

THE AMERICAN CHEMICAL SOCIETY.

(Continued)

DIVISION OF PHYSICAL AND INORGANIC CHEMISTRY

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Adsorption by precipitates V.: Adsorption during the precipitation of colloids by mixtures of electrolytes: HARRY B. WEISER. The precipitating action of mixtures of two electrolytes is approximately additive if the precipitation value of each is of the same order of magnitude such as frequently obtains when the precipitating ions have the same valence. The precipitating action of mixtures of electrolytes with widely varying precipitating power may be far from additive but under certain conditions may approach an additive relationship. The determining influences are (1) the effect of the presence of each precipitating ion on the adsorption of the other and (2) the magnitude of the stabilizing action of the ion having the same charge as the colloid.

The influence of the concentration of colloids on their precipitation by electrolytes: HARRY B. WEISER AND HENRY O. NICHOLAS. Burton and Bishop (*Jour. Phys. Chem.*, 24, 710 (1920)) state that the precipitating action of univalent ions increases and of trivalent ions decreases with decreasing concentration of colloid while that of divalent ions is almost independent of the colloid concentration. By an extended series of experiments with four different colloids this rule was shown to be far from general. With three of the colloids the precipitation value of all electrolytes decreased as the concentration of the colloid decreased, the effect being least marked with electrolytes having univalent precipitating ions. The determining factors are (1) the change in the amount of adsorption necessary for neutralization, (2) the change in the opportunity for collision of the particles, (3) the influence of the stabilizing ion particularly in the case of electrolytes that precipitate in high concentration.

Intermittent phosphorescence: HARRY B. WEISER. The luminescence of phosphorus is due to the rapid oxidation of phosphorus trioxide to phosphorus pentoxide. The luminescence is continuous only when the trioxide vapors are formed as rapidly as the luminescent reaction proceeds; the luminescence takes place in intermittent explosion waves when the velocity of formation of trioxide is less than the velocity of the explosion

wave. The pulsations may be very rapid or may occur at intervals of several hours. The number of luminescent waves in unit time is determined by (1) the temperature, (2) the partial pressure of oxygen, (3) the extent to which the heat of reaction is absorbed by the containing vessel, (4) the presence of "catalytic" vapors.

The ternary system: silver perchlorate-benzene-water: ARTHUR E. HILL. Silver perchlorate is very soluble in water, and moderately soluble in benzene. The system has been studied from the temperature of the ternary eutectic (-58°) up to the boiling points of the pure liquids. There occur four quintuple points, and twelve equilibria. Of most interest is the equilibrium in which three liquid phases are present, which may exist from -2.2° C. to $+22.3^{\circ}$ C. It appears to be the only three-component system showing three liquid layers derived from components in which only one pair (water and benzene) show the formation of two liquid phases.

Hydrated oxalic acid as an analytical standard: ARTHUR E. HILL AND THOMAS M. SMITH. The common drawbacks to the use of hydrated oxalic acid as a standard for oxidimetry and alkalimetry are its retention of included water and its irregularity in combined water due to its distinct vapor tension. These two sources of error should be eliminated by fine grinding, to offer an escape for included water, and by drying to constant weight in an atmosphere in which the aqueous tension is exactly that of the hydrate. We have found that grinding to pass a 100-mesh sieve meets the first requirement. To meet the second, we have dried the compounds over a mixture of hydrated and dehydrated oxalic acid, which is the only drying agent which can be in equilibrium with the compound at all temperatures. The compound can be brought to a constant composition within about three hours, and agrees in its reducing action upon KMnO_4 with Bureau of Standards sodium oxalate within 0.03 per cent.

Effect of the history of adsorbent on adsorption: R. C. WILEY AND N. E. GORDON. Silica gel was prepared containing various amounts of water of hydration, and shaken with varying concentrations of different salt solutions. It was found that the amount of hydration had some effect on the adsorption of some salts. In most instances the change was very small, but in these cases the analytical method used made the

small changes as certain as where the change was more pronounced.

Adsorption from solution: D. C. LICHTENWALNER, A. L. FLENNER AND N. E. GORDON. Varying concentrated solutions of calcium sulphate, calcium acid phosphate, magnesium sulphate, magnesium acid phosphate, potassium sulphate, and potassium acid phosphate were shaken with alumina hydrogel and iron hydrogel and the maximum adsorption determined by analyzing the solution before and after shaking. The water of hydration was all figured as water of dilution. Both gels show large adsorptions for each radical, and especially was this true in the case of the phosphate radical. The adsorption increased with increase of concentrate. The slow process of establishing equilibrium was also greatly marked.

Effect of hydrogen-ion concentration on adsorption: E. B. STARKEY AND N. E. GORDON. Hydrated gels of iron and silica were prepared in a very pure condition and shaken with a N/20 solution of KNO_3 , K_2SO_4 , KHPO_4 . The hydrogen-ion concentration had been varied by the introduction of sodium hydroxide or hydrochloric acid as the case might allow. The adsorption of each ion was followed by analyzing the solution before and after the shaking and figure the water of hydration as water of dilution. It was found that the adsorption of the metallic ion decreased with an increase of hydrogen-ion concentration, while the nitrate, sulphate, and phosphate radical varied between no change of adsorption as in the case of the nitrate radical to a very noticeable change of adsorption in the case of the phosphate radical.

The sorption of toluene and acetic acid and their mixtures by carbon: A. M. BAKER AND J. W. MCBAIN. A general method is described for determining the true sorption of both solvent and solute in place of the merely relative values obtained in the usual way for solutions. A maximum value for sorption is obtained which is independent of the absolute temperature; the ratio between the saturation values is that of the molecular weights (acetic acid being present as double molecules); and when solutions are employed, the total amount sorbed still corresponds to a complete monomolecular film in which a certain number of double molecules of acetic acid have replaced a corresponding number of molecules of toluene.

Drop weights of oils in solutions of emulsifying agents: ROBERT E. WILSON AND ALLEN ABRAMS.

The preparation and properties of ferric hydroxide gel: ROBERT E. WILSON, WILLIAM B. ROSS AND LEON W. PARSONS.

The measurement of the plasticity of clays: ROBERT E. WILSON AND F. P. HALL.

The transitional temperature of the sol and gel forms in gelatin: ROBERT HERMAN BOGUE. Bingham has shown that viscous liquids can be distinguished from plastic solids by a measurement of the viscosity at varying pressures and an extending of the curves downward till they intersect the axes. The former type intersect at the apex of the viscosity-pressure axes, while the latter type intersect upon the viscosity axis. By applying the principle to gelatin solutions at different temperatures and employing the MacMichael viscosimeter at varying speeds of rotation in place of the capillary type at varying pressures, it is found that the gelatine follows the law for a viscous liquid at temperatures above 33 degrees C., while at lower temperatures it follows the law for a plastic solid.

On the swelling and gelation of gelatin: ROBERT HERMAN BOGUE. Gelatine sols were treated with solutions of the silicates of sodium in which the $\text{Na}_2\text{O}:\text{SiO}_2$ ratio varied regularly from 1:4 to 1:1. The swelling, viscosity, alcohol number, and P_H values were determined. The data indicate that the effects resulting from such additions are due in all cases to changes in the P_H rather than to any other influence of the silicate. Gelation appears to be dependent upon the tendency of the substance to become solvated, the volume occupied by unit weight of dispersed phase being the determined factor. When this volume is very small or very large, the jelly consistency will be low, and at intermediate values of volume per unit weight the jelly consistency will reach its maximum.

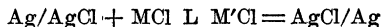
Plasticity of colloids: EUGENE C. BINGHAM.

The fluidity-pressure curves of gelatine solutions: S. E. SHEPPARD, FELIX A. ELLIOTT AND HARRY D. GIDEOUSE. Gelatine solutions were studied whose concentration varied from 1 per cent. to 8 per cent. at temperatures of 25°, 28° and 30° C. The fluidities were measured with an Ostwald type viscometer under pressures up to 900 mm. water. Ordinary, de-ashed and a mixture of de-ashed and autoclaved de-ashed gelatines were used. All measurable solutions showed little evidence of plastic flow, the curves being linear and approximately intersecting at a common point.

The method of preparing the solution was shown to influence the slope of the curves.

The action of dilute chloride solutions upon silver chloride: GEO. SHANNON FORBES AND H. ISABELLE COLE.

The potentials at the junctions of chloride solution: D. A. MACINNES AND Y. L. YEH. E.m.f. measurements were made on cells of the type:



(in which M and M' are the alkali metals and hydrogen) using a flowing junction similar to that developed by Lamb and Larson. With widely varying rates of flow the potentials were constant to ± 0.02 mv. for indefinite periods. With equal concentrations on both sides of the junction and assuming the chloride ion activity to be the same in all the solutions the measured e.m.f. is that of the liquid junction only. The results may be expressed by a simple additive relation in the few cases in which the formula of Lewis and Sargent does not hold.

Electrometric titration of ortho-phosphoric acid: E. T. OAKES AND HENRY M. SALISBURY. New curves for ortho-phosphoric acid titrated with sodium hydroxide and sodium carbonate are shown. These curves are plotted to show observed e.m.f. values as well as P_H values. Condenser method, and saturated calomel cell are used for measuring e.m.f. Technic of titrations, method of calculating results and sources of error are discussed briefly. Curves obtained by titrating phosphoric acid with sodium hydroxide, and sodium hydroxide with phosphoric acid are not mirror images. The second end point of phosphoric acid required more than twice as much alkali as the first. Curves obtained by titrating phosphoric acid with sodium carbonate, and sodium carbonate with phosphoric acid are vastly different. Equations conforming to these curves differ from those commonly accepted.

Oxidation-reduction potentials of certain indophenols and thiazine dyes: BARNETT COHEN AND W. MANSFIELD CLARK. A series of indophenols consisting of the condensation products of para-amino phenol with phenol, o-cresol, m-cresol, o-chlorophenol, guaiacol, thymol and carvacrol were synthesized. The potentials of mixtures of each of these with its reduction product were measured with a gold electrode at different P_H values. It is shown that the same general relations hold that were found by Clark in the study of methylene blue and indigo sulfonate, the potentials being a function of both the ratio of oxidation product

to reduction product and of the hydrogen-ion concentration. The effect of substitutions in changing the characteristic potentials is noted. Previous work with methylene blue has been extended to other thiazines. Characteristic constants for thionine, gentianine, toluidine blue o, thiocarmine R, methylene green G and new methylene blue N have been established.

Oxidation-reduction potentials of sulfonated indigos: M. X. SULLIVAN AND W. MANSFIELD CLARK. A trisulfonate and tetrasulfonate were found to have identical characteristic potentials when each was in definite ratio to its respective reduction product. These potentials are distinctly more positive than those of mono- and disulfonates. The potentials of the mono- and disulfonates are approximately the same but more refined measurements will have to be made to distinguish them.

A series of oxidation-reduction indicators: W. MANSFIELD CLARK AND H. F. ZOLLER. It is shown that certain dyes are as susceptible to precise electrode study as are certain inorganic oxidation-reduction combinations. The great importance of hydrogen-ion concentration is emphasized. The potentials for each dye can be reduced to a characteristic value from which there may be calculated the hypothetical hydrogen pressures in equilibrium with the oxidation-reduction products. These values are used in the form $\log (1/H_2)$ to which is given the symbol rH. Plotting the equilibria on the rH scale gives a picture of oxidation reduction indicators comparable with that of the acid base indicators plotted on the P_H scale. The following oxidation-reduction indicators were shown plotted on the rH scale: guaiacol indophenol, o-cresol indophenol, o-chloro indophenol, methylene green, thionine, methylene blue, indigo tetrasulfonate, new methylene blue, indigo disulfonate, neutral red and safranin. These constitute a series from rH 21.7, at the more oxidative end to rH 2.8 at the more reductive end of the scale.

Selenium galvanometric colorimeter: ALEXANDER LOWY AND OSWALD BLACKWOOD.

A submerged floating equilibrium bob that adjusts its weight to the density of the liquid in which it is placed: C. W. FOULK. This is a modification of the Richards floating equilibrium bob so that it can be used for the determination of the density of liquids over a considerable range. Preliminary experiments show that measurements of density can be made with it with an accuracy

of one or two in the fifth decimal place and probably in the sixth place, and that a given bob as modified will cover a range of about two decimal places, that is, with one instrument, for example, densities ranging from 1.00001 to 1.00010 could be read. The modification consists in attaching a light chain to the bob which is a fish-shaped, hollow glass, or silica bulb. It is evident that if the weight of such a bob (a certain amount of ballast is usually necessary) is approximately that of an equal volume of the liquid in which it is placed, it will assume a position of equilibrium between the surface of the liquid and the bottom of the containing vessel, the equilibrium being brought about by the chain suspended from its lower end. As the bob rises it lifts the chain link by link off the bottom of the vessel till the added weight counteracts the upward tendency and of course the reverse takes place if the bob tends to sink. A practical instrument utilizing this principle is made by having the bob in a tube open at both ends and with one end of the chain attached to the lower end of the tube, so that it hangs in a loop (catenary curve) between this point of support and the bob. The density of a liquid in which this instrument is placed can be determined by noting the position which the bob takes with respect to a scale on the tube. There are a number of interesting variations of the instrument that can not be given in a brief abstract.

The comparative value of different specimens of iodine for chemical measurements: C. W. FOULK AND SAMUEL MORRIS. Iodine was purified in various ways as described in the text-books of analytical chemistry and these preparations were then compared through the medium of a sodium thiosulphate solution with a specimen of iodine that had been purified as if for an atomic weight determination. Several new modifications of apparatus for purifying and drying iodine were also devised. The general conclusion drawn from the experiments was that the so-called "analytical" iodine is remarkably pure. Doubt, however, is thrown on the use of a sulphuric acid desiccator as a method of drying iodine when the water it contains had been entrained through the solidification of the iodine in the presence of liquid water.

Variation of grain size in photographic emulsions in relation to photochemical and photographic properties: E. P. WIGHTMAN, A. P. H. TRIVELLI AND S. E. SHEPPARD.

The physico-chemical properties of strong and weak flours III. Viscosity as a measure of hy-

dration capacity and the relation of the hydrogen-ion concentration to imbibition in the different acids: ROSS AIKEN GORTNER AND PAUL FRANCIS SHARP. In continuation of the work reported at the Chicago meeting of the Society, the authors have applied the use of the viscosimeter to the study of hydration of the emulsoid colloids present in wheat flour. Instead of using the washed out gluten as in previous work a 20 per cent. suspension of the entire flour was used in the present study. The results indicate (1) that the viscosimeter affords an accurate and rapid means of measuring imbibition, (2) the form of the viscosity curves is identical with that of the imbibitional curves obtained previously by weighing gluten discs, (3) "strong" flours give greater viscosity values than do weak flours at the corresponding concentration of acid calculated on either normality or hydrogen-ion concentration basis, (4) when the viscosity is plotted against hydrogen-ion concentration instead of against normality of acid a radically different form of curve results, with a maximum viscosity at about $P_H=3.00$, (5) the same value for maximum viscosity is not reached by all acids at the same hydrogen-ion concentration, (6) the order of the acids as influencing imbibition (lyotropic series) is not the same for all of the flours studied.

An interesting colloid gel: ROSS AIKEN GORTNER AND WALTER F. HOFFMAN. A rigid gel can be prepared from di benzoyl L. cystine containing as little as 0.15 per cent. of the compound. Viewed by dark field illumination this is apparently a crystal gel. It is suggested that this material may assist in studies regarding gel structure for it can be easily prepared in pure crystalline form and is consequently not affected by previous history as is gelatin, agar, etc.

Are electrolytes completely ionized at infinite dilution? HAROLD A. FALES AND HAROLD E. ROBERTSON. Measurements made on hydrochloric, acetic, sulphuric and phosphoric acids up to a dilution of three million liters per mol, by the electromotive force method using the ballistic galvanometer, show that the thermodynamic ionization passes through a minimum and approaches zero with increasing dilution. It seems that it is not until a dilution of one thousand liters per mol is reached that the thermodynamic concentration of hydrogen ion becomes equal to the ionic concentration.

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