

D.P.H.Disinfectants.

The following are qualitative tests for some of the commoner disinfectants. These tests, if positive are to be regarded as suggestive only and confirmatory tests would have to be employed in most instances.

Formalin. Formol (a 40 per cent. solution of formaldehyde - H_2CHO - in water).

- (a) Distinctive smell in strong solution particularly on warming.
- (b) Add a few drops of 5% phenol and then do a ring test with strong H_2SO_4 . Purple colour.

Phenol. Carbolic acid - $C_6H_5.OH$.

- (a) Ferric chloride solution gives a purple colour. *B purple colour*
- (b) Bromine water - a white precipitate of tribromophenol. *White ppt*

Mercuric chloride - corrosive sublimate.

- (a) KI solution gives a yellow precipitate of mercuric iodide soluble in excess.

Copper salts and zinc salts.

Same tests as in water analysis.

Sulphurous acid.

- (a) Smell of SO_2 (add acid if a sulphite).
- (b) $AgNO_3$ - white ppte soluble in strong HNO_3 . *A*

Chlorine.

- (a) KI - iodine is set free. *Dark blue*
- (b) Ortho - toluidine test.

Quantitative Methods.

(1) Determination of available chlorine in bleaching powder.

(a) Make a suspension - solution by weighing out about 1 gram (accurately) of the powder and grinding it up in water. Make up to 100 cc. in a volumetric flask.

Take out 10 cc. with a pipette.

Titrate with 0.1N sodium arsenite solution. To determine the approximate endpoint, a drop is taken out by means of a small glass rod and placed on starch-iodide paper. If free chlorine is still present a blue colour is produced on the paper owing to the liberation of iodine. As this end point is not very sharp a slight excess of the arsenite will have to be added before the test paper gives no colour. The amount of the excess added can now be determined by

1 gm powder in 100cc vol flask

Pip. 10 cc

Titrate c 0.1N ~~iodine~~ sodium arsenite sol

(b) excess arsenite titrate c 0.1N iodine starch as indicator

Soln arsen 22.5

2

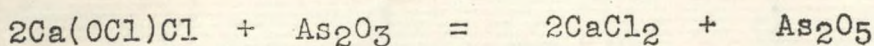
titrating the mixture of bleach and arsenite with 0.1N iodine solution using starch as an indicator.

Supposing that X cc. of the 0.1N arsenite were added originally and y cc. of 0.1N iodine are needed to produce a blue colour on back titration then (X - y) cc. of 0.1N arsenite solution have been required to use up the amount of available chlorine in 10 cc. of the original dilution of bleach.

Calculate first to a normality and then express your result as a percentage of available chlorine by weight in the original powder.

A newly-prepared bleaching powder contains about 33 per cent. of available chlorine.

Rationale of the process:-

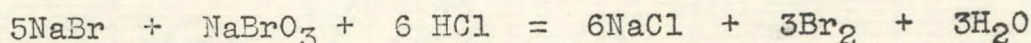


(b) An alternative method which however gives results which are too high in the presence of chlorates in the bleaching powder, is to take 10 cc. of the suspension-solution, acidify with acetic acid and then add KI. The free chlorine sets free iodine which is then estimated by the usual thiosulphate titration method.

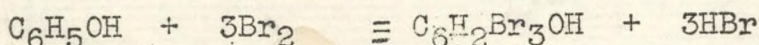
(2) Determination of the amount of phenol in a solution.

To a 200 cc. flask add 50 cc. of water, 5 cc. strong HCl, 25 cc. of the phenol solution followed by an excess (25 cc. for the given phenol solution) of 0.1N sodium bromide-bromate solution. Shake and allow to stand for 15 minutes. Add 5 cc. KI when iodine will be liberated and can then be titrated with thiosulphate. This titration determines the excess of bromide-bromate solution which has not been used up by the phenol.

The rationale of the process is, in the first place acid added to a mixture of bromide and bromate yields free bromine

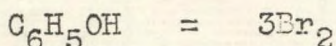


The free bromine then unites with the phenol:-



The excess bromine is then determined as stated by means of KI and thiosulphate titration.

In the calculation note that:-



and therefore a normal solution of phenol contains $\frac{M.W.}{6}$ grams per litre

Calculation.

Supposing 5 cc. of 0.1N thiosulphate are required to neutralize the iodine liberated by the residual bromine

$$\therefore 25 - 5 \text{ cc. } 0.1N \text{ bromide-bromate} = 25 \text{ cc. of the phenol solution,}$$

$$\text{Then the normality of the phenol solution} = \frac{20 \times 0.1}{25} = 0.09 N$$

From this calculate the percentage strength.

Adsorption.

Previously, in the lecture on colloids, the importance of electric charges and certain other physical properties of surfaces have been discussed, without considering the actual make up of the surface. Today we wish to extend our study to a consideration of the molecules present at a surface. We immediately find that even in many simple solutions the actual constitution of the surface layers of the solution is different from that in the body of the fluid, e.g. if air is blown through an aqueous solution of amyl alcohol so that a deep froth is formed, then on removing the froth and determining the amount of alcohol present in the fluid that makes up the froth, it is found that the concentration is much greater than is the concentration of alcohol in the underlying solution. The only difference between the froth and the underlying solution is that the former has a much greater surface or interface between the solution and air making up the froth. It is clear then that the concentration of alcohol present at the air-liquid interface is greater than that in the body of the fluid. This increase in concentration of a solution at a surface is due to the phenomenon known as adsorption.

Gibb's Adsorption Theorem states that a dissolved substance must increase its concentration at the surface if it tends to lower the surface tension. Or vice versa, a solute must decrease its concentration at a surface if it tends to raise the surface tension.

As adsorption does not depend solely upon the property of surface tension the theorem is best amplified thus:

Any substance in solution in a liquid in contact with the surface of another phase will increase its concentration at that surface, if by so doing the free energy (mechanical, electrical, chemical, etc.) present there is decreased.

Adsorption may be roughly defined as a loose fixation of a substance at an interface. It is not a true chemical combination.

Adsorption may take place at an interface between any two phases, e.g. a solid and a liquid, a solid and a gas, a liquid and another liquid, or a liquid and a gas. As a simple example we may take the adsorption of the dye, methylene blue, from solution by the solid, powdered charcoal. If the dye solution be shaken with charcoal then on filtering the filtrate is found to be colourless. In this experiment we have a loose combination between the dye (the adsorptive) and the charcoal (the adsorbent). This combination of adsorptive with adsorbent is termed the adsorbate.

Gaseous Adsorption.

Similarly charcoal will adsorb many gases, e.g. it will remove NH_3 from a mixture of this gas with air.

With gases it is usually found that the more easily a gas may be liquefied the more readily will it be adsorbed.

Generally speaking a rise in temperature decreases the amount of substance adsorbed. It follows, that when adsorption takes place heat is given out, e.g. the apparent temperature of a patient is higher if the thermometer is wrapped in flannel. This is due to the heat of adsorption of the moisture on the flannel.

If the temperature is kept constant it is found that the amount of gas adsorbed increases at first rapidly with increase in its pressure, but that the increase gradually falls off until a further rise in pressure does not lead to any further increase in the amount adsorbed. This result can be shown as a curve - an adsorption isotherm - if the amount of a gas adsorbed by unit area of an adsorbent when the system has reached equilibrium, is plotted against the concentration or pressure

Electrostatic adsorption

In adsorption of acetic acid and amyl alcohol by charcoal are dealing with mechanical adsorption due to the action of the surf tension in producing a change of concentration at a boundary surf. In these cases the amt adsorbed is related to the lowering of the surf tension produced by it in a liquid. ~~When~~ surface of an insoluble surf when immersed in a liquid becomes electrically charged. If therefore such a substance is placed in a soln in which particles with an opposite electrical charge are present e.g. ions or colloids, adsorption may take place owing to the electrostatic charge.

In such cases the amt of substance adsorbed is no way related to the influence of the dissolved substance or the ~~amt~~ the adsorbed substance on the surf tension of the soln. Thus charcoal may adsorb alkali salts from solutions even though these substances increase the surf tension of the liquid. - $KMnO_4$ decolorized passing through silica.

Changes following adsorption

The reversibility of an adsorption process is sometimes interfered with by the occurrence of secondary changes in the adsorbed material e.g. crystal growth - other changes are chemical.

Biological application of adsorption

In living organisms cells act as particles on which adsorption may occur as well as they themselves are packed full of colloids which also act as adsorbents and undergo changes (pptn, coagulation, swelling etc.). In living organisms therefore the properties and behavior of colloidal matter are of pre-eminent importance.

Agglutination of bacteria

Foreign protein injected into animal body \rightarrow antibodies \rightarrow neutralisation toxic or harmful action of the injected substance. Neutralization may be pptns - which pptn foreign substance, antibodies or agglutination of bacteria) by agglutination or adsorption processes + colloidal pptn.

Toxin - antitoxin

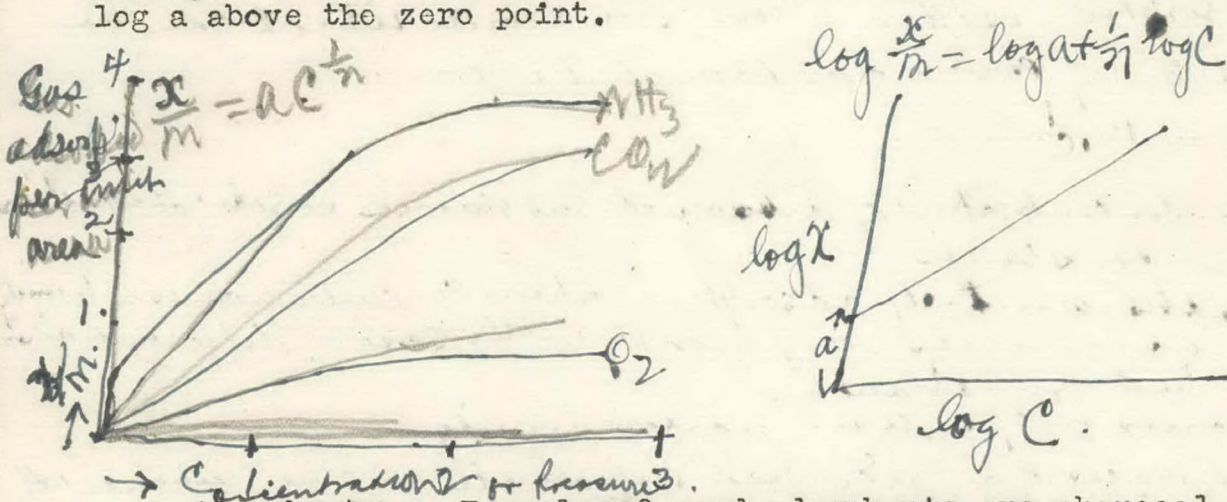
Darwin's phenomenon if you add small quantities of antitoxin to neutralize large amounts of toxin it will require a greater amt of antitoxin to neutralize the toxin action. In other words the toxin may develop a tolerance for the antitoxin similar to that which is shown by a suspension colloidal toward electrolytes and which is also found in the mutual precipitation of emulsions colloids.

Toxin + antitoxin reaction may be reversible early but soon toxin becomes fixed - Chemical reaction are also taking place in addition to adsorption + pptn process.

of the gas at that equilibrium. This result can be expressed mathematically (Freundlich):

$$\frac{x}{m} = aC^{\frac{1}{n}} \quad \text{or} \quad \log \frac{x}{m} = \log a + \frac{1}{n} \log C$$

where x = the amount of gas adsorbed by a surface of area m from a gaseous system in which the final concentration or pressure of the gas is C . If the logarithmic equation be plotted instead then a straight line is obtained, the line cutting the x axis at the point $\log a$ above the zero point.



Adsorbents. Examples of good adsorbents are charcoal, silicic acid gel, infusorial earth, kaolin, alumina, etc.

Examples of gaseous adsorption.

1. Charcoal respirators used to adsorb poisonous gases from inhaled air.
2. The recovery of benzene from the waste fumes of many chemical factories by passing the flue gases over charcoal.
3. The attainment of very high vacua by adsorbing Hg vapour by charcoal.

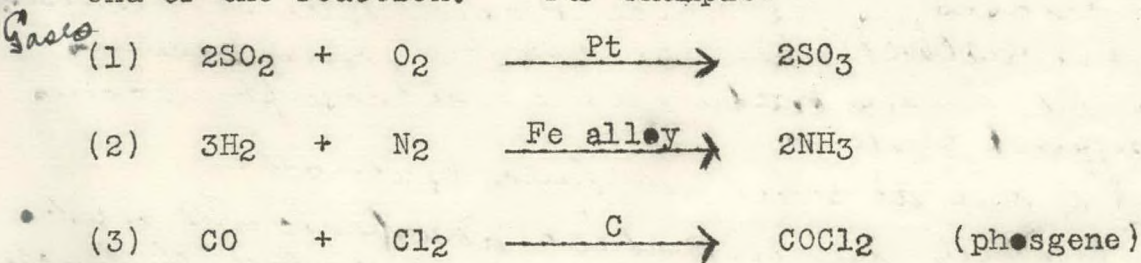
Adsorption in solution.

The laws governing gaseous adsorption apply equally to adsorption from dilute solutions. If the concentration be increased beyond the value giving maximum adsorption then the adsorption generally diminishes.

Catalysis.

Remember

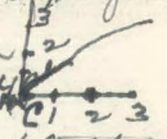
It is believed that adsorption is generally a preliminary stage in catalytic and enzymatic reactions, that is, in those reactions whose rate is increased immensely by the addition of some substance, e.g. finely divided platinum, which however appears to be unchanged at the end of the reaction. For example:



the amount adsorbed is definite, and depends on the nature of the adsorbent and of the solution

In other words, an Adsorption equilibrium is produced. On varying the concentration of the solution it is found that the amt. adsorbed is not proportional to the concentration, but is greater in diluted than in concentrated solutions.

This behaviour is illustrated by the adsorption isotherm.



The concentrations of solution at equilibrium are plotted as abscissa and the value $\frac{x}{m}$ or the amt. of substance (x) adsorbed by m grams of the adsorbing material as ordinates.

The adsorption isotherm forms a curve which can be represented by the equation of the form.

$$\frac{x}{m} = K \cdot C^n$$

where C = concentration of dissolved substance in soln at equilibrium

K + n = constants

K = coefficient of adsorption when concentration is = to unity and varies very greatly in the case of different adsorbed substances.

n = varies only within narrow limits

The last traces of an adsorbed substance can be removed only difficult because adsorption is relatively greater from dilute than from concentrated solution.

Application: Removal of dyes from cotton or wool by reversible equilibrium

• Adsorption in purification of enzymes - because diff. enzymes are adsorbed by different adsorbent under varying conditions e.g. pancreatic amylase adsorbed from 50% alcohol soln by aluminium gel ($Al(OH)_3$), the adsorption taking place at pH = 7.3

• for purifying insulin - adsorption is used. Insulin adsorbed by charcoal from a HCl soln pH 2.5; and impurities removed by washing with 5% soln acetic acid in 60% alcohol at pH 4.5

NB The adsorbed material can be removed by washing with alcohol or some other solvent of low surf. tension, owing to the fact that adsorption is generally greater from liquids of high surf. tension than from liquid of low surf. tension

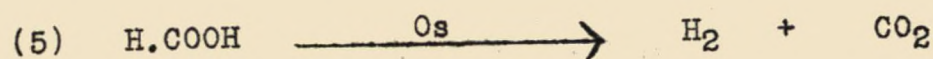
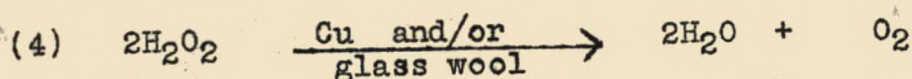
Adsorption Saturation

The amt. of substance adsorbed from a substance in solution from a soln increases as the concentration of the soln is increased until a point is reached when the adsorbing surf. becomes saturated. The concentration at which adsorption occurs differs for different systems.

Displacement of one adsorbed substance by another

The extent to which an inactive adsorbent will adsorb a substance from soln depends on the extent to which the dissolved substance lowers the surf. tension of the solvent, and it is possible to displace from adsorbent a substance which is relatively slightly adsorbed by one which is relatively more strongly adsorbed. Amyl alcohol will replace acetic acid from charcoal

or in solution



It has actually been shown that the rate of many homogeneous reactions in-solution depends upon the nature of the containing vessel.

Theories of Adsorption.

(1) Non-polar adsorption. Adsorption is due to the lowering of surface tension by the concentration of the adsorptive at the surface. Called non-polar because many substances that lower surface tension ionise little in solution, e.g. the group of substances known as fatty acids increase in both their power of being adsorbed and their power of lowering surface tension as the acid becomes more complex.

(2) Polar adsorption. Adsorption is due to the partial or complete neutralisation of the electric charge of a surface by the deposition of oppositely charged particles at that surface, e.g. by oppositely charged colloidal particles or ions.

For example - negatively charged charcoal particles adsorb positively charged $\text{Fe}(\text{OH})_3$ particles or positively charged ions such as H^+ , K^+ , Na^+ , etc.

(3) Chemical or Electro-chemical adsorption.

Neither (1) nor (2) can explain all examples of adsorption. For instance why should negative OH^- ions be adsorbed more readily by charcoal than positive Na^+ ions? As we investigate further, and especially in biological fields it becomes more and more obvious that a specificity of adsorption exists, which can only be explained by the view that certain groupings present in the surface have a specific affinity for certain other groupings in the adsorbed molecule. That is to say, that adsorption is really based on chemical attraction.

Examples of Adsorption of Interest in Biology.

(1) The power possessed by the humus of the soil to retain soluble salts, thereby preventing them from being washed away by rain.

(2) In sewage disposal works nitrifying organisms develop in the lower part of the contact filters. These organisms only develop, however, if certain organic impurities of sewage are removed from the liquors by adsorption on the upper layers of the filter.

(3) The permutit water softening system depends upon the exchange of the Na^+ ions of the zeolite for Ca and Mg ions of the water. This exchange may be an adsorption process.

(4) Catalytic and enzymatic reactions are probably dependent upon an initial adsorption of the reactants at the surface of the catalyst or enzyme.

(5) The action of certain poisons on micro-organisms has been shown to be proportional to the amount deposited on their surfaces.

Adsorption

1. Special properties of colloidal state dependent upon existence of very extensive surf.
2. At the boundary surf. bet 2 phases, whether these be solid liquid, gas, ~~there~~ an alteration in the distribution of matter or change of concentration occurs.
3. This change ^{of concentration} is brought about at a surf is brought about by the action of surf. forces called Adsorption.
4. An increase of concentration or a condensation of matter on a surf. is known as positive adsorption, while a decrease of concentration is spoken of as negative adsorption.
5. Increase of concentration at a solid surf. in contact with a gas is a known fact.

⑤ Amount of adsorption depends on temp.

(a) Adsorption increases on fall of temperature

Gas	Vol. of gas adsorb. by 1 cc. of charcoal at
Hydrogen	0.0
Helium	4 cc
Nitrogen	7 cc
Oxygen	15 cc

Hence effect of fall of temp made use of in producing high vacua. The vessel to be exhausted is connected to charcoal coated by liquid air. This charcoal in poison gas.

6. Rise in temp. reduces adsorption. Temp. drives off gas

7. At constant temp, when one determines amt of gas taken up by charcoal, it is found that the adsorption when the pressure or concentration of the gas is varied, is relatively much greater at lower than at higher pressures.

Pressure in mm P.	Concentration of CO_2 on charcoal	$\frac{x}{\sqrt[3]{P}}$
4.1	0.38	0.24
25.1	0.77	0.26
137.4	1.4	0.26
416.4	2.0	0.27
888.6	2.48	0.26

The concentration of CO_2 in the charcoal is proportional to the cube root of the pressure, or cube root of the concentration of the gas.

⑧ Adsorption varies according to chemical nature of solids. porous. surf. more adsorption.

Adsorption by a Solid from Solution

Adsorption takes place with very considerable velocity, so that the time required for equilibrium to be established bet a solid surf. and a solution depends mainly on the rate of diffusion of the solute to the solid. The production of equilibrium can be accelerated by stirring or shaking the solid with the solution.

Adsorption Isotherm

When a solid adsorbent (eg charcoal) is shaken with a solution of an adsorbable substance, the amount of substance adsorbed by unit mass of the adsorbent (or by unit area, since for a given material, the area may be regarded as proportional to the mass) depends on the concentration of the solution and on the temperature.

For a given concentration and temperature,

Colloids.

- A. It is better to speak of the 'Colloidal Condition' than simply of 'Colloids', since so many substances which are accepted as being crystalline, can be obtained in a colloidal condition by suitable methods.

The colloidal condition is assumed by many substances when their particles [in some other medium] have a diameter which is too small for them to be observed by ordinary methods of microscopy, [i.e. the particles are sub-microscopic], and yet are considerably larger than their constituent molecules. When the molecules as separate molecules can dissolve in a solvent, then we have a true molecular solution of a substance. The colloidal range of particle size is of 1-300 μ ($\mu = .001$ m.m.) in diameter.

Particles in true colloidal solution do not tend to settle out at the bottom of a vessel - but remain indefinitely in a state of almost even dispersion.

The particles can be observed by means of a Tyndale Beam applied suitably. This beam of light does not enable the eye to detect the actual particles, but it can observe light scattered from them. With actual molecules no such scattering is possible.

- B. The colloidal condition is characterized by the following:-

- (1) The Tyndale Beam effect.
- (2) The particles can be centrifuged down: not so in true molecular solutions.
- (3) (a) The particles are extremely slow to diffuse.
(b) The particles cannot pass through animal membranes, parchment, collodion, etc., i.e. cannot 'dialyse'.
- (4) Brownian movement is observed - by means of the Tyndale Beam.

- C. The total surface area of all the particles in a colloidal solution is enormous. A piece of matter in the form of a cube whose sides are each 1 cm. in length has an area of 6 cms.². If this cube be split up into 10^{29} cubes, each having a length now of only 0.01 μ for each of its sides, the total surface area of all the cubes is by this time 6×10^9 cms.², which is equal to 0.25 square mile. It can be imagined that any chemical or physical reactions which can occur at the surfaces of such particles will progress to a far extent at the innumerable surfaces presented by colloidal particles. This feature is one of great importance in many serum reactions and in clarification processes used in water and sewage purification.

D. Methods of Making Colloids.

- (a) By Dispersion, i.e. by reduction of the sizes of solids.

- (i) By grinding and milling a solid.
- (ii) By electrical dispersion, using a Bredig Arc.
- (iii) By use of Peptizing Agents.
- (iv) By 'weathering', as in clays and rocks.

- (b) By Condensation, i.e. by condensing molecules to form colloidal agglomerates. This is usually performed by methods of chemical reduction, i.e. by reducing agents.

- E. The colloidal conditions of chief interest in biology are of two classes, SOLS and GELS.

SOLS are liquid colloidal solutions; GELS are rigid colloidal solutions.

Peptisation - a small quantity of a ^{electrolyte} ~~substance~~ ^{helps facilitate} the dispersion of a substance and produce a colloidal sol. This process of deflocculation - the reverse of pptn or flocculation or precipitation - is called peptisation - resembling the conversion of insoluble protein into soluble peptone - due to differential adsorption of ^{ion} of the electrolyte which gives colloidal particles + or - charge according to charge of adsorbed ion.

* Peptisation = adsorption + lowering surf tension on H₂O side of adsorbed fil.

Emulsoids - albumen, starch, gelatin

Hydrophilic - stable because of electric charge on particles and adsorbed H₂O. Changes take place as a result of change in the hydration or water content of dispersed phase.

State of emulsoid more viscous than H₂O

viscosity of 1% cane sugar (suspensoid) = 2.45% > H₂O
 " " 1% gelatin emulsoid = 29% > H₂O

Precipitation - suspensoid colloids readily pptd. generally irreversibly by small amts of electrolytes. concentration Emulsoid less sensitive to electrolysis and are pptd by ^{neutral} salts - only when large amts are added - Salting out. Pptn is reversible on washing away the salt the colloid passes into a sol.

In the precipitation of emulsoids by salts, the nature of the ions and its power to alter the distribution of the water bet the internal and the external phases play an important part. Thus in pptn of egg white - lecithin the efficiency of different anions is in the order

- Citrate > tartrate > sulphate > acetate > chloride > nitrate
- Univalent cations > lithium > sodium > pot

Emulsoid are less sensitive to the complex ion than they are to the simple ion.

Protective action of Emulsoids

Suspensoid Colloids + smaller concentration of electrolytes > pptn

Suspensoid + emulsoid > suspensoid coated by adsorption with emulsoid and greater stability of emulsoid transferred to suspensoid.

In this way pptn of suspensoid by electrolytes is more or less effectively prevented.

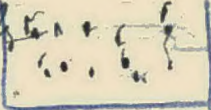
The emulsoids exercise protective action on suspensoids.

Application (a) Preparation of stable suspensoid, eg. ruby gold, ^{can be kept in colloidal state} prevents ^{from sedimentation} ~~spontaneous~~ ^{valuable substances} ~~precipitation~~ ^{physiological} Separation of acid waste of Na in blood prevented by protective colloids.

Sensitization of Colloid Sols (Sensitization) Addition of small amts of emulsoids to suspensoid may make suspensoid less stable or more easily pptd by electrolytes eg. Colloidal gold sol + gelatin or FeCl₃ + small amt serum

Formation of gel - When 1% Eohn gelatin in H₂O 20-25° is a readily flowing liquid, as cooled, it forms a jelly or gel. = pptn formed by agglomeration of the particles of a sol to gelatinous mass eg. Al(OH)₃

Ambiphotism is the property possessed by gels of taking up H₂O and swelling - influenced by presence of electrolytes

Gold particles
-2- Dispersed phase  *H₂O*
Cont. phase

F.(a) Colloidal solutions are such that there is a boundary wall or 'interface' between the colloidal particles and the surrounding medium. The colloidal particles form the DISPERSED PHASE, and the medium in which they are 'dissolved' or dispersed is the CONTINUOUS PHASE. For instance, in a colloidal gold sol, the gold particles form the Dispersed Phase, and water the Continuous Phase.

(b) DISPERSED PHASE is one of two kinds:-

(i) Emulsoid, or (ii) Suspensoid.

EMULSOIDS: are colloidal solutions, which are more viscous than water (or other solvent), and which are but little affected by the precipitating action of added electrolytes, i.e. salts.
Example - proteins, starch solution, gums, etc. *Hydrophilic*

or lyophilic i.e. affinity for H₂O or liquid
SUSPENSIDS: are colloidal solutions, whose viscosities are much the same as that of water: their particles are easily precipitated by added electrolytes.

Example - N/5 NaCl precipitates a red colloidal gold suspensoid as a blue precipitate of extremely small agglomerates of gold.

(c) The viscosity is high in emulsoids, because emulsoid particles 'bind' a considerable amount of the water of the continuous phase to themselves, leaving proportionately less 'free' water. Suspensoid particles have but little power of 'binding' water, and hence the viscosity of a suspensoid sol is almost that of water itself.

G. ELECTRICAL PROPERTIES of Colloidal Solutions.

In media having pH values of greater than 3-4, almost all colloidal particles have a negative electrical charge. The sign of the charge is demonstrated by the migration of colloidal particles towards a charged electrode, i.e. a positively charged electrode will attract negatively charged colloidal particles and increase their concentration in its vicinity, or will repel positively charged particles and decrease their concentration in its vicinity. Vice versa for a negatively charged electrode. Hence knowledge of a change of concentration of colloidal particles at an electrode of known electrical sign determines the sign of charge on colloidal particles. This process is known as Cataphoresis.

H.(a) PRECIPITATING POWERS of IONS.

The negative charge on a colloidal particle is neutralized by the positively charged ion, e.g. Na⁺, Ba⁺⁺, Al⁺⁺⁺ of ionized salts such as NaCl, BaCl₂, and AlCl₃ respectively. The negative charges on the colloidal particles repel the particles one from another and thus help to maintain stability of a colloidal solution. The repulsive charges being removed by addition of a salt, allow the colloidal particles to join together and later precipitate out. Negative ions of an added salt will remove the charge from a positively charged colloidal particle - with the same result.

(b) MUTUAL PRECIPITATION of COLLOIDAL PARTICLES.

Negatively charged colloidal particles, e.g. colloidal organic matter in sewage will be flocculated by a positively charged colloid such as Al(OH)₃ (at pH > 8.0). This is the basis of most processes of chemical clarification of water and sewage.

the addition of electrolytes to the colloidal sol, this potential is diminished, and the point of maximum stability of the colloid occurs at or very near the point of electric neutrality, the iso-electric point.

Solutions of electrolytes contain negatively charged particles or ions, and when these ions are added to a colloidal sol, the particles of the colloidal sol attract and combine with or adsorb on their surf. the ions of opp. charge, and the potential difference bet. the colloid and the medium is thereby diminished. We should expect that the greater the electric charge on the ions (the higher the valency of the ions) the more effective will the electrolyte be in diminishing the potential difference and in bringing about the pptn of the colloid. In other words the precipitating effect of an ion - of a positive ion on a neg. colloid and of a neg. ion on a positive colloid - depends on the valency of the ppting ion - Hardy Schulzky law (Partial law)

Precipitating efficiency depends on valency as well as chemical nature - e.g. ions of same valency have varying ppting efficiency - Ag⁺, H⁺, ions of heavy metals e.g. silver have high ppting efficiency.

The behaviour depends upon the readiness with which ions are adsorbed by the colloid.

1. The precipitation action of an electrolyte differs according as it is added all at once or in small portions at a time. When the electrolyte is added in small portions, a colloid becomes acclimatised and tolerant to the electrolyte, and requires more electrolyte than usual for pptn.

Adding as much large electrolyte than required no pptn owing to reversal of the sign of charge on the colloid or true suspension by the added electrolyte.

e.g. Small additions of $Al_2(SO_4)_3$ will cause pptn of flocculation of Ag or Au sol. but if excess $Al_2(SO_4)_3$ is added, Al_3^+ ions are adsorbed and positively charged Ag- or gold sol is obtained. ^{increasing amt} $FeCl_3$ Platinum sols, flocculation of the neg. colloid is first brought about, then a stable but a positively charged sol is produced, lastly when sufficiently large amts $FeCl_3$ added - complete pptn of the positively charged colloid is effected.

It must be noted that if the concentration of an electrolyte is below a certain value the potential bet. colloid and the dispersion medium is not lowered but raised so that minute traces of electrolytes may increase the stability of a colloidal sol. ^{this is why} e.g. a trace of $NaHCO_3$ is added to the water in the preparation of colloidal platinum sol. by the Bredig dispersion method.

Precipitation of suspensions - important diag application to the exam. of C.S. kind of patients suffering from diseases of C.N.S. (G.D. has meningitis). When gold is added to 0.4% soln $NaCl$ + C.S. fluid varying amts. the concentration at which pptn colloidal gold occurs differs according to general character of fluid.

In serum reactions, although at the pH of blood serum both antigen and antibody are negatively charged, the positive ions of electrolytes present [or added] tend to flocculate the, for instance, precipitinogen-precipitation complex.

(c) Divalent ions are more effective in precipitating colloidal particles than are monovalent ions, and trivalent ions are much more effective than either.

For maximum precipitation of colloidal particles, a definite quantity of an ion of opposite charge is required. More or less is not so efficient.

I. PROTECTION. Particles of a suspensoid sol may be protected from the precipitating action of ionized salts by having an emulsoid sol, such as gelatin sol, added to the suspension. The protective action of such an emulsoid appears to be due to its forming a coating round suspensoid particles, and in some manner preventing the charges of the suspensoid particles from being neutralized by the oppositely charged ions of an added salt. 'Colloidal Metals' such as colloidal manganese, iron.....etc., are protected from the precipitating action of the electrolytes in blood, etc., by the addition of emulsoid colloids in their preparation.

NaCl can just melt
Emulsoid alcohol
H₂O which condenses on its surf.
Water does not protect
Not ce

GELS: are two-phased systems like sols, but are rigid at ordinary temperatures. GELS may be changed into SOLS by warming; somewhat like the melting of a chemical compound. Cooling again may result in reforming the original GEL, e.g. agar, gelatin. Crystalloidal substances diffuse through gels almost as fast as they do through water, but other colloidal particles diffuse through gels only very slowly.

References to Literature.

Bayliss - General Physiology.
Freundlich - The Elements of Colloidal Chemistry.

Colloidal State.

Electrical Properties of Colloids - When a solid is introduced into a liquid of different dielectric constant, the solid becomes electrically charged. The attraction or repulsion between the two electric charges depend on the nature of the intervening medium represented by its "dielectric constant." The higher the dielectric constant of the medium, the weaker the mutual attraction between oppositely charged particles immersed in it.

Thus the particles of a suspension of clay and peat fibres are negatively charged, and if two electrodes connected with the poles of a high tension battery or dynamo are introduced into the suspension, the suspended particles are found to move towards the positively charged electrode.

This phenomenon is known as Cataphoresis.

So the electrical charge and the consequent mutual repulsion of the particles, the stability of the colloid sol, due.

Mutual Precipitation of Colloids

When two colloids of opposite electric charge are mixed, the charge of the one is neutralized by the other; aggregations of the particles and flocculation or precipitation of the colloids then take place. In order that pptn may be complete, the two colloids must be mixed in certain proportions within rather narrow limits.

Precipitation is due to the mutual neutralization of electric charges. The optimum is obtained when the proportions of the two colloids are charged sufficient to produce uncharged masses. They then coalesce and undergo pptn.

In the case of any two colloids the optimum amt will be definite and the adsorption complex is like a compound.

No pptn takes place when 2 colloids of same charges are mixed.

The mutual pptn of oppositely charged colloids can be made use of for the purpose of removing albumin from serum. Colloidal $\text{Fe}(\text{OH})_3$ is run from a burette into diluted serum. The mixture shaken after each addition.

$\text{Fe}(\text{OH})_3 + \text{Serum} \rightarrow$ mutual pptn: alb. removed from serum

Precipitation of Suspensions by Electrolytes

For colloid particles of different kinds, the potential difference bet. the particles + H_2O is approx. 0.05. By

Air.

Air is a mixture of Nitrogen [78.07%], Oxygen [20.95%] and CO₂ [0.03 - 0.04%]. These gases account for about 99% of the total, the remaining 1% consist of Hydrogen, Ammonia and the rare gases Neon, Argon and Krypton. Water vapour is also present to an extent of about 1% on the average.

Oxygen varies in amount only slightly under normal conditions, but in mines it may be as low as 18%. When at rest, an individual feels little discomfort at 11-12% of oxygen, and consciousness can be retained at 7%, although combustion is not supported much below 17%.

The CO₂ content of badly ventilated rooms frequently attains to 0.4%; 5-10% will cause discomfort in human beings.

Cases of Polluted Air.

Marsh Gas: or Methane. CH₄. Called 'marsh-gas' since it is generated in stagnant marshy pools as a result of gradual decay of vegetable matter, in a limited supply of oxygen [i.e. partially anaerobic].

The gas is often occluded by coal, sometimes under considerable pressure. When a new face is cut, a continuous stream of methane may be emitted. Hence methane is common in the atmospheres of coal-mines. 5-13% is inflammable in air.

Methane has no definite physiological action.

Poisoning by any of the following Gases in factories, etc. is notifiable.

Ferro-Silicon Gases. Ferro-silicon is used in the preparation of steels. Phosphorus and arsenic are often present as impurities, and combined exposure to moisture results in formation of the poisonous gases Phosphene and Arsine.

Hydrogen Sulphide, H₂S. Found in sewer gas and in chemical works and gas works. It is more dangerous than is usually thought; 0.2 to 0.4% may prove fatal, and with larger percentages sudden death can occur. The same remarks apply to [NH₄]₂S.

Carbon bisulphide, CS₂. Is a liquid solvent for rubber, and is used in vulcanising processes and in the artificial silk industry ('viscose'). It is very inflammable and very poisonous. An advanced degree of poisoning has serious consequences. Recovery is usual, but slow.

Benzene, C₆H₆. Benzene vapour is used in dry cleaning, and is found in petrol vapour. Causes anaemia and haemorrhage under the skin, and bleeding from the gums. Chronic benzene poisoning is a notifiable industrial disease, but acute poisoning is classed as an accident.

Aniline. Poisoning is usually by direct absorption of intermediate products of the dye industries by way of the skin, but fumes of such products enter the body by the respiratory and digestive tracts. The general action of aniline and its derivatives is to dissolve red blood corpuscles.

Tetrachlorethane, nitrobenzene, chloroform and trinitrotoluene occasionally cause toxic jaundice.

Chlorine, ammonia, nitric acid, hydrochloric acid and phosgene [COCl₂] are all dangerous irritants.

Carbon Monoxide. An extremely dangerous gas. It combines with oxyhaemoglobin to form CO-haemoglobin, a compound which is sufficiently stable to make the conversion back to oxyhaemoglobin difficult.

300 X affinity for hb than O₂
Besides being so poisonous it is unfortunately colourless and (as it occurs) is odourless. It is inflammable.

*With 0.08% CO in air hb becomes half saturated, with 0.16% CO man
hb. 2/3 saturated, thus doubling amt of CO in air does not necessarily double
degree of CO saturation in blood; 0.1% to causes symptoms headache & lethargy
within 1 hour.*

While 0.3% may produce unconsciousness in 2.0 minutes

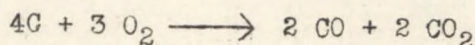
0.5-1.0% is fatal rapidly.

0.01% is permissible for several hours exposure

Symptoms - Vomiting, giddiness, headache, ringing in the ears and great lethargy. Convulsion & coma may supervene but loss of motor power usually occurs before unconsciousness. If active exercise is indulged in the rate of saturation increases & poisoning results more rapidly.

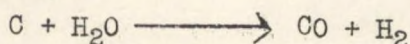
It occurs in several gases used for fuels in industry. Coal gas contains about 7.0%, but in some places as much as 12%. Anthracite stoves are sometimes a source of danger if the shaft is not quite intact.

① 'Producer gas' - much used in heavy industry - is made by passing air, or air mixed with steam, through a deep bed of coke. The following reaction occurs:-



The gas containing CO is now led away in pipes to any desired site and then is combusted. Any leakage from pipe lines may be dangerous.

② Water gas. Steam is passed over red-hot coke, causing "gasification" of the carbon:-



Here again the CO containing gas is led to its required site.

③ Blast-furnace gases always contain CO.

Other sources of CO are:-

④ Exhaust gases from motor cars. After explosions in coal mines CO may occur in the mine atmosphere. Brick and cement kilns. Coke ovens are possible sources. Carbon-arcs (as in cinemas). Patent water heaters, etc.

The smell of coal gas is not due, as some think, to the CO which it contains, but to the hydrocarbons of the gas.

Tests for Carbon Monoxide.

(a) The detection of CO is not easy. A piece of white filter paper moistened with palladium chloride - $PdCl_2$ - is turned pink, green, or black according to the amount of CO present in the atmosphere. But other organic substances produce the same reaction, and H_2S or NH_3 must be removed from the atmosphere.

(b) Vogels blood tests. If ordinary blood be diluted with 200 times its volume of water, a yellowish-red solution is obtained, but with blood containing CO, the solution is distinctly pink.

(c) Tannic acid test. Normal blood diluted 1 : 4 with water is shaken with equal volume of 1% tannic acid solution and allowed to stand 24 hours. A grey suspension results. Normal blood solution shaken in a CO containing atmosphere and treated as above gives a carmine red colour.

(d) NH_3 - $CuCl$ test. The reagent is NH_4Cl , $CuCl$, conc. NH_3 . The air suspected of containing CO must be free from CO_2 and O_2 by passing it through KOH and alkaline hydrosulphite. The CO then, on passing through the above reagent, forms a typical crystalline compound, which is probably $CuCl.CO.2H_2O$.

NOTE: KOH will absorb (i.e. react with) CO_2 , but it has no chemical reaction with CO.

(e) Spectroscopic test. - will detect CO when as little as 0.25%. If normal blood solution is placed so that the sun's rays pass through it before being admitted to a spectroscope, two dark bands [between the D and E lines] will be apparent, due to oxyhaemoglobin. A solution of blood containing CO-haemoglobin shows a very similar spectrum. But after adding a drop or two of $(NH_4)_2S$ and warming a little, and allowing to stand for 1/4 hour, the two bands persist, whereas with oxyhaemoglobin the original bands merge together [due to the $(NH_4)_2S$ reducing oxyhaemoglobin to haemoglobin].

P.M. Pupils dilated blood bright red and small haemorrhage into many body tissues may be found.
* artificial respiration and administration $O_2 + 7\% CO_2$ after patient has been removed from poisonous surroundings

Test for CO with small animal.

Introduced by Haldane in 1896 as a test for CO in dangerous concentrations in mine air. It depends upon the fact that small warm-blooded animals react far more quickly to CO than large animals, including man, and therefore act as safe indicators of CO.

A small bird, such as a linnet or canary, may be used; it becomes unsteady on its perch and falls off. But a bird is likely to die suddenly in a dangerous atmosphere and thus becomes useless as a further guide. A bird or mouse is affected within one-tenth of the time required to affect a man, and if a bird or mouse is affected, it will show effects within 10 minutes, depending on the CO concentration. The bird will probably die (unless promptly removed) with anything more than 0.2% CO, while a mouse will only be disabled at this concentration and may live at 0.4% to 0.5%. It appears that a concentration of more than 0.2% for a sufficient time is very dangerous to man, and a concentration of more than 0.02% will cause headache and partial disablement.

Wammalsh

Quantitative determination of CO.

(1) Carmine Titration. Small percentages of CO in air can be determined with considerable accuracy by a blood solution, of which the percentage saturation of haemoglobin with CO is titrated by means of a standard solution of Carmine.

Procedure. A solution consisting of 1 part of normal blood diluted to 100 parts with water is used. 5 cc.s of this normal blood solution is shaken up thoroughly with 200 to 300 cc.s of the air to be examined. This procedure brings the CO from the air sample into equilibrium with the haemoglobin. Call this solution A.

A further 5 cc.s of normal blood solution is saturated with CO by passing coal gas. The whole of the haemoglobin of this 5 cc. will then be combined with CO. Solution B.

To a third 5 cc.s of normal blood is added standard carmine solution from a burette until:-

(i) The colour matches tube A - say 2.2 cc.s and the titration then continued until:-

(ii) The colour matches tube B - say 6.2 cc.s.

From these two readings the 'percentage saturation' X, of the blood solution in equilibrium with the sample of air can be deduced from the formula:-

$$\frac{2.2}{2.2 + 5.0} : \frac{6.2}{6.2 + 5.0} :: X : 100.$$

Haldane has published curves correlating X the percentage saturation of haemoglobin with CO, with the percentage of CO in air. From these curves, therefore, we can determine the concentration of CO in an atmosphere.

This colorimetric titration is a peculiar one, since 'quality' and not 'depth' of colour is being estimated. The carmine has a bluer tint than blood solution saturated with CO, and the mixture of the carmine colour with the yellow of normal blood solution reproduces accurately the tint of the blood containing CO. The two solutions are not spectrally identical, the equality of tint is physiological only.

(2) Estimation of CO by Iodine Pentoxide.

The air sample is freed from CO₂, unsaturated hydrocarbon and aqueous vapour, and conducted through a U-tube containing 60-70 grams of pure I₂O₅ heated to 160°C.: by this means the CO alone is oxidised and iodine liberated according to the equation:- $5CO + I_2O_5 \longrightarrow 5CO_2 + I_2$. If the gas is now passed through two tubes containing KI solution, the iodine will be absorbed, and can be titrated with standard Na₂S₂O₃ solution.

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