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A Derivation of the Solubility Product Law

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A DERIVATION OF THE SOLUBILITY PRODUCT LAW

Warren C. Vosburgh

Stieglitz[1] pointed out in 1908 that the derivation of the solubility product law based on the application of the law of mass action to strong electrolytes is objectionable. Nevertheless many elementary textbooks still give it. Washburn[2] later gave a satisfactory thermodynamic derivation, and Butler[3] has more recently given a satisfactory statistical one. Another thermodynamic derivation is possible using the now familiar concepts of free energy and activity.

Lewis and Randall[4] have pointed out that in a saturated solution of an electrolyte the mean activity of the ions is constant. The reasoning by which this conclusion may be reached is as follows. A solid electrolyte is in equilibrium with its saturated solution when the free energy of the solid is equal to the partial molal free energy of the substance in solution,

$$F_s = \overline{F}_2. \tag{1}$$

By the definition of activity

$$F_s - \overline{F}_2 = R\,T\,\ln\frac{a_s}{a_2} \tag{2}$$

where a_s is the activity of the solid and $\overline{F}_s$ is its free energy, and a_2 is the activity of the solute and $\overline{F}_2$ is its partial molal free energy. Combining Equations 1 and 2 and simplifying shows that the two activities are equal. The activity of the solid is constant at constant temperature and pressure, and so the activity of the solute is constant also. The activity of the solute can be expressed in terms of the activities of its ions without assuming any particular theory of ionization. This gives

$$a_2 = a_+{}^{v+} \cdot a_-{}^{v-} = (a_\pm)^{v+ \,+\, v-} = K \tag{3}$$

where a_+ and a_- are the activities of the positive ion and the nega-

1 Stieglitz, *J. Amer. Chem. Soc.*, **30**, 946 (1908).
2 Washburn, *J. Amer. Chem. Soc.*, **32**, 487 (1910).
"Principles of Physical Chemistry," McGraw-Hill Book Co., New York, **1921**, p. 350.
3 Butler, *Chemistry and Industry*, **43**, 634 (1924).
4 Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, **1923**, p. 369.

tive ion, respectively, and v_+ and v_- are the numbers of moles of the two ions in one mole of the electrolyte. The mean activity is designated by a_+ and K is a constant. Lewis and Randall did not point out that Equation 3 is the solubility product law in an exact form.

In sufficiently dilute solutions, especially of uni-univalent electrolytes, the ion activities are approximately equal to their concentrations. Under such conditions concentrations can be substituted for activities in Equation 3, giving the ordinary form of the solubility product law. The latter can therefore be expected to hold when the concentrations are approximately equal to the activities and to fail when the concentrations differ appreciably from the activities.

STATE UNIVERSITY OF IOWA,
  IOWA CITY, IOWA.

THE RATE OF EVAPORATION THROUGH SURFACE FILMS

RAYMOND BARTLETT AND THOS. C. POULTER

The purpose of this investigation was to study the influence of surface tension on the rate of evaporation of water through surface films. We determined the rate of evaporation of pure water and water from solutions of calcium and sodium chlorides of concentrations varying from zero to nearly saturation.

These two solutions were selected because of the tendency of Ca. to increase the surface tension and of Na. to decrease the surface tension in water solutions. A mixture of these salts was also studied because of the tendency of one to overcome the effects of the other on the surface tension. The two curves for the rate of evaporation of Ca and Na solutions were determined and an increase in concentration caused a decrease in the rate of evaporation from each solution.

If, now, to a solution of NaCl of known concentration, of which the rate of evaporation has been determined, there be added a small amount of $CaCl_2$ without changing the concentration of Na, the vapor pressure of the solution would be lowered and the rate of evaporation would be decreased if it were a function of the vapor pressure only.

On the other hand, if the rate of evaporation remained constant, or increased, it would indicate that the rate of evaporation was not solely determined by the vapor pressure. The determinations

show a slight increase in the rate of evaporation, thereby indicating that the rate of evaporation is influenced to a small degree by the surface tension of the liquid.

IOWA WESLEYAN COLLEGE,
  MT. PLEASANT, IOWA.

THE COMMERCIAL PREPARATION OF OXYGEN FROM LIME AND CHLORINE

O. R. SWEENEY AND A. W. RALSTON

The reaction of chlorine on a suspension of lime in the presence of suitable catalysts, such as nickel, cobalt and iron salts, has been studied. It was found that the optimum temperature is 94° C.; that the greatest unit efficiency of the catalyst, nickel nitrate, is obtained at a concentration of .02 g. per 100 c.c; that the rate of generation of oxygen is almost directly proportional to the rate of flow of the chlorine and that nickel and cobalt salts are distinctly superior to all other catalysts which were used. In addition it has been found that the catalyst is not easily poisoned, and may be used throughout a number of runs.

An apparatus has been designed which is capable of producing pure oxygen from lime and chlorine, and which is capable of recovering the catalyst for further use.

By the process outlined chlorine, now a drug on the market, is converted into calcium chloride and yields oxygen, both of which are in demand. Commercial possibilities of this reaction were pointed out.

IOWA STATE COLLEGE,
  AMES, IOWA.

THE RATE OF SOLUTION OF Zn IN H_2SO_4 UNDER PRESSURES UP TO 347 ATMOSPHERES

THOS. C. POULTER AND GLEN E. FRAZER

A study is made of the factors influencing the rare of solution of Zn in H_2SO_4. The conditions of the surface, the local concentration of the acid at the surface of the Zn, and the size and shape of the pieces of Zn are found to be very important factors while pressures up to 347 atmospheres have very little direct influence upon the rate of reaction.

The pressure cell used for this work was exhibited.

A STUDY OF THE REACTIONS INVOLVED IN A SYSTEM OF Zn AND H_2SO_4 UNDER PRESSURES UP TO 16000 ATMOSPHERES

A continuation of the investigation described in the previous paper. A method is described for following the rate of the reaction at very high pressures in which the pressure can be varied rapidly and the rate of the reaction continuously read. Very little effect upon the rate of the reaction, directly due to pressure, was noticed up to pressures of 6000 atmospheres.

The pressure cells used for this work were exhibited including one that was ruptured at a very high pressure.

IOWA WESLEYAN COLLEGE,
    MT. PLEASANT, IOWA.

HEAT OF ADSORPTION ON CHARCOAL OF CERTAIN ORGANIC VAPORS

LLOYD MCKINLEY AND J. N. PEARCE

Previous work on the heat of adsorption has been carried out by the use of the ice calorimeter adapted only to those liquids of appreciable vapor pressure at 0°C, and affording no investigation of the effect of temperature upon the heat of adsorption.

In the present paper there is described a method for studying the heat of adsorption at different temperatures by employing a sensitive thermo-couple in a calorimeter system consisting of a known weight of low specific heat oil in a Dewar flask. With this arrangement we find that a change of 1 microvolt in the thermo-couple reading corresponds to 0.06 calories per gram of charcoal.

SOLUBILITY OF COPPER IN MILK

E. I. SOLOMAN WITH G. N. QUAM

The solubilities of copper in sweet whole raw milk held at a constant temperature for 30 minutes were determined for temperatures ranging from 20 degrees Centegrade to 100 degrees Centegrade. Copper sheets of known dimension were totally immersed and agitated in milk for 30 minutes at the specified temperature. Solubility values were determined by difference in weight of the copper sheets and also by determining colorimetrically with potassium ethyl xanthate the copper present in the ash of the milk.

Solubilities per unit area increase with rise in temperature up to 80 degrees Centegrade.

CoE College,
   Cedar Rapids.

THE ADSORPTION OF HYDROGEN, ETHYLENE AND ETHANE BY TIN OXIDE

Sylvia M. Goergen and J. N. Pearce

The adsorption of hydrogen, ethylene and ethane by tin oxide has been studied at several temperatures. Calculations of the adsorption magnitudes have been made on the assumption that helium is not adsorbed. The tin oxide used has been found to be very stable and is easily reproducible. The problem is being extended to include the study of the catalytic influence of the oxide upon the velocity of the reaction:

$$C_2H_4 + H_2 \rightleftarrows C_2H_6.$$
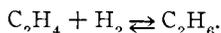
State University,
   Iowa City.

THE INFLUENCE OF HYDROGEN ION CONCENTRATION AND ELECTROLYTES UPON THE TURBIDITY, SENSITIVITY AND SETTLING RATES OF CERTAIN PLEISTOCENE CLAYS

Hoyt C. Graham and J. N. Pearce

The relative turbidity of the permanent colloidal suspensions from the different strata have been measured by means of a specially constructed tyndallmeter. The amount of clay which can be held in water suspension has been found to depend upon the stratum from which the clay was obtained, upon the hydrogen ion concentration, and upon the concentration of the electrolyte present in the suspension. In so far as the work has proceeded, we have found that the turbidity attainable is greater for the oxidized and leached strata than for the gumbotil; furthermore, for any one stratum, the maximum permanent turbidity is greater in the Kansan than in the Nebraskan.

The relative turbidity increases with increasing pH value until a certain maximum turbidity is reached, and then it decreases rapidly with further increase in pH. Except in the case of the

Nebraskan gumbotil, the maximum turbidity for each clay is found at almost identically the same pH, viz., 10.5.

STATE UNIVERSITY,
  IOWA CITY.

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A STUDY OF THE POTENTIALS AND OF THE ACTIV-ITIES OF THE METALS IN ZINC AMALGAM CELLS

J. N. PEARCE AND J. F. EVERSOLE

The electromotive forces of cells containing zinc amalgam elec-trodes in a saturated solution of zinc sulphate, have been deter-mined at 18°, 25° and 30°. The concentration of the zinc in the amalgams varied from N = 0.000302 to that of a two-phase amal-gam, N = 0.0638.

On the assumption that the amalgams form perfect solutions, the theoretical potentials have been calculated for a large number of cells in which each electrode is connected with the most dilute amalgam. The deviations between the observed and calculated values agree fairly well with the values obtained by Richards and Forbes.

Using the Hildebrand equation, and assuming that K = 11.2 for the equilibrium, $2\ Zn \rightleftarrows Zn_2$, we have calculated the potentials of the various cells and have found a close agreement between the observed and calculated values; especially is this true as the amal-gams approach infinite dilution.

The temperature coefficients of the cells have been determined and from these we have calculated the increase in free energy, in heat content, and in entropy accompanying the cell reaction.

Finally, the activities of the zinc and the mercury in the various amalgams have been calculated.

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  IOWA CITY.

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THE INFLUENCE OF SOLVENT UPON THE OPTICAL ROTATION OF DI-ETHYL TARTRATE

T. J. HEBERT AND J. N. PEARCE

A determination of the specific rotation of di-ethyl tartrate in various mixed-solvents has been made at 25° and 30°, using two different concentrations of the ester. The solvents used were ethyl alcohol, methyl alcohol, benzene and toluene and the binary mixt-

ures of each solvent with each of the remaining solvents. The mixed solvents were made on a mol fraction basis.

The specific rotation was found to be dependent on the composition of the mixed-solvent, upon the concentration of the ester and upon the temperature. It was also found to be influenced by the nature and proportions of the two solvents forming the binary mixture.

STATE UNIVERSITY,
  IOWA CITY.

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THE NEWLY COMPLETED WATERWORKS OF THE CITY OF ONEIDA, NEW YORK

NICHOLAS KNIGHT

The supply comes from Florence Creek, 22 miles north of the city. A 20-inch main conveys the water. The watershed contains 17 squuare miles, very sparsely settled and the danger from contamination is slight. There is an unusual amount of precipitation in that section of New York State, and in the dryest year of recent times, the rainfall was 41.28 inches.

A dam 400 feet long and 50 feet high, near the village of Taberg will impound the water, 200,000,000 gallons. It is estimated that this would furnish the city a three months' supply, should no rain fall during the period.

The paper contains a complete chemical analysis of the former supply which was unusually hard in $CaSO_4$; and also an analysis of the new supply which is unusually soft and pure. Both analyses were made in the Cornell College laboratories.

Oneida is a manufacturing city and it is already experiencing quite a boom on account of the quantity and excellent quality of its water supply.

CORNELL COLLEGE,
  MT. VERNON, IOWA.

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NEW HALOGENATED DERIVATIVES OF VANILLIN

L. CHAS. RAIFORD AND W. C. STOESSER

Carles [Bull. Soc., Chim., 17, 14 (1872)] prepared a monoiodovanillin in 1872, but did not prove its structure. Tiemann and Haarmann [Ber., 7, 615 (1874)] obtained a monobromo derivative that was shown by Dakin [Am. Chem. J., 42, 473 (1909)]

to have the halogen in position 5 (CHO = 1). Peratoner [Gazz. Chim. Ital., 28 (1) 235 (1898)] reported a monochloro compound in which the halogen was not oriented, but which may be a 5-derivative. The only dihalogenated vanillin on record is a diiodo compound obtained by Carles, for which no melting point was given, no derivatives prepared, and in which the halogen atoms were not ·oriented.

In the present work we have obtained the two remaining mono-bromo compounds, the 2- and 6-derivatives, and two of the possible dibromo substitution products, the 2, 5- and the 5, 6-compounds. Both mono- and dihalogenated compounds have been characterized by the study of several derivatives. All halogenated vanillins condense with amino compounds. No one of them has yet been found to undergo the benzoin condensation. Only one of the stereoisomeric oximes required by theory has been obtained in any case. The nitril obtained from the 5, 6-derivative, viz., 3-methoxy-4-hydroxy-5,6- dibromobenzonitril,   resists   hydrolysis with alkali to an extraordinary degree.

STATE UNIVERSITY,
    IOWA CITY, IOWA.

EFFECT OF SUBSTITUENTS IN THE FORMATION AND REACTIONS OF CERTAIN ETHERS

L. CHAS. RAIFORD AND GARRETT THIESSEN

In a previous report on this study it was found by Raiford and Colbert [Jour. Am. Chem. Soc., 48, 2652 (1926)] that the presence of a nitro radical in diphenyl ether interferes with the entrance of bromine to a much greater degree than could have been predicted on the ground of steric hindrance. Owing to lack of time the structures of several derivatives prepared to test this view were left undetermined, for future study. In the present study these have been determined in several cases and a number of other new halogenated derivatives prepared. These experiments have been conducted in the presence of aqueous alkali, a method which was in part standardized and designated in the previous work as the "wet method." In the present work this process has been shown to be capable of two modifications, each with somewhat specific applications which can, in general, be predicted.

A second point of interest in this work is the structure of the.

tetrabromo derivative of diphenyl ether obtained some years ago by Cook [J. Am. Chem. Soc., 32, 1286 (1910)] by direct bromination. A number of derivatives of this product have been obtained, but there is still some doubt as to the exact structure of the compound. Negative results are due in part to the stability of diphenyl ether derivatives, which makes it difficult to "split" the compounds in such a way as to recognize the character of the radicals present.

STATE UNIVERSITY,
  IOWA CITY, IOWA.

ORGANO-LEAD COMPOUNDS IN THE TREATMENT OF CANCER

HENRY GILMAN AND JACK ROBINSON

New organo-lead compounds have been prepared by means of the Grignard reagent. These compounds are being tested in cancer studies, as anti-knock agents, and as reagents to combat some plant diseases. Grignard reagents are being prepared from tetra-p-bromophenyl-lead, diphenyl-di-p-bromophenyl-lead, and halogeno-alkyl lead types by reaction with the special magnesium-copper alloy using mercuric salts as catalysts. Solubilizing groups like dialkylamino, diethyl-aminoethyl, and various carboxylic acid groups are being attached to the R groups which in turn are attached to lead.

For allied purposes the same types are being prepared where the lead has been replaced by tin, antimony, selenium and tellurium.

IOWA STATE COLLEGE,
  AMES, IOWA.

SOME ABNORMAL REACTIONS OF ORGANOMAGNESIUM HALIDES

HENRY GILMAN, J. E. KIRBY, R. E. FOTHERGILL AND
S. A. HARRIS

Nitro and nitroso groups react with methylmagnesium halides (and other RMgX compounds) to give methane and some ethane. The gases so evolved make it necessary to correct for the ordinary determination of active hydrogen by means of the Zerewitinoff method. Accordingly, the new hydroxy structure proposed for

o-nitrobenzaladehyde finds no support on the basis of gas evolved when treated with alkylmagnesium halides.

Benzylmagnesium halides, and related RMgX compounds like α-naphthylmethylmagnesium chloride (where the -MgX group is attached to a carbon that is attached in turn to an unsaturated carbon) have been found to give rearrangement products with new compounds like ethyl chlorocarbonate and ethylene oxide. In some cases (with benzylmagnesium chloride) rearrangement takes place to the para position. A study is in progress of the mechanism of such rearrangements.

In connection with the proof of the *non*-addition of RMgX compounds to an ethylenic linkage, it has been shown that cinnamyl chloride when treated with magnesium gives largely a Grignard reagent which when treated with carbon dioxide gives methyl atropic acid. The three other cases in the literature that have been offered as apparent proofs for the addition of RMgX compounds to an ethylenic linkage are also being investigated.

IOWA STATE COLLEGE,
    AMES, IOWA.

THE ACTION OF THE ALKYL CHLORIDES IN THE WURTZ REACTION

HARRY F. LEWIS

At the last meeting of the Iowa Academy, a report was made on the mechanism of the Wurtz reaction using butyl and isobutyl bromides. The preparation of octane in this manner is costly and an attempt has been made to replace the bromide by the chloride. This report covers such experiments. Either in the presence or absence of ether as a solvent, the reaction is difficult to control. Yields of octane up to 20% based on the butyl chloride have been obtained. An extremely inflammable by-product is produced and it is difficult to complete a preparation without at least one fire. Using octane itself as a solvent, several bad explosions resulted.

STERIC HINDRANCE IN THE BEHAVIOR OF PHENYL ALKYL ETHER AND DERIVATIVES

L. CHAS. RAIFORD AND D. M. BIROSEL

It is known that phenyl alkyl ethers substitute in the phenyl radical less easily than phenol; nevertheless, phenetol will give a

tribromophenyl compound. When the allyl derivative is used, both phenyl and allyl radicals may be involved in the change. Experiments now in progress show that rearrangement of the allyl ether by heat, according to Claisen's method may cause a loss of bromine.

STATE UNIVERSITY OF IOWA,
  IOWA CITY, IOWA.

DIPHENYLKETENE WITH NITROGEN TRICHLORIDE

G. H. COLEMAN AND A. W. CAMPBELL

Diphenylketene reacts with nitrogen trichloride in carbon tetra-chloride solution. When this solution is warmed to 50° C with sodium hydroxide the addition product undergoes a rearrange-ment with the formation of imidobenzophenone. This rearrange-ment is similar to the rearrangement in Hofmann's method for the preparation of primary amines from amides. On passing dry HCl into the carbon tetrachloride solution, the hydrochloride of this compound is precipitated.

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  IOWA CITY, IOWA.

NITROGEN TRICHLORIDE WITH BENZALACE-TOPHENONE

G. H. COLEMAN AND DAVID CRAIG

Nitrogen trichloride and benzalacetophenone in carbon tetra-chloride solution between 20° and -15° react to form free nitro-gen, ammonium chloride, benzalacetophenone dichloride, and a C-chloro-N-dichloroamino ketone. This compound can be reduced to the C-chloroamino ketone by means of concentrated hydro-chloric acid. The hydrochloride and the benzoyl derivative of this compound were isolated and analyzed.

STATE UNIVERSITY,
  IOWA CITY, IOWA.

MONOCHLOROAMINE WITH GRIGNARD REAGENTS

G. H. COLEMAN AND C. R. HOUSER

Certain Grignard reagents react with monochloroamine in dry ether solution to form amines. There is a wide variation in the

amount of amine produced. In some cases considerable ammonia is formed. With benzyl magnesium chloride, which thus far has given the best yield of amine, an 80 to 90% yield based on the monochloroamine is obtained.

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  IOWA CITY, IOWA.