KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed University Established Under Section 3 of UGC Act 1956)
COIMBATORE-21
DEPARTMENT OF CHEMISTRY
B.Sc Chemistry

Semester-III

16CHU301 PHYSICAL CHEMISTRY III 4H 4C
(Phase Equilibria and Chemical Kinetics)

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

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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DEPARTMENT OF CHEMISTRY
B.Sc Chemistry

ODD SEMESTER 2016 BATCH

LECTURE PLAN

Staff In charge : Mrs. H.Revathi
Class : II BSc Chemistry
Section : A
Subject : Physical chemistry III(Phase Equilibria and Chemical Kinetics)
Subject Code : 16CHU301
Semester / Year : III/II

UNIT-I

Phase Equilibria **Hour's required - 11**

S.No	Lecture Hour	Topics	Support Material
1	1	Concept of phases	**T1:**749-752
2	1	Components and degrees of freedom	**T1**:749-752
3	1	Derivation of Gibbs phase rule for reactive and nonreactive systems	**T1**:753-754
4	1	Clausius-clapeyron equation	**T1:**525-527
5	1	Applications of clapeyron equation to solid-liquid , liquid vapour and solid-vapour equilibria	**T1**:525-527
6	1	Phase diagram for one component systems(water and sulphur)	**T1**:756-757,761-762
7	1	Phase diagram for systems of solid-liquid equilibria involving eutectic points	**T1**:768-769, 770-771
8	1	Phase diagram for systems of solid-liquid equilibria involving ,congruent melting points	**T1**:774-778
9	1	Phase diagram for systems of solid-liquid equilibria involving incongruent melting points	**T1**:774-778
10	1	Phase diagram for systems of solid-liquid equilibria involving incongruent melting points	**T1**:774-778
11	1	Revision and discussin of question papers	

SUPPORTING MATERIALS:

Text Books:

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

UNIT-II

Three component systems **Hours required - 11**

S.No	Lecture Hour	Topics	Support Material
1	1	Three component systems:triangular plots	**T1**:782-784
2	1	Water-chloroform –acetic acid system	**T1:**782-784
3	1	Binary solutions:Gibbs-Duhem-Margules equation	**T1**:705-706
4	1	Derivation and applications to fractional distillation of binary miscible liquids	**T1**:713-716
5	1	Azeotropes, lever rule	**T1**:716
6	1	Partial miscibility of liquids	**T1**:718-721
7	1	CST, Misicible pairs, steam distillatin	**T1**:716-718
8	1	CST, Misicible pairs, steam distillatin	**T1**:786-791
9	1	Nernst distribution law:its derivation and applications	**T1**:786-791
10	1	Nernst distribution law:its derivation and applications	**T1**:786-791
11	1	Recaptulations and discussions of important questions	**T1**:786-791

SUPPORTING MATERIALS:

Text Books:

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

UNIT-III

Electrochemical cells **Hours required - 11**

S.No	Lecture Hour	Topics	Support Material
1	1	Rules of oxidation/reduction of ins based on half-cell potentials	**T1:**889-890
2	1	Applications of electrolysis in metallurgy and industry	**T1:**889-890
3	1	Chemical cells	**T2:**1.62-1.63
4	1	Reversible cells and irreversible cells with examples	**T2:**1.62-1.63
5	1	Electromotive force of a cell and its measurement	**T2:**1.47-1.48
6	1	Nernst equation	**T1:**886-888
7	1	Standard electrode potential	**T1:**889
8	1	Standard electrode potential	**T1:**889-891
9	1	Application to different kinds of half cells	**T1:**889-894
10	1	Application to different kinds of half cells	**T1:**889-894
11	1	Recaptulations and discussions of important questions	

SUPPORTING MATERIALS:

Text Books

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

T2:A.Sheik Mideen, *Engineering Chemistry-I*,2016,Shruthi publishers,Chennai

UNIT-IV

Application of EMF measurements **Hour's required-12**

S.No	Lecture Hour	Topics	Support Material
1	1	Application of EMF measurements in determining free energy, enthalpy and entropy of a cell reaction	**T1:**889-890
2	1	Application of EMF measurements in determining equilibrium constants	**T1**:886
3	1	Application of EMF measurements in determining pH values using hydrogen, quinine-hydroquinone, glass and SBO/Sb2O3 electrodes	**T1**:911-913
4	1	Concentration cells with and without transference	**T1**:895-902
5	1	Liquid junction potential	**T1**:902-903
6	1	Determination of activity coefficients	**T1**:906-909
7	1	Determination of activity coefficients	**T1**:906-909
8	1	Transference numbers	**T1:**914-921
9	1	Transference numbers	**T1:**914-926
10	1	Qualitative discussion of potentiometric titrations(acid-base, redox, precipitation)	**T1:**914-926
11	1	Qualitative discussion of potentiometric titrations(acid-base, redox, precipitation)	**T1:**914-926
12	1	Recaptulations and discussions of important questions	

SUPPORTING MATERIALS:

Text Books

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

UNIT-V

Surface chemistry **Hours required- 15**

S.No	Lecture Hour	Topics	Support Material
1	1	Physical adsorption	**T1:**4.3-4.4
2.	1	chemisorption	**T1:**4.3-4.4
3.	1	Adsorption isotherms(Langmuir)	**T1:**4.12-4.17
4	1	Adsorption isotherms(Langmuir)	**T1:**4.11-4.12
5	1	Adsorption isotherms(Langmuir)	**T1:**4.12-4.17
6	1	Adsorption isotherms(freundlich)	**T1:**4.11-4.12
7	1	Adsorption isotherms(freundlich)	**T1:**4.17-4.18
8	1	Nature of adsorbed state	**T1:**4.39-4.48
9	1	Nature of adsorbed state	**T1:**4.11-4.12
10	1	Qualitative discussion	**T1:**4.14-4.16
11	1	Qualitative discussion	**T1:**4.14-4.16
12	1	Recaptulations and discussions of important questions	
13	1	ESE question paper discussion	
14	1	ESE question paper discussion	
15	1	ESE question paper discussion	

SUPPORTING MATERIALS:

Text Books

T1:Engineering Chemistry-I,A.Sheik Mideen,2016,Shruthi publishers,Chennai

UNIT I

Phase Equilibria

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 .

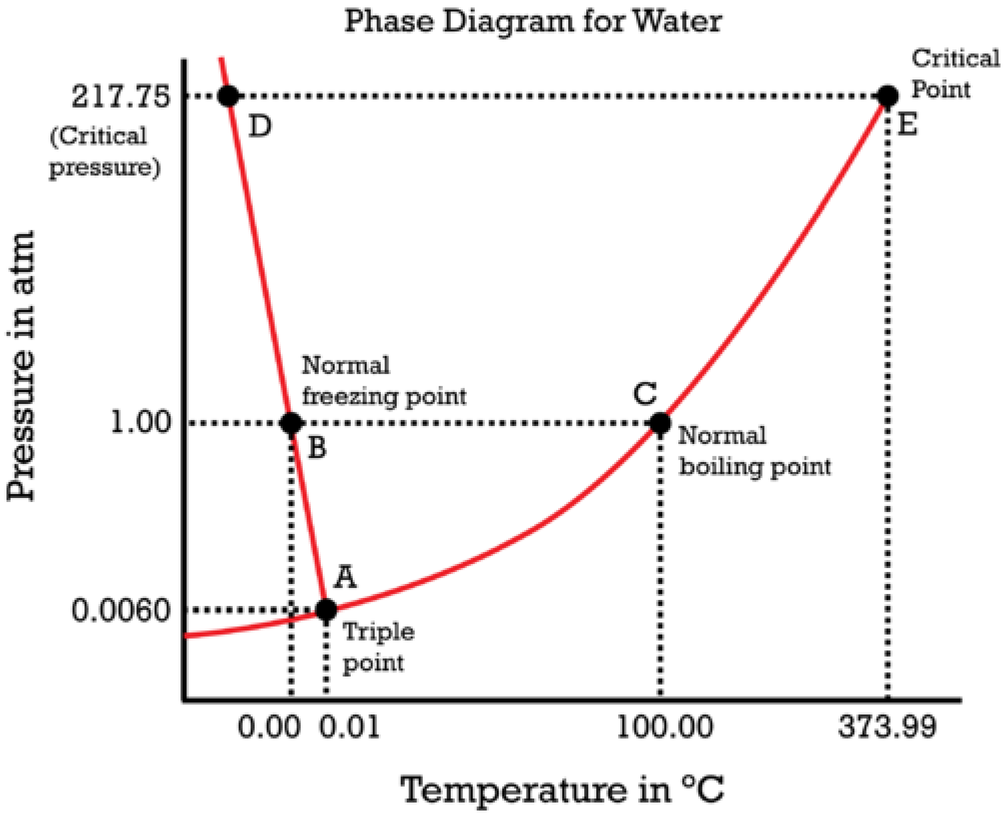


Figure 1

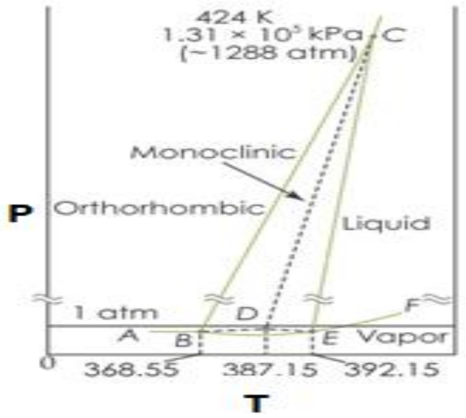
Notice one key difference between the general phase diagram and the phase diagram for water. In water's diagram, the slope of the line between the solid and liquid states is negative rather than positive. The reason is that water is an unusual substance in that its solid state is less dense than the 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.

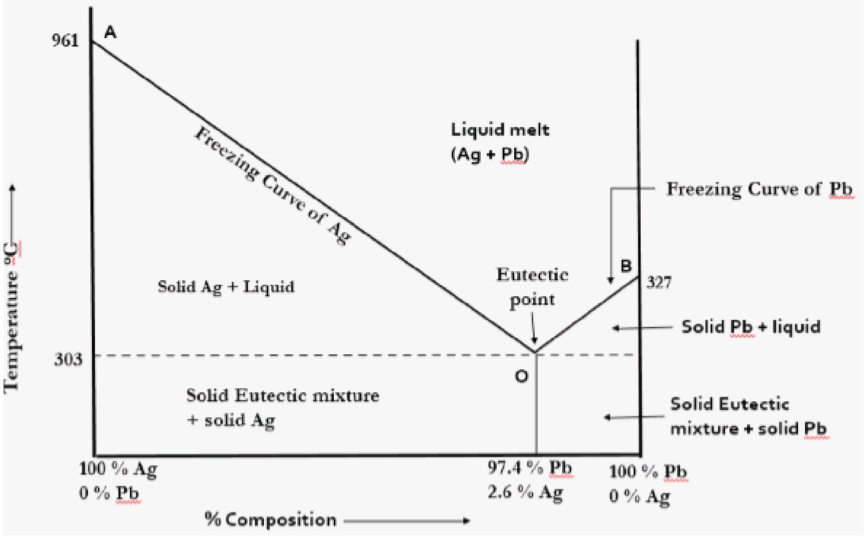
Metastable Equilibria The change of SR to SM takes place very slowly. If enough time for the change is not allowed and SR is heated rapidly, it is possible to pass well above the transition point without getting SM. In that case, there being three phases (SR, SL, SV) only and one component, the phase 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^{o}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.

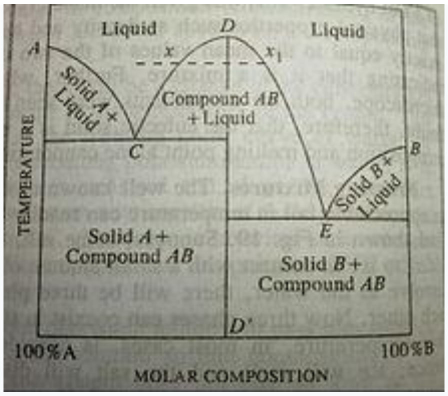
a) The region marked eutectic plus solid Ag in which crystalline silver and solid eutectic are stable.

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.



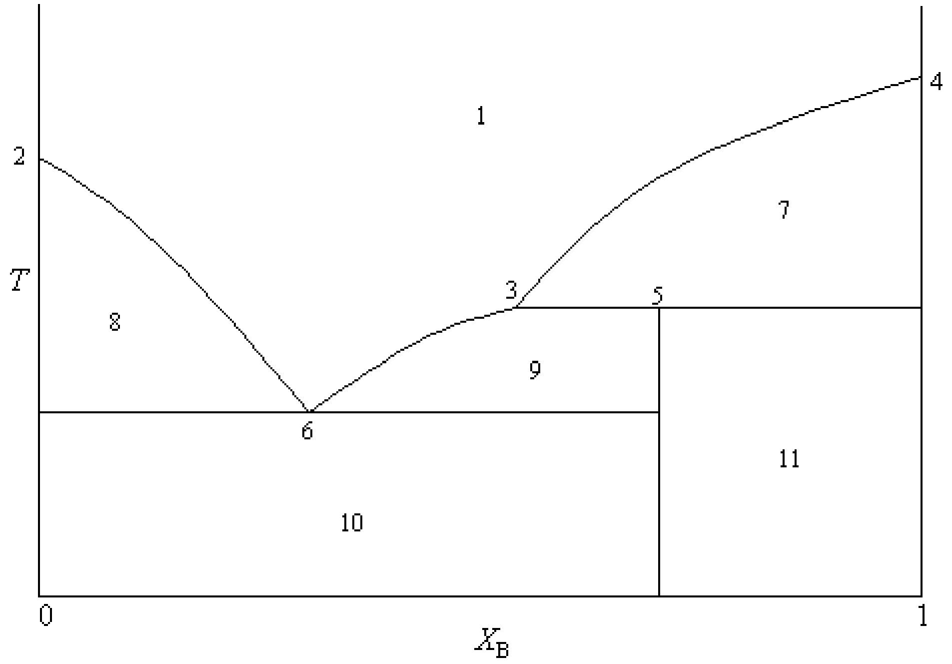
Phase Diagram for the Formation of a compound with congruent Melting Point

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

Part A(Each question carry one mark)

1.Benzene and alcohol constitutes

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

2. If F=0, the system is called

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

3. 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

4. On adding increasing amounts of ferric chloride in ferric chloride -water system there will be fall in----------------

a)pressure **b)temperature** c)composition d)temperature and composition

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

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

6. If F=2, the system is called

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

7. Water is an example for

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

8. Phase rule becomes -----------------for a three component system

a)F=5-P b)F=4-P c)F=3-P d)F=2-P

9. CCl4 and water forms

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

10. Sugar and water is and example for

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

11. All the phases must be at the ------------pressure otherwise the volume of one phase will increase at the expense of another

a)greater **b)same** c)lower d)same or lower

12. Reduced phase rule is otherwise known as

a)condensed phase rule b)phase rule equat c)Gibbs phase rule equation d)expanded phase rule

13. Benzene and alcohol constitutes
a) single phase b)two phase c)three phase d)four phase

14. If F=1, the system is called

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

15. All the phases must be at the ------------pressure otherwise the volume of one phase will increase at the expense of another

a)greater **b)same** c)lower d)same or lower

16. Reduced phase rule is otherwise known as

a)condensed phase rule b)phase rule equation c)Gibbs phase rule equation d)expanded phase rule

17.CCl4 and water forms

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

18. Sulphur exist in

a)three phase b)one phase c)two phase **d)four phase**

19. 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

20. On adding increasing amounts of ferric chloride in ferric chloride -water system there will be fall in----------------

a)pressure **b)temperature** c)composition d)temperature and composition

Part B(Each question carry two marks)

21.Define Phase.

22.Define Component.

23.Define Degree of freedom.

24.State reduced phase rule.

25.What is meant by triple point?

26.What is meant by eutectic point?

27.What is meant by congruent melting point?

28.What is meant by incongruent melting point?

Part C(Each question carry 8 marks)

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

30. Explain the phase diagram of water system.

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

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

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

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

KARPAGAM ACADEMY OF HIGHER EDUCATION
(Deemed to be University under Section 3 of UGC Act 1956)
COIMBATORE-641 021
(For the candidates admitted from 2016 & onwards)
II B.Sc. Chemistry
PHYSICAL CHEMISTRY

UNIT I

Multiple choice questions

S.No	Question	option 1	option 2	option 3	option 4	Answer
1	J.W.Gibbs enunciated the phase rule in	a)1876	b)1875	c)1874	d)1873	a)1876
2	A gas mixture constitutes	a) single phase	b)two phase	c)three phase	d)four phase	a) single phase
3	CCl4 and water forms	a)three phase	b)two phase	c)four phase	d)single phase	b)two phase
4	Benzene and alcohol constitutes	a) single phase	b)two phase	c)three phase	d)four phase	a) single phase
5	Calcium component is an example for	a)one component	b)two component	c)three component	d)four component	b)two component
6	Sulphur exist in	a)three phase	b)one phase	c)two phase	d)four phase	d)four phase
7	Sugar and water is and example for	a)two component	b)one component	c)three component	d)four component	a)two component
8	In a chemically reactive system, the number of components is given by	a)$C=N-m-N-R$	b)$C=n-M-N-r$	c)$C=N-m-n-R$	d)$C=R-N-n-m$	c)$C=N-m-n-R$
9	If $F=0$, the system is called	a)bivariant	b)univariant	c)invariant	d)trivariant	c)invariant
10	If $F=1$, the system is called	a)bivariant	b)univariant	c)invariant	d)trivariant	b)univariant
11	If $F=2$, the system is called	a)bivariant	b)univariant	c)invariant	d)trivariant	a)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	a)greater	b)lower	c)greater and lower	d)constant	a)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	a)greater	b)smaller	c)greater and smaller	d)constant	b)smaller
14	For a given number of components, the number of phases is --------- when the number of degrees of freedom is zero	a)maximum	b)minimum	c)constant	d)maximum and minimum	a)maximum
15	All the phases must be at the ------------temperature otherwise there will be flow of heat from one phase to another	a)greater	b)same	c)lower	d)same or lower	b)same
16	All the phases must be at the ------------pressure otherwise the volume of one phase will increase at the expense of another	a)greater	b)same	c)lower	d)same or lower	b)same
17	Gibbs phase rule equation for one component system is	a)$F=C-P+2$	b)$F=C-P+1$	c)$F=C-P$	d)$F=P-C+2$	a)$F=C-P+2$
18	Gibbs phase rule equation for two component system is	a)$F=C-P+2$	b)$F=C-P+1$	c)$F=C-P$	d)$F=P-C+2$	b)$F=C-P+1$
19	Water is an example for	a)three component	b)two component	c)one component	d)four component	c)one component
20	Sulphur is an example for	a)four component	b)two component	c)three component	d)one component	d)one component
21	The temperature at which all the three phases will be equilibrium is known as	a)eutectic point	b)congruent melting point	c)incongruent melting point	d)triple point	d)triple point
22	The temperature at which two solid and one liquid phase are in equilibrium is known as	a)incongruent melting point	b)congruent melting point	c)triple point	d)eutectic point	d)eutectic point
23	Carbon di-oxide is an example for	a)three component	b)two component	c)one component	d)four component	c)one component
24	Reduced phase rule is otherwise known as	a)condensed phase rule	b)phase rule equation	c)Gibbs phase rule equation	d)expanded phase rule	a)condensed phase rule
25	Lead-Silver is an example for	a)three component	b)two component	c)one component	d)four component	b)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	a)incongruent melting point	b)congruent melting point	d)triple point	d)eutectic point	b)congruent melting point
27	Ferric chloride -water is an example for	a)congruent melting point	b)triple point	c)incongruent melting point	d)eutectic point	a)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 a solution with a composition different from that of the solid phase. Such a compound is said to possess a	a)incongruent melting point	b)congruent melting point	d)triple point	d)eutectic point	a)incongruent melting point
29	Transition temperature is otherwise known as	a)peritectic temperature	b)melting temperature	c)sublimation temperature	d)vapour pressure temperature	a)peritectic temperature
30	Phase rule becomes -----------------for a three component system	a)F=5-P	b)F=4-P	c)F=3-P	d)F=2-P	a)F=5-P
31	Isothermal critical point is otherwise known as	a)plait point	b)melting point	c)sublimation point	d)plait and melting point	a)plait point
32	Acetic acid-chloroform and water is an example for	a)three component	b)two component	c)one component	d)four component	a)three component
33	An equation of fundamental importance which finds extensive application in one-component, two phase systems was derived independently by	a)Clausius	b)Einstein	c)Gibbs	d)Henry	a)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	a)liquid to solid	b)solid to vapour	c)liquid to vapour	d)solid to liquid	c)liquid to vapour
35	G is known as	a)enthalpy	b)entropy	c)free energy	d)work	c)free energy
36	Clapeyron equatiion gives change in pressure d P which accompany the change in-----------	a)temperature	b)volume	c)composition	d)temperature and composition	a)temperature
37	ΔHv is known as	a)molar heat of sublimation	b)molar heat of vaporisation	c)molar heat of fusion	d)molar heat of enthalpy	b)molar heat of vaporisation
38	ΔHf is known as	a)molar heat of sublimation	b)molar heat of vaporisation	c)molar heat of fusion	d)molar heat of enthalpy	c)molar heat of fusion
39	ΔS is known as	a)change in free energy	b)change in entropy	c)change in enthalpy	d)change in energy	b)change in entropy
40	Lewis introduce the concept of	a)fugacity	b)volume	c)pressure	d)temperature	a)fugacity
41	Calculate F in water↔vapour equilibria	a)1	b)2	c)3	d)4	a)1
42	Calculate F in solid↔liquid equilibria	a)2	b)1	c)3	d)4	b)1
43	Calculate F in solid↔vapour equilibria	a)3	b)5	c)4	d)1	d)1
44	calculate F in ice↔liquid↔vapour equilibria	a)0	b)1	c)2	d)4	a)0
45	Pressure-temperature axis is drawn for-------------------	a)two component	b)one component	c)three component	d)one and two component	b)one component
46	Temperature-composition axis is drawn for	a)two component	b)one component	c)three component	d)one and two component	a)two component
47	The simplest three component systems are those in which a liquid system breaks down into ---------- phases	a)one	b)two	c)three	d)four	b)two
48	Application of the phase rule to a systme corresponding to a point in the two phase region gives F=	a)3	b)2	c)1	b)0	a)3
49	Tie lines are drawn in	a)one component	b)two component	c)three component	d)four component	c)three component
50	A system of two salts and water furnishes an example of a	a)two component	b)three component	c)one component	d)four component	b)three component

51	Bismuth-cadmium is an example for	a)incongruent melting point	b)congruent melting point	c)eutectic system	d)triple point	c)eutectic system
52	Potassium iodide-water is an example for	a)eutectic system	b)one component	b)three component	d)four component	a)eutectic system
53	The well known observation that the addition of salt to ice produces an appreciable fall in -----------------------------	a)temperature	b)pressure	c)pressure and temperature	d)composition	a)temperature
54	On adding increasing amounts of ferric chloride in ferric chloride -water system there will be fall in----------------	a)pressure	b)temperature	c)composition	d)temperature and composition	b)temperature
55	S1↔S2+-----------------	a)solution	b)S3	c)S2	d)S1+S2	a)solution
56	Number of phases in water↔solid is	a)1	b)2	c)3	d)4	b)2
57	Number of phases in water↔vapour is	a)1	b)2	c)3	d)4	b)2
58	Number of phases in solid ↔vapour is	a)2	b)3	c)1	d)0	c)1
59	Number of component in NaCl and water is	a)1	b)2	c)3	d)4	b)2
60	Number of component in alcohol and water is	a)2	b)1	c)3	d)4	a)2

UNIT II

Three Component System

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

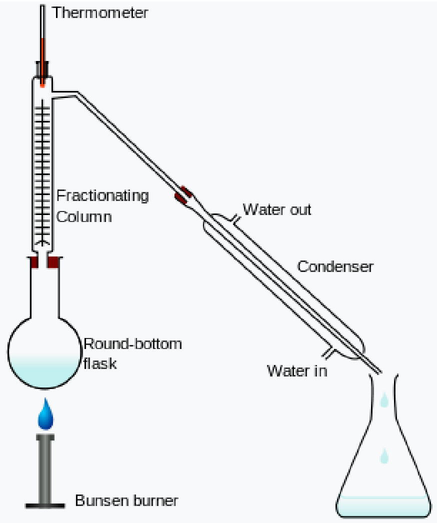
all at some fixed temperature.

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:

$$nA \Leftrightarrow A_n \; nA$$

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

Part A(Each carry one mark)

1. Isothermal critical point is otherwise known as

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

2. In Gibbs-Duhem-Margules equation, if the vapour behaves as an ideal gas,the fugacity can be replaced by

a)temperature b)pressure c)concentration **d)vapour pressure**

3. For a three component system, the phase rule becomes

a)F=4-P **b)F=5-P** c)F=3-P d)F=2-P

4. Minimum boiling point is said to be

a)high volatile b)least volatile c)no volatile d)volatility increases and then decreases

5. complex ions are studied in

a)nernst distribution law b)gibbs distribution law c)einstein distribution law d)albert distribution law

6. Existence of similar molecular species in the two phases in-----------with other

a)contact b)no contact c)contact and no contact d)bonded

7. 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

8. In Gibbs-Duhem-Margules equation, if the vapour behaves as an ideal gas,the fugacity can be replaced by

a)temperature b)pressure c)concentration **d)vapour pressure**

9. Tie lines are represented in

a)two component sytem b)one component system **c)three component system** d)four component system

10. In type I of fractional distillation

a)possible to isolate both the pure consituents from each other
b) not possible to isolate both the pure consituents from each other
c)possible as well as not possible to isolate both the pure constituents from each other
d)possible to isolate one constituent

11. Ethanol in type II fractional distillation is obtained as

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

12. Minimum boiling point is said to be

a)high volatile b)least volatile c)no volatile d)volatility increases and then decreases

13. 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

a)ideal b)real c)ideal and real d)non-ideal

14. In type III of fractional distillation

a)possible to isolate both the pure consituents from each other

b) not possible to isolate both the pure consituents from each other

c)possible as well as not possible to isolate both the pure constituents from each other

d)possible to isolate one constituent

15. Water-ethanol system is an example for

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

16. 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

17. 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

18. In Gibbs-Duhem-Margules equation, if the vapour behaves as an ideal gas,the fugacity can be replaced by

a)temperature b)pressure c)concentration **d)vapour pressure**

19. In type II constant boiling mixture obtained as

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

20. Critical solution temperature is otherwise known as

a)consolute temperature b)solubility temperature c)misicibility temperature d)melting temperature

Part B(Each carry two marks)

21.What is known as CST?

22.What is known as UCST?

23.What is known as LCST?

24.State Nernst distribution law.

25.Mention few examples for three component system.

26.Mention the applications of Nernst distribution law.

27.What are miscible pairs.

Part C(Each carry 8 marks)

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

29.Derive Nernst distribution law and mention its important applications

30.Derive Gibbs-Duhem Margules equation.
31.Explain fractional distillation in detail
32.write notes on
(i)Fractional distillation

(ii)Steam distillation

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

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

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UNIT II
Multiple choice questions

S.No	Question	option 1	option 2	option 3	option 4	Answer
1	For a three component system, the phase rule becomes	a)F=4-P	b)F=5-P	c)F=3-P	d)F=2-P	b)F=5-P
2	The simplest three component systems are those in which a liquid system breaks down into	a)two phases	b)three phases	c)four phases	d)five phases	a)two phases
3	Isothermal critical point is otherwise known as	a)eutectic point	b)triple point	c)plait point	d)melting point	c)plait point
4	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	b)F=3
5	Tie lines are represented in	a)two component sytem	b)one component system	c)three component system	d)four component system	c)three component system
6	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	a)three component
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	a)ideal	b)real	c)ideal and real	d)non-ideal	a)ideal
8	A binary solution of components A and B in equilibrium with their vapours, at constant temperature and pressure is given by	a)Gibbs equation	b)Margules equation	c)Gibbs-Duhem-Margules equation	d)Duhem equation	c)Gibbs-Duhem-Margules equation
9	nA and n B are the numbers of moles of components A and B	a)Gibbs equation	b)Margules equation	c)Gibbs-Duhem-Margules equation	d)Duhem equation	c)Gibbs-Duhem-Margules equation
10	In Gibbs-Duhem-Margules equation, if the vapour behaves as an ideal gas,the fugacity can be replaced by	a)temperature	b)pressure	c)concentration	d)vapour pressure	d)vapour pressure
11	The process of separating mixtures by repeated distillation and condensation is known as	a)steam distillation	b)fractional distillation	c)distillation	d)condensation	b)fractional distillation
12	In type I of fractional distillation	a)possible to isolate both the pure consituents from each other	b) not possible to isolate both the pure consituents from each other	c)possible as well as not possible to isolate both the pure constituents from each other	d)possible to isolate one constituent	a)possible to isolate both the pure consituents from each other
13	In type II of fractional distillation	a)possible to isolate both the pure consituents from each other	b) not possible to isolate both the pure consituents from each other	c)possible as well as not possible to isolate both the pure constituents from each other	d)possible to isolate one constituent	d)possible to isolate one constituent
14	In type III of fractional distillation	a)possible to isolate both the pure consituents from each other	b) not possible to isolate both the pure consituents from each other	c)possible as well as not possible to isolate both the pure constituents from each other	d)possible to isolate one constituent	d)possible to isolate one constituent
15	In type II constant boiling mixture obtained as	a)residue	b)distillate	c)residue and distillate	d)vapour	b)distillate
16	In type II Pure A or Pure B obtained as	a)residue	b)distillate	c)residue and distillate	d)vapour	a)residue
17	In type III constant boiling mixture obtained as	a)residue	b)distillate	c)residue and distillate	d)vapour	a)residue

18	In type III pure A or pure B obtained as	a)residue	b)distillate	c)residue and distillate	d)vapour	b)distillate
19	The constant boiling point in type II is	a)minimum	b)maximum	c)increases and then decreases	d)decreases and then increases	a)minimum
20	The constant boiling point in type III is	a)minimum	b)maximum	c)increases and then decreases	d)decreases and then increases	b)maximum
21	Pure water boils at	a)100 degree celsius	b)50 degree celsius	c)120 degree celsius	d0110 degree celsius	a)100 degree celsius
22	pure hydrogen chloride boils at	a)65 degree celsius	b)100 degree celsius	c)-85 degree celsius	d)85 degree celsius	c)-85 degree celsius
23	In water-ethanol system, the constant boiling mixture correspoding to the point has a composition of	a)100% ethanol	b)95.6%ethanol	c)93%ethanol	d)94%ethanol	b)95.6%ethanol
24	Ethanol in type II fractional distillation is obtained as	a)residue	b)distillate	c)residue and distillate	d)vapour	b)distillate
25	pure water is obtained as	a)residue	b)distillate	c)residue and distillate	d)vapour	a)residue
26	Ethanol boils at----------------------- under a presuure of 1 atmosphere	a)78.13 degree celsius	b)80 degree celsius	c)100 degree celsius	d)20 degree celsius	a)78.13 degree celsius
27	Water-ethanol system is an example for	a)type I	b)type II	c)type III	d)type IV	b)type II
28	Mixture of acetone and chloroform is an example for	a)type I	b)type II	c)type III	d)type IV	c)type III
29	Mixture of water and hydrogen chloride are example for	a)type I	b)type II	c)type III	d)type IV	c)type III
30	Mixture of water and nitric acid are example for	a)type I	b)type II	c)type III	d)type IV	c)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	a)azeotropic mixture	b)liquid mixture	c)solid mixture	d)gaseous mixture	a)azeotropic mixture
32	azeotropic mixture is otherwise known as	a)constant boiling mixture	b)liquid mixture	c)gaseous mixture	d)solid mixture	a)constant boiling mixture
33	maximum boling point is said to be	a)high volatile	b)least volatile	c)no volatile	d)volatility increases and then decreases	b)least volatile
34	minimum boiling point is said to be	a)high volatile	b)least volatile	c)no volatile	d)volatility increases and then decreases	a)high volatile
35	------------------------ are used in fractional distillation	a)fractionating column	b)distillation column	c)condensation column	d)fractionating and distillation column	a)fractionating column
36	compostion of liquid and vapour phases can be determined with the help of	a)phase rule	b)lever's rule	c)gibbs rule	d)charles rule	b)lever's rule
37	The masses of the liquids in the distillate will be in the ratio of their vapour pressures and molar masses	a)fractional distillation	b)steam distillation	c)fractional and steam distillation	d)column distillation	b)steam distillation
38	Any mixture of two immiscible liquids will boil at a temperature ----------------------than that at which any pure constituent of the misture boils	a)lower	b)higher	c)lower and higher	d)constant	a)lower
39	The boiling point of aniline is	a)180 degree celsius	b)100 degree celsius	c)120 degree celsius	d)85 degree celsius	a)180 degree celsius
40	A compound immisicible or nearly so in water is	a)benzene	b)aniline	c)phenol	d)amide	b)aniline
41	partial miscibility increases on increasing the temperature	a)phenol-water	b)water-nicotine			a)phenol-water
42	partial miscibility increases on lowering the temperature	a)phenol-water	b)(C2H5)2 NH-H2O	c)water-picotine	d)ether-water system	b)(C2H5)2 NH-H2O
43	parital misicibility increases on both rasing as well as lowering the temperature	a)water-nicotine	b)phenol-water	c)water-benzene	d)ether-water system	a)water-nicotine
44	complete miscibility temperature cannot be obtained	a)water-benzene	b)phenol-water	c)ether-water	d)water-nicotine	c)ether-water
45	The temperature above which a pair of partially miscible liquids become miscible in all proportions is called	a)lower critical solution temperatue	b)higher critical solution tmeperature	c)critical solution temperature	d)critical temperature	c)critical solution temperature
46	critical solution temperature is otherwise known as	a)consolute temperture	b)solubility temperature	c)misicibility temperature	d)melting temperature	a)consolute temperture

47	Liquid pairs attain complete misicibility above a certain temperature in which case they are said to have the	a)LCST	b)UCST	b)CST	d)ST	b)UCST
48	Liquid pairs show complete miscibility below a certain temperature when they are said to have	a)LCST	b)UCST	b)CST	d)ST	a)LCST
49	The composition points of the conjugate phases are joined by	a)tie lines	b)conjugate lines	c)upper lines	d)lower lines	a)tie lines
50	The two phases having dissimilar composition in equilibrium with each other at a given temperature constitute a pair of	a)conjugate phase	b)non-conjugate phase	c)tie phase	d)gibbs phase	a)conjugate phase
51	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	a)conjugate solutions
52	aniline-hexane is an example for	a)partial miscibility increases on increasing the temperature	b)partial miscibility increases on lowering the temperature	c)parital misicibility increases on both rasing as well as lowering the temperature	d)complete miscibility temperature cannot be obtained	a)partial miscibility increases on increasing the temperature
53	triethylamine-water system is an example for	a)partial miscibility increases on increasing the temperature	b)partial miscibility increases on lowering the temperature	c)parital misicibility increases on both rasing as well as lowering the temperature	d)complete miscibility temperature cannot be obtained	b)partial miscibility increases on lowering the temperature
54	partition coefficient is otherwise known as	a)distribution coefficient	b)diffusion coefficient	c)viscosity coefficient	d)freezing coefficient	a)distribution coefficient
55	The Nernst distribution law is calid only for --------------------- of single molecules in the two phases	a)concentrations	b)pressure	b)volume	d)temperature	a)concentrations
56	benzene-water	a)mutually insoluble	b)mutually soluble	c)insoluble	d)completely soluble	a)mutually insoluble
57	The mutual solubility is not altered by the presence of the solute in	a)aniline-water	b)benzene-water	c)amide-water	d)chloroform-water	b)benzene-water
58	complex ions are studied in	a)nernst distribution law	b)gibbs distribution law	c)einstein distribution law	d)albert distribution law	a)nernst distribution law
59	One of the important validity in Nernst distribution law is	a)constant temperature	b)constant pressure	c)constant volume	d)constant composition	a)constant temperature
60	Existence of similar molecular species in the two phases in----------with other	a)contact	b)no contact	c)contact and no contact	d)bonded	a)contact

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UNIT III
Multiple choice questions

S.No	Question	option 1	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	a)daniel cell	b)galvanic cell	c)laclanche cell	d)voltaic cell	b)galvanic cell
2	The electrode in which oxidation occurs is	a)anode	b)cathode	c)Anode and Cathode	d)Electrolyte	a)anode
3	The salt bridge is filled with a solution of	a)potassium chromate	b)sodium chloride	c)potassium chloride	d)zinc chloride	c)potassium chloride
4	If the electricity produced by the cell is equal to the EMF, the cell is	a)reversible	b)irreversible	c)Sometimes reversible	d)Sometimes irreversible	b)irreversible
5	In quinhydrone electrode, platinum wire is placed	a)hydroquinone and quinone	b)only hydroquinone	c)only quinone	d)Water	b)only hydroquinone
6	An example for metal-metal ion electrodes is	a)daniel cell	b)hydrogen electrode	c)chlorine electrode	d)calomel electrode	a)daniel cell
7	An example for gas electrode is	a)hydrogen electrode	b)chlorine electrode	c)oxygen electrode	d)hydrogen, Chlorine and oxygen electrode	d)hydrogen, Chlorine and oxygen electrode
8	calomel is a	a)potassium chloride	b)sodium chloride	c)mercurous chloride	d)barium chloride	c)mercurous chloride
9	The wire used in the calomel electrode is made of	a)platinum	b)copper	c)titanium	d)iron	a)platinum
10	An example for oxidation-reduction electrode is	a)calomel electrode	b)chlorine electrode	c)quinhydrone electrode	d)hydrogen electrode	c)quinhydrone electrode
11	In quinhydrone electrode, the platinum wire is placed in a solution containing	a)hydroquinone and quinone	b)only hydroquinone	c)only quinone	d)Water	b)only hydroquinone
12	The tendency of an electrode to lose or gain electrons when contact with its own ions in solution, is called	a)electrode potential	b)reduction potential	c)oxidation potential	d)Concentration potential	a)electrode potential
13	The electrode in which reduction occurs is	a)anode	b)cathode	c)Anode and Cathode	d)Electrolyte	b)cathode
14	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	c)electrochemical series
15	Any two suitable half cells can be combained to form a	a)daniel cell	b)electrochemical cell	c)galvanic cell	d)leclanche cell	c)galvanic cell
16	If the electricity produced by the cell is greater than the applied EMF, then the cell is	a)reversible	b)irreversible	c)Sometimes reversible	d)Sometimes irreversible	a)reversible
17	In the calomel electrode, the wire used is made of	a)platinum	b)copper	c)titanium	d)iron	a)platinum
18	The salt bridge is made of	a)potassium chromate	b)sodium chloride	c)potassium chloride	d)zinc chloride	c)potassium chloride
19	An example for metal-insoluble metal salt electrode is	a)calomel electrode	b)standard hydrogen electrode	c)silver-silver chloride electrode	d)Gas electrode	a)calomel electrode
20	The voltaic cell Zn-Cu, the standard EMF is	a)1.20 v	b)1.15 v	c)1.25 v	d)1.10 v	d)1.10 v
21	Which one is Metal-insoluble metal salt electrode	a)calomel electrode	b)standard hydrogen electrode	c)silver-silver chloride electrode	d)Gas electrode	a)calomel electrode

22	The EMF is measured in	a)volts	b)coulomb	c)faraday	d)joules	a)volts
23	The electrical energy is measured in	a)volts	b)joules	c)coulomb	d)meter	b)joules
24	The EMF generated by an electrochemical cell is given by the symbol	a)E	b)E°	c)V	d)V°	a)E
25	The EMF is measured by	a)voltmeter	b)galvanometer	c)potentiometer	d)ammeter	c)potentiometer
26	The EMF of the unknown half cell is calculated from	a)$E^{\circ}=E_R-E_L$	b)$E^{\circ}=E_L-E_R$	c)$E^{\circ}=E_L+E_R$	d)$E^{\circ}=E_L+Es$	a)$E^{\circ}=E_R-E_L$
27	The potential of a single electrode in a half cell is called the	a)electromotive force	b)single electrode potential	c)standard reduction potential	d)cell potential	b)single electrode potential
28	If the standard emf E° is positive, the reaction is	a)feasible	b)not feasible	c)reversible	d)Irreversible	a)feasible
29	The Nernst equation is	a)$E= 2.303\ RT/nF \log K$	b)$E= 2.303/nF\ RT \log K$	c)$E= 2.303\ RT/nF-E^{\circ}$	d)$E=E^{\circ}- 2.303\ RT/nF \log K$	b)$E= 2.303/nF\ RT \log K$
30	The Nernst equation for the oxidation half cell is	a)$E=E^{\circ}- 2.303/n \log [Zn^{2+}]$	b)$E= 2.303\ RT/nF \log K$	c)$E=E^{\circ}- 0.0591 /n \log [Mn^{+}]$	d)$E= 2.303/nF \log K$	a)$E=E^{\circ}- 2.303/n \log [Zn^{2+}]$
31	Which compound is used in the salt bridge	a)potassium chromate	b)sodium chloride	c)potassium chloride	d)zinc chloride	c)potassium chloride
32	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)$\Delta F= nEG$	a)$\Delta G= -nFE$
33	The metals near the bottom of the electrochemical series is	a)strong reducing agents	b)strong oxidising agent	c)weak reducing agent	d)weak oxidising agents	a)strong reducing agents
34	The feasibility of a redox reaction can be predicted with the help of	a)electronegativity	b)electrochemical series	c)electron affinity	d)equivalent conductance	b)electrochemical series
35	The emf of a cell with 1M solution of reactants and products in solution at 25°c is called	a)half cell potential	b)standard emf	c)single electrode potential	d)redox potential	b)standard emf
36	The relationship between equilibrium constant and the standard emf of a cell is	a)$E^{\circ}= 0.0591 \log k$	b)$0.0591E^{\circ}= \log k$	c)$nE^{\circ}= 0.0951 \log k$	d)$nE^{\circ}= 0.0591 \log k$	b)$0.0591E^{\circ}= \log k$
37	Which one of the following is not present in the calomel electrode	a)mercurous chloride	b)mercury	c)KCl	d)ZnCl	d)ZnCl
38	The electrochemical or electrolytic processes are carried out in a device known as	a)battery	b)galvanometer	c)potentiometer	d)electrolyte	b)galvanometer
39	When the electrodes are connected externally, then the circuit is said to be	a)open	b)closed	c)ideal	d)constant	a)open
40	What is SHE	a)standard hydrogen electrode	b)standard helium electrode	c)simple half electrode	d)standard reference electrode	a)standard hydrogen electrode
41	The overall reaction taking place in the daniel cell is	a)oxidation	b)reduction	c)redox	d)forward	c)redox
42	If the reduction potential of the electrode is 1.5v then its oxidation potential is	a)0 v	b)1 v	c)negative 1.5	d)2	c)negative 1.5
43	Daniel cell is called as	a)voltaic cell	b)half cell	c)anode cell	d)cathode half cell	b)half cell
44	Metal-insoluble metal salt electrode is	a)calomel electrode	b)standard hydrogen electrode	c)silver-silver chloride electrode	d)Gas electrode	a)calomel electrode
45	The standard EMF of Zn-Cu voltaic cell is	a)1.20 v	b)1.15 v	c)1.25 v	d)1.10 v	d)1.10 v
46	The standard emf can be determined at standard temperature is	a)32°c	b)20°c	c)25°c	d)27°c	c)25°c

47	The standard electrode potential at 25°c is zero for	a)Hydrogen electrode	b)Gas electrode	c)Calomel electrode	d)Metal electrode	a)Hydrogen electrode
48	The standard hydrogen electrode can act as	a)anode	b)cathode	c)Anode and Cathode	d)Electrolyte	c)Anode and Cathode
49	The emf of the standard hydrogen electrode is arbitrarily assigned the value of	a)0 v	b)0.1 v	c)0.001 v	d)1 v	a)0 v
50	The reduction potential of the electrode is 1.5v then its oxidation potential is	a)0 v	b)1 v	c)negative 1.5	d)2	c)negative 1.5
51	The standard temperature at which the standard emf can be determined is	a)32°c	b)20°c	c)25°c	d)27°c	c)25°c
52	For Zn-Cu voltaic cell, the standard EMF is	a)1.20 v	b)1.15 v	c)1.25 v	d)1.10 v	d)1.10 v
53	Which one the following is example for Metal-insoluble metal salt electrode	a)calomel electrode	b)standard hydrogen electrode	c)silver-silver chloride electrode	d)Gas electrode	a)calomel electrode
54	The unit of electrical energy is	a)volts	b)joules	c)coulomb	d)meter	b)joules
55	In IUPAC conventions, the double vertical line represents	a)two half cell	b)cathode half cell	c)salt bridge	d)anode half cell	c)salt bridge
56	Platinum is a	a)positive electrode	b)negative electrode	c)Positve and negative electrode	d)Inert electrode	d)Inert electrode
57	If the emf acts in the opposite direction through the cell circuit it is denoted as a	a)positive	b)negative	c)zero	d)cannot be determined	c)zero
58	What is the potential of a half cell consisting of zinc electrode in 0.01M $ZnSO_4$ solution 25°c. E$^{\circ}$= 0.763 V	a)0.0591 V	b)0.6521 V	c)0.7532 V	d)0.8221 V	a)0.0591 V
59	What is R in Nernst equation	a)rate of the reaction	b)redox reaction	c)gas constant	d)reduction of gas	c)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	a)25.59 kJ	b)29.52 kJ	c)28.95 kJ	d)data inadequate	a)25.59 kJ

UNIT IV

Application of EMF Measurements

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.

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

- 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".

$$n = 2 \text{ moles of electrons}$$

- 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:

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

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

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.

$$E^0\ cell=Ecathode-E^0\ anode$$

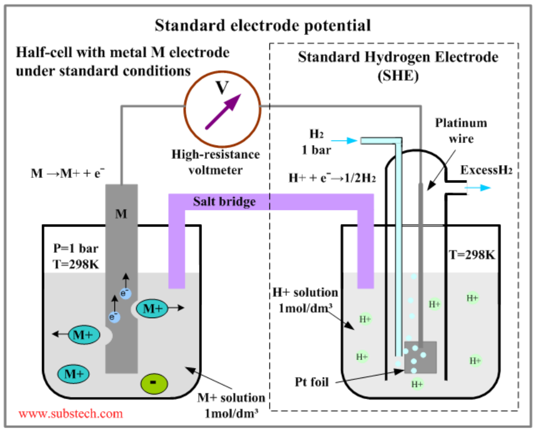


Fig.1 An example of a concentration cell

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

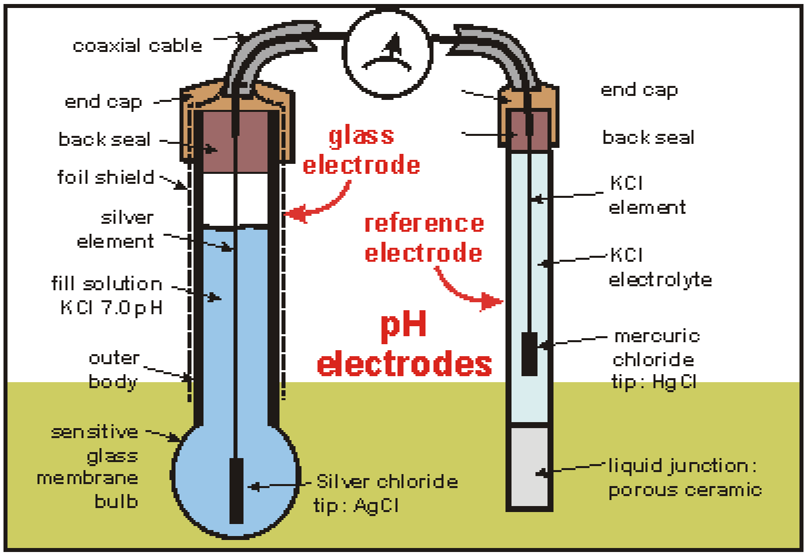
Corrosion can occur on a concentration cell when the metal being used is in contact with different concentrations, causing parts of the metal to have different electric potential than the other parts. One element that is often linked to this corrosion is oxygen. In the areas in which there is a low oxygen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

Part A(Each carry one mark)

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. Quinhydrone electrode is preferred to the ------------electrode

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→Cu2++ 2e- and** **$2Na + 2H_2O \rightarrow 2NaOH + H_2$**

5. Emf is measured in

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

6. A solution of -----------molar HCl which 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. The reference electrode employed is usually the --------------------in glass electrode

a)hydrogen **b)calomel** c)quinine d)hydroquinone

10. Two like electrodes with different concentration are immersed in an electrolyte are known as

a)electrode-concentration cell **b)electrolyte concentration cell** c)cell concentration d)cell constant

11. 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

12. Electrical energy forced in electrochemical cell is

a)Spontaneous **b)Non-Spontaneous** c)Exothermic d)Endothermic

13. . 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

14. The electrical energy produced by a galvanic cell is given by the ------------- of its electromotive force and the quantity of electricity which passes

a)sum **b)product** c)sum and product d)divided

15. Electricity is measured in

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

16 The potential of a hydrogen electrode in contact with a solution of H+ ions involving the reaction is given by

a)Nernst equation b)Gibbs equation c)Duhem equation d)Clausius equation

17. Glass electrodes can be used in

a)strong oxidising solutions b)week oxidising solutions c)strong reducing solutions d)week reducing solutions

18. Why not pH cannot be measured through potentiometer or voltmeter, but can be done through electronic voltmeter

a)resistance of the glass membrane is very high and the current is small

b) resistance of the glass membrane is low and the current is large

c)different salt bridges are used

d) glass electrode compares pH, while electrode measures P H

19. Liquid junction potential depends on

a)transference number of anion and cation b)removal of anion and cation

c)transfer of only anion d)transfer of only cation

20. When does L.J.P becomes negative

a)$t_- = t_+$ b)$t_- \neq t_+$ **c)$t_- > t_+$** d)$t_- < t_+$

Part A(Each carry two marks)

21.What is known as liquid junction potential?

22.What is the principle behind potentiometric titration?

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

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

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

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

27.Define transport number.

28.What is known as activity coefficient?

Part B(Each carry 8 marks)

29.Explain potentiometric precipitation reaction.

30. Explain the following

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

31.Explain concentration cells with and without transference.

32.Describe potentiometric titrations of a redox reaction

33.Explain concentration cells with and without transference.

34. Explain the following

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

35.How to determine pH using the following electorodes

    (i)Hydrogen electrode
    (ii)Quinhydrone electrode
    (iii) Glass electrode

36.Explain potentiometric redox titration.

37.Write short note on

    (i)Liquid junctional potential

    (ii)EMF measurements in determining equilibrium constant

38.Explain potentiometric acid-base titration..

KARPAGAM ACADEMY OF HIGHER EDUCATION
(Deemed to be University under Section 3 of UGC Act 1956)
COIMBATORE-641 021
(For the candidates admitted from 2016 & onwards)
II B.Sc. Chemistry
PHYSICAL CHEMISTRY

UNIT IV
Multiple choice questions

S.No	Question	option 1	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	a)sum	b)product	c)sum and product	d)divided	b)product
2	Electricity is measured in	a)volts	b)amperes	c)coulombs	d)ohm	c)coulombs
3	Emf is measured in	a)volts	b)amperes	c)coulombs	d)ohm	a)volts
4	Electrical energy of a reversible cell originated from the ------------------- in the enthalpy of the cell reaction	a)decrease	b)increase	c)decreases and then increases	d)increases and the decreases	a)decrease
5	The standard free energy change of a cell reaction is given by	a)$\Delta G=-n FE$	b)$\Delta F=n FE$	c)$\Delta G=n FE$	d)$\Delta G=FE$	a)$\Delta G=-n FE$
6	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	a)free energy	b)entropy	c)enthalpy	d)equilibrium constant	d)equilibrium constant
7	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	a)standard EMF
8	The potential of a hydrogen electrode in contact with a solution of H+ ions involving the reaction is given by	a)Nernst equation	b)Gibbs equation	c)Duhem equation	d)Clausius equation	a)Nernst equation
9	Instead of taking quinone and hydroquinone, a small amount of -----------is taken	a)quinhydrone	b)glass	c)hydroquinone	d)quinone	a)quinhydrone
10	Quinhydrone electrode is preferred to the ----------- electrode	a)hydrogen	b)calomel	c)glass	d)platinum	a)hydrogen
11	The quinhydrone electrode is combined with a saturated-------------electrode to form a cell	a)hydrogen	b)calomel	c)glass	d)platinum	b)calomel
12	The quinhydrone electrode cannot be used for solutins p H more than	a)7	b)9	c)8	d)5	c)8
13	Hydroquinone ionises appreaciably as an acid and also gets --------------partly by atmospheric oxygen	a)oxidised	b)reduced	c)oxidised and then reduced	d)reduced and then oxidised	a)oxidised
14	The glass electrode is made of a special glass of relativley -----melting point and then ------------ electrical conductivity	a)high and low	b)low and high	c)high and high	d)low and low	b)low and high

15	A solution of -----------molar HCl which furnishes a constant hydrogen ion concentration	a)0.01	b)0.1	c)0.2	d)0.001	b)0.1
16	The reference electrode employed is usually the --------------------in glass electrode	a)hydrogen	b)calomel	c)quinone	d)hydroquinone	b)calomel
17	The EMF can be determined by means of a ------------	a)potentiometer	b)conductivity meter	d)p H meter	d)voltmeter	a)potentiometer
18	Glass electrodes can be used in	a)strong oxidising solutions	b)week oxidising solutions	c)strong reducing solutions	d)week reducing solutions	a)strong oxidising solutions
19	calomel electrode consists of mercury,solid mercurous chloride and a solution of ------------	a)KCl	b)NaCl	c)NaOH	d)KOH	a)KCl
20	Standard cell potential is measured	a)at a temperature of 25°c	b)when ion concentration of aqueous reactants are 1.00 M	c)under the condition of 1.00 atm for gaseous reactants	d)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	d)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
21	The standard electrode commonly used are	a)hydrogen electrode	b)quinhydrone electrode	c)glass electrode	d)nitrogen electrode	a)hydrogen electrode
22	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
23	Why not pH cannot be measured through potentiometer or voltmeter, but can be done through electronic voltmeter	a)resistance of the glass membrane is very high and the current is small	b)resistance of the glass membrane is low and the current is large	c)different salt bridges are used	d)glass electrode compares pH, while electrode measures Ph	b)resistance of the glass membrane is low and the current is large
24	PH of the cell can be found out	a)given the E_{cell} value	b)given the $E^{\circ}G$	c)given the E0 value	d)given the $E^{\circ}G$ and given the Ecell value	d)given the $E^{\circ}G$ and given the Ecell value
25	How does electrical energy is obtained from the cell	a)due to ions	b)chemical reaction inside the cell	c)due to water	d)chemical reactionoutside the cell	b)chemical reaction inside the cell
26	Transfer of matter with respect to concentration is known as	a)cell equilibrium	b)cell constant	c)cell concentration	d)Electolyte concentration	c)cell concentration
27	Two like electrodes with different concentration are immersed in an electrolyte are known as	a)electrode-concentration cell	b)electrolyte concentration cell	c)cell concentration	d)cell constant	b)electrolyte concentration cell
28	Electrode-concentration cell are evidently independent of	a)concentration of electrolyte	b)concentration of ions	c)concentration in electrode	d)electrolyte concentration cell	a)concentration of electrolyte
29	The whole process will be spontaneous only when the	a)emf is negative	b)emf is partially negative	c)emf is partially positive	d)emf is positive	a)emf is negative
30	Solution with same electrolyte with different concentration is found in	a)electrolyte concentration cell	b)electrode-concentration cell	c)concentration of ions	d)electrode-concentration cell and electrolyte concentration cell	b)electrode-concentration cell

31	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	b)concentration cell without transfer
32	Transfer of ions takes place directly at	a)concentration cell without transfer	b)concentration cell with transfer	c)emf is partially negative	d)concentration cell without transfer and concentration cell with transfer	b)concentration cell with transfer
33	Liquid junction potential depends on	a)transference number of anion and cation	b)removal of anion and cation	c)transfer of only anion	d)transfer of only cation	a)transference number of anion and cation
34	When does L.J.P becomes null/zero	a)$t_-=t_+$	b)$t_-\neq t_+$	c)$t_->t_+$	d)$t_-<t_+$	a)$t_-=t_+$
35	When does L.J.P becomes negative	a)$t_-=t_+$	b)$t_-\neq t_+$	c)$t_->t_+$	d)$t_-<t_+$	c)$t_->t_+$
36	When does L.J.P becomes positive	a)$t_-=t_+$	b)$t_-\neq t_+$	c)$t_->t_+$	d)$t_-<t_+$	d)$t_-<t_+$
37	Which among the following electrolytes have the same transfer number of anions and cations	a)potassium chloride and ammonium nitrate	b)potassium nitrate and ammonium chloride	c)potassium sulphate and ammonium nitrate	d)potassium nitrate and ammonium sulphate	c)potassium sulphate and ammonium nitrate
38	Reversibility of electrode with respect to cation will determine	a)transfer number of anion	b)transfer number of cation	c)emf is partially negative	d)concentration cell with transfer	a)transfer number of anion
39	Reversibility of electrode with respect to anion will determine	a)transfer of anion	b)transfer of cation	c)emf is partially negative	d)concentration cell with transfer	b)transfer of cation
40	Potential of any electrode depends on	a)concentration of ions	b)concentration of anion	c)concentration of cation	d)transfer of cation	a)concentration of ions
41	Why an indicator is not required for a potentiometric titration that is carried out with a coloured solution	a)no indicator required	b)self indicator	c)no indicator required and self indicator	d)External indicator	c)no indicator required and self indicator
42	In a potentiometric titration, the EMF slowly changes when	a)the end point changes	b)before the end point	c)when the end point approaches	d)emf is partially negative	c)when the end point approaches
43	Which among the following electrode is used as oxidation- reduction electrode	a)copper	b)silver-silver	c)platinum	d)tin	b)silver-silver
44	The Liquid junction potential becomes positive	a)$t_-=t_+$	b)$t_-\neq t_+$	c)$t_->t_+$	d)$t_-<t_+$	d)$t_-<t_+$
45	Which among the following will come under potentiometric titration	a)acid-base titration	b)redox titration	c)precipitation titration	d)acid-base titration, redox titration and precipitation titration	d)acid-base titration, redox titration and precipitation titration
46	Which among the following is taken as indicator in the precipitation titration of silver nitrate against potassium chloride	a)potassium electrode	b)silver electrode	c)hydrogen electrode	d)silver-silver electrode	b)silver electrode
47	Organic compounds which can exist in oxidised form as well as reduced form are said to be	a)amphoteric indicator	b)redox indicator	c)acid indicator	d)base indicator	b)redox indicator
48	Which is that one main feature of redox indicators	a)different concentration	b)different colour	c)different cell	d)same colour	b)different colour
49	When does a redox indicator can be successfully used	a)measured potential to be about 0.03 volt	b)more than 0.03 volt	c)0 potential	d)1	b)more than 0.03 volt
50	Which among the following is a redox indicator for titration of ferrous ions against dichromate ions	a)diphenylamine	b)KCl	c)NaCl	d)CaCl2	a)diphenylamine
51	Determination of transport number, valency of a ion, coefficient of electrolyte are purely based upon	a)cell constant	b)equilibrium constant	c)EMF	d)Concentration	a)cell constant

52	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)	c)oxidation of $Cu^{3+}(aq)$
53	The site of oxidation in an electrochemical cell is	a)the anode	b)cathode	c)electrodes	d)salt bridge	a)the anode
54	Which statement below is not true for the reaction $Fe^{3+} + e^{-} \rightarrow Fe^{2+}$	a)Fe^{3+} is being reduced	b)the oxidation state of Fe has charged	c)Fe^{3+} could be referred ta as an oxidizing agent in this reaction	d)both Fe^{2+} and Fe^{2+} are called anions	d)both Fe^{2+} and Fe^{2+} are called anions
55	In any electrochemical cell, the cathode is always	a)non metal	b)attached to battery	c)the electrode at which some species gain electrons	d)the electrode at which some species lose electrons	a)non metal
56	Electrical energy forced in electrochemical cell is	a)Spontaneous	b)Non-Spontaneous	c)Exothermic	d)Endothermic	b)Non-Spontaneous
57	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→Cu2++ 2e- and 2Na+ $2H_2O \rightarrow 2NaOH + H_2$	d)Cu→Cu2++ 2e- and 2Na+ $2H_2O \rightarrow 2NaOH + H_2$
58	A voltaic cell has an E° value of -1.00 v the reaction is	a)spontaneous	b)has positive ΔG°	c)has negative ΔG°	d)0	b)has positive ΔG°
59	Which of the following can we use to measure Ph?	a)a glass electrode	b)a concentration cell	c)a hydrogen electrode	d)a glass electrode, a concentration cell and a hydrogen electrode	d)a glass electrode, a concentration cell and a hydrogen electrode
60	What is ΔG° at 298k for the reaction Hg(l) + $2Fe^{3+}(aq) \rightarrow Hg^{2+}(aq) + 2Fe^{2+}(aq)$	a)positive 314 Kelectrode	b)negative 16 KJ	c)negative 314 Kelectrode	d)positive 16 KJ	d)positive 16 KJ

UNIT V

Surface Chemistry

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

Surface chemistry

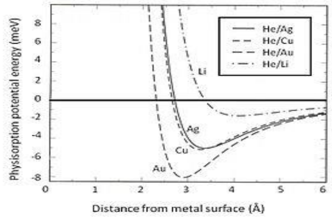
Physical adsorption

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 **R** = (0, 0, *Z*), and the position coordinate of its electron, **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.[5] 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 $(1 - \theta)$.

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

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

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

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**.

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,

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

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

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

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

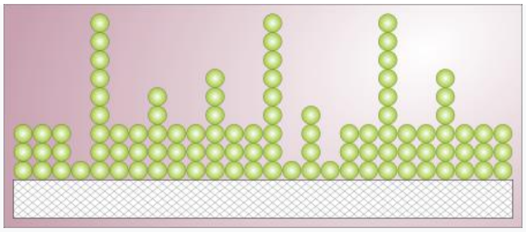
Equation (3) is in agreement with Freundlich adsorption equation.

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 QUESTIONS

Part A(Each question carry one mark)

1. The substance adsorbed or attached is called the------------

a)adsorbent **b)adsorbate** c)sorbate d)desorption

2. Ps called as

a)pressure **b)saturation pressure** c)temperature d)volume

3. In physical adsorption, there a regular decrease in extent of adsorption as------------increases

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

4. 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

5. . charcoal and silica gel are excellent-------------

a)adsorbate **b)adsorbent** c)sorbent d)absorbate

6. Freundlich adsoprtion isotherm fails if concentration of adsorbate is very-------------

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

7. According to Langmuir if a bond is weak, a-------------------adsorption takes place

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

8. The surface area of catalysts is an important factor in------------------ activity

a)activity coefficients b)viscosity coefficients c)diffusion coefficients **d)catalytic**

9. charcoal and silica gel are excellent-------------

a)adsorbate **b)adsorbe** c)sorbent d)absorbate

10. Freundlich adsoprtion isotherm fails if concentration of adsorbate is very-------------

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

11. Activated charcoal is used for removing-------------

a)colouring matter b)dust c)sediments d)coagulant

12. In order to increase the rate of adsorption,----------------------is very necessary

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

13. The adsorption is accompanied by a ----------------------in residula surface forces

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

14. x/m is known as

a)nature of adsorption **b)extent of adsorption** c)rate of adsorption d)magnitude of adsorption

15. According to Langmuir if a bond is weak, a--------------------adsorption takes place

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

16. The surface area of catalysts is an important factor in------------------ activity

a)activity coefficients b)viscosity coefficients c)diffusion coefficients **d)catalytic**

17. The adsorption is accompanied by a ----------------------in residula surface forces

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

18. x/m is known as

a)nature of adsorption **b)extent of adsorption** c)rate of adsorption d)magnitude of adsorption

19. BET finds application in

a)catalysis b)activity of coefficients c)diffusion coefficients d)viscosity coefficient

20. The surface area of catalysts is an important factor in------------------ activity

a)activity coefficients b)viscosity coefficients c)diffusion coefficients **d)catalytic**

Part B(Each question carry 2 marks)

21.What is known as physical adsorption?

22.What is known as chemical adsorption?

23.Define adsorption.

24.Define absorption.

25.Define adsorbate.

26.Define adsorbent.

27.Write down an equation for BET.

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

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

Part C (Each question carry 8 marks)

30. Differentiate physical adsorption with chemical adsorption.

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

32.What is adsorption and absorption.Derive Freundlich adsorption isotherm and mention its conditions.
33. Discuss BET in detail.
34.What is adsorption and absorption.Derive Freundlich adsorption isotherm and mention its conditions.
35.What is adsorption and absorption.Derive Freundlich adsorption isotherm and mention its conditions.
36.What is adsorption and absorption. Explain BET

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II B.Sc. Chemistry
PHYSICAL CHEMISTRY

UNIT V
Multiple choice questions

S.No	Question	option 1	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	a)adsorption	b)absorption	c)sorption	d)desorption	a)adsorption
2	The adsorption is accompanied by a ----------------------in residula surface forces	a)decrease	b)increase	c)increase and then decreases	d)decrease and then increases	a)decrease
3	The adsorption of a gas on a solid is sometimes called	a)inclusion	b)occlusion	c)sorption	d)desorption	b)occlusion
4	The material providing the surface upon which adsorption occurs is known as the -----------------	a)adsorbent	b)adsorbate	c)sorbate	d)desorption	a)adsorbent
5	The substance adsorbed or attached is called the------------	a)adsorbent	b)adsorbate	c)sorbate	d)desorption	b)adsorbate
6	The removal of adsorbed substance from the surface is called	a)inclusion	b)occlusion	c)sorption	d)desorption	d)desorption
7	The amount of heat evolved when 1 mole of any gas is adsorned on solid adsorbent surface is called----------------of adsorption	a)entropy	b)enthalpy	c)free energy	d)work function	b)enthalpy
8	When the concentration of the adsorbate is more on the surface of the adsorbent than the bulk, it is called-----------------adsorption	a)positive	b)negative	c)inclusion	d)occlusion	a)positive
9	When the concentration of the adsorbate is less on the surface of the adsorbent than the bulk, it is called-----------------adsorption	a)positive	b)negative	c)inclusion	d)occlusion	b)negative
10	Adsorption is a -------------phenomenon	a)surface	b)bulk	c)layer	d)negative	a)surface
11	Adsorption is a ------------process	a)slow	b)fast	c)medium	d)average	b)fast
12	Absorption is a----------process compared to adsorption	a)slow	b)fast	c)medium	d)average	a)slow
13	Adsorption involves the-------------------into the interior of the matter	a)diffusion	b)penetration	c)occlusion	d)inclusion	a)diffusion
14	In-------------------, a gas gets adsorbed on the solid only if it forms chemical bonds	a)adsorption	b)desorption	c)chemisorption	d)absorption	c)chemisorption
15	Greater the surface area of the adsorbent, ---------------is its adsorption capacity	a)greater	b)lower	c)average	d)medium	a)greater
16	charcoal and silica gel are excellent-------------	a)adsorbate	b)adsorbent	c)sorbent	d)absorbate	b)adsorbent
17	charcoal is ------------porous and hence possess-------------surface areas	a)high and large	b)low and small	c)high and small	d)low and large	a)high and large
18	The extent of adsorption depends upon the-------------	a)temperature	b)pressure	c)volume	c)concentration	b)pressure
19	Adsorption isotherm is a graph plotted between magnitude of adsorption and --------------at constant temperature	a)temperature	b)pressure	c)volume	c)concentration	b)pressure
20	Ps called as	a)pressure	b)saturation pressure	c)temperature	d)volume	b)saturation pressure
21	Ps becomes ------------ to the rate of desorption and further increase of pressure does not alter the equilibrium	a)equal	b)greater	c)lower	d)greater than or equal to	a)equal
22	x/m is known as	a)nature of adsorption	b)extent of adsorption	c)rate of adsorption	d)magnitude of adsorption	b)extent of adsorption
23	At low pressure in Freundlich isotherm the graph is almost a ------------	a)parallel	b)perpendicular	c)straight line	d)slope	c)straight line
24	At high pressure in Freundlich isotherm the graph is almost--------------to X-axis	a)parallel	b)perpendicular	c)straight line	d)slope	a)parallel
25	At intermediate pressure in Freundlich isotherm x/m depends on	a)0 to 1	b)1 to 2	c)0 to 2	d)0 to 3	a)0 to 1
26	Freundlich adsorption isotherm fails is pressure is----------	a)high	b)low	c)medium	d)average	a)high
27	Freundlich adsoprtion isotherm fails if concentration of adsorbate is very-------------	a)high	b)low	c)medium	d)average	a)high
28	Adsorption isobar is a graph plotted between magnitude of adsorption and -------------- at constant pressure	a)temperature	b)volume	c)concentration	d)composition	a)temperature
29	The amount absorbed x/m should ---------------with an increase in temperature	a)decrease	b)increase	c)remain constant	d)decrease and then increases	a)decrease

30	chemisorption requires-----------	a)activation energy	b)entropy	c)enthalpy	d)free energy	a)activation energy
31	adsorption-----------can be used to distinguish between physical and chemical adsorption	a)isobar	b)isotherm	c)isochore	d)isotherm and isochore	a)isobar
32	In physical adsorption, there a regular decrease in extent of adsorption as------------increases	a)pressure	b)concentration	c)volume	d)temperature	d)temperature
33	In chemisorption, there is initial increase and then decrease in extent of adsorption as --------------------increases	a)pressure	b)concentration	c)volume	d)temperature	d)temperature
34	In order to increase the rate of adsorption,----------------------is very necessary	a)catalyst	b)reactant	c)activation	d)sorption	c)activation
35	mechanical rubbing can be done to increase	a)speed	b)activation	c)reaction	d)speed of catalyst	b)activation
36	Adsorption from solutions decreases with rise of temperature and decrease in-----------------------of solution	a)increase	b)decrease	c)decreases and then increases	d)increases and the decreases	b)decrease
37	Activated charcoal is used for removing-------------	a)colouring matter	b)dust	c)sediments	d)coagulant	a)colouring matter
38	Activated charcoal is used in --------------	a)sedimentation	b)coagulation	c)colouration	d)gas masks	d)gas masks
39	Adsorption process is used in production of vacuum by using activated charcoal in ------------flask	a)condenser	b)distillation	c)Dewar's	d)air condenser	c)Dewar's
40	Lake test for aluminium is based upon ---------------of litmus colour	a)absorption	b)adsorption	c)sorption	d)desorption	b)adsorption
41	According to Langmuir, valencies at the surface of adsorbent atoms are ----------------	a)fully satisfied	b)not fully satisfied	c)partially satisfied	d)satisfied	b)not fully satisfied
42	According to Langmuir if a bond is weak, a--------------------adsorption takes place	a)chemical	b)physical	c)oxidation	d)reduction	b)physical
43	According to Langmuir if a bond is strong, a--------------------adsorption takes place	a)chemical	b)physical	c)oxidation	d)reduction	a)chemical
44	The residual valency force on the surface of adsorbent is effective only up to a small distance and hence, the adsorbed gas layer is only-----------molecule thick	a)one	b)two	c)zero	d)three	a)one
45	The phenomenon of adsorption consists of two opposing processes namely condensation and -------------------	a)distillation	b)evaporation	c)circulation	d)floatation	b)evaporation
46	When the adsorption starts the whole adsorbent surface is bare and consequently the initial rate of absorption is-------------	a)lowest	b)highest	c)constant	d)medium	b)highest
47	When the adsorption starts the whole adsorbent surface is bare and consequently the rate of condensation----------------	a)increases	b)decreases	c)decreases and then increases	d)increases and the decreases	b)decreases
48	The rate of evaporation of the condensed molecules gradually---------	a)increases	b)decreases	c)decreases and then increases	d)increases and the decreases	a)increases
49	A dynamic equilibrium is set up, when the rate of condensation becomes equal to the rate of ------------------	a)distillation	b)evaporation	c)circulation	d)floatation	b)evaporation
50	P/w against P, we should get a----------------	a)decrease	b)straight line	c)increase	d)increases and the decreases	b)straight line
51	Brunauer–Emmett–Teller (BET) theory aims to explain the physical adsorption of gas molecules on a ---------------- surface	a)solid	b)liquid	c)gaseous	d)semi liquid	a)solid
52	The concept of BET is extension of -------------------isotherm	a)Freundlich	b)Langmuir	c)Emmett	d)Teller	b)Langmuir
53	The BET method is widely used in---------------science	a)surface	b)adsorption	c)material	d)polymer	a)surface
54	According to BET,adsorptions occur only on well-defined sites of the sample --------------	a)bulk	b)surface	c)surface as well as bulk	d)layered	b)surface
55	According to BET,the uppermost molecule layer is in equilibrium with the -------------- phase	a)liquid	b)gas	c)solid	d)gas as well as liquid	b)gas
56	The--------------- is a kinetically-limited process	a)adsorption	b)desorption	c)sorption	d)adsorbent	b)desorption
57	At the saturation pressure, the molecule layer number tends to-----------	a)infinity	b)low	c)high	d)low and high	a)infinity
58	By application of the BET theory it is possible to determine the inner surface of hardened ------------paste	a)composite	b)cement	c)matrix	d)concreate	b)cement
59	BET finds application in	a)catalysis	b)activity of coefficients	c)diffusion coefficients	d)viscosity coefficient	a)catalysis
60	The surface area of catalysts is an important factor in------------------ activity	a)activity coefficients	b)viscosity coefficients	c)diffusion coefficients	d)catalytic	d)catalytic

Reg. No. : ---------------

[16CHU301]

KARPAGAM UNIVERSITY

COIMBATORE-21
(For the candidates admitted from 2016 & onwards)
II B.Sc CHEMISTRY
I INTERNAL TEST
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. A gas mixture constitutes a

a) Two phase b) three phase c) one phase d) four phase

2. Calcium carbonate is an example for a system of

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

3. Sulphur is an example for

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

4. F=C-P+2, Here F is

a) Degree of freedom b) component c) phase d) freedom

5. In a chemically reactive system, the number of components is given by

a) C=N-m-n-R b) C=R-N-m-n c) C=m-n-R-C d) C=n-m-r-N

6. Phase rule was enunciated by

a) J.Willard Gibbs b) Albert Einstein c) Antoine Lavoisier c) Dmitri Mendeleev

7. The phase rule equation for one 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+1 c) F=C-P+3 d) F=C-P

85 copies

9. The temperature at which three phases are in equilibrium is known as

a) triple point b) eutectic point c)congruent melting point

d) incongruent melting 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-Clapeyron

d) Dmitri Mendeleev

12. Water and sulphur are examples for

a) One component b) two component c) three component

d) four component

13. Picric aid-benzene is an example for

a) One component b) formation of compounds with congruent melting point

c) three component d) formation of compounds with incongruent melting point

14. Ferric chloride-water system is an example for

a) One component b) formation of compounds with congruent melting point

c) three component d) formation of compounds with incongruent melting point

15. $CH_3COOH-CHCl_3-H_2O$ is an example for

a) One component b) two component

c) three component d) four component

16. Gibbs-Duhem Margules equation is applicable for

a) Binary mixtures　b) tertiary mixtures

c) quaternary mixtures　d) binary and tertiary mixtures

17. In Gibbs-Duhem Margules equation fugacity can be replaced by

a) Temperature　b) volume

c) vapour pressure　d) composition

18. Reduced phase rule is otherwise known as

a) phase rule equation　b) condensed phase rule

c) Gibbs phase rule　d) phase rule equation and Gibbs phase rule

19. In a system the composition of the liquid and vapour phases can be determined with the help of

a) Lever's rule　b) Gibbs phase rule

c) Lever's rule and Gibbs phase rule　d) condensed phase rule

20. Any mixture of two immiscible liquids will boil at a temperature -------------- than that at which any pure constituent of the mixture boils

a) Lower　b) higher

c) constant　d) lower and then increases

PART- B (3 x 2 = 6 Marks)

Answer ALL the Questions

21. What is eutectic point and triple point?

22. Difference between congruent and incongruent melting point.

23. Calculate the degree of freedom for the following equation: ice and water

PART- C (3 x 8 = 24 Marks)

Answer ALL the Questions

24. (a) What is phase rule equation. Define the terms phases, components and degree of freedom with at least two examples.

(OR)

(b) Explain one component-water system with a neat diagram.

25. (a) What is a triangular plot. Explain CH_3COOH-$CHCl_3$-H_2O with a neat diagram.

(OR)

(b) Derive Gibbs-Duhem-Margules equation.

26. (a) Analyze two component system, taking lead silver system as an example.

(OR)

(b) Justify sodium-potassium form compounds with incongruent melting point.

[16CHU301]

KARPAGAM ACADEMY OF HIGHER EDUCATION
(Deemed to be University under Section 3 of UGC Act 1956)
COIMBATORE-21
(For the candidates admitted from 2016 & onwards)
B.Sc. Degree Internal Examination,July 2017
PHYSICAL CHEMISTRY III
(Phase Equilibria and Chemical Kinetics)

INTERNAL I

PART- A

ANSWER KEY

1.c)one phase

2.b)two component

3.a)one component

4.a)degree of freedom

5.a)C=R-N-m-n

6.a)J.Willard Gibbs

7.a)F=C-P+2

8.a) F=C-P+2

9.a)triple point

10.b)eutectic point

11.c)clausius-clapeyron

12.a)one component

13.d)formation of compounds with incongruent melting point

14.b)formation of compounds with congruent melting point

15.c)three component

16.a)binary mixtures

17.c)vapour pressure

18.b)condensed phase rule

19.a)lever's rule

20.a)lower

PART- B

21.The point where solid, liquid and vapours phases are equilibrium is known as triple point

The point where two solid and liquid are equilibrium is known as eutectic point

22. **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.

Incongruent melting occurs when a solid substance does not melt uniformly, decomposing into another solid and a liquid with different compositions. For example, potassium feldspar ($KAlSi_3O_8$) decomposes to leucite ($KAlSi_2O_6$) when it melts. T

23.F=C-P+2

F=1-2+2

F=1(Uni variant)

PART- C

24.a) **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,) 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.)

b) **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 .

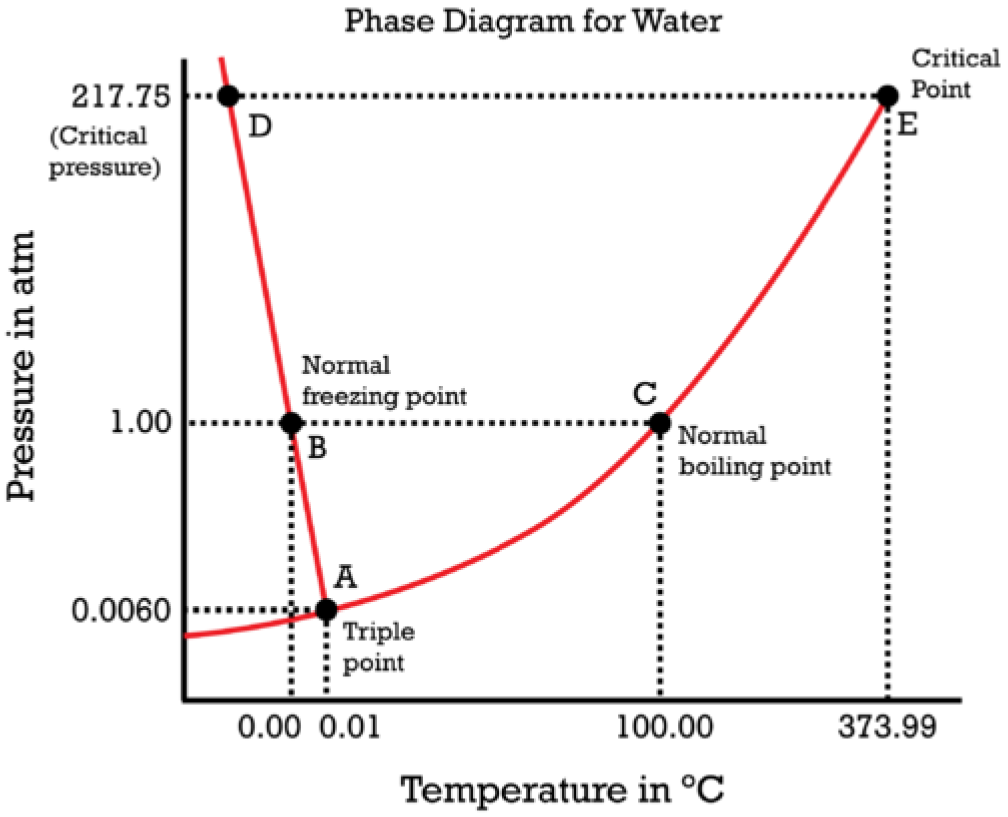


Figure 1

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.

Refer again to water's phase diagram (Figure above). Notice point E, labeled the critical point . What does that mean? 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.

25.a) 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.

b) **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:

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

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

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

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

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

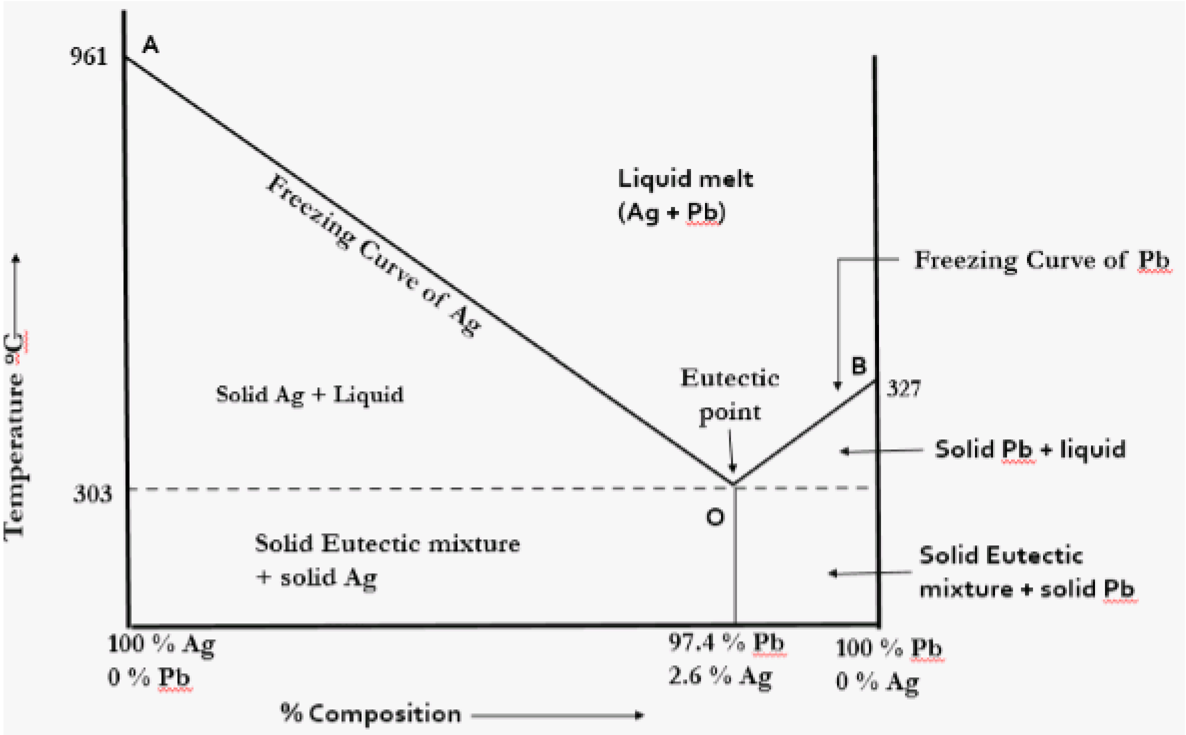
(i) Gibbs-duhem equation is helpful in calculating partial molar quantity of a binary mixture by measuring the composition of the mixture which depends on the total molar quantity.

(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.

26.a) **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.

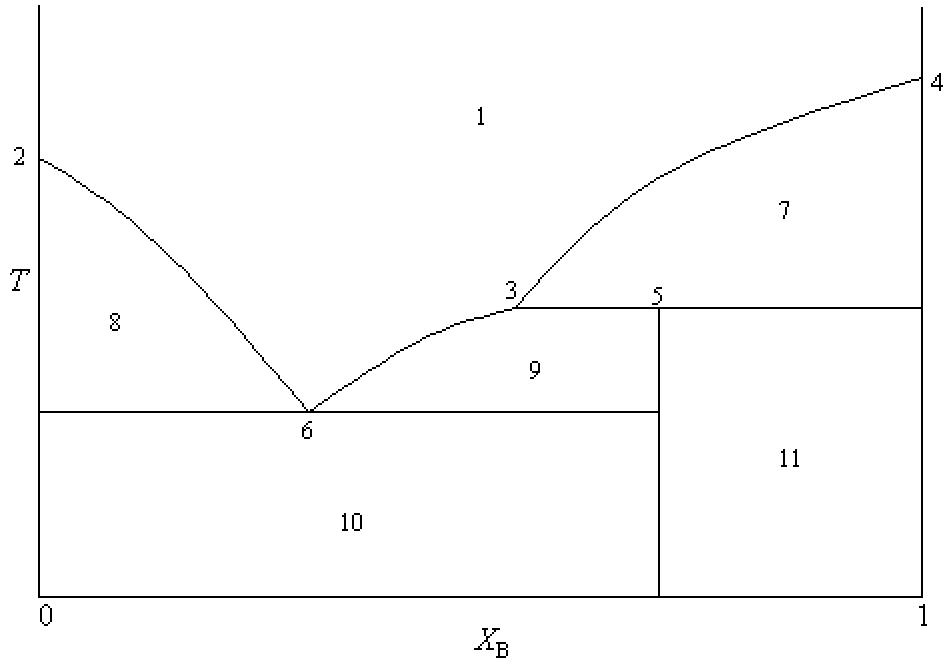
a) The region marked eutectic plus solid Ag in which crystalline silver and solid eutectic are stable.

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.

b)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)

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Reg. No. : ------------- [16CHU301]

KARPAGAM UNIVERSITY

COIMBATORE-21
(For the candidates admitted from 2016 & onwards)
II - B.Sc CHEMISTRY
II INTERNAL TEST
PHYSICAL CHEMISTRY III
(Phase Equilibria and Chemical Kinetics)

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

Date : 7. 8 . 2017 FN

PART- A **(20 x 1= 20 Marks)**

Answer ALL the Questions

1. Partition coefficient is otherwise known as

a) Distribution coefficient b) diffusion coefficient

c) Viscosity coefficient d) freezing coefficient

2. The Nernst distribution law is calid only for --------------------of single molecules in the two phases

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

3. benzene-water

a) Mutually insoluble b) mutually soluble c) insoluble d) completely soluble

4. The mutual solubility is not altered by the presence of the solute in

a) aniline-water b) benzene-water c) amide-water d) chloroform-water

5. Complex ions are studied in

a) Nernst distribution law b) gibbs distribution law

c) Einstein distribution law d)albert distribution law

6. One of the important validity in Nernst distribution law is

a) Constant temperature b) constant pressure

c) Constant volume d) constant composition

7. Existence of similar molecular species in the two phases in-----------with other

a) Contact b) no contact c) contact and no contact d) bonded

8. In quinhydrone electrode, platinum wire is placed

a) Hydroquinone and quinone b) only hydroquinone

c) Only quinone d) Water

9. An example for metal-metal ion electrodes is

a) Daniel cell b) hydrogen electrode c) chlorine electrode d) calomel electrode

10. An example for gas electrode is

A) Hydrogen electrode b) chlorine electrode

c) Oxygen electrode d) hydrogen, Chlorine and oxygen electrode

11. Calomel is a

a) Potassium chloride b) sodium chloride

c) mercurous chloride d) barium chloride

12. The wire used in the calomel electrode is made of

a) Platinum b) copper c) titanium d) iron

13. An example for oxidation-reduction electrode is

a) Calomel electrode b) chlorine electrode

c) quinhydrone electrode d) hydrogen electrode

14. The Nernst equation is

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

c) $E= 2.303\ RT/nF - E^\circ$ d) $E=E^\circ - 2.303\ RT/nF \log K$

15. The Nernst equation for the oxidation half cell is

a) $E=E^\circ - 2.303/n \log [Zn^{2+}]$ b) $E= 2.303\ RT/nF \log K$

c) $E=E^\circ - 0.0591\ /n \log [Mn^+]$ d) $E= 2.303/nF \log K$

16. Which compound is used in the salt bridge

a) Potassium chromate b) sodium chloride

c) Potassium chloride d)zinc chloride

17. 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) $\Delta F= nEG$

18. The metals near the bottom of the electrochemical series is

a) Strong reducing agents b) strong oxidising agent

c) Weak reducing agent d) weak oxidising agents

19. The feasibility of a redox reaction can be predicted with the help of

a) Electro negativity b) electrochemical series

c) Electron affinity d) equivalent conductance

20. What is R in Nernst Equation?

a) Rate of the reaction b) redox reaction c) gas constant d) reduction of gas

PART- B **Answer ALL the Questions** **(3 x 2 = 6 Marks)**

21. State Nernst distribution law?

22. What is known electrochemical cell?

23. What is known electrolytic cell?

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

24. a. Explain Nernst distribution law and mention its applications.

(OR)

b. Explain fractional distillation in detail

25. a. Derive Nernst equation for EMF of a cell.

(OR)

b. Discuss the following

(i) Reversible and irreversible cells

(ii) Standard electrode potential

26. a. Explain electromotive force of a cell and its measurement.

(OR)

b. What is known as standard electrode potential and derive an expression for Nernst equation for an oxidation potential.

[16CHU301]

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COIMBATORE-21
(For the candidates admitted from 2016 & onwards)
B.Sc. Degree Internal Examination,July 2017
PHYSICAL CHEMISTRY III
(Phase Equilibria and Chemical Kinetics)

INTERNAL II

PART- A

ANSWER KEY

1.a)distribution coefficient

2.a)concentrations

3.a)mutually insoluble

4.b)benzene-water

5.a)Nernst distribution law

6.a)constant temperature

7.a)contact

8.b)only hydroquinone

9.a)Daniel cell

10.d)hydrogen, chlorine and oxygen electrode

11.c)mercurous chloride

12.a)platinum

13.c)quinhydrone electrode

14.a)$E=2.303\ RT/n\ F \log K$

15.a)$E=E^0-2.303/n \log[Zn^{2+}]$

16.c)potassium chloride

17.a)$\Delta G=-n\ F\ E$

18.a)strong reducing agents

19.b)electrochemical series

20.c)gas constant

PART- B

21. 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.

22. 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.

23. An **electrolytic cell** is an electrochemical cell that drives a non-spontaneous redox reaction through the application of electrical energy. They are often used to decompose chemical compounds, in a process called electrolysis.

PART- C

24.a) **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:

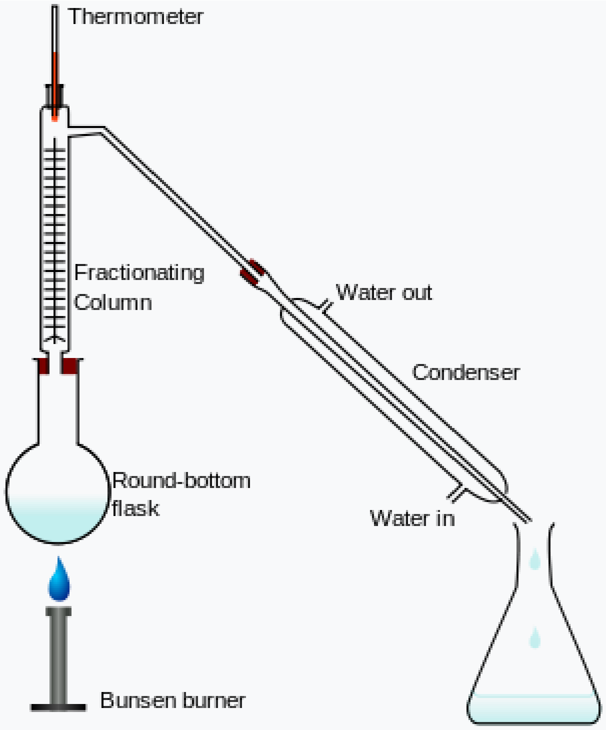
$$nA \Leftrightarrow A_n \; \mathrm{nA}$$

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

b) **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.

Discussion

As an example consider t he 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.[*citation needed*] 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.

25.a) **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 $E^{\ominus}$ (with a superscript plimsoll character, pronounced "standard" or "nought"), is the measure of individual potential of a reversible electrode[clarification needed] 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.

b)(i) Cells produce electricity when electrochemical reactions take place in the cell. If the cell is reversible (like a lead-acid car battery, or a nickel cadmium battery) you can use a higher voltage to force current backwards through the battery, causing the reverse electrochemical reactions to occur, recharging the battery. Regular and alkaline dry cell batteries also produce electricity via electrochemical reactions, but if you force current backwards through them, different reactions take place and the battery heats up, explodes, or just quits working.

(ii) 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

26.a) **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.

b) 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 table

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.

Reg. No. : ---------------- **[16CHU301]**

KARPAGAM UNIVERSITY

COIMBATORE-21
(For the candidates admitted from 2016 & onwards)
II - B.Sc CHEMISTRY
III INTERNAL TEST
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. 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. The potential of a hydrogen electrode in contact with a solution of H^+ ions involving the reaction is given by

   a) Nernst equation b) Gibbs equation c) Duhem equation d) Clausius equation

3. Instead of taking quinone and hydroquinone, a small amount of -----------is taken

   a) quinhydrone b) glass c) hydroquinone d) quinone

4. Quinhydrone electrode is preferred to the ------------electrode

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

5. The EMF can be determined by means of a -----------

   a) Potentiometer b) conductivity meter c) pH meter d) voltmeter

6. Glass electrodes can be used in

   a) Strong oxidizing solutions b) week oxidising solutions

   c) Strong reducing solutions d) week reducing solutions

No of copies (37)

7. Calomel electrode consists of mercury,solid mercurous chloride and a solution of -----------

   a) KCl b) NaCl c) NaOH d) KOH

8. A voltaic cell has an E° value of -1.00 v the reaction is

   a) Spontaneous b) has positive ΔG° c) has negative ΔG° d) 0

9. Which of the following can we use to measure pH?

   a) A glass electrode

   b) A concentration cell

   c) A hydrogen electrode

   d) A glass electrode, a concentration cell and a hydrogen electrode

10. What is ΔG° at 298k for the reaction $Hg_{(l)} + 2Fe^{3+}(aq) \rightarrow Hg^{2+}(aq) + 2Fe^{2+}(aq)$

    a) Positive 314 K electrode b) negative 16 KJ

    c) Negative 314 K electrode d) positive 16 KJ

11. The substance adsorbed or attached is called the-----------

    a) Adsorbent b) adsorbate c) sorbate d) desorption

12. The removal of adsorbed substance from the surface is called

    a) Inclusion b) occlusion c) sorption d) desorption

13. The amount of heat evolved when 1 mole of any gas is adsorned on solid adsorbent surface is called---------------of adsorption

    a) Entropy b) enthalpy c) free energy d) work function

14. When the concentration of the adsorbate is more on the surface of the adsorbent than the bulk, it is called-----------------adsorption

    a) Positive b) negative c) inclusion d) occlusion

15. In chemisorption, there is initial increase and then decrease in extent of adsorption as ------------------increases

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

16. In order to increase the rate of adsorption,--------------------is very necessary

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

17. Mechanical rubbing can be done to increase

a) Speed b) activation c) reaction d) speed of catalyst

18. Adsorption from solutions decreases with rise of temperature and decrease in----------of solution

a) Increase b) decrease

c) Decreases and then increases d) increases and the decreases

19. The concept of BET is extension of ------------------isotherm

a) Freundlich b) Langmuir c) Emmett d) Teller

20. The BET method is widely used in--------------science

a) Surface b) adsorption c) material d) polymer

PART- B **Answer ALL the Questions** **(3 x 2 = 6 Marks)**

21. What is said to be liquid junction potential?

22. Define EMF.

23. What is known as physisorption?

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

24. a. Write short note on

(i) Liquid junctional potential

(ii) EMF measurements in determining equilibrium constant

(OR)

b. Explain potentiometric acid-base titration.

25. a. Differentiate physical adsorption with chemical adsorption.

(OR)

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

26. a. Explain potentiometric redox titration.

(OR)

b. What is adsorption and absorption? Explain BET

[16CHU301]

KARPAGAM ACADEMY OF HIGHER EDUCATION
(Deemed to be University under Section 3 of UGC Act 1956
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(For the candidates admitted from 2016 & onwards)
B.Sc. Degree Internal Examination,July 2017
PHYSICAL CHEMISTRY III
(Phase Equilibria and Chemical Kinetics)

INTERNAL III

PART- A

ANSWER KEY

1.a)standard EMF

2.a)Nernst equation

3.a)quinhydrone

4.a)hydrogen

5.a)potentiometer

6.a)strong oxidizing solutions

7.a)KCl

8.b)has positive ΔG^0

9.a)A glass electrode

10.d)positive 16 KJ

11.a)adsorbent

12.b)occulusion

13.b)enthalpy

14.a)positive

15.d)temperature

16.c)activation

17.b)activation

18.d)increases and then decreases

19.b)Langmuir

20.a)surface

PART- B

21. **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

22. **Electromotive force**, also called **emf** (denoted and measured in volts),is the voltage developed by any source of electrical energy such as a battery or dynamo. It is generally defined as the electrical potential for a source in a circuit.A device that converts other forms of energy to electrical energy supplies an emf to a circuit.

23. 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

PART- C

24.a) **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.

(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:

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

b. **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)

- 25.a) 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.

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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 – 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

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

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

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) 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.

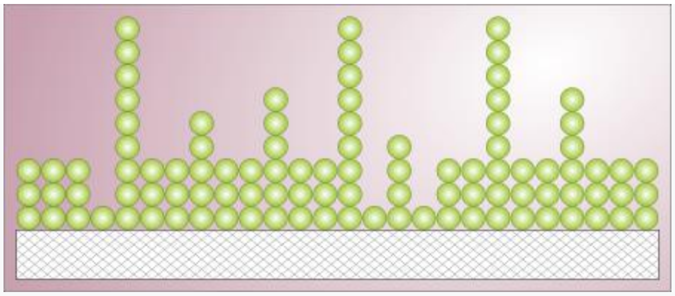
Most often of all, the reduction of iodine to iodide is the last step in a series of reactions where the initial reactions are used to convert an unknown amount of the solute (the substance being analyzed) to an equivalent amount of iodine, which may then be titrated. Sometimes other halogens (or haloalkanes) 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}.

b) **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. 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.

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]

KARPAGAM UNIVERSITY
Karpagam Academy of Higher Education
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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
(Under Section 3 of UGC Act 1956)
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

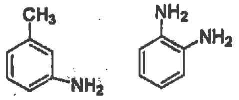
GENERAL CHEMISTRY IV

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?
