GPAT ONLINE CLASSES

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Physical Chemistry

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BCOP R&D CENTER

M.pharm - Pharmaceutics Pharmaceutical Analysis Pharmacology

B.pharm

Topics to be covered in this session

- 1. Composition and Physical States of Matter
- 2. Colligative Properties
- 3. Thermodynamics
- 4. Refractive index
- 5. Solutions
- 6. Ionic equilibrium
- 7. Electrochemistry



Composition and Physical States of Matter

- 1. Intermolecular forces & their impact on the states of matter
- 2. Physical properties of matter
- 3. Dipole moment
- 4. Dielectric constant
- 5. Van Der Waals equation
- 6. Critical phenomenon
- 7. liquefaction of gases

1. Intermolecular forces & their impact on the states of matter

- Cohesion or the attraction of like molecules
- Adhesion or the attraction of unlike molecules
- Minimum potential energy at 3-4 angstroms

Importance of intermolecular forces

- Understanding the properties of solids, liquids and gases
- Flocculation of suspensions
- Stabilization of dispersions
- Compaction of powders
- Compression of granules

Various types of attractive intermolecular forces

 Van der Waals forces
 Ion-dipole and ion- induced dipole forces
 Hydrogen Bonds
 Hydrophobic interactions

> Van der Waals forces

- Dipole-dipole interaction, orientation effect or Keesom forces 1- 7 kcal/mole $\propto 1/r^4$
- Dipole-induced dipole interaction, induction effect or Debye forces1-3 kcal'mole
- Induced dipole-induced dipole interaction, dispersion effect or London force 0.5 -1 kcal/mole $\propto 1/r^7$



> Ion-dipole and ion- induced dipole forces

Solubility of ionic crystalline substances in water

 $I_2 + KI - KI_3$ Na+

> Hydrogen Bonds

- Interaction between hydrogen and fluorine, oxygen or nitrogen
- Tetrahedra structure of water, dimer in formic and acetic acids
- Intra and intermolecular hydrogen bonding in salicylic acid
- Bond energy in between 2 -8 kcal/mole
- Measured by IR and NMR spectroscopy

> Hydrophobic interactions

- Association of nonpolar groups in aqueous solutions
- Stabilization of protein structure, drug-protein binding, drug-receptor interaction

2. Physical properties of matter

- Extensive and intensive physical properties
- Additive, constitutive and colligative
- Appearance, texture ,density, colour, odour, hardness,
 solubility, polarity and volume
- Pressure, volume and temperature for gases
- Molecular weight of a gas= gRT/PV
- Determined by Regnault and VictorMeyer methods
- Vapour pressure and boiling point for liquids

Cont

2. Physical properties of matter

Clausius- clapeyron equation

$$\log \frac{p_2}{p_1} = \frac{\Delta H_e (T_2 - T_1)}{2.303 R T_1 T_2}$$

- Viscosity and surface tension are also exhibited by liquids
- Melting point of a solid
- Clapeyron equation

$$\frac{\Delta T}{\Delta P} = T \frac{V_t - V_s}{\Delta H_f}$$

3. Dipole moment

- Permanent dipole moment and induced dipole moment
- The magnitude of permanent dipole moment μ is expressed in Debye(10⁻¹⁸esu cm)
- Total molar polarization=P_i+P₀

$$P_0 = 4\Pi N \mu^2 / 9kT$$

- Induced or electronic polarization is the shift of electronic cloud due to electric field or electromagnetic waves
- Pi is determined by molar refraction using D line of sodium lamp
 Cont

3. Dipole moment

Lorentz- Lorenz equation

$$P_{i} = \frac{n D^{2} - 1}{n D^{2} + 2} X \frac{M}{d} = MR$$

 It can also be calculated with electron group refraction given by Smyth or atomic refractivity complied by Fajans

$$P = P_i + A\frac{1}{T}$$

Related to solubility and biological activity

4. Dielectric constant

- Capacitance ratio
- Determined by oscilometry

Clausius-Mosssotti equation

$$\left(\frac{\varepsilon-1}{\varepsilon+2}\right)\frac{M}{\rho} = \frac{4}{3}\frac{\Pi nM\alpha_p}{\rho} = \frac{4}{3}\Pi N\alpha_p = P_i$$

5. Van Der Waals equation

$$\left(P + \frac{an^2}{V^2}\right) \left(V - b\right) = RT$$

Internal pressure and excluded volume

6. Critical phenomenon

- Critical point
- Certain value above or below which, certain physical change will not takes place
- Critical temperature of water is 374°c, critical pressure is 218 atm

7. Liquefaction of gases

- Adiabatic expansion in a Dewar or vacuum flask
- Joule Thomson effect
- Cooling with freezing mixtures
- Compressing the gas below its critical temperature
- Work against an external force
- Work against its own internal forces
- LPG and LNG

CHAPTER – 2 Colligative Properties

- Ideal behavior and deviations
- Activity and activity coefficients and colligative properties
- Practical applications of colligative properties

- Lowering of vapor pressure Raoults law, manometers, isopiestic methods, thermoelectric methods
- Elevation of boiling point Cottrell boiling point apparatus
- Depression of freezing point Beckmann and equilibrium method
- Osmotic pressure
- Vant Hoffs equation

π v=nRT

Morse equation



Ideal behavior and deviations

- Obeys Raoults law at all temperatures and concentrations without any change in heat and volume
- Hydrogen bonding, solvate exhibit negative deviation
- Chloroform- ethyl alcohol, benzene- ethyl alcohol shows positive deviation

Activity and activity coefficients and colligative properties

Practical applications of colligative properties

- Preparation of intravenous and lacrimal solutions
- Experimental physiology
- Determination of molecular weight of solutes
- Extent of ionization of electrolytes

- Choice of colligative property
- Cryoscopic and vapour pressure techniques
- are preferable
- **Osmotic pressure for high polymers**

- 1. First law of Thermodynamics
- 2. Second law of Thermodynamics
- 3. Third law of Thermodynamics
- 4. Free Energy
- 5. Thermochemistry
- 6. Isothermal and Adiabatic and reversible process

CHAPTER-3 Thermodynamics

- Quantitative relationship between heat and mechanical, electric, chemical, radiation and other energies
 - Thermodynamic properties E,V,P and T
 - Open and closed systems based on exchange of heat, work and matter
 - Work is a product of intensity and capacity factors

1. First law of Thermodynamics

∆E=Q-W

- Under adiabatic conditions $\Delta E=-W$
- In case of ideal gases Q=W
- Enthalpy H=E+PV
- Heat capacity at constant pressure $C_P = dqp/dt = \Delta H/\Delta T$
- Heat capacity at constant volume Cv=dqv/dt
- To calculate change of energy associated with chemical reaction and physical changes in the state

2. Second law of Thermodynamics

- Increase in value of entropy of an isolated system undergoing a spontaneous process
- Entropy S=k In W Δ S=Q/T
- Δ S=0 for reversible process and > 0 for irreversible process
- Efficiency=W/Q

3. Third law of Thermodynamics

4. Free Energy

Helmholtz free energy

A=E-TS

- Pressure-volume work for reversible isothermal process
- Gibbs free energy

G=E+PV-TS

• Energy involved in chemical reaction conducted at constant temperature and pressure

Requirements for spontaneous

- Isolated system dS > 0
- Isothermal and isochoric process dA<0= -SdT-PdV
- Isothermal and isobaric process dG < 0 =-SdT+VdP
- Constant volume and entropy dE < 0 =TdS-PdV

5. Thermochemistry

- Heat of formation
- Heat of combustion
- Hess law of constant heat summation
- Differential and integral heats of solution
- Heat of hydration
- Heat of mixing
- Heat of neutralization
- Number of calories obtained from food

6. Isothermal and Adiabatic and reversible process

Large constant temperature bath, Dewar flask or

vacuum flask

- Q=0 in adiabatic process w=-dE
- Work of expansion

W=P Δ V



CHAPTER- 4 Refractive index

- Refraction
- Specific refractivity
- Molar refractivity

Refraction

- N=sin i/sin r
- Refractive index is greater than 1 for materials denser than air
- Influenced by wavelength and temperature
- D- Line emission of sodium at 589 nm at 20⁰ c nD²⁰
- Identify a substance, measure the purity, determine the concentration

Specific refractivity

- Parameter charactering the electronic polarizability of a substance in high frequency electromagnetic field of a light wave
- It is the ratio of molar refraction to molecular weight

$$r = \frac{1}{\rho} \left[\frac{n^2 - 1}{n^2 + 2} \right]$$

Molar refractivity

Related to refractive index and molecular properties

$$Rm = \frac{M}{\rho} \left[\frac{n^2 - 1}{n^2 + 2} \right]$$

- Additive constitutive property
- Used to distinguish the structurally different compounds such as keto and enol tautomers



SOLUTIONS

Contents

- Solubility
- Solubility curves
- Types of solutions
- Effect of co-solvency, pH & other factors on solubility
- Solubility of gases in liquids
- Solubility liquids in liquids
- Solubility of solids in liquids
- Critical solution temperature
- Law of partitioning and its applications
- Solute- solvent interactions
 - **Expression of concentrations**



- Concentration of a solute in a saturated solution at a certain temperature
 - Phase rule F=C-P+2
 - Rate of solution $= \frac{DA}{L}(C_1 C_2)$
 - Particle size, stirring, solubility and viscosity of solvent affect rate of solution
- Descriptive terms for solubility

Descriptive term	Part of solvent required per part of solute
Very soluble	Less than 1
Freely soluble	From 1 to 10
Soluble	From 10 to 30
Sparingly soluble	From 30 to 100
Slightly soluble	From 100 to 1000
Very slightly soluble	From 1000 to 10,000
Practically insoluble	10,000 and over
Solubility curves



Types of solutions

- Solutions of solids in liquids
- Solutions of liquids in liquids
- Solutions of gases in liquids
- Solutions of solids in solids



Effect of co-solvency, PH & other factors on solubility

- Co-solvent increases the solubility of un ionized species by adjusting the polarity of the solvent
- It may decrease the dissociation of a weak electrolyte
- The solubility of week electrolyte is influenced by the pH



Solubility of gases in liquids

- Hcl, NH₃, effervescent preparations and aerosols
- Depends on pressure ,temperature, salts and chemical reaction
- Henrys law C2= σp = product of solubility coefficient and partial pressure of the gas
- Solubility decreases with temperature
- Salting out
- Henrys law not applicable in a chemical reaction
- Solubility of a gas in liquid is expressed by Henrys law constant or Bunsen absorption coefficient α

Solubility liquids in liquids



- Molecular connectivity (χ , zero, first and higher order). Sum of the reciprocal of square root number
- Molecular surface area related properties like the total surface area(TSA), hydrocarbon surface area(HYSA) and functional group



Solubility of solids in liquids

- With or without accompanying chemical reaction in the solvent
- Effect of temperature
- Effect of salts salting in, salting out or no alteration
- Solubility of solutes containing two or more species common ion effect
- Solubility following a chemical reaction
- In ideal solutions heat of solution is equal to heat of fusion

Solubility of solids in liquids

- Solubility of a solid in ideal solution depends on temperature, melting point and molar heat of fusion
- In ideal solutions, the slope of the line drawn between log solubility (mole fraction) vs reciprocal of absolute temperature is $-\Delta H_f/2,303R$
- In non ideal solutions, the concentration is replaced with activity, solubility parameter determined from heat of vaporization, internal pressure and surface tension
 - EHS Solubility approach

Critical solution temperature

Phenol and water system phase diagram.

Temperature fixed at 50 °C

Point a, system containing 100% pure water.

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Addition of phenol to water will result in the formation of a single liquid phase until the point b is reached.

*At point b, appears a second phase.

Phase A: water rich phase containing 11% phenol

Phase B: phenol rich phase containing 63% phenol





2. <u>Systems showing a decrease in miscibility</u> with rise in temperature

TRIETHYLAMINE & WATER

The solubility of liquid pairs may increase as the temperature is lowered

The system will exhibit a lower consolute temp.

<u>Below which</u> the two members are soluble in all proportions <u>Above which</u> two separate layers are formed.



Systems Showing Upper and Lower CSTs

The $\widehat{\square}$ miscibility with $\widehat{\square}$ temp. in systems having a lower CST is not indefinite.

> a certain temperature miscibility starts to $\hat{\parallel}$ again with further $\hat{\parallel}$ in temperature.

Closed-phase diagram, i.e. nicotinewater system.



Law of partitioning and its applications

 $K=c_1/c_2$

- Effect of ionic dissociation and molecular association on partition
- Extraction
- Solubility
- Preservative action
- Biological activity

Solute- solvent interactions

- Like dissolves like
- Dipole moment
- Hydrogen bond
- Difference in acidic and basic constituents
- Ratio of polar to non polar groups of the molecule

Expression of concentrations

- Volume of the solvent required to dissolve one gram of solute (g/ml)
- Quantity of solute in grams dissolves in 100 ml
- Quantity of solute in grams dissolved in 100 gm
- Number of moles of solute in 1 liter of solvent
- 100 ml of saturated solution contains gms of solute
- %w/w, %w/v, %v/v
- Molarity, molality and mole fraction

CHAPTER-6

lonic equilibrium

- Theory of conductivity
- Equivalent conductance
- Mobility of ion/

Theory of conductivity

- Conductivity is the ability of a solution to conduct electric current
- Conductivity is determined from the voltage and current values according to ohms law
- Conductivity is proportional to ion concentration
- Ionic interactions can alter the linear relationship between conductivity and concentration of ions in concentrated solutions
- The basic unit of conductivity is Siemens and the unit of specific conductivity unit is Siemens/cm
- Conductivity measurements are temperature dependent; it varies from solution to solution

Equivalent conductance

- Conductance of a solution containing 1 gm equivalent of the solute when the electrodes are spaced 1 cm apart in a cell
- Expressed in mho cm²
- Increases on dilution
- Kohlrausch found that the equivalent conductance was a linear function of square root of concentration
- The intercept of the graph between the equivalent conductance vs corresponding square root of concentration is known as equivalent conductance at infinite dilution.

Mobility of ions

- Velocity attained by an ion moving through a gas under unit electric field
- The unit is m²s-¹ vol⁻¹
- It's known as ion mobility spectrometry in gas phase and electrophoresis in liquid phase
- It's characterized by charge (q), shape and size.

$$v = \frac{E \times q}{f}$$
$$n = v/E$$

CHAPTER-7

ELECTROCHEMISTRY

- Properties of electrolyte solutions
- Electrolysis
- Electrical cell
- Electron transport
- Faradays laws of electrolysis
- Single electrode potential
- Concentration cells
- Half-cells
- Half cell potential
- Types of half cells
- Nernst equation
- Salt bridge
- Electromotive series
- Standard electrode potential
- Reference &indicator electrodes



Properties of electrolyte solutions

- Substances that dissociate into oppositely charged mobile, solvated ions when dissolved in appropriate solvent
- The activity and activity coefficient of electrolytes include the Coulomb interaction effect among ions
- The chemical potential of the electrolyte solution is lower than the solution of uncharged solute species
- The charge density is related to electric potential by the Poisson equation
- Debye-Huckel theory states that attraction or repulsion between two ions depends only on their charge and separation distance and not on their chemical identity

Electrolysis

- A chemical reaction observed in electrolyte cell under a potential of several volts.
- Electrons enter into the solution from the battery or generator at the cathode and combine with the cations in the solution
- Cations are reduced and carry electrons towards the anode and are oxidized
- Reduction is addition of electrons and oxidation is the removal of electrons
- Oxidation occurs at anode and reduction at cathode
- Platinum electrode is generally used as it is not attackable metal

Electrical cell



10000000

1 minimum

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Electron transport

- Flow of electrons from right to left by the movement of cations to the right and anions to the left
- The fraction of current carried by cations or anions is known as transference number
- t₊=current carried by cations/total current
- t_= current carried by anions/total current
- The sum of two transference numbers is 1
- The transference number is related to velocity of the ions
- The quantity of electric charge is coulombs= 3 X10⁹ esu

Electron transport



Faradays laws of electrolysis

- Laws of electricity introduced in 1833 and 1834
- Passage of 96,500 coulombs of electricity through a conductivity cell produces a chemical change of 1 gm equivalent weight of any substance.
- The quantity 96,500 is one faraday
- The passage of one faraday of electricity results in the transport of 6.02X10²³ electrons in the cell
- Faradays law can be used to determine the charge on an electron

Single electrode potential

- The amount of the charge produced on an individual electrode determines single electrode potential
- Electrochemical cell contains two half cells
- The potential of a single electrode in half cell is called single electrode potential
- In Daniel cell, the electrodes Zn/Zn⁺²(anode) develops a negative charge and the cathode Cu/Cu⁺², a positive charge
- The single electrode potential depends on
 - Concentration of ions in solution
 - Tendency to form ions
 - temperature

Single electrode potential



Concentration cells

- The emf results from the differences in activities of solutions of same material constituting the two half-cells
- The general equation of a concentration cell is

$$E_{cell} = \frac{0.0592}{n} \cdot \log \frac{a_1}{a_2}$$

Concentration cells



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minimum

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Half-cells

- A half cell is one of the two electrodes in a galvanic cell or simple battery
- A standard half- cell consists of a metal electrode in a 1 molar aqueous solution of metals salt at25°c
- In Zn-Cu battery, the two half cells make an oxidizing- reducing couple
- On the cathode

Oxidant +ne⁻ reluctant $Cu^{+2}+2e^{-}$ Cu On the anode Reluctant \longrightarrow oxidant + ne⁻ Zn \longrightarrow Zn²⁺+2e⁻

Half-cells

- The standard electrode potential is the potential difference between the metal half- cells in a circuit with a standard hydrogen half cell connected by a salt bridge
- No reaction takes place unless it's connected to another half cell via electric conductor and salt bridge

Half-cells



GALVANIC CELL

Energy released by spontaneous redox reaction is converted to electrical energy.

Oxidation half-reaction: $Y \rightarrow Y^+ + e^-$

Reduction half-reaction: $Z^+ + e^- \rightarrow Z$

Overall cell reaction: $Y + Z \rightarrow Y^+ + Z^-$ (G < 0)



ELECTROLYTIC CELL

Electrical energy is used to drive nonspontaneous redox reaction.

Oxidation half-reaction: $Z^- \rightarrow Z + e^-$

Reduction half-reaction: $Y^+ + e^- \rightarrow Y$

Overall cell reaction: $Y^+ + Z^- \rightarrow Y + Z (G > 0)$

Half cell potential



- Potential developed at the electrode of a half cell due to the presence of oxidation or reduction
- Used to indicate corrosion activity and measure the tendency of oxidation/ reduction
- It's associated with an electrode- solution potential difference
- The potential magnitude depends upon the nature of specific electrode reaction and on the concentration of dissolved solution
- The sign of potential difference depends on the direction of electrode reaction

Types of half cells

- Gas electrodes
 - Hydrogen electrode
 - Chlorine electrode
- Metal- Metal ion electrodes
- Redox electrodes
- Metal- insoluble Metal salt- anion electrodes



Types of Half Cell



1. <u>Metal in contact with a solution of its ions</u> Metal electrode in contact with a solution containing ions of the same metal. Examples include copper, tin and zinc; $Cu^{2+}+2e^{-} \rightarrow Cu$; Sn $^{2+}+2e^{-} \rightarrow Sn$; Zn $^{2+}+2e^{-} \rightarrow Zn$



2. Gas in contact with a solution of its ions Platinum inert electrode in contact with a solution of the ions of the gas present. Examples include the standard hydrogen electrode and chlorine: $2H^+ + 2e^- \rightarrow H_2$; $Cl_2 + 2e^- \rightarrow 2Cl^-$



3. Ions of different oxidation states in solution

An inert platinum electrode is used to allow electrons to pass into the half cell. The concentrations of the different ions must be the same, 1.0 moldm⁻³. Examples of this include iron (III) and iron (II), copper (II) and copper (I); non metal examples include iodine and iodide, bromine and bromide, and manganate (VII) and manganese (II).
Gas electrodes

- Hydrogen electrode
- Hydrogen gas bubbling in a solution of an acid
- Hydrogen is non conducting, so platinum or other metal is used for adsorption of gas
- **Chlorine electrode**
- Chlorine gas at a given pressure is bubbled into a solution of HCI



Calomel Electrode

 Mercury in contact with a saturated mercury chloride(Calomel) and known conc. of KCI.



Cell Diagram



- Metal- Metal ion electrodes
 - Electrodes of Daniel cell and silver- silver ion electrode
 - May be made of an amalgam of the metal in mercury to study electro chemistry of

highly reactive metals in their pure state.

Ag/AgCl (sat'd),KCl (xM) I



- Redox electrodes
 - Consists of ions of two different oxidatio states and a non reactive metal like platinum
 - May be made with organic molecules like quinine and hydroquinone



- Metal- insoluble Metal salt- anion electrodes
 - Constructed with a metal with its insoluble metal salt dipped in a solution containing the common anion of the salt
 - A rod of Ag coated with a paste of AgCI dipped in a solution of CI- ions.

Nernst equation

$$\mathbf{E} = \frac{E^o - 0.0592}{n} \cdot \log \frac{a_{products}}{a_{reactants}}$$

- E° is the standard potential.
- emf when the activities of all reactants and products are unity
- This equation is used to calculate individual electrode potential or a cell emf from known E^o at a specified temperature.

Salt bridge

- A laboratory device used to connect the oxidation and reduction half cells
- Maintains electrical neutrality within the internal circuit
- Slow down the rate of equilibrium
- Glass tube and filter paper bridges are available
- Glass tube is with U shape (to prevent over heating). 2.5% agar solution in 1M solution of sodium sulfate
- Filter paper is soaked with sodium sulfate solution
- Negatively charged sulfate ions enter the solution of Zinc sulfate to neutralize the positively charged Zn ions and viceversa

Electromotive series

- Listing of chemical species (atoms, ions and molecules) in the order of their tendency to gain or loss electrons
- Expressed in volts and measured with reference to hydrogen electrode as standard and assigned a voltage zero
- The electrodes above hydrogen have negative reduction potential and vice- versa

Standard electrode potential

It's determined based on Debye-Huckel limiting law

E+0.1184 log c=E⁰+0.0603 \sqrt{c}

Intercept of the graph drawn between

E+0.1184 log c and \sqrt{c}

Reference & indicator electrodes

- The unknown electrode is the cathode in the cell (right side)
- E _{cell}=E _{reference}+E _{unknown electrode}
- E⁰ cell = E ° reference + E ° unknown electrode
- Hydrogen electrode, 0.1 N calomel electrode, 1N calomel electrode, saturated calomel electrode and Silver-Silver chloride electrodes

Reference & indicator electrodes

- KCI solution acts as the electrolyte solution in all the secondary reference electrodes (salt bridge)
- Indicator electrode forms an electrochemical half cell with the interested ions in the solution
- Ion selective electrodes (ISE) are most important class of indicator electrodes

Example for Gas Non Metal Ion Half Cell



Although gases are reactive, they are usually more difficult to manage in the laboratory. As a result, gaseous half-cells are not very common. In a gaseous half-cell, the gas bubbles over an inert electrode that is connected to the external wire. Its conjugate redox non-metal ion is in solution.

THANK YOU



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