolyte.

Electromotive force of a cell and its measurement

The **electromotive force (EMF)** is the maximum potential difference between two electrodes of a galvanic or voltaic cell. This quantity is related to the tendency for an element, a compound or an ion to acquire (i.e. gain) or release (loss) electrons. For example, the maximum potential between Zn and Cu of a well known cell

$Zn\ (s)\ |\ Zn^{2+}\ (1\ M)\ ||\ Cu^{2+}\ (1\ M)\ |\ Cu\ (s)$

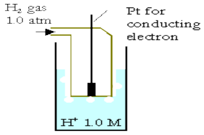
has been measured to be 1.100 V. A concentration of 1 M in an ideal solution is defined as the standard condition, and 1.100 V is thus the **standard electromotive force, DE^o,** or **standard cell potential** for the Zn-Cu galvanic cell.



The standard cell potential, DE^o, of the a galvanic cell can be evaluated from the standard reduction potentials of the two half cells E^o. The reduction potentials are measured against the standard hydrogen electrode (SHE):

$Pt\ (s)\ |\ H_2\ (g,\ 1.0\ atm)\ |\ H^+\ (1.0\ M).$

Its reduction potential or oxidation potential is defined to be exactly zero.



Standard Hydrogen Electrode (SHE)

The reduction potentials of all other half-cells measured in volts against the SHE are the difference in electrical potential energy per coulomb of charge.

Note that the unit for energy J = Coulomb volt, and the Gibbs free energy G is the product of charge q and potential difference E:

G in J = q E in C V

for electric energy calculations.

Evaluating Standard Cell Potential DE° of Galvanic Cells

A galvanic cell consists of two half-cells. The convention in writing such a cell is to put the (reduction) cathode on the right-hand side, and the (oxidation) anode on the left-hand side. For example, the cell

$$\mathrm{Pt} \mid \mathrm{H_2} \mid \mathrm{H^+} \parallel \mathrm{Zn^{2+}} \mid \mathrm{Zn}$$

consists of the oxidation and reduction reactions:

$H_2 = 2\,e + 2\,H^+$ . . . . anode (oxidation) reaction
$Zn^{2+} + 2\,e = Zn$ . . . . cathode (reduction) reaction

If the concentrations of H^+ and Zn^{2+} ions are 1.0 M and the pressure of H_2 is 1.0 atm, the voltage difference between the two electrodes would be -0.763 V (the Zn electrode being the negative electrode). The conditions specified above are called the **standard conditions** and the EMF so obtained is **the standard reduction potential**.

Note that the above cell is in reverse order compared to that given in many textbooks, but this arrangement gives the standard reduction potentials directly, because the Zn half cell is a reduction half-cell. The negative voltage indicates that the reverse chemical reaction is spontaneous. This corresponds to the fact that Zn metal reacts with an acid to produce H_2 gas. As another example, the cell

$Pt \mid H_2 \mid H^+ \parallel Cu^+ \mid Cu$

consists of an oxidation and a reduction reaction:

$H_2 \leftrightarrow 2\ e + 2\ H^+$ . . . . anode reaction
$Cu^{2+} + 2\ e \leftrightarrow Cu$ . . . . cathode reaction

and the standard cell potential is 0.337 V. The positive potential indicates a spontaneous reaction,

$Cu^{2+} + H_2 \leftrightarrow Cu + 2\ H^+$

but the potential is so small that the reaction is too slow to be observed.

Example 1

What is the potential for the cell

$Zn \mid Zn^{2+}(1.0\ M) \parallel Cu^{2+}(1.0\ M) \mid Cu$

Solution

From a table of standard reduction potentials we have the following values

$Cu^{2+} + 2\ e \leftrightarrow Cu$ . . . $E° = 0.337$ - - - (1)
$Zn \leftrightarrow Zn^{2+} + 2\ e$ . . . $E^* = 0.763$ - - - (2)

Add (1) and (2) to yield

$Zn + Cu^{2+} \leftrightarrow Zn^{2+} + Cu$ . . . DE° = E° + E* = 1.100 V

Note that E* is the oxidation standard potential, and E° is the reduction standard potential, E* = -E°. The standard cell potential is represented by dE°.

Discussion

The positive potential confirms your observation that zinc metal reacts with cupric ions in solution to produce copper metal.

Example 2

What is the potential for the cell

$Ag \mid Ag^+(1.0\ M) \parallel Li^+(1.0\ M) \mid Li$

Solution

From the table of standard reduction potentials, you find

$Li^+ + e \leftrightarrow Li$ . . . E° = -3.045, - - - (3)
$Ag \leftrightarrow Ag^+ + e$ . . . E* -0.799, - - - (4)

According to the convention of the cell, the reduction reaction is on the right. The cell on your left-hand side is an oxidation process. Thus, you add (4) and (3) to obtain

$Li^+ + Ag \leftrightarrow Ag^+ + Li$ . . . dE° = -3.844 V

Discussion

The negative potential indicates that the reverse reaction should be spontaneous.

Some calculators use a lithium battery. The atomic weight of Li is 6.94, much lighter than Zn (65.4).

Summary

- The **electromotive force (EMF)** is the maximum potential difference between two electrodes of a galvanic or voltaic cell.
- The standard reduction potential of M^{n+}, 1 M / M couple is the standard cell potential of the galvanic cell:

  $$Pt \mid H_2, 1\ atm \mid H^+, 1\ M \parallel M^{n+}, 1\ M \mid M$$

- The standarde oxidation potential of M | M^{n+}, 1 M couple is the standard cell potential of the galvanic cell:

  $$M \mid M^{n+}, 1\ M \parallel H^+, 1\ M \mid H_2, 1\ atm \mid Pt$$

- If the cell potential is negative, the reaction is reversed. In this case, the electrode of the galvanic cell should be written in a reversed order.

Nernst equation

In electrochemistry, the **Nernst equation** is an equation that relates the reduction potential of an electrochemical reaction (half-cell or full cell reaction) to the standard electrode potential, temperature, and activities (often approximated by concentrations) of the chemical species undergoing reduction and oxidation. It is the most important equation in the field of electrochemistry. It is named after the German physical chemist who first formulated it, Walther Nernst.

Standard electrode potential and its application to different kinds of half-cells

In electrochemistry, the **standard electrode potential**, abbreviated E° or E⊖ (with a superscript plimsoll character, pronounced "standard" or "nought"), is the measure of individual potential of a reversible electrode at standard state, which is with solutes at an effective concentration of 1 mol dm^{-3}, and gases at a pressure of 1 atm. The reduction potential is an intensive property. The values are most often tabulated at 25 °C. The basis for an electrochemical cell such as the galvanic cell is always a redox reaction which can be broken down into two half-reactions: oxidation at anode (loss of electron) and reduction at cathode (gain of electron). Electricity is generated due to electric potential difference between two electrodes. This potential difference is created as a result of the difference between individual potentials of the two metal electrodes with respect to the electrolyte. (Reversible electrode is an electrode that owes its potential to changes of a reversible nature, in contrast to electrodes used in electroplating which are destroyed during their use.)

Although the overall potential of a cell can be measured, there is no simple way to accurately measure the electrode/electrolyte potentials in isolation. The electric potential also varies with temperature, concentration and pressure. Since the oxidation potential of a half-reaction is the negative of the reduction potential in a redox reaction, it is sufficient to calculate either one of the potentials. Therefore, standard electrode potential is commonly written as standard reduction potential.

Calculation of standard electrode potentials

The electrode potential cannot be obtained empirically. The galvanic cell potential results from a pair of electrodes. Thus, only one empirical value is available in a pair of electrodes and it is not possible to determine the value for each electrode in the pair using the empirically obtained galvanic cell potential. A reference electrode, standard hydrogen electrode (SHE), for which the potential is defined or agreed upon by convention, needed to be established. In this case SHE is set to 0.00 V and any electrode, for which the electrode potential is not yet known, can be paired with SHE—to form a galvanic cell—and the galvanic cell potential gives the unknown electrode's potential. Using this process, any electrode with an unknown potential can be paired with either the SHE or another electrode for which the potential has already been derived and that unknown value can be established.

Since the electrode potentials are conventionally defined as reduction potentials, the sign of the potential for the metal electrode being oxidized must be reversed when calculating the overall cell potential. Note that the electrode potentials are independent of the number of electrons transferred —they are expressed in volts, which measure energy per electron transferred—and so the two electrode potentials can be simply combined to give the overall cell potential even if different numbers of electrons are involved in the two electrode reactions.

For practical measurements, the electrode in question is connected to the positive terminal of the electrometer, while SHE is connected to the negative terminal.

Standard reduction potential

The larger the value of the standard reduction potentials, the easier it is for the element to be reduced (accept electrons); in other words, they are better oxidizing agents. For example, F_2 has 2.87 V and Li^+ has −3.05 V. F reduces easily and is therefore a good oxidizing agent. In contrast, $Li_{(s)}$ would rather undergo oxidation (hence a good reducing agent). Thus Zn^{2+} whose standard reduction potential is −0.76 V can be oxidized by any other electrode whose standard reduction potential is greater than −0.76 V (e.g. H^+(0 V), Cu^{2+}(0.16 V), F_2(2.87 V)) and can be reduced by any electrode with standard reduction potential less than −0.76 V (e.g. H_2(−2.23 V), Na^+(−2.71 V), Li^+(−3.05 V).

In a galvanic cell, where a spontaneous redox reaction drives the cell to produce an electric potential, Gibbs free energy ΔG° must be negative, in accordance with the following equation:

$$\Delta G^\circ_{cell} = -nFE^\circ_{cell}$$

where n is number of moles of electrons per mole of products and F is the Faraday constant, ~96485 C/mol. As such, the following rules apply:

If $E^\circ_{cell} > 0$, then the process is spontaneous (galvanic cell)

If $E°_{cell} < 0$, then the process is nonspontaneous (electrolytic cell)

Thus in order to have a spontaneous reaction ($\Delta G° < 0$), $E°_{cell}$ must be positive, where:

$$E°_{cell} = E°_{cathode} - E°_{anode}$$

where $E°_{anode}$ is the standard potential at the anode and $E°_{cathode}$ is the standard potential at the cathode as given in the table of standard electrode potential.

EMF and its measurement

EMF measurements are measurements of ambient (surrounding) electromagnetic fields that are performed using particular sensors or probes, such as EMF meters. These probes can be generally considered as *antennas* although with different characteristics. In fact probes should not perturb the electromagnetic field and must prevent coupling and reflection as much as possible in order to obtain precise results. There are two main types of EMF measurements:

- *broadband measurements* performed using a broadband probe, that is a device which senses any signal across a wide range of frequencies and is usually made with three independent diode detectors;
- *frequency selective measurements* in which the measurement system consists of a field antenna and a frequency selective receiver or spectrum analyzer allowing to monitor the frequency range of interest.

EMF probes may respond to fields only on one axis, or may be tri-axial, showing components of the field in three directions at once. Amplified, active, probes can improve measurement precision and sensitivity but their active components may limit their speed of response.

POSSIBLE QUESTIONS

UNIT III

Part-A(20 MARKS)

(Q.NO 1 TO 20 Online Examination)

Part-B (2 Marks)

1.What are electrochemical cells?
2.What are reversible and irreversible cells.
3.Define EMF.
4.What is known as standard electrode potential?
5.What is known as single electrode potential?

6.What are half cells?

7.Write down Nernst equation for oxidation potential.

8.Write down Nernst equation for reduction potential.

Part-C (6 MARKS)

1.Derive Nernst equation for EMF of a cell.

2. Discuss the following

    (i)Reversible and irreversible cells
    (ii)Standard electrode potential

3.Explain electromotive force of a cell and its measurement.
4.write notes on
    (i)reversible and irreversible cells
    (ii)rules of oxidation/reduction of ions based on half-cell potentials

5.What is known as standard electrode potential and derive an expression for Nernst equation for an oxidation potential.
6.What is known as electrochemical cell and write down the rules of oxidation/reduction of ions based on half-cell potentials.

KARPAGAM ACADEMY OF HIGHER EDUCATION

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

COIMBATORE-641 021

(For the Canditates admitted from 2017 & onwards)

II B.Sc Chemistry

PHYSICAL CHEMISTRY III(Phase equilibria and chemical kinetics)

Unit III (ELECTROCHEMICAL CELLS)

S.No	Question	Option1	Option 2	Option 3	Option 4	Answer
1	The device in which the free energy of a physical or chemical process is converted into electrical energy is called	daniel cell	galvanic cell	laclanche cell	voltaic cell	galvanic cell
2	The electrode in which oxidation occurs is	anode	cathode	Anode and Cathode	Electrolyte	anode
3	The salt bridge is filled with a solution of	potassium chromate	sodium chloride	potassium chloride	zinc chloride	potassium chloride
4	If the electricity produced by the cell is equal to the EMF, the cell is	reversible	irreversible	Sometimes reversible	Sometimes irreversible	irreversible
5	In quinhydrone electrode, platinum wire is placed	hydroquinone and quinone	only hydroquinone	only quinone	Water	only hydroquinone
6	An example for metal-metal ion electrodes is	daniel cell	hydrogen electrode	chlorine electrode	calomel electrode	daniel cell
7	An example for gas electrode is	hydrogen electrode	chlorine electrode	oxygen electrode	hydrogen, Chlorine and oxygen electrode	hydrogen, Chlorine and oxygen electrode
8	calomel is a	potassium chloride	sodium chloride	mercurous chloride	barium chloride	mercurous chloride
9	The wire used in the calomel electrode is made of	platinum	copper	titanium	iron	platinum
10	An example for oxidation-reduction	calomel electrode	chlorine electrode	quinhydrone electrode	hydrogen electrode	quinhydrone electrode

	electrode is					
11	In quinhydrone electrode, the platinum wire is placed in a solution containing	hydroquinone and quinone	only hydroquinone	only quinone	Water	only hydroquinone
12	The tendency of an electrode to lose or gain electrons when contact with its own ions in solution, is called	electrode potential	reduction potential	oxidation potential	Concentration potential	electrode potential
13	The electrode in which reduction occurs is	anode	cathode	Anode and Cathode	Electrolyte	cathode
14	The value of standard electrode potential arranged in the decreasing order is called	chemical series	potential series	electrochemical series	electricity series	electrochemical series
15	Any two suitable half cells can be combained to form a	daniel cell	electrochemical cell	galvanic cell	leclanche cell	galvanic cell
16	If the electricity produced by the cell is greater than the applied EMF, then the cell is	reversible	irreversible	Sometimes reversible	Sometimes irreversible	reversible
17	In the calomel electrode, the wire used is made of	platinum	copper	titanium	iron	platinum
18	The salt bridge is made of	potassium chromate	sodium chloride	potassium chloride	zinc chloride	potassium chloride
19	An example for metal-insoluble metal salt electrode is	calomel electrode	standard hydrogen electrode	silver-silver chloride electrode	Gas electrode	calomel electrode
20	The voltaic cell Zn-Cu, the standard EMF is	1.20 v	1.15 v	1.25 v	1.10 v	1.10 v
21	Which one is Metal-insoluble metal salt electrode	calomel electrode	standard hydrogen electrode	silver-silver chloride electrode	Gas electrode	calomel electrode
22	The EMF is measured in	volts	coulomb	faraday	joules	volts
23	The electrical energy is measured in	volts	joules	coulomb	meter	joules
24	The EMF generated by an electrochemical	E	E°	V	V°	E

	cell is given by the symbol					
25	The EMF is measured by	voltmeter	galvanometer	potentiometer	ammeter	potentiometer
26	The EMF of the unknown half cell is calculated from	$E^{\circ}=ER-EL$	$E^{\circ}=EL-ER$	$E^{\circ}=EL+ER$	$E^{\circ}=EL+Es$	$E^{\circ}=ER-EL$
27	The potential of a single electrode in a half cell is called the	electromotive force	single electrode potential	standard reduction potential	cell potential	single electrode potential
28	If the standard emf E° is positive, the reaction is	feasible	not feasible	reversible	Irreversible	feasible
29	The Nernst equation is	$E= 2.303\ RT/nF \log K$	$E= 2.303/nF\ RT \log K$	$E= 2.303\ RT/nF- E^{\circ}$	$E=E^{\circ}- 2.303\ RT/nF \log K$	$E= 2.303/nF\ RT \log K$
30	The Nernst equation for the oxidation half cell is	$E=E^{\circ}- 2.303/n \log [Zn^{2+}]$	$E= 2.303\ RT/nF \log K$	$E=E^{\circ}- 0.0591 /n \log [M^{n+}]$	$E= 2.303/nF \log K$	$E=E^{\circ}- 2.303/n \log [Zn^{2+}]$
31	Which compound is used in the salt bridge	potassium chromate	sodium chloride	potassium chloride	zinc chloride	potassium chloride
32	The relationship between free energy change and emf of a cell is	$\Delta G= -nFE$	$\Delta H= -nFE$	$\Delta E= nFG$	$\Delta F= nEG$	$\Delta G= -nFE$
33	The metals near the bottom of the electrochemical series is	strong reducing agents	strong oxidising agent	weak reducing agent	weak oxidising agents	strong reducing agents
34	The feasibility of a redox reaction can be predicted with the help of	electronegativity	electrochemical series	electron affinity	equivalent conductance	electrochemical series
35	The emf of a cell with 1M solution of reactants and products in solution at 25°c is called	half cell potential	standard emf	single electrode potential	redox potential	standard emf
36	The relationship between equilibrium constant and the standard emf of a cell is	$E^{\circ}= 0.0591 \log k$	$0.0591E^{\circ}= \log k$	$nE^{\circ}= 0.0951 \log k$	$nE^{\circ}= 0.0591 \log k$	$0.0591E^{\circ}= \log k$
37	Which one of the following is not present in the	mercurous chloride	mercury	KCl	ZnCl	ZnCl

	calomel electrode					
38	The electrochemical or electrolytic processes are carried out in a device known as	battery	galvanometer	potentiometer	electrolyte	galvanometer
39	When the electrodes are connected externally, then the circuit is said to be	open	closed	ideal	constant	open
40	What is SHE	standard hydrogen electrode	standard helium electrode	simple half electrode	standard reference electrode	standard hydrogen electrode
41	The overall reaction taking place in the daniel cell is	oxidation	reduction	redox	forward	redox
42	If the reduction potential of the electrode is 1.5v then its oxidation potential is	0 v	1 v	negative 1.5	2	negative 1.5
43	Daniel cell is called as	voltaic cell	half cell	anode cell	cathode half cell	half cell
44	Metal-insoluble metal salt electrode is	calomel electrode	standard hydrogen electrode	silver-silver chloride electrode	Gas electrode	calomel electrode
45	The standard EMF of Zn-Cu voltaic cell is	1.20 v	1.15 v	1.25 v	1.10 v	1.10 v
46	The standard emf can be determined at standard temperature is	32°c	20°c	25°c	27°c	25°c
47	The standard electrode potential at 25°c is zero for	Hydrogen electrode	Gas electrode	Calomel electrode	Metal electrode	Hydrogen electrode
48	The standard hydrogen electrode can act as	anode	cathode	Anode and Cathode	Electrolyte	Anode and Cathode
49	The emf of the standard hydrogen electrode is arbitrarily assigned the value of	0 v	0.1 v	0.001 v	1 v	0 v
50	The reduction potential of the electrode is 1.5v then its oxidation potential	0 v	1 v	negative 1.5	2	negative 1.5

	is					
51	The standard temperature at which the standard emf can be determined is	32°c	20°c	25°c	27°c	25°c
52	For Zn-Cu voltaic cell, the standard EMF is	1.20 v	1.15 v	1.25 v	1.10 v	1.10 v
53	Which one the following is example for Metal-insoluble metal salt electrode	calomel electrode	standard hydrogen electrode	silver-silver chloride electrode	Gas electrode	calomel electrode
54	The unit of electrical energy is	volts	joules	coulomb	meter	joules
55	In IUPAC conventions, the double vertical line represents	two half cell	cathode half cell	salt bridge	anode half cell	salt bridge
56	Platinum is a	positive electrode	negative electrode	Positve and negative electrode	Inert electrode	Inert electrode
57	If the emf acts in the opposite direction through the cell circuit it is denoted as a	positive	negative	zero	cannot be determined	zero
58	What is the potential of a half cell consisting of zinc electrode in 0.01M $ZnSO_4$ solution 25°c. E°= 0.763 V	0.0591 V	0.6521 V	0.7532 V	0.8221 V	0.0591 V
59	What is R in Nernst equation	rate of the reaction	redox reaction	gas constant	reduction of gas	gas constant
60	What is the free energy change for the reaction $Sn^{4+} + 2e \rightarrow Sn^{2+}$. If its standard reduction potential is +0.15	25.59 kJ	29.52 kJ	28.95 kJ	data inadequate	25.59 kJ

UNIT IV

SYLLABUS

APPLICATION OF EMF MEASUREMENTS: Application of EMF measurements in determining (i)free energy,enthalpy and entropy of a cell reaction, (ii) equilibrium constants, and (iii)p H values, using hydrogen, quinine-hydroquinone glass and SbO/Sb_2O_3 electrodes. Concentration cells with and without transference, liquid junction potential;determination of activity coefficients and transference numbers. Qualitative discussion of potentiometric tirations9acid-base, redox, precipitation)

APPLICATION OF EMF MEASUREMENTS

Electrode at which oxidation takes place is anode and the electrode at which reduction takes place is cathode. When a metal is in contact with its own ion solution it develops a potential with respect to the electrolyte. The potential difference developed at the anode - electrolyte interface is called oxidation potential and the potential difference developed at the cathode -electrolyte interface is called reduction potential. The potential difference between the anode and cathode is called the EMF of the cell. The potential difference measured at standard conditions (1 atm pressure, 273K) is called standard electrode potential. Standard electrode potential gives the tendency of the electrode to get oxidized or reduced. If the electrolytes are different the two compartments are joined by a salt bridge, which is a tube containing a concentrated electrolyte solution in agar jelly that completes the electrical circuit and enables the cell to function.

Electrochemical Series:

A series in which metals are arranged in the decreasing order of reduction potential.

Electrodes	**E^0 in volt**
$F_2(g) + 2e^- \rightarrow 2F$ -(aq)	+2.87
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$	+1.77
$Au^+(aq) + e^- \rightarrow Au(s)$	+1.68
$Cl_2(g)$ +2e- → 2Cl- (aq)	+1.36
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	+1.23
$Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$	+1.09
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	+0.77
$I_2(s) + 2e^- \rightarrow 2I^-(aq)$	+0.54
$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$	+0.40
$Cu_2^+(aq) + 2e^- \rightarrow Cu(s)$	+0.34
$S(s) + 2H^+(aq) + 2e^- \rightarrow H_2S(g)$	+0.14
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00
$Pb_2^+(aq) + 2e^- \rightarrow Pb(s)$	-0.13
$Sn_2^+(aq) + 2e^- \rightarrow Sn(s)$	-0.14

$Ni_2^+(aq) + 2e^- \rightarrow Ni(s)$	-0.23
$Co_2^+(aq) + 2e^- \rightarrow Co(s)$	-0.28
$Fe_2^+(aq) + 2e^- \rightarrow Fe(s)$	-0.44
$Zn_2^+(aq) + 2e^- \rightarrow Zn(s)$	-0.76
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	-0.83
$Mn_2^+(aq) + 2e^- \rightarrow Mn(s)$	-1.03
$Al_3+(aq) + 3e- \rightarrow Al(s)$	-1.67
$Mg_2^+(aq) + 2e^- \rightarrow Mg(s)$	-2.34
$Na^+(aq) + e^- \rightarrow Na(s)$	-2.71
$Ca_2^+(aq) + 2e^- \rightarrow Ca(s)$	-2.87
$K^+(aq) + e^- \rightarrow K(s)$	-2.93
$Li^+(aq) + e^- \rightarrow Li(s)$	-3.02

We can construct innumerable number of galvanic cells by taking combinations of different half cells. Each half cell consists of a metallic road dipped in to an electrolyte. The metal with higher reduction potential act as cathode and the other will act as anode.

Standard EMF of the cell:

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

A galvanic cell is represented by putting a vertical line between metal and electrolyte solution and putting a double vertical line between the two electrolytes connected by a salt bridge.

Eg: The symbolic representation of Daniel cell is given below,

$$(-)Zn/Zn^{2+},SO_4^{2-}{}_{(conc_1)}//Cu^{2+},SO_4^{2-}{}_{(conc_2)}/Cu(+)$$

First, the reduced form of the metal to be oxidized at the anode (Zn) is written. This is separated from its oxidized form by a vertical line, which represents the limit between the phases (oxidation changes). The double vertical lines represent the saline bridge on the cell. Finally, the oxidized form of the metal to be reduced at the cathode, is written, separated from its reduced form by the vertical line. The electrolyte concentration is given as it is an important variable in determining the cell potential.

Standard Hydrogen Electrode (S.H.E.):

The potential of Standard hydrogen electrode used as the reference electrode has been arbitrarily taken as zero. The electrode consist of a glass jacket consisting of dry hydrogen gas bubbled at one atmosphere. There is a platinum wire sealed in the glass jacket. The entire system is immersed in 1M HCl solution. Standard hydrogen electrode can be represented as,

$$Pt,H_2\ (g)/H^+(aq)$$

Electrode potential at any concentration can be calculated using Nernst equation. For the reaction,

$$aA + cC^{a+} \rightarrow cC + aA^{c+}$$

Nernst Equation,

$$E_{cell} = E^0_{cell} \frac{2.303RT}{nF} - \frac{\log[C^{a+}]^c}{[A^{c+}]^a}$$

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

$$n = c \quad \text{if} \quad c = a$$

$$n = c \times a \quad \text{if} \quad c \neq a$$

Where;

n=number of electrons.

E^0= electrode potential of cell at standard conditions.

T=temperature.

R=universal gas constant.

F=Faraday constant.

When a cell reaction takes place electrical energy is produced which results in decrease in the free energy of the system.

Electrical work = Decrease in free energy

In an electro chemical cell,

Electric work done = Quantity of electric charge produced x E.M.F of the cell

For one mole of electrons quantity of electric charge is 1F (96500 coulomb)

Therefore, for n moles it is nF.

$$Electric\ \ work\ \ done = nFE_{cell}$$

$$-\triangle G = nFE_{cell}$$

For a standard cell,

$$-\triangle G^0 = nFE^0_{cell}$$

By van 't Hoff relation,

$$\triangle G^0 = \ -RT\ln K$$

$$E^0_{cell} = \frac{RT}{nF}\ln K$$

$$\ln K = \frac{nFE^0}{RT}E^0_{cell}$$

K=equilibrium constant

Spontaneity or Feasibility of Reaction:

ΔG	K	E^0_{cell}	**Reaction**
Negative	>1	Positive	Spontaneous
Zero	=1	Zero	Equilibrium
Positive	<1	Negative	Non - spontaneous

Application of Emf measurements in determining

Measurement of entropy and enthalpy of a cell reaction

FromGibbs-Helmholtzequationwehave

$$\Delta G = \Delta H + T\left[\frac{\partial(\Delta G)}{\partial T}\right]_p$$

DG = – nEF and differentiating DG with respect to temperature at constant pressure yields

$$\left[\frac{d(\Delta G)}{\partial T}\right]_p = -nF\left(\frac{\partial F}{\partial F}\right)_p$$

The quantity $\left(\frac{\partial E}{\partial T}\right)_p$ is the temperature coefficient of the cell. Substituting the value of $\left[\frac{\partial(\Delta G)}{\partial T}\right]_p$ inequation,weget

$$\Delta G = \Delta H - nFT\left(\frac{\partial E}{\partial T}\right)_p$$

AlsodG=dH–TdS

$$\Delta S = nF\left(\frac{\partial E}{\partial T}\right)_p$$

Equation can be used for calculating the entropy changes for the cell reaction in terms of the temperature coefficient of the cell emf. Equation can also be written as

$$-nFE = \Delta H - nFT\left(\frac{\partial E}{\partial T}\right)_p$$

or

$$\Delta H = nF\left[T\left(\frac{\partial E}{\partial T}\right)_p - E\right]$$

From equation, the enthalpy change for cell reaction can be determined from the measurement of cell emf and the temperature coefficient of the emf.

Determination of equilibrium constant

To calculate the equilibrium constant for an electrochemical cell we need to know:

- the standard state potential for a cell
- the half-reactions involved

The Nernst equation is used in calculating the equilibrium constant.

$$E^o_{cell} = \frac{RT}{nF} \ln Q$$

At equilibrium Q = K. Substituting in K for Q, and the values for R, T, and F, we get:

$$E^o_{cell} = \frac{0.0257}{n} \ln K = \frac{0.0592}{n} \log K$$

Example: Find the value of the equilibrium constant at 25°C for the cell reaction for the following electrochemical cell:

$$Cu \mid Cu^{2+}(1\ M) \parallel Ag^{+}(1\ M) \mid Ag.$$

- Write the equations for the cell half-reactions, calculate the standard cell potential, and determine the number of electrons transferred.

$2\ Ag^{+}(aq) + 2\ e^{-} \rightarrow 2\ Ag(s)$ $E^{o}_{reduction} = +\ 0.799\ V$

$Cu(s) \rightarrow Cu^{2+}(aq) + 2\ e^{-}$ $E^{o}_{oxidation} = -\ 0.518\ V$

$2\ Ag^{+}(aq) + Al(s) \rightarrow 2\ Ag(s) + Cu^{2+}(aq)$ $E^{o}_{cell} = +\ 0.281\ V$

n = 2 moles of electrons

- Substitute into the above equation and solve for K
- Substitute into the above equation and solve for K.

$$E^{o}_{cell} = \frac{0.0592}{n} \log K$$

$$0.281 = \frac{0.0592}{2} \log K$$

$$\log K = 9.49$$

$$K = 10^{9.49} = 3.1 \times 10^{9}$$

Note: values for the equilibrium constant for electrochemical cell reactions are sometimes very large.

Determining the Standard State Free Energy Change from E^o_{cell}

To determine the standard state free energy change for a cell reaction

- determine the E^o_{cell}
- determine the number of moles of electrons transfered in the reaction.
- solve for dG^o using the equation

$$dG^o = - nFE^o_{cell}$$

DG^o = standard state free energy change (joules)

n = number of moles of electrons transferred

F = Faraday's constant (96,485 C/mol e^-)

E^o_{cell} = standard state cell potential (volts or joules/C)

Example: Find the value of the equilibrium constant at 25°C for the cell reaction for the following electrochemical cell:

$$Cu \mid Cu^{2+}(1\ M) \parallel Ag^{+}(1\ M) \mid Ag.$$

(The solution for the determination of the E^o_{cell} and the number of moles of electrons, n, are shown in the example in the previous section. Click HERE to see the solution.)

- Determine the E^o_{cell}.

$$E^o_{cell} = + 0.281 \text{ volts}$$

- Determine the number of moles of electrons transfered.

$$n = 2 \text{ moles of } e^-$$

- Substitute into the equation and solve.

$$DG^o = - (2 \text{ mol } e^-)(96{,}485 \text{ C/mol } e^-)(0.281 \text{ J/C})$$

$$DG^o = - 54{,}200 \text{ J or } - 54.2 \text{ kJ}$$

Determining the Non-Standard State Free Energy Change

To determine the non-standard state free energy change:

- calculate the standard cell potential, E^o_{cell}
- determine the number of moles of electrons transferred, n
- calculate the reaction quotient, Q
- calculate the non-standard cell potential, E_{cell}, using the Nernst equation
- Calculate the non-standard free energy change using the equation:

$$dG = - nFE_{cell}$$

Example: Calculate the free energy change for the following electrochemical cell.

$$Zn(s) \mid Zn^{2+} (1.50 \text{ M}) \parallel Cu^{2+} (0.25 \text{ M}) \mid Cu(s)$$

- Calculate E^o_{cell}.

$Zn(s) \rightarrow Zn^{2+}(aq) + 2 e^-$ $E^o_{oxidiation} = + 0.762$ volts

$Cu^{2+}(aq) + 2 e^- \rightarrow Cu(s)$ $E^o_{reduction} = + 0.339$ volts

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ $E^o_{cell} = + 1.101$ volts

- Determine "n".

n = 2 moles of electrons

- Calculate Q

$$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]} = \frac{1.50}{0.25} = 6.0$$

- Calculate E_{cell}

$$E_{cell} = 1.101 \text{ volts} - \frac{0.0257}{2} \ln 6 = 1.078 \text{ volts}$$

- Calculate DG.

$$\Delta G = -nFE_{cell} = -(2 \text{ mole } e^-)(96{,}485 \text{ C/mole } e^-)(1.078 \text{ volts})$$
$$\Delta G = -208,000 \text{ joules or } -208 \text{ kJ}$$

Application of EMF measurements in determing pH values

Hydrogen ions play a central role in the lives of cells. For example, changes in hydrogen ion concentration are intimately tied to the charge of side chains in proteins. This charge state, in turn, affects the activity of enzymes as well as their folding and even localization. Further, the famed ATP synthases that churn out the ATPs that power many cellular processes are driven by gradients in hydrogen ions across membranes.

The abundance of these ions and, as a result, the charge state of many compounds is encapsulated in the pH defined as

$pH=-\log_{10}([H^+]/1)$

where [H^+] denotes the concentration or more formally the activity of the charged hydrogen ions (H^+, or more accurately the sum of hydronium, H_3O^+, as well as the functionally important but often overlooked Zundel, $H_5O_2^+$, and Eigen, $H_7O_3^+$, cations). We are careful to divide the hydrogen ion concentration by a so-called "standard state" concentration, the agreed upon value is 1M, in order to ensure that when taking the log we have a unitless quantity.

The integer 7 is often etched in our memory from school as the pH of water, but there is nothing special about the integral value of 7. Water has a neutral pH of about 7, with the exact value varying with temperature, ionic strength and pressure. What is the pH inside the cell? Just like with other parameters describing the "state" of molecules and cells, the answer depends on physiological conditions and which compartment within the cell we are considering (i.e. which organelle). Despite these provisos, crude generalizations about the pH can be a useful guide to our thinking.

Concentration cells with and without transference:A concentration cell is an electrolytic cell that is comprised of two half-cells with the same electrodes, but differing in concentrations. A concentration cell acts to dilute the more concentrated solution and concentrate the more dilute solution, creating a voltage as the cell reaches an equilibrium. This is achieved by transferring the electrons from the cell with the lower concentration to the cell with the higher concentration.

The standard electrode potential, commonly written as E^o_{cell}, of a concentration cell is equal to zero because the electrodes are identical. But, because the ion concentrations are different, there is a potential difference between the two half-cells. One can find this potential difference via the Nernst Equation,

$$Ecell=E^0\ cell-0.0592nlogQ$$

at 25°C. The E stands for the voltage that can be measured using a voltmeter (make sure if the voltmeter measures it in millivolts that you convert the number before using it in the equation). Note that the Nernst Equation indicates that cell potential is dependent on concentration, which results directly from the dependence of free energy on concentration. Remember that to find Q you use this equation:

$$aA+bB\rightleftharpoons cC+dDaA+bB\rightleftharpoons cC+dD$$

$$Q=(C)c\ast(D)d(A)a\ast(B)bQ=(C)c\ast(D)d(A)a\ast(B)b$$

When Q=1, meaning that the concentrations for the products and reactants are the same, then taking the log of this equals zero. When this occurs, the E_{cell} is equal to the E^{o}_{cell}.

Another way to use the E^{o}_{cell} , or to find it, is using the equation below.

$$E^{0}\ \text{cell}=\text{Ecathode}-E^{0}\ \text{anode}$$

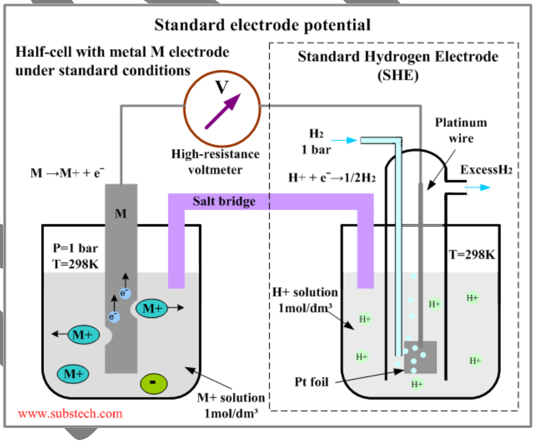


Fig.1 An example of a concentration cell

Connected Information

These concepts are useful for understanding the electron transfer and what occurs in half-cells.

Use of a Salt Bridge

The two compartments of a cell must be separated so they do not mix, but cannot be completely separated with no way for ions to be transferred. A wire cannot be used to connect the two compartments because it would react with the ions that flow from one side to another. Because of this, a salt bridge is an important part of a concentration cell. It solves the major problem of electrons beginning to pile up too much in the right beaker. This buildup is due to electrons moving from the left side, or left beaker, to the right side, or right beaker. The salt bridge itself can be in a few different forms, such as a salt solution in a U-tube or a porous barrier (direct contact). It evens the charge by moving ions to the left side, or left beaker. In the written expression which shows what is occurring in specific reactions, the salt bridge is represented by the double lines. An example of this would be:

Zn(s)|Zn2+(1M)||Cu2+(1M)|CuZn(s)|Zn2+(1M)||Cu2+(1M)|Cu

The double lines between the Zn^{2+} (1M) and the Cu^{2+} (1M) signify the salt bridge. The single lines, however, do not represent bridges; they represent the different phase changes, for example, from solid zinc to liquid zinc solution. If there is a comma where you would expect to see a single line, this is not incorrect. It simply means that no phase changes occurred.

Electrode Use

In this type of reaction, there are two electrodes which are involved. These are known as the anode and the cathode, or the left and right side, respectively. The anode is the side which is losing electrons (oxidation) while the cathode is the side which is gaining electrons (reduction).

Use of a Voltmeter

A voltmeter (not to be confused with a different kind of voltmeter which also measures a type of energy) is used to measure the cell potential that is passed between the two sides. It is typically located in between the two cells. This cell potential (also known as an electromotive force) occurs due to the flow of electrons. The value it shows can be negative or positive depending on the direction in which the electrons are flowing. If the potential is positive then the transfer of electrons is spontaneous, but the reverse reaction is NONspontaneous. Conversely, if the value of the potential is negative, the transfer of electrons is nonspontaneous and the reverse reaction. The voltmeter measures this potential in volts or millivolts.

Electrons

The tendency of electrons to flow from one chemical to another is known as electrochemistry. This is what occurs in a concentration cell. The electrons flow from the left side (or left beaker) to the right side (or right beaker). Because the left side is losing electrons and the right is gaining them, the left side is called the oxidation side and the right side is the reduction side. Although you could switch the two to be on the opposite sides, this is the general way in which the set up is done. The oxidation side is called the anode and the reduction side is the cathode. It is the flow of the electrons that cause one side to be oxidized and the other to be reduced.

Corrosion

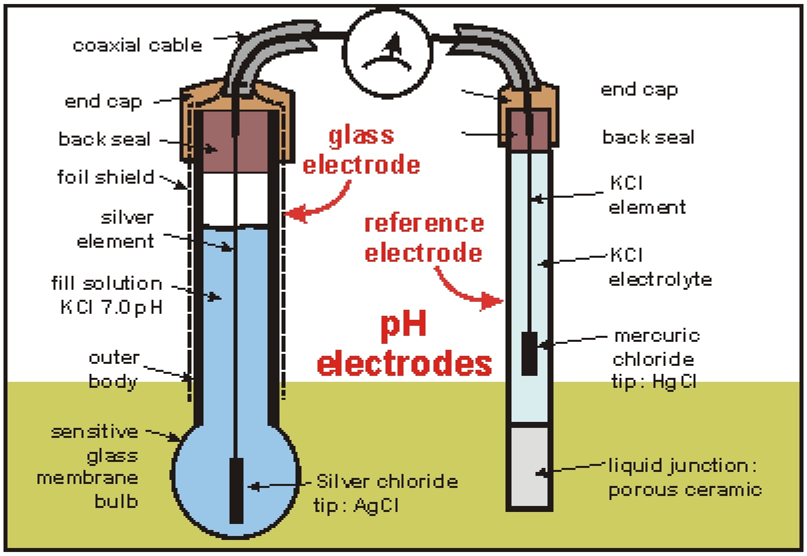
Corrosion can occur on a concentration cell when the metal being used is in contact with different concentrations, causing parts of the metal to have different electric potential than the other parts. One element that is often linked to this corrosion is oxygen. In the areas in which there is a low oxygen concentration corrosion occurs.

This can be somewhat prevented through sealing off the cell and keeping it clean, but even this cannot prevent any corrosion from occurring at some point.

Corrosion is most frequently a problem when the cell is in contact with soil. Because of the variations that occur within soil, which is much greater than the variations that occur within a fluid, contact with soil often causes corrosion for the cell.

Uses of Concentration Cells

A pH meter is a specific type of concentration cell that uses the basic setup of a concentration cell to determine the pH, or the acidity/basicity, of a specific solution. It is comprised of two electrodes and a voltmeter. One of the electrodes, the glass one has two components: a metal (commonly silver chloride) wire and a separate semi-porous glass part filled with a potassium chloride solution with a pH of 7 surrounding the AgCl. The other electrode is called the reference electrode, which contains a potassium chloride solution surrounding a potassium chloride wire. The purpose of this second electrode is to act as a comparison for the solution being tested. When the glass electrode comes into contact with a solution of different pH, an electric potential is created due to the reaction of the hydrogen ions with the metal ions. This potential is then measured by the voltmeter, which is connected to the electrode. The higher the voltage, the more hydrogen ions the solution contains, which means the solution is more acidic.



Liquid junction potential

Liquid junction potential occurs when two electrolytic solutions of different concentrations are in contact with each other. The more concentrated solution will have a tendency to diffuse into the comparatively less concentrated one. The rate of diffusion of each ion will be roughly proportional to its speed in an electric field. If the anions diffuse more rapidly than the cations, they will diffuse ahead into the dilute solution, leaving the latter negatively charged and the concentrated solution positively charged. This will result in an electrical double layer of positive and negative charges at the junction of the two solutions. Thus at the point of junction, a potential difference will develop because of the ionic transfer. This potential is called liquid junction potential or diffusion potential which is non-equilibrium potential. The magnitude of the potential depends on the relative speeds of the ions' movement.

Calculation

The liquid junction potential cannot be measured directly but calculated. The Electromotive force (EMF) of a concentration cell with transference includes the liquid junction potential.

where a_1 and a_2 are activities of HCl in the two solutions, R is the Universal Gas Constant, T is the temperature and F is Faraday's Constant.

where a_2 and a_1 are activities of HCl solutions of right and left hand electrodes respectively and t_M be transport number of Cl^-

Liquid Junction potential = $E_{wt} - E_{nt} = (t_M - 1)\ RT/F\ .\ \ln (a_2/a_1)$

Elimination of liquid junction potential

Go

The liquid junction potential interferes with the exact measurement of the electromotive force of a chemical cell, so its effect should be minimized as much as possible for accurate measurement. The most common method of eliminating the liquid junction potential is to place a salt bridge consisting of a saturated solution of potassium chloride(KCl) and ammonium nitrate(NH_4NO_3) with lithium acetate(CH_3COOLi) between the two solutions constituting the junction. When such a bridge is used, the ions in the bridge are present in large excess at the junction and they carry almost the whole of the current across the boundary. The efficiency of KCl/NH_4NO_3 is connected with the fact that in these salts, the transport numbers cation.

Potentionmetric titrations

Potentiometric titration is a technique similar to direct titration of a redox reaction. It is a useful means of characterizing an acid. No indicator is used; instead the potential is measured across the analyte, typically an electrolyte solution. To do this, two electrodes are used, an indicator electrode (the glass electrode and metal ion indicator electrode) and a reference electrode. Reference electrodes generally used are hydrogen electrodes, calomel electrodes, and silver chloride electrodes. The indicator electrode forms an electrochemical half cell with the interested ions in the test solution. The reference electrode forms the other half cell,

The overall electric potential is calculated as $E_{cell} = E_{ind} - E_{ref} + E_{sol}$. E_{sol} is the potential drop over the test solution between the two electrodes. E_{cell} is recorded at intervals as the titrant is added. A graph of potential against volume added can be drawn and the end point of the reaction is halfway between the jump in voltage. E_{cell} depends on the concentration of the interested ions with which the indicator electrode is in contact. For example, the electrode reaction may be

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

As the concentration of M^{n+} changes,the E_{cell} changes correspondingly. Thus the potentiometric titration involve measurement of $E_{cell}$with the addition of titrant. types of potentiometric titration: acid-base titration (total alkalinity and total acidity), redox titration (HI/HY and cerate), precipitation titration (halides), and complexometric titration (free EDTA)

The first potentiometric titration was carried out in 1893 by Robert Behrend at Ostwald's Institute in Leipzig. He titrated mercurous solution with potassium chloride, potassium bromide, and potassium iodide. He used a mercury electrode along with a mercury/mercurous nitrate reference electrode. He found that in a cell composed of mercurous nitrate and mercurous nitrate/mercury, the initial voltage is 0. If potassium chloride is added to mercurous nitrate on one side, mercury (I) chloride is precipitated. This decreased the osmotic pressure of mercury (I) ions on the side and creates a potential difference. This potential difference increases slowly as additional potassium chloride is added, but then increases more rapidly. He found the greatest potential difference is achieved once all of the mercurous nitrate has been precipitated. This was used to discern end points of titrations.

Wilhelm Bottger then developed the tool of potentiometric titration while working at Ostwald's Institute. He used potentiometric titration to observe the differences in titration between strong and weak acids, as well as the behavior of polybasic acids. He introduced the idea of using potentiometric titrations for acids and bases that could not be titrated in conjunction with a colorimetric indicator

Potentiometric titrations were first used for redox titrations by Crotogino. He titrated halide ions using potassium permanganate using a shiny platinum electrode and a calomel electrode. He says that if an oxidizing agent is added to a reducing solution then the equilibrium between the reducing substance and reaction product will shift towards the reaction product. The changes the potential very slowly until the amount of reducing substance becomes very small. A large change in potential will occur then once a small addition of the titrating solution is added, as the final amounts of reducing agent are removed and the potential corresponds solely to the oxidizing agent. This large increase in potential difference signifies the endpoint of the reaction.

Redox titration

A **redox titration** is a type of titration based on a redox reaction between the analyte and titrant. Redox titration may involve the use of a redox indicator and/or a potentiometer. A common example of a redox titration is treating a solution of iodine with a reducing agent to produce iodide using a starch indicator to help detect the endpoint. Iodine (I_2) can be reduced to iodide (I^-) by e.g. thiosulfate ($S_2O_3^{2-}$), and when all iodine is spent the blue colour disappears. This is called an iodometric titration.

Most often of all, the reduction of iodine to iodide is the last step in a series of reactions where the initial reactions are used to convert an unknown amount of the solute (the substance being analyzed) to an equivalent amount of iodine, which may then be titrated. Sometimes other halogens (or haloalkanes) than iodine are used in the intermediate reactions because they are available in better measurable standard solutions and/or react more readily with the solute. The extra steps in iodometric titration may be worth while because the equivalence point, where the blue turns a bit colourless, is more distinct than some other analytical or may be by volumetric methods.

To evaluate a redox titration we need to know the shape of its titration curve. In an acid–base titration or a complexation titration, the titration curve shows how the concentration of H_3O^+ (as pH) or M^{n+} (as pM) changes as we add titrant. For a redox titration it is convenient to monitor the titration reaction’s potential instead of the concentration of one species.

The Nernst equation relates a solution's potential to the concentrations of reactants and products participating in the redox reaction. Consider, for example, a titration in which a titrand in a reduced state, A_{red}, reacts with a titrant in an oxidized state, B_{ox}.

Precipitation titration

Titration involving precipitation at end of process is called as precipitation titration. Most of metallic halides are titrated by precipitation method.

It is also called as argentimetric titration. There are three methods used for determining end point in precipitation titration.

Application of Precipitation titration:

Use for determination of halides and pseudo-halides

To determine solubility constant of compounds

To determine electrode potential

For determining chloride, cyanides and thiosulphites

POSSIBLE QUESTIONS

UNIT IV

Part-A(20 MARKS)

(Q.NO 1 TO 20 Online Examinations)

Part -B(2 MARKS)

1.What is known as liquid junction potential?

2.What is the principle behind potentiometric titration?

3.Mention the application of EMF measurements in determining free energy.

4. Mention the application of EMF measurements in determining enthalpy.

5. Mention the application of EMF measurements in determining entropy.

6. Mention the application of EMF measurements in determining equilibrium constant.

7.Define transport number.

8.What is known as activity coefficient?

Part- C(6 MARKS)

1.Explain potentiometric precipitation reaction.

2 Explain the following

(i)application of EMF measurements in determining enthalpy
(ii)application of EMF measurements in determining free energy of a cell

3.Explain concentration cells with and without transference.

4.Describe potentiometric titrations of a redox reaction

5.Explain concentration cells with and without transference.

6. Explain the following

(i)application of EMF measurements in determining enthalpy
(ii)application of EMF measurements in determining free energy of a cell

7.How to determine pH using the following electorodes
(i)Hydrogen electrode
(ii)Quinhydrone electrode
(iii) Glass electrode

8.Explain potentiometric redox titration.

9.Write short note on

(i)Liquid junctional potential

(ii)EMF measurements in determining equilibrium constant

10.Explain potentiometric acid-base titration..

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(For the Canditates admitted from 2017 & onwards)

II B.Sc Chemistry

PHYSICAL CHEMISTRY III(Phase equilibria and chemical kinetics)

Unit IV (APPLICATION OF EMF MEASUREMENTS)

S.No	Question	Option1	Option 2	Option 3	Option 4	Answer
1	The electrical energy produced by a galvanic cell is given by the-------------- of its electromotive force and the quantity of electricity which passes	sum	product	sum and product	divided	product
2	Electricity is measured in	volts	amperes	coulombs	ohm	coulombs
3	Electrical energy of a reversible cell originated from the -------------------- in the enthalpy of the cell reaction	decrease	increase	decreases and then increases	increases and the decreases	decrease
4	The standard free energy change of a cell reaction is given by	ΔG=-n FE	ΔF=n FE	ΔG=n FE	ΔG=FE	ΔG=-n FE
5	Knowing the EMF of the cell and the concentrations of reactants and products of the cell reaction, we can calculate the ---------------------- of the cell reaction	free energy	entropy	enthalpy	equilibrium constant	equilibrium constant
6	If the ----------------------------------of a particular cell is known the	standard EMF	entropy	free energy	enthalpy	standard EMF

	equilibrium constant of the cell reaction can be calculated					
7	The potential of a hydrogen electrode in contact with a solution of H+ ions involving the reaction is given by	Nernst equation	Gibbs equation	Duhem equation	Clausius equation	Nernst equation
8	Instead of taking quinone and hydroquinone, a small amount of -----------is taken	quinhydrone	glass	hydroquinone	quinone	quinhydrone
9	Quinhydrone electrode is preferred to the ------------ electrode	hydrogen	calomel	glass	platinum	hydrogen
10	The quinhydrone electrode is combined with a saturated------------- electrode to form a cell	hydrogen	calomel	glass	platinum	calomel
11	The quinhydrone electrode cannot be used for solutins p H more than	7	9	8	5	8
12	Hydroquinone ionises appreaciably as an acid and also gets ---------------partly by atmospheric oxygen	oxidised	reduced	oxidised and then reduced	reduced and then oxidised	oxidised
13	The glass electrode is made of a special glass of relativley ----- melting point and then ------------ electrical conductivity	high and low	low and high	high and high	low and low	low and high
14	A solution of ----------- molar HCl which furnishes a constant hydrogen ion concentration	0.01	0.1	0.2	0.001	0.1
15	The reference electrode employed is usually the -----------	hydrogen	calomel	quinone	hydroquinone	calomel

	---------in glass electrode					
16	The EMF can be determined by means of a ------------	potentiometer	conductivity meter	d)p H meter	voltmeter	potentiometer
17	Glass electrodes can be used in	strong oxidising solutions	week oxidising solutions	strong reducing solutions	week reducing solutions	strong oxidising solutions
18	calomel electrode consists of mercury,solid mercurous chloride and a solution of ------------	KCl	NaCl	NaOH	KOH	KCl
19	Standard cell potential is measured	at a temperature of 25°c	when ion concentration of aqueous reactants are 1.00 M	under the condition of 1.00 atm for gaseous reactants	at a temperature of 25°c, when ion concentration of aqueous reactants are 1.00 M and under the condition of 1.00 atm for gaseous reactants	at a temperature of 25°c, when ion concentration of aqueous reactants are 1.00 M and under the condition of 1.00 atm for gaseous reactants
20	The standard electrode commonly used are	hydrogen electrode	quinhydrone electrode	glass electrode	nitrogen electrode	hydrogen electrode
21	Which of the following is a different between glass electrode and hydrogen electrode	glass electrode measures Ph while hydrogen electrode compares Ph	different salt bridges are used	glass electrode compares pH, while electrode measures Ph	different electrolyte are used	glass electrode measures Ph while hydrogen electrode compares Ph
22	Why not pH cannot be measured through potentiometer or voltmeter, but can be done through electronic voltmeter	resistance of the glass membrane is very high and the current is small	resistance of the glass membrane is low and the current is large	different salt bridges are used	glass electrode compares pH, while electrode measures Ph	resistance of the glass membrane is low and the current is large

23	PH of the cell can be found out	given the Ecell value	given the E°G	given the E0 value	given the E°G and given the Ecell value	given the E°G and given the Ecell value
24	How does electrical energy is obtained from the cell	due to ions	chemical reaction inside the cell	due to water	chemical reactionoutside the cell	chemical reaction inside the cell
25	Transfer of matter with respect to concentration is known as	cell equilibrium	cell constant	cell concentration	Electolyte concentration	cell concentration
26	Two like electrodes with different concentration are immersed in an electrolyte are known as	electrode-concentration cell	electrolyte concentration cell	cell concentration	cell constant	electrolyte concentration cell
27	Electrode-concentration cell are evidently independent of	concentration of electrolyte	concentration of ions	concentration in electrode	electrolyte concentration cell	concentration of electrolyte
28	The whole process will be spontaneous only when the	emf is negative	emf is partially negative	emf is partially positive	emf is positive	emf is negative
29	Solution with same electrolyte with different concentration is found in	electrolyte concentration cell	electrode-concentration cell	concentration of ions	electrode-concentration cell and electrolyte concentration cell	electrode-concentration cell
30	Transfer of ions from one electrolytic solution to the other does not take place at	concentration cell with transfer	concentration cell without transfer	emf is partially negative	concentration cell without transfer and concentration cell with transfer	concentration cell without transfer
31	Transfer of ions takes place directly at	concentration cell without transfer	concentration cell with transfer	emf is partially negative	concentration cell without transfer and concentration cell with transfer	concentration cell with transfer
32	Liquid junction potential depends on	transference number of anion and cation	removal of anoin and cation	transfer of only anion	transfer of only cation	transference number of anion and cation
33	When does L.J.P becomes null/zero	t-=t+	t-≠t+	t->t+	t-<t+	t-=t+

34	When does L.J.P becomes negative	$t- = t+$	$t- \neq t+$	$t- > t+$	$t- < t+$	$t- > t+$
35	When does L.J.P becomes positive	$t- = t+$	$t- \neq t+$	$t- > t+$	$t- < t+$	$t- < t+$
36	Which among the following electrolytes have the same transfer number of anions and cations	potassium chloride and ammonium nitrate	potassium nitrate and ammonium chloride	potassium sulphate and ammonium nitrate	potassium nitrate and ammonium sulphate	potassium sulphate and ammonium nitrate
37	Reversibility of electrode with respect to cation will determine	transfer number of anion	transfer number of cation	emf is partially negative	concentration cell with transfer	transfer number of anion
38	Reversibility of electrode with respect to anion will determine	transfer of anion	transfer of cation	emf is partially negative	concentration cell with transfer	transfer of cation
39	Potential of any electrode depends on	concentration of ions	concentration of anion	concentration of cation	transfer of cation	concentration of ions
40	Why an indicator is not required for a potentiometric titration that is carried out with a coloured solution	no indicator required	self indicator	no indicator required and self indicator	External indicator	no indicator required and self indicator
41	In a potentiometric titration, the EMF slowly changes when	the end point changes	before the end point	when the end point approaches	emf is partially negative	when the end point approaches
42	Which among the following electrode is used as oxidation-reduction electrode	copper	silver-silver	platinum	tin	silver-silver
43	The Liquid junction potential becomes positive	$t- = t+$	$t- \neq t+$	$t- > t+$	$t- < t+$	$t- < t+$
44	Which among the following will come under potentiometric titration	acid-base titration	redox titration	precipitation titration	acid-base titration, redox titration and precipitation titration	acid-base titration, redox titration and precipitation titration
45	Which among the following is taken as indicator in the precipitation titration of silver nitrate against potassium	potassium electrode	silver electrode	hydrogen electrode	silver-silver electrode	silver electrode

	chloride					
46	Organic compounds which can exist in oxidised form as well as reduced form are said to be	amphoteric indicator	redox indicator	acid indicator	base indicator	redox indicator
47	Which is that one main feature of redox indicators	different concentration	different colour	different cell	same colour	different colour
48	When does a redox indicator can be successfully used	measured potential to be about 0.03 volt	more than 0.03 volt	0 potential	1	more than 0.03 volt
49	Which among the following is a redox indicator for titration of ferrous ions against dichromate ions	diphenylamine	KCl	NaCl	CaCl2	diphenylamine
50	Determination of transport number, valency of a ion, coefficient of electrolyte are purely based upon	cell constant	equilibrium constant	EMF	Concentration	cell constant
51	In given reaction $2Cr(s) + 3Cu^{2+}(aq) \rightarrow 3Cr^{3+}(aq) + 3Cr(s)$ which reaction occurs of the cathode in an electrochemical cell	reduction of Cu2+(aq)	reduction of Cu(s)	oxidation of Cu3+(aq)	oxidation of Cr(s)	oxidation of Cu3+(aq)
52	The site of oxidation in an electrochemical cell is	the anode	cathode	electrodes	salt bridge	the anode
53	Which statement below is not true for the reaction $Fe^{3+} + e^{-} \rightarrow Fe^{2+}$	Fe3+ is being reduced	the oxidation state of Fe has charged	Fe3+ could be referred ta as an oxidizing agent in this reaction	both Fe2+ and Fe2+ are called anions	both Fe2+ and Fe2+ are called anions
54	In any electrochemical cell, the cathode is always	non metal	attached to battery	the electrode at which some species gain electrons	the electrode at which some species lose electrons	non metal
55	Electrical energy forced in electrochemical cell	Spontaneous	Non-Spontaneous	Exothermic	Endothermic	Non-Spontaneous

	is					
56	Which of the following shows a metal being oxidized	2Na+ 2H2O→2NaOH+ H2	Cu→Cu2++ 2e-	Cu2++ 2e+→Cu	Cu→Cu2++ 2e- and 2Na+ 2H2O→2NaOH+ H2	Cu→Cu2++ 2e- and 2Na+ 2H2O→2NaOH + H2
57	A voltaic cell has an E° value of -1.00 v the reaction is	spontaneous	has positive ΔG°	has negative ΔG°	0	has positive ΔG°
58	Which of the following can we use to measure Ph?	a glass electrode	a concentration cell	a hydrogen electrode	a glass electrode, a concentration cell and a hydrogen electrode	a glass electrode, a concentration cell and a hydrogen electrode
59	What is ΔG° at 298k for the reaction Hg(l) + $2Fe^{3+}$(aq)→Hg^{2+}(aq) + $2Fe^{2+}$(aq)	positive 314 Kelectrode	negative 16 KJ	negative 314 Kelectrode	positive 16 KJ	positive 16 KJ
60	Why not pH cannot be measured through potentiometer or voltmeter, but can be done through electronic voltmeter	resistance of the glass membrane is very high and the current is small	resistance of the glass membrane is low and the current is large	different salt bridges are used	glass electrode compares pH, while electrode measures Ph	resistance of the glass membrane is low and the current is large

UNIT V

SYLLABUS

Surface Chemistry: Physical adsorption, chemisorptions adsorption isotherms(Langmuir and Freundlich), nature of adsorbed state. Qualitative discussion of BET

Surface chemistry

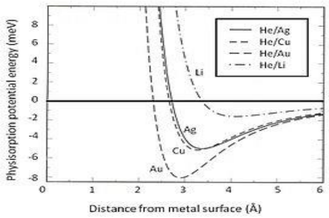
Physical adsorption

The fundamental interacting force of physisorption is caused by van der Waals force. Even though the interaction energy is very weak (~10–100 meV), physisorption plays an important role in nature. For instance, the van der Waals attraction between surfaces and foot-hairs of geckos provides the remarkable ability to climb up vertical walls. Van der Waals forces originate from the interactions between induced, permanent or transient electric dipoles.

In comparison with chemisorption, in which the electronic structure of bonding atoms or molecules is changed and covalent or ionic bonds form, physisorption, generally speaking, can only be observed in the environment of low temperature (thermal energy at room temperature ~26 meV) and the absence of the relatively strong chemisorptions. In practice, the categorisation of a particular adsorption as physisorption or chemisorption depends principally on the binding energy of the adsorbate to the substrate.

To give a simple illustration of physisorption, we can first consider an adsorbed hydrogen atom in front of a perfect conductor, as shown in Fig. 1. A nucleus with positive charge is located at $\mathbf{R} = (0, 0, Z)$, and the position coordinate of its electron, $\mathbf{r} = (x, y, z)$ is given with respect to the nucleus. The adsorption process can be viewed as the interaction between this hydrogen atom and its image charges of both the nucleus and electron in the conductor. As a result, the total electrostatic energy is the sum of attraction and repulsion terms:

Physisorption potential



Even though the van der Waals interaction is attractive, as the adsorbed atom moves closer to the surface the wavefunction of electron starts to overlap with that of the surface atoms. Further the energy of the system will increase due to the orthogonality of wavefunctions of the approaching atom and surface atoms.

This Pauli exclusion and repulsion are particularly strong for atoms with closed valence shells that dominate the surface interaction. As a result, the minimum energy of physisorption must be found by the balance between the long-range van der Waals attraction and short-range Pauli repulsion. For instance, by separating the total interaction of physisorption into two contributions- a short-range term depicted by Hartree–Fock theory and a long-range van der Waals attraction, the equilibrium position of physisorption for rare gases adsorbed on jellium substrate can be determined. Fig. 2 shows the physisorption potential energy of He adsorbed on Ag, Cu, and Au substrates which are described by the jellium model with different densities of smear-out background positive charges. It can be found that the weak van der Waals interaction leads to shallow attractive energy wells (<10 meV). One of the experimental methods for exploring physisorption potential energy is the scattering process, for instance, inert gas atoms scattered from metal surfaces. Certain specific features of the interaction potential between scattered atoms and surface can be extracted by analyzing the experimentally determined angular distribution and cross sections of the scattered particles.

Comparison with chemisorption

- Physisorption is a general phenomenon and occurs in any solid/fluid or solid/gas system. Chemisorption is characterized by chemical specificity.
- In physisorption, perturbation of the electronic states of adsorbent and adsorbate is minimal. For chemisorption, changes in the electronic states may be detectable by suitable physical means.
- Typical binding energy of physisorption is about 10–100 meV. Chemisorption usually forms bonding with energy of 1–10 eV.
- The elementary step in physisorption from a gas phase does not involve an activation energy. Chemisorption often involves an activation energy.
- For physisorption, under appropriate conditions, gas phase molecules can form multilayer adsorption. In chemisorption, molecules are adsorbed on the surface by valence bonds and only form monolayer adsorption.

Langmuir adsorption isotherm

In 1916, Irving Langmuir proposed another Adsorption Isotherm which explained the variation of Adsorption with pressure. Based on his theory, he derived Langmuir Equation which depicted a relationship between the number of active sites of the surface undergoing adsorption and pressure.

Assumptions of Langmuir Isotherm

Langmuir proposed his theory by making following assumptions.

1. Fixed number of vacant or adsorption sites are available on the surface of solid.
2. All the vacant sites are of equal size and shape on the surface of adsorbent.
3. Each site can hold maximum of one gaseous molecule and a constant amount of heat energy is releasedduringthisprocess.

4. Dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules.

$$A(g) + B(S) \underset{\text{desorption}}{\overset{\text{Adsorption}}{\rightleftharpoons}} AB$$

Where A (g) is unadsorbed gaseous molecule, B(s) is unoccupied metal surface and AB is Adsorbed gaseous molecule.

5. Adsorption is monolayer or unilayer.

Derivations of the Langmuir Adsorption Equation

Calculation of Equilibrium Constant

Langmuir proposed that dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules. Using the equilibrium equation, equilibrium constant can be calculated.

$$A(g) + B(S) \underset{K_d}{\overset{K_a}{\rightleftharpoons}} AB$$

Where K_a represents equilibrium constant for forward reaction and K_d represents equilibrium constant for backward direction.

According to Kinetic theory,

Rate of forward reaction = K_a [A] [B]

Rate of backward reaction = K_d [AB]

At equilibrium, Rate of forward reaction is equal to Rate of backward reaction

$$K_a [A] [B] = K_d [AB]$$

$$\text{Or, } \frac{K_a}{K_d} = \frac{[AB]}{[A][B]}$$

$$K = \frac{K_a}{K_d} = \frac{[AB]}{[A][B]}$$

The above equation represents the equilibrium constant for distribution of adsorbate between the surface and the gas phase.

Derivation

Langmuir Equation which depicts a relationship between the number of active sites of the surface undergoing adsorption (i.e. extent of adsorption) and pressure.

To derive Langmuir Equation and new parameter ‘ θ ’ is introduced. Let θ the number of sites of the surface which are covered with gaseous molecules. Therefore, the fraction of surface which are unoccupied by gaseous molecules will be (1 – θ).

Now, Rate of forward direction depends upon two factors: Number of sited available on the surface of adsorbent, (1 – θ) and Pressure, P. Therefore rate of forward reaction is directly proportional to both mentioned factors.

$$\text{Rate of forward reaction} \propto P\,(1 - \theta)$$

$$\text{Rate of adsorption} \propto P\,(1 - \theta)$$

$$\text{Or, Rate of adsorption} = K_a P\,(1 - \theta)$$

Similarly, Rate of backward reaction or Rate of Desorption depends upon number of sites occupied by the gaseous molecules on the surface of adsorbent.

$$\text{Rate of desorption} \propto \theta$$

$$\text{Or, Rate of desorption} = K_d\,\theta$$

At equilibrium, rate of adsorption is equal to rate of desorption.

$$K_a P (1 - \theta) = K_d \theta$$

We can solve the above equation to write it in terms of θ.

$$K_aP - K_aP \theta = K_d \theta$$

$$K_aP = K_aP \theta + K_d \theta$$

$$K_aP = (K_d + K_aP) \theta$$

$$\theta = \frac{K_aP}{K_d + K_aP}$$

Divide numerator and denominator on RHS by K_d, we get

$$\theta = \frac{\frac{K_a}{K_d}P}{\frac{K_d}{K_d} + \frac{K_a}{K_d}P}$$

Now put

$$K = \frac{K_a}{K_d}$$

in above equation we get

$$\theta = \frac{KP}{1 + KP}$$

Langmuir Adsorption Equation

This is known as Langmuir Adsorption Equation.

Alternate form of Langmuir Adsorption Equation

Langmuir adsorption equation can be written in an alternate form in terms of volume of gas adsorbed. Let V be volume of gas adsorbed under given sets of conditions of temperature and pressure and V_{mono} be the adsorbed volume of gas at high pressure conditions so as to cover the surface with a unilayer of gaseous molecules.

$$\theta = \frac{V}{V_{mono}}$$

Substituting the value of θ in Langmuir equation

$$\frac{V}{V_{mono}} = \frac{KP}{1+KP}$$

$$\text{Or} \quad V_{mono} = 1 + \frac{1}{KP}$$

Or in terms of pressure P we get,

$$\frac{P}{V} = \frac{P}{V_{mono}} + \frac{1}{KV_{mono}}$$

Langmuir Adsorption Equation in alternate form

Thus, if we plot a graph between P/V Vs P, we will obtain a straight line with

$$slope = \frac{1}{V_{mono}} \quad \text{and} \quad Intercept = \frac{1}{KV_{mono}}$$

Limitations of Langmuir Adsorption Equation

1. The adsorbed gas has to behave ideally in the vapor phase. This condition can be fulfilled at low pressure conditions only. Thus Langmuir Equation is valid under low pressure only.

2. Langmuir Equation assumes that adsorption is monolayer. But, monolayer formation is possible only under low pressure condition. Under high pressure condition the assumption breaks down as gas molecules attract more and more molecules towards each other. *BET theory* proposed by Brunauer, Emmett and Teller explained more realistic multilayer adsorption process.
3. Another assumption was that all the sites on the solid surface are equal in size and shape and have equal affinity for adsorbate molecules i.e. the surface of solid if homogeneous. But we all know that in real solid surfaces are heterogeneous.
4. Langmuir Equation assumed that molecules do not interact with each other. This is impossible as weak force of attraction exists even between molecules of same type.
5. The adsorbed molecules has to be localized i.e. decrease in randomness is zero ($\Delta S = 0$).This is not possible because on adsorption liquefaction of gases taking place, which results into decrease in randomness but the value is not zero.

From above facts we can conclude that, **Langmuir equation is valid under low pressure conditions**.

Freundlich Adsorption Equation: A Special Case of Langmuir Equation

We consider Langmuir Equation

$$\theta = \frac{KP}{1+KP}$$

At low pressure value of KP<<1. Therefore,

$$\theta = KP \quad \text{Or } \theta \propto P \qquad \text{... (1)}$$

The above equation shows linear variation between extent of adsorption of gas and pressure.

At high pressure value of KP>>1

$$\therefore \theta = \frac{KP}{KP} = 1 \qquad \ldots (2)$$

The extent of adsorption, θ is independent of pressure at high pressure conditions. The reaction at this stage becomes zero order

Combining the results of equation (4) and (5), we can conclude that

$$\theta = Kp^{0-1}$$
$$or\, \theta = Kp^{1/n} \qquad \ldots (3)$$

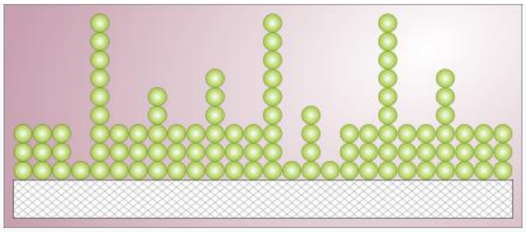
Equation (3) is in agreement with Freundlich adsorption equation.

We can say that Freundlich adsorption equation is a special case of Langmuir equation.

Qualitative discussion of BET

Brunauer–Emmett–Teller (**BET**) **theory** aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of materials. In 1938, Stephen Brunauer, Paul Hugh Emmett, and Edward Teller published the first article about the BET theory in the Journal of the American Chemical Society.[1] The BET theory applies to systems of multi layer adsorption, and usually utilizes probing gases that do not chemically react with material surfaces as adsorbates to quantify specific surface area. Nitrogen is the most commonly employed gaseous adsorbate used for surface probing by BET methods. For this reason, standard BET analysis is most often conducted at the boiling temperature of N_2 (77 K). Further probing adsorbates are also utilized, albeit with lower frequency, allowing the measurement of surface area at different temperatures and measurement scales. These have included argon, carbon dioxide, and water. Specific surface area is a scale-dependent property, with no single true value of specific surface area definable, and thus quantities of specific surface area determined through BET theory may depend on the adsorbate molecule utilized and its adsorption cross section.

Concept



BET model of multilayer adsorption, that is, a random distribution of sites covered by one, two, three, etc., adsorbate molecules.

The concept of the theory is an extension of the Langmuir theory, which is a theory for monolayer molecular adsorption, to multilayer adsorption with the following hypotheses:

1. gas molecules physically adsorb on a solid in layers infinitely;
2. there is no interaction between each adsorption layer; and
3. the Langmuir theory can be applied to each layer.

POSSIBLE QUESTION

UNIT V

Part-A(20 MARKS)

(Q.NO 1 TO 20 Online Examination)

Part-B(2 MARKS)

1.What is known as physical adsorption?

2.What is known as chemical adsorption?

3.Define adsorption.

4.Define absorption.

5.Define adsorbate.

6.Define adsorbent.

7.Write down an equation for BET.

8.What is the condition for Freundlich adsorption isotherm at high pressure.

9.Write down the condition for Langmuir adsorption isotherm at low pressure.

Part-C(6 MARKS)

1. Differentiate physical adsorption with chemical adsorption.

2.Explain the postulates of Langmuir adsorption isotherm and derive the same .

3.What is adsorption and absorption.Derive Freundlich adsorption isotherm and mention its conditions.
4. Discuss BET in detail.
5.What is adsorption and absorption.Derive Freundlich adsorption isotherm and mention its conditions.

6.What is adsorption and absorption.Derive Freundlich adsorption isotherm and mention its conditions.

7.What is adsorption and absorption. Explain BET

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(For the Canditates admitted from 2017 & onwards)

II B.Sc Chemistry

PHYSICAL CHEMISTRY III(Phase equilibria and chemical kinetics)

Unit V (SURFACE CHEMISTRY)

S.No	Question	Option1	Option 2	Option 3	Option 4	Answer
1	The phenomenon of concentration or assimilation of gas at the surface of a solid with which it is in close proximity is called	adsorption	absorption	sorption	desorption	adsorption
2	The adsorption is accompanied by a ----------------------in residula surface forces	decrease	increase	increase and then decreases	decrease and then increases	decrease
3	The adsorption of a gas on a solid is sometimes called	inclusion	occlusion	sorption	desorption	occlusion
4	The material providing the surface upon which adsorption occurs is known as the -----------------	adsorbent	adsorbate	sorbate	desorption	adsorbent
5	The substance adsorbed or attached is called the------------	adsorbent	adsorbate	sorbate	desorption	adsorbate
6	The removal of adsorbed substance from the surface is called	inclusion	occlusion	sorption	desorption	desorption
7	The amount of heat evolved when 1 mole of any gas is adsorned on solid adsorbent surface is called----------------of adsorption	entropy	enthalpy	free energy	work function	enthalpy
8	When the concentration of the	positive	negative	inclusion	occlusion	positive

	adsorbate is more on the surface of the adsorbent than the bulk, it is called-----------------adsorption					
9	When the concentration of the adsorbate is less on the surface of the adsorbent than the bulk, it is called-----------------adsorption	positive	negative	inclusion	occlusion	negative
10	Adsorption is a -------------phenomenon	surface	bulk	layer	negative	surface
11	Adsorption is a ------------process	slow	fast	medium	average	fast
12	Absorption is a-----------process compared to adsorption	slow	fast	medium	average	slow
13	Adsorption involves the-------------------into the interior of the matter	diffusion	penetration	occlusion	inclusion	diffusion
14	In ------------------, a gas gets adsorbed on the solid only if it forms chemical bonds	adsorption	desorption	chemisorption	absorption	chemisorption
15	Greater the surface area of the adsorbent, ---------------is its adsorption capacity	greater	lower	average	medium	greater
16	charcoal and silica gel are excellent-------------	adsorbate	adsorbent	sorbent	absorbate	adsorbent
17	charcoal is ------------porous and hence possess-------------surface areas	high and large	low and small	high and small	low and large	high and large
18	The extent of adsorption depends upon the-------------	temperature	pressure	volume	c)concentration	pressure
19	Adsorption isotherm is a graph plotted between magnitude of adsorption and --------------at constant temperature	temperature	pressure	volume	c)concentration	pressure
20	Ps called as	pressure	saturation	temperature	volume	saturation

			pressure			pressure
21	Ps becomes ------------ to the rate of desorption and further increase of pressure does not alter the equilibrium	equal	greater	lower	greater than or equal to	equal
22	x/m is known as	nature of adsorption	extent of adsorption	rate of adsorption	magnitude of adsorption	extent of adsorption
23	At low pressure in Freundlich isotherm the graph is almost a ------------	parallel	perpendicular	straight line	slope	straight line
24	At high pressure in Freundlich isotherm the graph is almost--------------to X-axis	parallel	perpendicular	straight line	slope	parallel
25	At intermediate pressure in Freundlich isotherm x/m depends on	0 to 1	1 to 2	0 to 2	0 to 3	0 to 1
26	Freundlich adsorption isotherm fails is pressure is----------	high	low	medium	average	high
27	Freundlich adsoprtion isotherm fails if concentration of adsorbate is very-------------	high	low	medium	average	high
28	Adsorption isobar is a graph plotted between magnitude of adsorption and --------------- at constant pressure	temperature	volume	concentration	composition	temperature
29	The amount absorbed x/m should --------------- with an increase in temperature	decrease	increase	remain constant	decrease and then increases	decrease
30	chemisorption requires-----------	activation energy	entropy	enthalpy	free energy	activation energy
31	adsorption-----------can be used to distinguish between physical and chemical adsorption	isobar	isotherm	isochore	isotherm and isochore	isobar
32	In physical adsorption, there a regular	pressure	concentration	volume	temperature	temperature

	decrease in extent of adsorption as------------increases					
33	In chemisorption, there is initial increase and then decrease in extent of adsorption as ---------------------increases	pressure	concentration	volume	temperature	temperature
34	In order to increase the rate of adsorption,----------------------is very necessary	catalyst	reactant	activation	sorption	activation
35	mechanical rubbing can be done to increase	speed	activation	reaction	speed of catalyst	activation
36	Adsorption from solutions decreases with rise of temperature and decrease in-----------------------of solution	increase	decrease	decreases and then increases	increases and the decreases	decrease
37	Activated charcoal is used for removing-------------	colouring matter	dust	sediments	coagulant	colouring matter
38	Activated caharcoal is used in --------------	sedimentation	coagulation	colouration	gas masks	gas masks
39	Adsorption process is used in production of vacuum by using activated charcoal in ------------flask	condenser	distillation	Dewar's	air condenser	Dewar's
40	Lake test for aluminium is based upon ---------------of litmus colour	absorption	adsorption	sorption	desorption	adsorption
41	According to Langmuir, valencies at the surface of adsorbent atoms are ----------------	fully satisfied	not fully satisfied	partially satisfied	satisfied	not fully satisfied
42	According to Langmuir if a bond is weak, a--------------------adsorption takes place	chemical	physical	oxidation	reduction	physical
43	According to Langmuir if a bond is strong, a--------------------adsorption takes place	chemical	physical	oxidation	reduction	chemical
44	The residual valency force on the surface of	one	two	zero	three	one

	adsorbent is effective only up to a small distance and hence, the adsorbed gas layer is only ----------molecule thick					
45	The phenomenon of adsorption consists of two opposing processes namely condensation and --------------------	distillation	evaporation	circulation	floatation	evaporation
46	When the adsorption starts the whole adsorbent surface is bare and consequently the initial rate of absorption is-------------	lowest	highest	constant	medium	highest
47	When the adsorption starts the whole adsorbent surface is bare and consequently the rate of condensation----------------	increases	decreases	decreases and then increases	increases and the decreases	decreases
48	The rate of evaporation of the condensed molecules gradually---------	increases	decreases	decreases and then increases	increases and the decreases	increases
49	A dynamic equilibrium is set up, when the rate of condensation becomes equal to the rate of ------------------	distillation	evaporation	circulation	floatation	evaporation
50	P/w against P, we should get a----------------	decrease	straight line	increase	increases and the decreases	straight line
51	Brunauer–Emmett–Teller (BET) theory aims to explain the physical adsorption of g as molecules on a ---------------- surface	solid	liquid	gaseous	semi liquid	solid
52	The concept of BET is extension of ------------------isotherm	Freundlich	Langmuir	Emmett	Teller	Langmuir
53	The BET method is	surface	adsorption	material	polymer	surface

	widely used in---------------science					
54	According to BET,adsorptions occur only on well-defined sites of the sample ---------------	bulk	surface	surface as well as bulk	layered	surface
55	According to BET,the uppermost molecule layer is in equilibrium with the -------------- phase	liquid	gas	solid	gas as well as liquid	gas
56	The ---------------is a kinetically-limited process	adsorption	desorption	sorption	adsorbent	desorption
57	At the saturation pressure, the molecule layer number tends to-----------	infinity	low	high	low and high	infinity
58	By application of the BET theory it is possible to determine the inner surface of hardened ------------paste	composite	cement	matrix	concreate	cement
59	BET finds application in	catalysis	activity of coefficients	diffusion coefficients	viscosity coefficient	catalysis
60	The surface area of catalysts is an important factor in------------------ activity	activity coefficients	viscosity coefficients	diffusion coefficients	catalytic	catalytic

Reg. No. : ------------------ **[17CHU301]**

KARPAGAM ACADEMY OF HIGHER EDUCATION
(Deemed to be University)
(Established Under Section 3 of UGC Act 1956)
COIMBATORE-21
B.Sc. Degree Internal Examination,July 2018
(For the candidates admitted from 2017& onwards)
II B.Sc CHEMISTRY
INTERNAL EXAM I
PHYSICAL CHEMISTRY III
(Phase Equilibria and Chemical Kinetics)

Time: 2 hours **Maximum: 50 marks**

PART- A (20 x 1= 20 Marks)
Answer ALL the Questions

1.J.W.Gibbs enunciated the phase rule in

a)1876 b)1875 c)1874 d)1873

2.Benzene and alcohol constitutes

a) single phase b)two phase c)three phase d)four phase

3.Sugar and water mixture is an

a)two component b)one component c)three component d)four component

4.If F=0, the system is called

a)bivariant b)univariant c)invariant d)trivariant

5.A compound which melts sharply at a constant temperature into a liquid of the same composition as the solid is said to possess a

a)incongruent melting point b)congruent melting point

d)triple point d)eutectic point

6.Transition temperature is otherwise known as

a)peritectic temperature b)melting temperature

c)sublimation temperature d)vapour pressure temperature

7.The phase rule equation for two component system
a)F=C-P+2 b) F=C-P+1 c) F=C-P+3 d) F=C-P

8. The phase rule equation for one component system
a)F=C-P+2 b) F=C-P+1c) F=C-P+3 d) F=C-P
9.The temperature at which solid phase gets converted to liquid phase is known as

a)triple point b)eutectic point c)melting point d)boiling point

10.The temperature at which two solid phase are in equilibrium with a liquid phase is known as
a)triple point b)eutectic point c)congruent melting point d)incongruent melting point

11.An equation of fundamental importance which finds extensive application in one-component, two-phase systems, was derived by
a)J.Willard Gibbs b)Albert Einstein c)Clausius-Clapeyrond) Dmitri Mendeleev

12.Water and sulphur are examples for
a)one component b)two component c)three component d)four component

13.ΔHv is known as

a)molar heat of sublimation b)molar heat of vaporisation

c)molar heat of fusion d)molar heat of enthalpy

14.Clapeyron equatiion gives change in pressure d P which accompany the change in-----------

a)temperature b)volume c)composition d)temperature and composition

15.Carbon di-oxide system is an example for
a)one component b)two component c)three component d)four component
16.Tie lines are represented in

a)two component sytem b)one component system

c)three component system d)four component system

17.In Gibbs-DuhemMargules equation fugacity can be replaced by
a)temperature b)volume c)vapour pressure d)composition

18.InReduced phase rule which one of the factor is neglected
a)pressure b)temperature c)volume d)composition

19.A system of two salts and water furnishes an example of a ---------------------- system involving solids and liquids

a)three component b)two component c)one component d)four component

20.Isothermal critical point is otherwise known as

a)eutectic point b)triple point c)plait point d)melting point

PART- B(3 x 2= 6 Marks)

Answer ALL the Questions
21.Calculate degrees of freedom for the following system
Liquid melt ↔ solid Pb

22.What is meant by eutectic point
23.Justify decomposition of calcium carbonate is a two component system.

PART- C(3 x 8= 24 Marks)
Answer ALL the Questions

24.a.Apply phase rule to one component system by taking water as an example..

(OR)

b. Compute degrees of freedom for sulphur system with a neat diagram.

25.a.What are binary solutions? Derive Gibbs-Duhem-Margules equation.

(OR)

b. What is a triangular plot. Explain CH_3COOH-$CHCl_3$-H_2O with a neat diagram

26.a.State reduced phase rule. Justify reduced phase rule for Lead- Silver system with a neat diagram.

(OR)

b.Compare phase and component. How solid, liquid and vapour phases differ and mention two examples for each.

[17CHU301]

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II B.Sc CHEMISTRY
INTERNAL EXAM I
PHYSICAL CHEMISTRY III
(Phase Equilibria and Chemical Kinetics)

ANSWER KEY
PART- A

1.a)1876

2.a)single phase

3.a)two component

4.c)invariant

5.b)congruent melting point

6.a)peritectic temperature

7.b)F=C-P+1

8.a)F=C-P+2

9.c)melting point

10.b)eutectic point

11.c)Clausius clapeyron equation

12.a)one component

13.a)molar heat of vaporization

14.a)temperature

15.a)one component

16.c)three component system

17.c)vapour pressure

18.a)pressure

19.a)three component

20.c)plaint point

PART B

21.F=C-P+1

=2-2+1

F=1

22.Eutectic point is one in which two solid phase and one liquid phase will be in equilibrium.

23.The composition of each phase in decomposition of calcium carbonate can be explained by taking one phases. Hence it is a two component system.

PART C

24.a) Water is a unique substance in many ways. One of these special properties is the fact that solid (ice) is less dense than liquid water just above the freezing point. The phase diagram for water is shown in the Figure below .

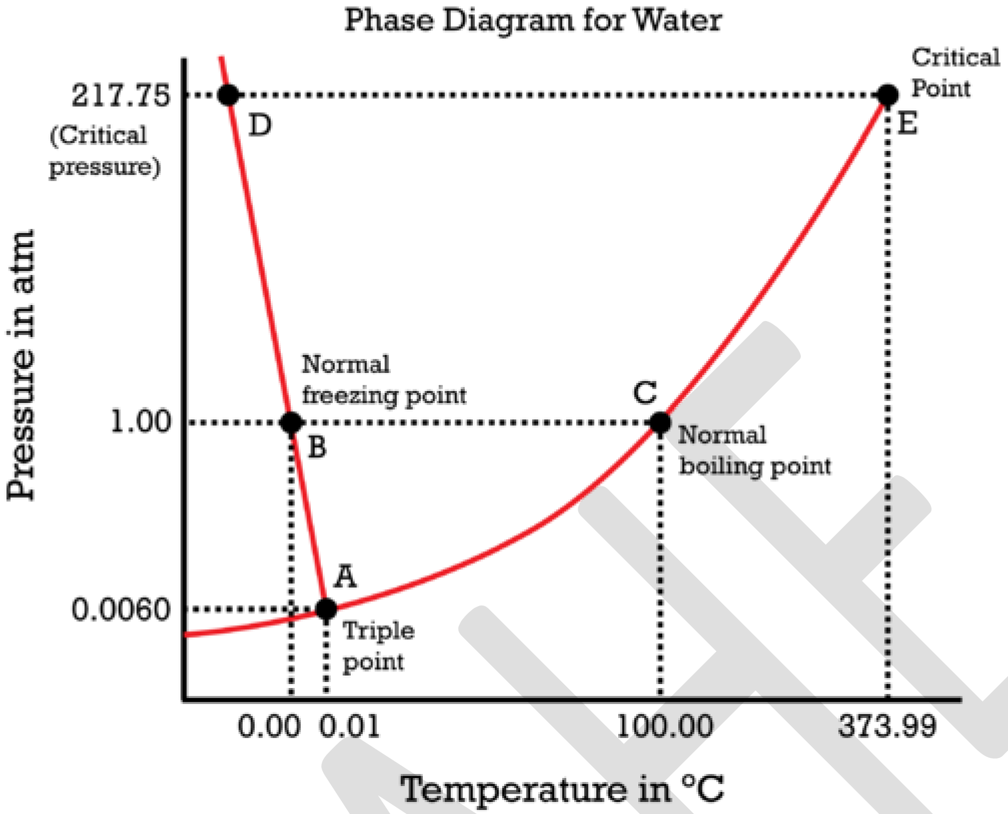


Figure 1

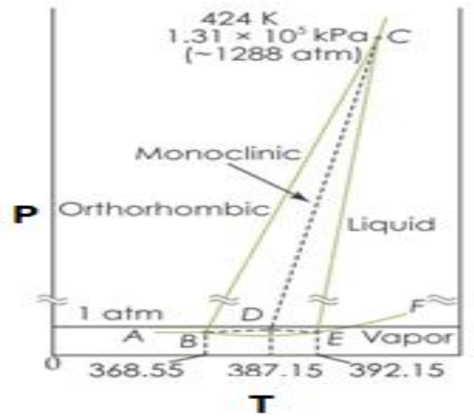
Notice one key difference between the general phase diagram and the phase diagram for water. In water's diagram, the slope of the line between the solid and liquid states is negative rather than positive. The reason is that water is an unusual substance in that its solid state is less dense than the liquid state. Ice floats in liquid water. Therefore, a pressure change has the opposite effect on those two phases. If ice is relatively near its melting point, it can be changed into liquid water by the application of pressure. The water molecules are actually closer together in the liquid phase than they are in the solid phase.

The point E in the above phase diagram labeled the critical point . At 373.99°C, particles of water in the gas phase are moving very, very rapidly. At any temperature higher than that, the gas phase cannot be made to liquefy, no matter how much pressure is applied to the gas.
The critical pressure (P_c) is the pressure that must be applied to the gas at the critical

temperature in order to turn it into a liquid. For water, the critical pressure is very high, 217.75 atm. The critical point is the intersection point of the critical temperature and the critical pressure.

b. **PHASE DIAGRAM OF SULPHUR**

Phase Diagram of Sulphur In the following example, we will use the phase diagram of sulphur in the form of overhead projector (OHPI transparencies to illustrate such overlapping. Fig.6.1 shows the phase diagram of sulphur pressure . Except that a different presentation of the lines (eg. the dotted lines, the continuous lines and a solid dark line) is used to show the three fundamental parts of this phase diagram.



The curves AB, BC, CD, BE, CE, EG divide the diagram into four areas. Curve AB, the Vapour Pressure curve of SR. It shows the vapour pressure of solid rhombic sulphur (SR) at different temperatures. Along this curve the two phases SR and sulphur vapour (SV) are in equilibrium. The system SR/SV has one degree of freedom, F = C – P + 2 = 1 – 2 + 2 = 1 i.e., it is monovariant.

Curve BC, the Vapour Pressure curve of SM. It shows variation of the vapour pressure of monoclinic sulphur (SM) with temperature. SM and SV coexist in equilibrium along this curve. The system SM/SV is monovariant. Curve CD, the Vapour Pressure curve of SL. It depicts the variation of the vapour pressure of liquid sulphur (SL) with temperature. SL and SV are in equilibrium along CD. The two phase system SL/SV is monovariant. One atmosphere line meets this curve at a temperature (444.6ºC) which is the boiling point of sulphur. Curve BE, the Transition curve. It shows the effect of pressure on the transition temperature for SR and SM. As two solid phases are in equilibrium along the curve, the system SR/SM is monovariant. The transformation of SR and SM is accompanied by increase of volume (density of SR = 2.04; SM = 1.9) and absorption of heat i.e., SR + Q (heat energy) YZZ ZZX SM Thus the increase of pressure will shift the equilibrium to the left (Le Chatelier's Principle) and the transition temperature will, therefore, be raised. This is why the line BE slopes away from the pressure axis showing thereby that the transition temperature is raised with increase of pressure. Curve CE, the Fusion curve of SM. It represents the effect of pressure on the melting point of SM. The two phases in equilibrium along this curve are SM and SL. The system SM/SL is monovariant. As the melting or fusion of SM is accompanied by a slight increase of volume, the melting point will rise by increase of pressure (Le Chatelier's principle). Thus the curve CE slopes slightly away from the pressure axis. The curve ends at E because SM ceases to exist beyond this point. Curve EG, the Fusion curve for SR. Here the two phases in equilibrium are SR and SL. The number of phases being two, the system SR/SL is monovariant.

The Triple points B, C, E Triple point B. This is the meeting point of the three curves AB, BC and BE. Three phases, solid SR, solid SM and SV are in equilibrium at the point B. There being three phases and one component, the system SR/SM/SL is nonvariant. F = C – P + 2 = 1 – 3 + 2 = 0 At B, SR is changed to SM and the process is reversible. Thus the temperature corresponding to B is the transition temperature (95.6ºC). Triple point C. The curves BC, CD, CE meet at this point. The three phases in equilibrium are SM, SL and SV. There being three phases and one component, the system SM/SL/SV is nonvariant. The temperature corresponding to C as indicated on the phase diagram is 120ºC. This is the melting point of SM. Triple point E. The two lines CE and BE, having different inclinations away from the pressure axis, meet at E where a third line EG also joins. The three phases SR, SM and SL are in equilibrium and the system at the point E is nonvariant. This point gives the conditions of existence of the system SR/SM/SL at 155ºC and 1290 atmospheres pressure. (3) The Areas The phase diagram of the sulphur system has four areas or regions. These are labelled as rhombic sulphur, monoclinic sulphur, liquid sulphur and vapour. These represent single phase systems which have two degrees of freedom, F = C – P + 2 = 1 – 1 + 2 = 2 That is, each of the systems SR, SM, SL, and SV are bivariant.

Metastable Equilibria The change of SR to SM takes place very slowly. If enough time for the change is not allowed and SR is heated rapidly, it is possible to pass well above the transition point without getting SM. In that case, there being three phases (SR, SL, SV) only and one component, the phase diagram, like that of water system, will consist of three curves, one triple point and three areas. The dashed curve BF, the Vapour Pressure curve of metastable SR. This is a continuation of the vapour pressure curve AB of stable SR. The metastable phases SR and SV are in equilibrium along this curve. It is a monovariant system. The dashed curve CF, the Vapour Pressure curve of supercooled SL. On supercooling liquid sulphur, the dashed curve CF is obtained. It is, in fact, the back prolongation of DC. The curve CF represents the metastable equilibrium between supercooled SL and SV. Thus it may be designated as the vapour pressure curve of supercooled SL. It meets the dashed curve BF at F. The dashed curve FE, the Fusion curve of metastable SR. The two metastable phases SR and SL are in equilibrium along this curve and the system is monovariant. This shows that the melting point of metastable SR is increased with pressure. Beyond E, this curve depicts the conditions for the stable equilibrium SR/SL as the metastable SR disappears. The metastable Triple point F. At this point, three metastable phases SR, SL and SV are in equilibrium. The system is a metastable triple point with no degree of freedom. The corresponding temperature is the melting point of metastable SR (114ºC)

Phase diagrams for systems of solid liquid equilibria involving eutectic points.

25.a) The Gibbs free energy can be defined in two different ways once by subtracting off combinations of entropy S, enthalpy H and temperature T and other as a sum of chemical potentials and amounts of species. The fact that they are equal gives a new relation known as “Gibbs-Duhem Relation.” The Gibbs-Duhem relation helps us to calculate relationships between quantities as a system which remains in equilibrium. One example is the Clausius-Clapeyron equation which states that two phases at equilibrium with each other having equaled amount of a given substance must have exactly the same free energy i.e. it relates equilibrium changes in pressure to changes in temperature as a function of material parameters.

Deriving the Gibbs-Duhem equation from thermodynamics state equations is very easy. The Gibbs free energy G in equilibrium can be expressed in terms of thermodynamics as:

$dG=\mu_1\, dn_1 + n_1\, d\mu_1 + \mu_2\, dn_2 + n_2\, d\mu_2 \ldots\ldots\ldots\ldots \mu_j\, dn_j + n_j\, d\mu_j$

$= (\mu_1\, dn_1 + \mu_2\, dn_2 + \ldots\ldots\ldots \mu_j\, dn_j) + (n_1\, d\mu_1 + n_2\, d\mu_2 + \ldots\ldots\ldots\ldots n_j\, d\mu_j)$

At constant temperature and pressure, the above equation can be written as:

$\mathbf{n_1\, d\mu_1 + n_2\, d\mu_2 + \ldots\ldots\ldots\ldots n_j\, d\mu_j = 0}$

$\mathbf{\sum n_i\, d\mu_i = 0}$ ……………………..(1)

Because at constant temperature and pressure, $(\mu_1\, dn_1 + \mu_2\, dn_2 + \ldots\ldots\ldots \mu_j\, dn_j) = dG$

The equation (1) is known as the Gibbs-Duhem equation.

ApplicationsofGibbs-Duhemequation:

(i) Gibbs-duhem equation is helpful in calculating partial molar quantity of a binary mixture by measuring the composition of the mixture which depends on the total molar quantity.

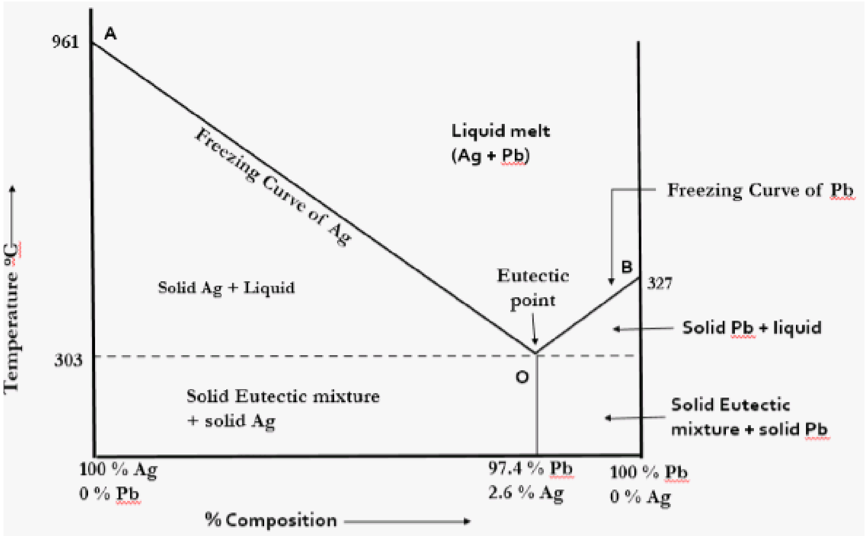
(ii) Gibbs-duhem equation is helpful in calculating the partial vapor pressures by calculating the total vapor pressure. All these calculations require a curve-fitting procedure. Using tabulated experimental data the accuracy of the calculated quantities was found to be comparable to the accuracy of the original experimental data.

b. The system acetic acid - chloroform - water is one of the classical examples of partial miscibility in a ternary system, first studied by Wright, Thompson, and Leon in 1891 (1). Thanks to the subsequent workers Brancker, Hunter, and Nash (2), the equilibrium relations at 25" are very well known, as far as the compositions of equilibrium liquid layers are concerned. Nothing, however, is known about: (a) the solid-liquid equilibria at low temperatures; (b) equilibrium liquid compositions at temperatures other than 25"; (c) the critical phenomena, L1-V (L1 = chloroform layer) and L2-V (Lz = aqueous layer). So far no study has been made of critical phenomena in any system exhibiting partial miscibility in the liquid state and the results arrived at in this paper have general applicability to all systems of this kind. A previous paper (3) has dealt with the thermodynamics of this system, as exemplified by the vapor pressures and densities

Because of the chemical natures of the substances named in the title, formation of compounds or of solid solutions is inherently improbable and therefore the study of the freezing point curves was expected to yield little of interest. The study was, however, carried out for the binary systems chloroform - acetic acid and chloroform - water, and for the ternary system, using a double-junction copper-constantan thermocouple, a Brown Elektronik recorder, and liquid nitrogen as a coolant. The system acetic acid -water was previously studied by various workers (4) and the eutectic found to lie at 58.1% acetic acid and -28.5 to -27.0'. The eutectic of the chloroform - acetic acid system was found to lie at 91.8% CHCl3 by weight, and -67.5" (Fig. 1). In the system chloroform-water, the eutectic lies at O.lyo Hz0 and -64.0". The ternary eutectic was found to lie at -70" and 90.7% chloroform, 8.3% acetic acid, and 1.0% water. The eutectic trough leading from the acetic acid -water eutectic to the acetic acid -chloroform eutectic was determined experimentally.

26.a) **TWO–COMPONENT SYSTEMS** When a single phase is present in a two-component system, the degree of freedom is three, $F = 2 – 1 + 2 = 3$ This means that three variables must be specified in order to describe the condition of the phase.

Phase diagram of Ag-Pb system



In two component systems there are four possible phases solid Ag, solid Pb, solution of Ag, + Pb and vapour. Since the pressure has no effect on equilibrium so the system can be represented by temperature concentration diagram at constant atmospheric pressure. As pressure is neglected the phase rule is called condensed phase rule.

1) Curve AO. It is a freezing point curve of Ag. Ag Co exists as solid and liquid. Melting point of Ag falls gradually on adding Pb till the lowest point is reached. The solution gets saturated with respective to lead.

2) Curve BO. It is a freezing point curve of Pb. At this curve the melting point gradually falls on the addition of Ag till lowest point it reach.

3) Point O. It is eutectic point. Here 3 phases co-exists and point O represents a fixed composition and system is in variant.

Below the temperature line of eutectic temperature, we have two regions.

a) The region marked eutectic plus solid Ag in which crystalline silver and solid eutectic are stable.

b) The region marked eutectic plus solid Pb in which crystalline lead and solid eutectic are stable.

4) Area AOB. It represents solution of Pb Ag. On lowering temperature the lead begins to separate out till the point O is reached.

b) **Phase**:It is defined as any homogeneous, physically distinct and mechanically separable portion of a system, which is separated from other such parts of the system by definite boundary surfaces in a system.

Component- It is defined as the smallest number of independently variable constituents taking part in the state of equilibrium by means of which the composition of each phase can be expressed directly or in the form of chemical equation.

Degree of freedom- It is defined as the minimum number of the independently variable factors such as the temperature, pressure and composition of the phases which must be arbitrarily specified in order to represent perfectly the condition of a system.

A phase is a form of matter that is homogeneous in chemical composition and physical state. Typical phases are solid, liquid and gas. Two immiscible liquids (or liquid mixtures with different compositions) separated by a distinct boundary are counted as two different phases, as are two immiscible solids.

The number of components (C) is the number of chemically independent constituents of the system, i.e. the minimum number of independent species necessary to define the composition of all phases of the system.[2] For examples see component (thermodynamics).

The number of degrees of freedom (F) in this context is the number of intensive variables which are independent of each other.

The basis for the rule is that equilibrium between phases places a constraint on the intensive variables. More rigorously, since the phases are in thermodynamic equilibrium with each other, the chemical potentials of the phases must be equal. The number of equality relationships determines the number of degrees of freedom. For example, if the chemical potentials of a liquid and of its vapour depend on temperature (T) and pressure (p), the equality of chemical potentials will mean that each of those variables will be dependent on the other. Mathematically, the equation $\mu_{liq}(T, p) = \mu_{vap}(T, p)$, where μ = chemical potential, defines temperature as a function of pressure or vice versa. (Caution: do not confuse p = pressure with P = number of phases.)

To be more specific, the composition of each phase is determined by $C - 1$ intensive variables (such as mole fractions) in each phase. The total number of variables is $(C - 1)P + 2$, where the extra two are temperature T and pressure p. The number of constraints is $C(P - 1)$, since the chemical potential of each component must be equal in all phases. Subtract the number of constraints from the number of variables to obtain the number of degrees of freedom as

$F = (C - 1)P + 2 - C(P - 1) = C - P + 2.$

The rule is valid provided the equilibrium between phases is not influenced by gravitational, electrical or magnetic forces, or by surface area, and only by temperature, pressure, and concentration.

[17CHU301] **Reg. No……………**

KARPAGAM ACADEMY OF HIGHER EDUCATION

COIMBATORE-641 021

(For the candidates admitted from 2017 & Onwards)

B.Sc., DEGREE INTERNAL EXAMINATION, AUGUST 2018

CHEMISTRY

INTERNAL TEST-II

PHYSICAL CHEMISTRY-III

(Phase Equilibrium and Chemical Kinetics)

Time: 2 Hours **Maximum : 50 marks**

PART - A (20 x 1 =20)

Answer all Questions

1. Critical solution temperature is otherwise known as

a) consolute temperature b)solubility temperature

c) misicibility temperature d)melting temperature

2. Water-ethanol system is an example for

a)type I b)type II c)type III d)type IV

3. Solutions of different composition coexisting with one another are termed as

a)conjugate solutions b)non-conjugate solutions

c)mixed solutions d)non-mixed solutions

4. Ethanol in type II fractional distillation is obtained as

a)residue b)distillate c)residue and distillate d)vapour

5. Azeotropic mixture is otherwise known as

a) constant boiling mixture b) liquid mixture

c) gaseous mixture d) solid mixture

6. Application of the phase rule to a system corresponding to a point in the two phase region gives

a)F=2 b)F=3 c)F=1 d)F=0

7. The electrode in which oxidation occurs is
a)anode b)cathode c)Anode and Cathode d)Electrolyte

8. The value of standard electrode potential arranged in the decreasing order is called
a)chemical series b)potential series
c)electrochemical series d)electricity series

9. The electrical energy is measured in
a)volts b)joules c)coulomb d)meter

10. What is the potential of a half cell consisting of zinc electrode in 0.01M $ZnSO_4$ Solution?
T=25°C. E°= 0.763 V
a)0.0591 V b)0.6521 V c)0.7532 V d)0.8221 V

11. An example for metal-metal ion electrodes is
a)daniel cell b)hydrogen electrode c)chlorine electrode d)calomel electrode

12. Which one is Metal-insoluble metal salt electrode?
a)calomel electrode b)standard hydrogen electrode
c)silver-silver chloride electrode d)Gas electrode

13. The reduction potential of the electrode is 1.5v then its oxidation potential is
a)0 V b)1 V c)negative 1.5 V d)2 V

14. The relationship between free energy change and emf of a cell is
a)$\Delta G = -nFE$ b)$\Delta H = -nFE$ c)$\Delta E = nFG$ d)$\Delta F = nEG$

15. The electrochemical or electrolytic processes are carried out in a device known as
a)battery b)galvanometer c)potentiometer d)electrolyte

16. The salt bridge is filled with a solution of
a)potassium chromate b)sodium chloride
c)potassium chloride d)zinc chloride

17. The electrode in which reduction occurs is
a)anode b)cathode c)anode and cathode d)Electrolyte

18. The EMF generated by an electrochemical cell is given by the symbol
a)E b)E° c)V d)V°

19. If the standard emf E° is positive, the reaction is

a) feasible b)not feasible c) reversible d) Irreversible

20. The Nernst equation is

a)E= 2.303 RT/nF log K b) E= 2.303/nF RT log K

c) E= 2.303 RT/nF-E° d) E=E°- 2.303 RT/nF log K

PART B (3x2=6)

Answer All the Questions

21. Define Critical Solution Temperature.

22. What is meant by an electrolytic cell?

23. Write down Nernst equation for an oxidation and reduction potential.

PART C (3x8=24)

Answer All the Questions

24. a) Write notes on (i)Fractional distillation (ii)Steam distillation

(OR)

b) Derive Nernst distribution law and mention its applications.

25. a) What is known as electrochemical cell and write down the rules of oxidation/reduction of ions based on half-cell potentials.

(OR)

b) Derive Nernst equation for EMF of a cell.

26. a) What are the applications of Electrolysis in metallurgy and industry?

(OR)

b) Discuss the following

(i) Reversible and irreversible cells

(ii) Standard electrode potential

.

[17CHU301] **Reg. No……………**

KARPAGAM ACADEMY OF HIGHER EDUCATION

COIMBATORE-641 021

(For the candidates admitted from 2017 & Onwards)

B.Sc., DEGREE INTERNAL EXAMINATION, AUGUST 2018

CHEMISTRY

INTERNAL TEST-II

PHYSICAL CHEMISTRY-III
(Phase Equilibrium and Chemical Kinetics)

Time: 2 Hours **Maximum : 50 marks**

PART - A (20 x 1 =20)

Answer all Questions

1. Critical solution temperature is otherwise known as
a) consolute temperature b)solubility temperature
c) misicibility temperature d)melting temperature

2. Water-ethanol system is an example for
a)type I **b)type II** c)type III d)type IV

3. Solutions of different composition coexisting with one another are termed as
a)conjugate solutions b)non-conjugate solutions
c)mixed solutions d)non-mixed solutions

4. Ethanol in type II fractional distillation is obtained as
a)residue **b)distillate** c)residue and distillate d)vapour

5. Azeotropic mixture is otherwise known as
a)constant boiling mixture b) liquid mixture
c) gaseous mixture d) solid mixture

6. Application of the phase rule to a system corresponding to a point in the two phase region gives
a)F=2 **b)F=3** c)F=1 d)F=0

7. The electrode in which oxidation occurs is
a)anode b)cathode c)Anode and Cathode d)Electrolyte

8. The value of standard electrode potential arranged in the decreasing order is called
a)chemical series b)potential series
c)electrochemical series d)electricity series

9. The electrical energy is measured in
a)volts **b)joules** c)coulomb d)meter

10. What is the potential of a half cell consisting of zinc electrode in 0.01M $ZnSO_4$ Solution?
T=25°C. E°= 0.763 V
a)0.0591 V b)0.6521 V c)0.7532 V d)0.8221 V

11. An example for metal-metal ion electrodes is
a)daniel cell b)hydrogen electrode c)chlorine electrode d)calomel electrode

12. Which one is Metal-insoluble metal salt electrode?
a)calomel electrode b)standard hydrogen electrode
c)silver-silver chloride electrode d)Gas electrode

13. The reduction potential of the electrode is 1.5v then its oxidation potential is
a)0 V b)1 V **c)negative 1.5 V** d)2 V

14. The relationship between free energy change and emf of a cell is
a)$\Delta G= -nFE$ b)$\Delta H= -nFE$ c)$\Delta E= nFG$ d)$\Delta F= nEG$

15. The electrochemical or electrolytic processes are carried out in a device known as
a)battery **b)galvanometer** c)potentiometer d)electrolyte

16. The salt bridge is filled with a solution of
a)potassium chromate b)sodium chloride
c)potassium chloride d)zinc chloride

17. The electrode in which reduction occurs is
a)anode **b)cathode** c)anode and cathode d)Electrolyte

18. The EMF generated by an electrochemical cell is given by the symbol
a)E b)E° c)V d)V°

19. If the standard emf E° is positive, the reaction is

a) feasible b)not feasible c) reversible d) Irreversible

20. The Nernst equation is

a)E= 2.303 RT/nF log K **b) E= 2.303/nF RT log K**

c) E= 2.303 RT/nF-E° d) E=E°- 2.303 RT/nF log K

PART B (3x2=6)

Answer All the Questions

21. Define Critical Solution Temperature.

22. What is meant by an electrolytic cell?

23. Write down Nernst equation for an oxidation and reduction potential.

PART C (3x8=24)

Answer All the Questions

24. a) Write notes on (i)Fractional distillation (ii)Steam distillation

(OR)

b) Derive Nernst distribution law and mention its applications.

25. a) What is known as electrochemical cell and write down the rules of oxidation/reduction of ions based on half-cell potentials.

(OR)

b) Derive Nernst equation for EMF of a cell.

26. a) What are the applications of Electrolysis in metallurgy and industry?

(OR)

b) Discuss the following

(i) Reversible and irreversible cells

(ii) Standard electrode potential

[17CHU301]

KARPAGAM ACADEMY OF HIGHER EDUCATION
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COIMBATORE-21
B.Sc. Degree Internal Examination,July 2018
(For the candidates admitted from 2017& onwards)
II B.Sc CHEMISTRY
INTERNAL EXAM II
PHYSICAL CHEMISTRY III
(Phase Equilibria and Chemical Kinetics)

ANSWER KEY
PART- A

1.a)consolute temperature

2.b)type II

3.a)conjugate solutions

4.b)distillate

5.a)constant boiling mixture

6.b)F=3

7.a)anode

8.c)electrochemical series

9.b)joules

10.a)0.0591 V

11.a)Daniel cell

12.a)calomel electrode

13.c)negative 1.5 V

14.a)ΔG=-Nfe

15.b)galvanometer

16.c)potassium chloride

17.b)cathode

18.a)E

19.a)feasible

20.$E=E^0-2.303\ RT/n\ F\ \log K$

PART B

21. The temperature at which complete miscibility is reached as the temperature is raised or in some cases lowered —used of two liquids that are partially miscible under ordinary conditions

22.Electrolytic cell is one in which electrical energy is converted into chemical energy

23.Nernst equation for oxidation potential $E=E^0-RT/n\ F\ \log [M^+]$

Nernst equation for reducation potential $E=E^0+RT/n\ F\ \log [M^+]$

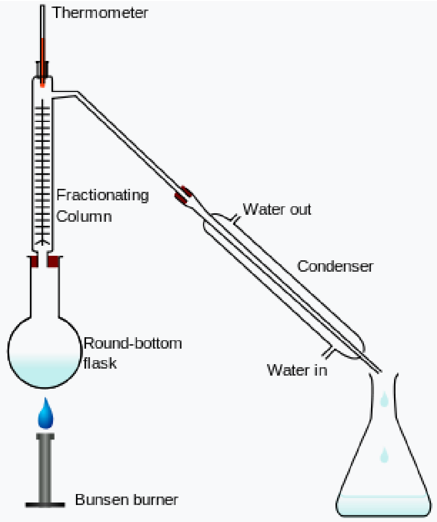
PART C

24.a)(i)Fractional distillation

Fractional distillation is the separation of a mixture into its component parts, or fractions. Chemical compounds are separated by heating them to a temperature at which one or more fractions of the compound will vaporize. It uses distillation to fractionate. Generally the component parts have boiling points that differ by less than 25 °C from each other under a pressure of one atmosphere. If the difference in boiling points is greater than 25 °C, a simple distillation is typically used.

Fractional distillation in a laboratory makes use of common laboratory glassware and apparatuses, typically including a Bunsen burner, a round-bottomed flask and a condenser, as well as the single-purpose fractionating column.

Apparatus



Fractional distillation

An Erlenmeyer flask is used as a receiving flask. Here the distillation head and fractionating column are combined in one piece.[1]

- heat source, such as a hot plate with a bath, and ideally with a magnetic stirrer.
- distilling flask, typically a round-bottom flask
- receiving flask, often also a round-bottom flask
- fractionating column
- distillation head
- thermometer and adapter if needed
- condenser, such as a Liebig condenser or Allihn condenser
- vacuum adapter (not used in image to the right)
- boiling chips, also known as anti-bumping granules
- Standard laboratory glassware with ground glass joints, e.g. quickfit apparatus.

As an example consider the distillation of a mixture of water and ethanol. Ethanol boils at 78.4 °C while water boils at 100 °C. So, by heating the mixture, the most volatile component (ethanol) will concentrate to a greater degree in the vapor leaving the liquid. Some mixtures form azeotropes, where the mixture boils at a lower temperature than either component. In this example, a mixture of 96% ethanol and 4% water boils at 78.2 °C; the mixture is more volatile than pure ethanol. For this reason, ethanol cannot be completely purified by direct fractional distillation of ethanol-water mixtures.

The apparatus is assembled as in the diagram. (The diagram represents a batch apparatus as opposed to a continuous apparatus.) The mixture is put into the round bottomed flask along with a few anti-bumping granules (or a Teflon coated magnetic stirrer bar if using magnetic stirring), and the fractionating column is fitted into the top. The fractional distillation column is set up with the heat source at the bottom on the still pot. As the distance from the stillpot increases, a temperature gradient is formed in the column; it is coolest at the top and hottest at the bottom. As the mixed vapor ascends the temperature gradient, some of the vapor condenses and revaporizes along the temperature gradient. Each time the vapor condenses and vaporizes, the composition of the more volatile component in the vapor increases. This distills the vapor along the length of the column, and eventually the vapor is composed solely of the more volatile component (or an azeotrope). The vapor condenses on the glass platforms, known as trays, inside the column, and runs back down into the liquid below, refluxing distillate. The efficiency in terms of the amount of heating and time required to get fractionation can be improved by insulating the outside of the column in an insulator such as wool, aluminium foil or preferably a vacuum jacket. The hottest tray is at the bottom and the coolest is at the top. At steady state conditions, the vapor and liquid on each tray are at *equilibrium*. The most volatile component of the mixture exits as a gas at the top of the column. The vapor at the top of the column then passes into the condenser, which cools it down until it liquefies. The separation is more pure with the addition of more trays (to a practical limitation of heat, flow, etc.) Initially, the condensate will be close to the azeotropic composition, but when much of the ethanol has been drawn off, the condensate becomes gradually richer in water. The process continues until all the ethanol boils out of the mixture. This point can be recognized by the sharp rise in temperature shown on the thermometer.

The above explanation reflects the theoretical way fractionation works. Normal laboratory fractionation columns will be simple glass tubes (often vacuum-jacketed, and sometimes internally silvered) filled with a packing, often small glass helices of 4 to 7 mm diameter. Such a column can be calibrated by the distillation of a known mixture system to quantify the column in terms of number of theoretical trays. To improve fractionation the apparatus is set up to return condensate to the column by the use of some sort of reflux splitter (reflux wire, gago, Magnetic swinging bucket, etc.) - a typical careful fractionation would employ a reflux ratio of around 4:1 (4 parts returned condensate to 1 part condensate take off).

In laboratory distillation, several types of condensers are commonly found. The Liebig condenser is simply a straight tube within a water jacket, and is the simplest (and relatively least expensive) form of condenser. The Graham condenser is a spiral tube within a water jacket, and the Allihn condenser has a series of large and small constrictions on the inside tube, each increasing the surface area upon which the vapor constituents may condense.

Alternate set-ups may use a multi–outlet distillation receiver flask (referred to as a "cow" or "pig") to connect three or four receiving flasks to the condenser. By turning the cow or pig, the distillates can be channeled into any chosen receiver. Because the receiver does not have to be removed and replaced during the distillation process, this type of apparatus is useful when distilling under an inert atmosphere for air-sensitive chemicals or at reduced pressure. A Perkin triangle is an alternative apparatus often used in these situations because it allows isolation of the receiver from the rest of the system, but does require removing and reattaching a single receiver for each fraction.

Vacuum distillation systems operate at reduced pressure, thereby lowering the boiling points of the materials. Anti-bumping granules, however, become ineffective at reduced pressures

(ii) **Steam distillation** is a special type of distillation (a separation process) for temperature sensitive materials like natural aromatic compounds. It once was a popular laboratory method for purification of organic compounds, but has become obsolete by vacuum distillation. Steam distillation remains important in certain industrial sectors.[1]

Many organic compounds tend to decompose at high sustained temperatures. Separation by distillation at the normal (1 atmosphere) boiling points is not an option, so water or steam is introduced into the distillation apparatus. The water vapor carries small amounts of the vaporized compounds to the condensation flask, where the condensed liquid phase separates, allowing for easy collection. This process effectively allows for distillation at lower temperatures, reducing the deterioration of the desired products. If the substances to be distilled are very sensitive to heat, steam distillation may be applied under reduced pressure, thereby reducing the operating temperature further.

After distillation the vapors are condensed. Usually the immediate product is a two-phase system of water and the organic distillate, allowing for separation of the components by decantation, partitioning or other suitable methods.

Applications

A boiling water distiller. Boiling tank on top and holding tank on the bottom.

Steam distillation is employed in the isolation of essential oils, for use in perfumes, for example. In this method, steam is passed through the plant material containing the desired oils. Eucalyptus oil and orange oil are obtained by this method on an industrial scale. Steam distillation is also sometimes used to separate intermediate or final products during the synthesis of complex organic compounds.

Steam distillation is also widely used in petroleum refineries and petrochemical plants where it is commonly referred to as "steam stripping".

Steam distillation also is an important means of separating fatty acids from mixtures and for treating crude products such as tall oils to extract and separate fatty acids, soaps and other commercially valuable organic compounds.

b) At constant temperature, a solute distributes itself between two immiscible solvents only in a particular ratio”This statement is a Nernst Distribution Law – i.e. the law that determines the relative distribution of a component that is soluble in two liquids, these liquids being immiscible or miscible to a limited extent. This law is one of the laws applying to ideal dilute solutions. It was discovered by W. Nernst in 1890. The Nernst distribution law states that, at equilibrium, the ratio of the concentrations of a third component in two liquid phases is constant. The law may be expressed in the form

$$c_1/c_2 = k$$

where c_1 and c_2 are the molar equilibrium concentrations of the third component in the first and second phase, respectively; the constant k is the distribution coefficient, which is temperature dependent.

The Nernst distribution law permits us to determine the most favorable conditions for the extraction of substances from solutions. If the dissolved compound in one of the solvents can associate:

$$nA \Leftrightarrow A_n \; nA$$

than the ration c_1/c_2 is **not** stable at constant temperature

25.a) Rules of oxidation/reduction of ions based on half-cell potentials

A **half-cell** is a structure that contains a conductive electrode and a surrounding conductive electrolyte separated by a naturally occurring Helmholtz double layer. Chemical reactions within this layer momentarily pump electric charges between the electrode and the electrolyte, resulting in a potential difference between the electrode and the electrolyte. The typical anode reaction involves a metal atom in the electrode dissolved and transported as a positive ion across the double layer, causing the electrolyte to acquire a net positive charge while the electrode acquires a net negative charge. The growing potential difference creates an intense electric field within the double layer, and the potential rises in value until the field halts the net charge-pumping reactions. This self-limiting action occurs almost instantly in an isolated half-cell; in applications two dissimilar half-cells are appropriately connected to constitute a Galvanic cell.

A standard half-cell, used in electrochemistry, consists of a metal electrode in a 1 molar (1 mol/L) aqueous solution of the metal's salt, at 298 kelvin (25 °C).[1] The electrochemical series, which consists of standard electrode potentials and is closely related to the reactivity series, was generated by measuring the difference in potential between the metal half-cell in a circuit with a standard hydrogen half-cell, connected by a salt bridge.

The standard hydrogen half-cell:

$2H^+(aq) + 2e^- \rightarrow H_2(g)$

The half-cells of a Daniell cell:

Original equation

$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

Half-cell (anode) of Zn

$Zn \rightarrow Zn^{2+} + 2e^-$

Half-cell (cathode) of Cu

$Cu^{2+} + 2e^- \rightarrow Cu$

b) In electrochemistry, the **Nernst equation** is an equation that relates the reduction potential of an electrochemical reaction (half-cell or full cell reaction) to the standard electrode potential, temperature, and activities (often approximated by concentrations) of the chemical species undergoing reduction and oxidation. It is the most important equation in the field of electrochemistry. It is named after the German physical chemist who first formulated it, Walther Nernst.

Standard electrode potential and its application to different kinds of half-cells

In electrochemistry, the **standard electrode potential**, abbreviated E° or E⊖ (with a superscript plimsoll character, pronounced "standard" or "nought"), is the measure of individual potential of a reversible electrode at standard state, which is with solutes at an effective concentration of 1 mol dm^{-3}, and gases at a pressure of 1 atm. The reduction potential is an intensive property. The values are most often tabulated at 25 °C. The basis for an electrochemical cell such as the galvanic cell is always a redox reaction which can be broken down into two half-reactions: oxidation at anode (loss of electron) and reduction at cathode (gain of electron). Electricity is generated due to electric potential difference between two electrodes. This potential difference is created as a result of the difference between individual potentials of the two metal electrodes with respect to the electrolyte. (Reversible electrode is an electrode that owes its potential to changes of a reversible nature, in contrast to electrodes used in electroplating which are destroyed during their use.)

Although the overall potential of a cell can be measured, there is no simple way to accurately measure the electrode/electrolyte potentials in isolation. The electric potential also varies with temperature, concentration and pressure. Since the oxidation potential of a half-reaction is the negative of the reduction potential in a redox reaction, it is sufficient to calculate either one of the potentials. Therefore, standard electrode potential is commonly written as standard reduction potential.

Calculation of standard electrode potentials

The electrode potential cannot be obtained empirically. The galvanic cell potential results from a pair of electrodes. Thus, only one empirical value is available in a pair of electrodes and it is not possible to determine the value for each electrode in the pair using the empirically obtained galvanic cell potential. A reference electrode, standard hydrogen electrode (SHE), for which the potential is defined or agreed upon by convention, needed to be established. In this case SHE is set to 0.00 V and any electrode, for which the electrode potential is not yet known, can be paired with SHE—to form a galvanic cell—and the galvanic cell potential gives the unknown electrode's potential. Using this process, any electrode with an unknown potential can be paired with either the SHE or another electrode for which the potential has already been derived and that unknown value can be established.

Since the electrode potentials are conventionally defined as reduction potentials, the sign of the potential for the metal electrode being oxidized must be reversed when calculating the overall cell potential. Note that the electrode potentials are independent of the number of electrons transferred —they are expressed in volts, which measure energy per electron transferred—and so the two electrode potentials can be simply combined to give the overall cell potential even if different numbers of electrons are involved in the two electrode reactions.

For practical measurements, the electrode in question is connected to the positive terminal of the electrometer, while SHE is connected to the negative terminal.[1]

Standard reduction potential

The larger the value of the standard reduction potentials, the easier it is for the element to be reduced (accept electrons); in other words, they are better oxidizing agents. For example, F_2 has 2.87 V and Li^+ has −3.05 V. F reduces easily and is therefore a good oxidizing agent. In contrast, $Li_{(s)}$ would rather undergo oxidation (hence a good reducing agent). Thus Zn^{2+} whose standard reduction potential is −0.76 V can be oxidized by any other electrode whose standard reduction potential is greater than −0.76 V (e.g. H^+(0 V), Cu^{2+}(0.16 V), F_2(2.87 V)) and can be reduced by any electrode with standard reduction potential less than −0.76 V (e.g. H_2(−2.23 V), Na^+(−2.71 V), Li^+(−3.05 V)).

In a galvanic cell, where a spontaneous redox reaction drives the cell to produce an electric potential, Gibbs free energy ΔG° must be negative, in accordance with the following equation:

$$\Delta G^\circ_{cell} = -nFE^\circ_{cell}$$

where n is number of moles of electrons per mole of products and F is the Faraday constant, ~96485 C/mol. As such, the following rules apply:

If $E^\circ_{cell} > 0$, then the process is spontaneous (galvanic cell)

If $E^\circ_{cell} < 0$, then the process is nonspontaneous (electrolytic cell)

Thus in order to have a spontaneous reaction ($\Delta G^\circ < 0$), E°_{cell} must be positive, where:

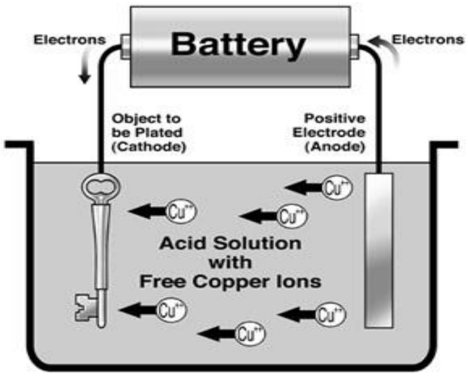
$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

where E°_{anode} is the standard potential at the anode and $E^\circ_{cathode}$ is the standard potential at the cathode as given in the table of standard electrode potential.

26.a) Applications of electrolysis in metallurgy and industry

Electroplating is used to coat one metal with another metal by using electrolysis. Electroplating is usually done to improve the appearance of the metal or prevent the corrosion of the metal.

Chromium plating is used to prevent iron from rusting.



The cathode is the object to be plated, while anode is the desired metal to coat the object. The electrolyte solution must contain ions of the same metal for plating. During electrolysis, the anode will dissolve into the solution. The ions produced will migrate to the cathode where they are discharged and deposited as a layer on the cathode.

It is important to ensure that the cathode is electrically conductive. (If not, the electrolysis does not work.)

Example:Silver Plating

Electrodes: Silver anode, Cathode is object to be plated with silver

Electrolyte: Solution of soluble silver salt. (E.g. Silver nitrate, $AgNO_3(aq)AgNO_3(aq)$)

$$AgNO_3(aq)\leftrightarrow Ag^{+(}aq)+NO^{-3}(aq)$$

$$H_2O(l)\leftrightarrow H^{+}(aq)+OH^{-}(aq)$$

Ions present in solution: $Ag^{+}Ag^{+}$, $H^{+}H^{+}$, $NO^{-3}NO^{-3}$, $OH^{-}OH^{-}$
Reaction at CATHODE:

- Ag^{+} and $H^{+}$is attracted to the cathode.
- Ag^{+} is preferentially discharged.

- Silver metal is deposited on the cathode.
- $Ag^{+}(aq)+e- \longrightarrow Ag(s)$

Reaction at ANODE:

- $NO^{-3}$and OH^{-} is attracted to the anode.
- Neither NO^{-3} nor OH^{-} is discharged.
- Each silver atom loses one electron to form one Ag^{+} ion.
- The silver anode dissolves into the solution.
- $Ag(s) \rightarrow Ag^{+}(aq)+e-$

b)Reversibel and irrerversible cells

Cells in which cells and reactions are reversed is known as reversible cells

Eg., lead acid battery

Cells in which cells and reactions are not reversed is known as irreversible cell

Eg., dry cell

(ii) In electrochemistry, the **standard electrode potential**, abbreviated E° or $E^{\ominus}$ (with a superscript plimsoll character, pronounced "standard" or "nought"), is the measure of individual potential of a reversible electrode at standard state, which is with solutes at an effective concentration of 1 mol dm^{-3}, and gases at a pressure of 1 atm. The reduction potential is an intensive property. The values are most often tabulated at 25 °C. The basis for an electrochemical cell such as the galvanic cell is always a redox reaction which can be broken down into two half-reactions: oxidation at anode (loss of electron) and reduction at cathode (gain of electron). Electricity is generated due to electric potential difference between two electrodes. This potential difference is created as a result of the difference between individual potentials of the two metal electrodes with respect to the electrolyte. (Reversible electrode is an electrode that owes its potential to changes of a reversible nature, in contrast to electrodes used in electroplating which are destroyed during their use.)

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KARPAGAM ACADEMY OF HIGHER EDUCATION

COIMBATORE-641 021

(For the candidates admitted from 2017 & Onwards)

B.Sc., DEGREE INTERNAL EXAMINATION, OCTOBER 2018

CHEMISTRY

INTERNAL TEST-III

PHYSICAL CHEMISTRY-III

(Phase Equilibrium and Chemical Kinetics)

Time: 2 Hours **Maximum : 50 marks**

PART - A (20 x 1 =20)

Answer all Questions

1. If the --------------of a particular cell is known, the equilibrium constant of the cell reaction can be calculated.

a)standard EMF b)entropy c)free energy d)enthalpy

2. Which one of the electrodes is preferred to Quinhydrone?

a)hydrogen b)calomel c)glass d)platinum

3. Electrode-concentration cell are evidently independent of

a)concentration of electrolyte b)concentration of ions

c)concentration in electrode d)electrolyte concentration cell

4. Which of the following shows a metal being oxidized

a)$2Na + 2H_2O \rightarrow 2NaOH + H_2$ b)$Cu \rightarrow Cu^{2+} + 2e^-$

c)$Cu^{2+} + 2e^+ \rightarrow Cu$ d)$Cu \rightarrow Cu^{2+} + 2e-$ and $2Na + 2H_2O \rightarrow 2NaOH + H_2$

5. Emf is measured in

a)volts b)amperes c)coulombs d)ohm

6. Which molar of HCl solution furnishes a constant hydrogen ion concentration?

a)0.01 b)0.1 c)0.2 d)0.001

7. Glass electrodes can be used in

a)strong oxidising solutions b)week oxidising solutions

c)strong reducing solutions d)week reducing solutions

8. In given reaction $2Cr(s) + 3Cu^{2+}(aq) \rightarrow 3Cr^{3+}(aq) + 3Cr(s)$ which reaction occurs of the cathode in an electrochemical cell

a)reduction of $Cu^{2+}(aq)$ b)reduction of Cu(s)

c)oxidation of $Cu^{3+}(aq)$ d)oxidation of Cr(s)

9. Transfer of ions from one electrolytic solution to the other does not take place at

a)concentration cell with transfer
b)concentration cell without transfer
c)emf is partially negative
d)concentration cell without transfer and concentration cell with transfer

10. Electrical energy forced in electrochemical cell is
a)Spontaneous b)Non-Spontaneous c)Exothermic d)Endothermic

11.The adsorption is accompanied by a ---------------------in residual surface forces

a)decrease b)increase c)increase and then decreases d)decrease and then increases

12. x/m is known as

a)nature of adsorption b)extent of adsorption

c)rate of adsorption d)magnitude of adsorption

13. According to Langmuir if a bond is weak, which type of adsorption takes place?

a)chemical b)physical c)oxidation d)reduction

14. Which one of the activity is important factor in the surface area of catalysts?

a)activity coefficients b)viscosity coefficients

c)diffusion coefficients d)catalytic

15.Charcoal and silica gel are excellent a)adsorbate b)adsorbent c)sorbent d)absorbate

16. Freundlich adsoprtion isotherm fails if concentration of adsorbate is very

a)high b)low c)medium d)average

17. Adsorption involves the-------------------into the interior of the matter

a)diffusion b)penetration c)occlusion d)inclusion

18. Which among the following is very necessary in order to increase the rate of adsorption?

a)catalyst b)reactant c)activation d)sorption

19.In physical adsorption there is a increase in which one there is a decrease in extent of adsorption.

a)pressure b)concentration c)volume d)temperature

20. By application of the BET theory it is possible to determine the inner surface of hardened ------------paste

a)composite b)cement c)matrix d)concrete

PART B (3x2=6)

Answer All the Questions

21**.** What is said to be activity coefficient?

22.Write down BET equation.

23.Differentiate adsorbate and adsorbent.

PART C (3x8=24)

Answer All the Questions

24. a)How to determine pH using the following electrodes
(i)Hydrogen electrode
(ii)Quinhydrone electrode
(iii)Glass electrode

(OR)

b. Explain potentiometric redox titration.

25. a) . What is known as absorption? Derive Freundlich adsorption isotherm and mention its conditions.

(OR)

b. Explain the postulates of Langmuir adsorption isotherm and derive the same .

26. a) . Write short note on

(i) Liquid junctional potential

(ii) EMF measurements in determining equilibrium constant

(OR)

b) Differentiate physical adsorption and chemical adsorption.

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[17CHU301]

KARPAGAM ACADEMY OF HIGHER EDUCATION
(Deemed to be University)
(Established Under Section 3 of UGC Act 1956)
COIMBATORE-21
B.Sc. Degree Internal Examination,July 2018
(For the candidates admitted from 2017& onwards)
II B.Sc CHEMISTRY
INTERNAL EXAM III
PHYSICAL CHEMISTRY III
(Phase Equilibria and Chemical Kinetics)

ANSWER KEY
PART- A

1.a)standard EMF

2.a)hydrogen

3.a)concentration

4.d)$Cu \rightarrow Cu^{2+} + 2e^-$ and $2Na+2H_2O \rightarrow 2NaOH+H_2$

5.a)volts

6.b)0.1

7.a)strong oxidizing solutions

8.c)oxidation of Cu^{+3}

9.b)concentrations cell without transfer

10.b)Non-spontaneous

11.a)decrease

12.b)extent of adsorption

13.b)physical

14.d)catalytic

15.b)adsorbent

16.a)high

17.a)diffusion

18.c)activation

19.d)temperature

20.b)cement

PART B

21. An **activity coefficient** is a factor used in thermodynamics to account for deviations from ideal behaviour in a mixture of chemical substances.[1] In an ideal mixture, the microscopic interactions between each pair of chemical species are the same (or macroscopically equivalent, the enthalpy change of solution and 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.

22. $1/v[(p0/p)-1]=c-1/v_m c\ p/p0 +1/v_m c$

23. adsorbate is a substance that's gets adsorbed on the surface

Adsorbent is a substance where adsorption takes place

PART C

24.a(i)Hydrogen electrode

The **Standard hydrogen electrode** (abbreviated **SHE**), is a redox electrode which forms the basis of the thermodynamic scale of oxidation-reduction potentials. Its absolute electrode potential is estimated to be 4.44 ± 0.02 V at 25 °C, but to form a basis for comparison with all other electrode reactions, hydrogen's standard electrode potential (E^0) is declared to be zero volts only at 298K.[1] Potentials of any other electrodes are compared with that of the standard hydrogen electrode at the same temperature.

Hydrogen electrode is based on the redox half cell:

$$2\ H^+(aq) + 2\ e^- \rightarrow H_2(g)$$

This redox reaction occurs at a platinized platinum electrode. The electrode is dipped in an acidic solution and pure hydrogen gas is bubbled through it. The concentration of both the reduced form and oxidised form is maintained at unity. That implies that the pressure of hydrogen gas is 1 bar (100 kPa) and the activity of hydrogen ions in the solution is unity. The activity of hydrogen ions is their effective concentration, which is equal to the formal concentration times the activity coefficient. These unit-less activity coefficients are close to 1.00 for very dilute water solutions, but usually lower for more concentrated solutions.

(ii)Quinhydrone electrode

The **quinhydrone electrode** is a type of redox electrode which used to measure the hydrogen ion concentration (pH) of a solution in a chemical experiment. It provides an alternative to the commonly used glass electrode in a pH meter.[1]

The electrode consists of an inert metal electrode (usually a platinum wire) in contact with quinhydrone crystals and a water-based solution. Quinhydrone is slightly soluble in water, dissolving to form a mixture of two substances, quinone and hydroquinone, with the two substances present at equal concentration. Each one of the two substances can easily be oxidised or reduced to the other.

The potential at the inert electrode depends on the ratio of the activity of two substances (quinone-hydroquinone), and also the hydrogen ion concentration. The electrode half-reaction is:

$$\text{Hydroquinone} \leftrightarrow \text{Quinone} + 2H^+ + 2e^-$$

Because the electrode half-reaction involves hydrogen ions, the electrode potential depends on the activity of hydrogen ions.

(iii)Glass electrode

A **glass electrode** is a type of ion-selective electrode made of a doped glass membrane that is sensitive to a specific ion. The most common application of ion-selective glass electrodes is for the measurement of pH. The pH electrode is an example of a glass electrode that is sensitive to hydrogen ions. Glass electrodes play an important part in the instrumentation for chemical analysis and physico-chemical studies. The voltage of the glass electrode, relative to some reference value, is sensitive to changes in the activity of certain type of ions.

A typical modern pH probe is a combination electrode, which combines both the glass and reference electrodes into one body. The combination electrode consists of the following parts (see the drawing):

1. a sensing part of electrode, a bulb made from a specific glass
2. internal electrode, usually silver chloride electrode or calomel electrode
3. internal solution, usually a pH=7 buffered solution of 0.1 mol/L KCl for pH electrodes or 0.1 mol/L MCl for pM electrodes
4. when using the silver chloride electrode, a small amount of AgCl can precipitate inside the glass electrode
5. reference electrode, usually the same type as 2
6. reference internal solution, usually 0.1 mol/L KCl
7. junction with studied solution, usually made from ceramics or capillary with asbestos or quartz fiber.
8. body of electrode, made from non-conductive glass or plastics.

The bottom of a pH electrode balloons out into a round thin glass bulb. The pH electrode is best thought of as a tube within a tube. The inner tube contains an unchanging 1×10^{-7} mol/L HCl solution. Also inside the inner tube is the cathode terminus of the reference probe. The anodic terminus wraps itself around the outside of the inner tube and ends with the same sort of reference probe as was on the inside of the inner tube. It is filled with a reference solution of KCl and has contact with the solution on the outside of the pH probe by way of a porous plug that serves as a salt bridge.

b) A **redox titration** is a type of titration based on a redox reaction between the analyte and titrant. Redox titration may involve the use of a redox indicator and/or a potentiometer. A common example of a redox titration is treating a solution of iodine with a reducing agent to produce iodide using a starch indicator to help detect the endpoint. Iodine (I_2) can be reduced to iodide (I^-) by e.g. thiosulfate ($S_2O_3^{2-}$), and when all iodine is spent the blue colour disappears. This is called an iodometric titration.

Most often of all, the reduction of iodine to iodide is the last step in a series of reactions where the initial reactions are used to convert an unknown amount of the solute (the substance being analyzed) to an equivalent amount of iodine, which may then be titrated. Sometimes other halogens (or haloalkanes) than iodine are used in the intermediate reactions because they are available in better measurable standard solutions and/or react more readily with the solute. The extra steps in iodometric titration may be worth while because the equivalence point, where the blue turns a bit colourless, is more distinct than some other analytical or may be by volumetric methods.

To evaluate a redox titration we need to know the shape of its titration curve. In an acid–base titration or a complexation titration, the titration curve shows how the concentration of H_3O^+ (as pH) or M^{n+} (as pM) changes as we add titrant. For a redox titration it is convenient to monitor the titration reaction's potential instead of the concentration of one species.

The Nernst equation relates a solution's potential to the concentrations of reactants and products participating in the redox reaction. Consider, for example, a titration in which a titrand in a reduced state, A_{red}, reacts with a titrant in an oxidized state, B_{ox}.

25.a) Freundlich Adsorption Equation: A Special Case of Langmuir Equation

We consider Langmuir Equation

$$\theta = \frac{KP}{1+KP}$$

At low pressure value of KP<<1. Therefore,

$$\theta = KP \quad \text{Or } \theta \propto P \qquad \ldots (1)$$

The above equation shows linear variation between extent of adsorption of gas and pressure.

At high pressure value of KP>>1

$$\therefore \ \theta = \frac{KP}{KP} = 1 \qquad \ldots (2)$$

The extent of adsorption, θ is independent of pressure at high pressure conditions. The reaction at this stage becomes zero order

Combining the results of equation (4) and (5), we can conclude that

$$\theta = Kp^{0-1}$$

$$or\ \theta = Kp^{1/n} \qquad \ldots (3)$$

Equation (3) is in agreement with Freundlich adsorption equation.

We can say that Freundlich adsorption equation is a special case of Langmuir equation.

b) **Langmuir adsorption isotherm**

In 1916, Irving Langmuir proposed another Adsorption Isotherm which explained the variation of Adsorption with pressure. Based on his theory, he derived Langmuir Equation which depicted a relationship between the number of active sites of the surface undergoing adsorption and pressure.

Assumptions of Langmuir Isotherm

Langmuir proposed his theory by making following assumptions.

1. Fixed number of vacant or adsorption sites are available on the surface of solid.
2. All the vacant sites are of equal size and shape on the surface of adsorbent.
3. Each site can hold maximum of one gaseous molecule and a constant amount of heat energy is releasedduringthisprocess.
4. Dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules.

$$A(g) + B(S) \underset{\text{desorption}}{\overset{\text{Adsorption}}{\rightleftharpoons}} AB$$

Where A (g) is unadsorbed gaseous molecule, B(s) is unoccupied metal surface and AB is Adsorbed gaseous molecule.

5. Adsorption is monolayer or unilayer.

Derivations of the Langmuir Adsorption Equation

Calculation of Equilibrium Constant

Langmuir proposed that dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules. Using the equilibrium equation, equilibrium constant can be calculated.

$$A(g) + B(S) \underset{K_d}{\overset{K_a}{\rightleftharpoons}} AB$$

Where K_a represents equilibrium constant for forward reaction and K_d represents equilibrium constant for backward direction.

According to Kinetic theory,

Rate of forward reaction = K_a [A] [B]

Rate of backward reaction = K_d [AB]

At equilibrium, Rate of forward reaction is equal to Rate of backward reaction

$$K_a [A] [B] = K_d [AB]$$

$$\text{Or, } \frac{K_a}{K_d} = \frac{[AB]}{[A][B]}$$

$$K = \frac{K_a}{K_d} = \frac{[AB]}{[A][B]}$$

The above equation represents the equilibrium constant for distribution of adsorbate between the surface and the gas phase.

Derivation

Langmuir Equation which depicts a relationship between the number of active sites of the surface undergoing adsorption (i.e. extent of adsorption) and pressure.

To derive Langmuir Equation and new parameter ‘ θ ’ is introduced. Let θ the number of sites of the surface which are covered with gaseous molecules. Therefore, the fraction of surface which are unoccupied by gaseous molecules will be (1 – θ).

Now, Rate of forward direction depends upon two factors: Number of sited available on the surface of adsorbent, $(1 - \theta)$ and Pressure, P. Therefore rate of forward reaction is directly proportional to both mentioned factors.

$$\text{Rate of forward reaction} \propto P\,(1 - \theta)$$

$$\text{Rate of adsorption} \propto P\,(1 - \theta)$$

$$\text{Or, Rate of adsorption} = K_a P\,(1 - \theta)$$

Similarly, Rate of backward reaction or Rate of Desorption depends upon number of sites occupied by the gaseous molecules on the surface of adsorbent.

$$\text{Rate of desorption} \propto \theta$$

$$\text{Or, Rate of desorption} = K_d\,\theta$$

At equilibrium, rate of adsorption is equal to rate of desorption.

$$K_a\,P\,(1 - \theta) = K_d\,\theta$$

We can solve the above equation to write it in terms of θ.

$$K_aP - K_aP\,\theta = K_d\,\theta$$

$$K_aP = K_aP\,\theta + K_d\,\theta$$

$$K_aP = (K_d + K_aP)\,\theta$$

$$\theta = \frac{K_aP}{K_d + K_aP}$$

Divide numerator and denominator on RHS by K_d, we get

$$\theta = \frac{\frac{K_a}{K_d}P}{\frac{K_d}{K_d} + \frac{K_a}{K_d}P}$$

Now put

$$K = \frac{K_a}{K_d}$$

in above equation we get

$$\theta = \frac{KP}{1+KP}$$

Langmuir Adsorption Equation

This is known as Langmuir Adsorption Equation.

Alternate form of Langmuir Adsorption Equation

Langmuir adsorption equation can be written in an alternate form in terms of volume of gas adsorbed. Let V be volume of gas adsorbed under given sets of conditions of temperature and pressure and V_{mono} be the adsorbed volume of gas at high pressure conditions so as to cover the surface with a unilayer of gaseous molecules.

$$\theta = \frac{V}{V_{mono}}$$

Substituting the value of θ in Langmuir equation

$$\frac{V}{V_{mono}} = \frac{KP}{1+KP}$$

Or $V_{mono} = 1 + \frac{1}{KP}$

Or in terms of pressure P we get,

$$\frac{P}{V} = \frac{P}{V_{mono}} + \frac{1}{KV_{mono}}$$

Langmuir Adsorption Equation in alternate form

Thus, if we plot a graph between P/V Vs P, we will obtain a straight line with

$$slope = \frac{1}{V_{mono}} \quad \text{and} \quad Intercept = \frac{1}{KV_{mono}}$$

Limitations of Langmuir Adsorption Equation

1. The adsorbed gas has to behave ideally in the vapor phase. This condition can be fulfilled at low pressure conditions only. Thus Langmuir Equation is valid under low pressure only.
2. Langmuir Equation assumes that adsorption is monolayer. But, monolayer formation is possible only under low pressure condition. Under high pressure condition the assumption breaks down as gas molecules attract more and more molecules towards each other. *BET theory* proposed by Brunauer, Emmett and Teller explained more realistic multilayer adsorption process.
3. Another assumption was that all the sites on the solid surface are equal in size and shape and have equal affinity for adsorbate molecules i.e. the surface of solid if homogeneous. But we all know that in real solid surfaces are heterogeneous.
4. Langmuir Equation assumed that molecules do not interact with each other. This is impossible as weak force of attraction exists even between molecules of same type.
5. The adsorbed molecules has to be localized i.e. decrease in randomness is zero ($\Delta S = 0$).This is not possible because on adsorption liquefaction of gases taking place, which results into decrease in randomness but the value is not zero.

From above facts we can conclude that, **Langmuir equation is valid under low pressure conditions**.

26.a)(i) **Liquid junction potential** occurs when two electrolytic solutions of different concentrations are in contact with each other. The more concentrated solution will have a tendency to diffuse into the comparatively less concentrated one. The rate of diffusion of each ion will be roughly proportional to its speed in an electric field. If the anions diffuse more rapidly than the cations, they will diffuse ahead into the dilute solution, leaving the latter negatively charged and the concentrated solution positively charged. This will result in an electrical double layer of positive and negative charges at the junction of the two solutions. Thus at the point of junction, a potential difference will develop because of the ionic transfer. This potential is called liquid junction potential or diffusion potential which is non-equilibrium potential. The magnitude of the potential depends on the relative speeds of the ions' movement.

(ii) To calculate the equilibrium constant for an electrochemical cell we need to know:

- the standard state potential for a cell
- the half-reactions involved

The Nernst equation is used in calculating the equilibrium constant.

$$E^o_{cell} = \frac{RT}{nF} \ln Q$$

At equilibrium Q = K. Substituting in K for Q, and the values for R, T, and F, we get:

$$E^o_{cell} = \frac{0.0257}{n} \ln K = \frac{0.0592}{n} \log K$$

Example: Find the value of the equilibrium constant at 25^{o}C for the cell reaction for the following electrochemical cell:

$$\mathrm{Cu} \mid \mathrm{Cu^{2+}(1\ M)} \parallel \mathrm{Ag^{+}(1\ M)} \mid \mathrm{Ag}.$$

- Write the equations for the cell half-reactions, calculate the standard cell potential, and determine the number of electrons transferred.

$2\ Ag^+(aq) + 2\ e^- \rightarrow 2\ Ag(s)$ $\qquad$ $E^o_{reduction} = +\ 0.799\ V$

$Cu(s) \rightarrow Cu^{2+}(aq) + 2\ e^-$ $\qquad$ $E^o_{oxidation} = -\ 0.518\ V$

$2\ Ag^{+}(aq) + Al(s) \rightarrow 2\ Ag(s) + Cu^{2+}(aq)$ $E^{o}_{cell} = +\ 0.281\ V$

n = 2 moles of electrons

- Substitute into the above equation and solve for K
- Substitute into the above equation and solve for K.

$$E^{o}_{cell} = \frac{0.0592}{n} \log K$$

$$0.281 = \frac{0.0592}{2} \log K$$

$$\log K = 9.49$$

$$K = 10^{9.49} = 3.1 \times 10^{9}$$

Note: values for the equilibrium constant for electrochemical cell reactions are sometimes very large.

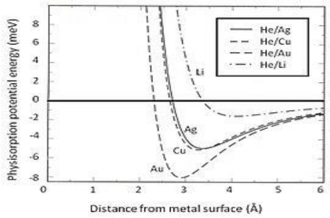
b) **Physical adsorption**

The fundamental interacting force of physisorption is caused by van der Waals force. Even though the interaction energy is very weak (~10–100 meV), physisorption plays an important role in nature. For instance, the van der Waals attraction between surfaces and foot-hairs of geckos provides the remarkable ability to climb up vertical walls.[4] Van der Waals forces originate from the interactions between induced, permanent or transient electric dipoles.

In comparison with chemisorption, in which the electronic structure of bonding atoms or molecules is changed and covalent or ionic bonds form, physisorption, generally speaking, can only be observed in the environment of low temperature (thermal energy at room temperature ~26 meV) and the absence of the relatively strong chemisorptions. In practice, the categorisation of a particular adsorption as physisorption or chemisorption depends principally on the binding energy of the adsorbate to the substrate.

To give a simple illustration of physisorption, we can first consider an adsorbed hydrogen atom in front of a perfect conductor, as shown in Fig. 1. A nucleus with positive charge is located at $\mathbf{R} = (0, 0, Z)$, and the position coordinate of its electron, $\mathbf{r} = (x, y, z)$ is given with respect to the nucleus. The adsorption process can be viewed as the interaction between this hydrogen atom and its image charges of both the nucleus and electron in the conductor. As a result, the total electrostatic energy is the sum of attraction and repulsion terms:

Physisorption potential



Even though the van der Waals interaction is attractive, as the adsorbed atom moves closer to the surface the wavefunction of electron starts to overlap with that of the surface atoms. Further the energy of the system will increase due to the orthogonality of wavefunctions of the approaching atom and surface atoms.

This Pauli exclusion and repulsion are particularly strong for atoms with closed valence shells that dominate the surface interaction. As a result, the minimum energy of physisorption must be found by the balance between the long-range van der Waals attraction and short-range Pauli repulsion. For instance, by separating the total interaction of physisorption into two contributions- a short-range term depicted by Hartree–Fock theory and a long-range van der Waals attraction, the equilibrium position of physisorption for rare gases adsorbed on jellium substrate can be determined. Fig. 2 shows the physisorption potential energy of He adsorbed on Ag, Cu, and Au substrates which are described by the jellium model with different densities of smear-out background positive charges. It can be found that the weak van der Waals interaction leads to shallow attractive energy wells (<10 meV). One of the experimental methods for exploring physisorption potential energy is the scattering process, for instance, inert gas atoms scattered from metal surfaces. Certain specific features of the interaction potential between scattered atoms and surface can be extracted by analyzing the experimentally determined angular distribution and cross sections of the scattered particles.

Comparison with chemisorption

- Physisorption is a general phenomenon and occurs in any solid/fluid or solid/gas system. Chemisorption is characterized by chemical specificity.
- In physisorption, perturbation of the electronic states of adsorbent and adsorbate is minimal. For chemisorption, changes in the electronic states may be detectable by suitable physical means.
- Typical binding energy of physisorption is about 10–100 meV. Chemisorption usually forms bonding with energy of 1–10 eV.
- The elementary step in physisorption from a gas phase does not involve an activation energy. Chemisorption often involves an activation energy.
- For physisorption, under appropriate conditions, gas phase molecules can form multilayer adsorption. In chemisorption, molecules are adsorbed on the surface by valence bonds and only form monolayer adsorption.

Reg. No.................................

[13CHU401]

KARPAGAM UNIVERSITY
(Under Section 3 of UGC Act 1956)
COIMBATORE – 641 021
(For the candidates admitted from 2013 onwards)

B.Sc. DEGREE EXAMINATION, APRIL 2016
Fourth Semester

CHEMISTRY

GENERAL CHEMISTRY - IV

Time: 3 hours

Maximum : 60 marks

PART – A (10 x 2 = 20 Marks)
Answer any TEN Questions

1. What is meant by Mond's process?
2. What are the ores of Iron?
3. How cobalt is purified by electrolysis?
4. Write any two commercial uses of phenol.
5. Describe the preparation of cresols.
6. How will you prepare catechol from salicylaldehyde?
7. How will you synthesise aniline from benzoic acid?
8. Draw the structure of p-toluidine.
9. How is diazomethane prepared?
10. Define degrees of freedom.
11. Define the stability of phase of a system.
12. What is meant by components in phase?
13. Write the definition of a real solution.
14. How will you calculate the relative lowering of vapour pressure?
15. State Nernst distribution law.

PART B (5 X 8= 40 Marks)
Answer ALL the Questions

16. a. What are alloy steels? Mention three elements that are used in preparing them? What are the special properties of the alloys?

Or

b. How is steel manufactured from wrought iron?

17. a. Discuss the basicity of aromatic amines.

Or

b. Describe the mechanism of action of nitrous acid on aromatic primary, secondary and tertiary amines.

18. a. Derive Gibbs phase rule thermodynamically.

Or

b. Discuss the main features of the phase diagram of water system, explaining especially why the slope of solid-liquid line is negative for water.

19. a. State and derive Raoult's law for lowering of vapour pressure. How is this law used for the determination of molecular mass of a non-volatile solute?

Or

b. Define osmosis. How molecular weight of a substance can be determined by osmotic pressure method?

20. **Compulsory : -**

i. Why phenol is having high melting point?
ii. Why phenol is more soluble in water compared with hexanol with a comparable molecular weight?
iii. o-salicylaldehyde and o-nitrophenol showed lower solubility relative to their meta and para isomers. Why?

Reg. No……………………………

[14CHU401]

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Karpagam Academy of Higher Education
(Established Under Section 3 of UGC Act 1956)
COIMBATORE – 641 021
(For the candidates admitted from 2014onwards)
B.Sc., DEGREE EXAMINATION, APRIL 2016

Fourth Semester

CHEMISTRY

GENERAL CHEMISTRY - IV

Time: 3 hours Maximum : 60 marks

PART – A (20 x 1 = 20 Marks) (30 Minutes)
(Question Nos. 1 to 20 Online Examinations)

PART B (5 x 8 = 40 Marks) (2 ½ Hours)
Answer ALL the Questions

21. a) How is pure nickel extracted from its ore? Discuss.

Or

b) Give a detailed account on the properties of platinum group metals.

22. a) Justify the following statements with proper chemical equations.
    i. Phenol is acidic.
    ii. Electrophilic substitution takes place at ortho- and para- positions to –OH group in phenol.
    iii. Phenol on condensation with phthalic anhydride gives phenolphthalein whereas resorcinol gives fluorescein.

Or

b) Prepare (i) Phloroglucinol from 2,4,6-trinitrobenzoic acid
(ii) resacetophenone from resorcinol (iii) Salicylaldehyde from phenol
(iv)1-naphthol from naphthalene.

23. a) (i) Arrange the following in the increasing order of basicity and Justify your answer:
methyl amine, ammonia , N-methyl aniline, aniline, dimethyl amine.
(ii) How are primary, secondary and tertiary amines in a mixture separated by Hinsberg's method?

Or

b) (i) What is Arndt-Eistert synthesis?
(ii) How does diazoacetic ester react with (I) ethylene (II) benzene, hv
(iii) acetic acid (IV) Zn/acetic acid?

24. a) (i) Discuss the phase diagram for the sulphur system.
(ii) Define : Phase and degree of freedom.

Or

b) (i) Describe the phase diagram of Bi-Cd system.
(ii) Determine the number of components for the following systems: (i) Br_2 dissolved in CCl_4 solution (ii) a mixture of $N_2(g)$, $H_2(g)$ and $NH_3(g)$.

25. a) (i) State and explain Henry's law and Raoult's law as applied to ideal and non-ideal solutions.
(ii) How is molar mass determined from osmotic pressure measurement?

Or

b) Derive the relation between the boiling point elevation of a solution and the mole fraction of the dissolved solute. How is the expression used for determining molar mass of a nonvolatile solute?

Reg. No.................................

[14CHP203]

KARPAGAM UNIVERSITY

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COIMBATORE – 641 021
(For the candidates admitted from 2014 onwards)

M.Sc. DEGREE EXAMINATION, APRIL 2015

Second Semester

CHEMISTRY

PHYSICAL CHEMISTRY – II (Chemical Kinetics and Electro Chemistry)

Time: 3 hours Maximum : 60 marks

PART – A (10 x 2 = 20 Marks)

Answer any TEN Questions

1. Explain volume of activation.
2. What is the effect of Pressure on rate of reaction?
3. Explain the use of NMR in Studying fast reaction.
4. Write Michelis – menten equation and explain the terms.
5. Write a note on effect of pH on enzyme catalysis.
6. Write Bronsted catalysis law.
7. Define activity coefficient.
8. Explain Falkehagen effect.
9. Explain Wien effect
10. Write some important application of electro analytical methods.
11. Define halfwave potential.
12. Explain dropping mercury electrode
13. Define activation polarization.
14. Write a note on Tafel Plots.
15. What are the different types of polarization in electrodes?

PART B (5 X 8= 40 Marks)

Answer ALL the Questions

16. a. Discuss Pulse method in studying fast reaction.

Or

b. Discuss about graphical presentation involved in Kinetics of Corrosion.

17. a. Derive Langumuir adsorption isotherm.

Or

b. Discuss an experimental observation of corrosion and its Kinetics.

18. a. Write Deby- Huckel limiting law and its application.

Or

b. Discuss Langumuir-Rideal – Elay mechanism.

19. a. Discuss the principle and applications of ampere metric titrations

Or

b. Discuss Gouy Chappmantheory

20. **Compulsory : -**

Discuss elaborately about ARRT theory.

Reg. No................................

[12CHU401]

KARPAGAM UNIVERSITY
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COIMBATORE – 641 021
(For the candidates admitted from 2012 onwards)

B.Sc. DEGREE EXAMINATION, APRIL 2014
Fourth Semester

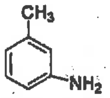
CHEMISTRY

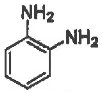
GENERAL CHEMISTRY IV

Time: 3 hours Maximum : 100 marks

PART – A (15 x 2 = 30 Marks)
Answer ALL the Questions

1. What is the composition of matte in the extraction of nickel?
2. Write the formula of pentlandite ore.
3. What is the use of black iron oxide?
4. Discuss the toxic character of phenol.
5. How are aromatic amines prepared?
6. Describe the preparation of phenol from Bakelite.
7. How is the basicity of aniline affected by substituent on the ring?
8. Give an example for primary, secondary and tertiary amines.
9. Name the structure of the following:





10. Explain the phase rule.
11. What is meant by components in the system?
12. What are the four phases in the sulphur system?
13. Define Raoult's law.
14. What is depression of freezing point?
15. What are colligative properties?

PART B (5 X 14= 70 Marks)
Answer ALL the Questions

16. (a) Discuss the metallurgy of cobalt.

Or

(b) Explain the metallurgy of platinum.

17. (a) Give anyfive important methods of introducing OH group in an aromatic ring.

Or

(b) Describe the mechanism of
(i) Reimer-Tiemann reaction (ii) Schotten-Baumann reaction
(iii) Kolbe reaction

18. (a) (i) Discuss the relative basic character of ammonia, methylamine and aniline.
(ii) Explain the weak basic character of aniline in particular.

Or

(b) Give the general chemical reactions of amines.

19. (a) Deduce the expression for
(i) Claypeyron equation (ii) Claypeyron-Clasius equation.

Or

(b) Discuss main features of the phase diagram of water system, explaining especially why the slope of solid-liquid line is negative for water.

20. (a) Explain the following terms:
(i) Nernst's distribution law (ii) Henry's law

Or

(b) Define osmosis. How molecular weight of a substance can be determined by osmotic pressure method?
