work. Studies of soil conditions and plant reactions are being carried on in the endeavor to interpret more fully this phenomenon.

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THE AMERICAN CHEMICAL SOCIETY[1]

PHYSICAL AND INORGANIC CHEMISTRY

Arthur E. Hill, *Chairman*
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The application of the Lewis-Langmuir structure of the atom to the theory of coordination: C. J. BROCKMAN. In building up his theory of complex compounds Werner postulated the existence of a "coordination number" for certain elements, the theory being more or less at variance with the accepted ideas concerning valence, etc. Now it is suggested that the formation of complex compounds be due to an inherent desire on the part of certain elements to complete its outer shell of electrons to that configuration which is characteristic of the next higher inert gas, by taking on single or pairs of electrons from ions in solution or from molecules, etc., as they are available for such absorption. When electrons in such ions are absorbed by the central element the union between coordinated atoms or radicals becomes noniogenic. In support of this theory complexes containing Pt, Cr, Co and Fe as the central atoms have been studied.

The electric moments of the molecules of monocarboxylic acids and their esters: CHARLES P. SMYTH. The electric moments of the molecules of a number of monocarboxylic acids and esters are calculated from their structures, which are assumed to be formed by the linking of atoms by electron pairs symmetrically located at the apices of regular tetrahedra. The ratio of the moments thus obtained to those previously calculated in a similar manner for the molecules of the ketones, aldehydes and alcohols is in good agreement with that of the moments obtained from experimental data on these substances. The principal moments of the molecules induce secondary moments on the carbon chains of the esters, but, in conformity with the structures indicated by the X-ray measurements of Müller and Shearer, these induced moments oppose and nearly cancel one another in the carbon chain of the acyl radical of the ester, but reenforce one another in the chain of the alcohol radical, so that the moment of the molecule as a whole increases with increasing length of this chain, but changes little with increasing length of the acyl chain. The fact that the variations among the electric moments of different molecules may be explained by the assumption of electrons pairs shared between atoms which tend strongly to maintain their effective positions in definite symmetrical locations in the molecules seems to support the idea that valence forces are highly localized and directive in character, as indicated by the X-ray study of solids and the recent conclusions of Vorländer upon liquid crystals.

Adsorption and Schulze's law: HARRY B. WEISER. Schulze's law, that the precipitating power of an electrolyte is greater the higher the valence of the precipitating ion, is but little more than a qualitative rule. In so far as the rule holds, the adsorbability of an ion is greater the higher the valence. The conclusion of Dhar and his collaborators that ions with the lowest precipitating power are adsorbed the most and *vice versa* is both theoretically and experimentally unsound. An indirect method has been devised for determining the relative adsorbability of weakly adsorbed univalent ions. With strong electrolytes containing weakly adsorbed precipitating ions and the same stabilizing ion there is a direct relation between the relative adsorbability of the precipitating ions and the coagulating power of the electrolytes in the sense that the electrolyte containing the most readily adsorbed precipitating ion coagulates a sol in lowest concentration.

Mechanism of the photochemical reaction between hydrogen and chlorine: A. L. MARSHALL. An investigation has been made of the reaction between atomic hydrogen and a mixture of hydrogen and chlorine at low pressures. It has been found that below 0.001 cm pressure there is a yield of one molecule of hydrogen chloride per atom of hydrogen, while at 0.60 cm pressure the yield is ten molecules per atom of hydrogen. An explanation of these results can be found assuming the reactive form of chlorine to be an energy-rich chlorine molecule. It can be shown from kinetic theory considerations that at pressures below 0.01 cm the mean free time between impacts is longer than the average life of excited chlorine molecules which is taken as of the order of (10) -6 secs. Hence a yield of one molecule of hydrogen chloride per atom of hydrogen is to be expected. At higher pressures where the kinetic mean free time is shorter than this the yield per atom should increase. The mechanism postulated for the reaction is

$$\mathrm{H} + \mathrm{Cl_2} = \mathrm{HCl}\ (\text{active}) + \mathrm{Cl}$$
$$\mathrm{HCl}\ (\text{active}) + \mathrm{Cl_2} = \mathrm{Cl_2}\ (\text{active}) + \mathrm{HCl}$$
$$\mathrm{Cl_2}\ (\text{active}) + \mathrm{H_2} = 2\ \mathrm{HCl}\ (\text{active})$$

On the basis of this mechanism an explanation is given for the effect of water vapor in the photochemical reaction between hydrogen and chlorine. The primary action of light in this reaction is assumed to be the production of energy-rich chlorine molecules and not atomic chlorine.

Primary and secondary valence. An attempt to improve the classification of valence: ARTHUR A. BLANCHARD. Valence is classified in terms of the nuclear atom with the aid of certain general postulates concerning the extra nuclear electrons. Polar valence is the algebraic charge. Non-polar valence in the number of pairs of electrons held in common in the sheath of the atom

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[1] Baltimore meeting, April, 1925.

in question and other atoms. Submerged polar valence is the net charge of an atom if the electrons held in common are credited wholly either to that atom or the other atoms according as to which is supposed to have the greater affinity for them. The maximum number of electrons possible in the successive layers or levels is 2. 8. 18. 32. . . . These numbers give stable layers, but the number rises with difficulty above 8 unless there is an accumulation in an outer layer. The number in the sheath rises above eight only in exceptional cases when the atom is surrounded by other atoms and the electrons of the sheath are all shared, *e.g.*, in the ammoniates and the carbonyls. In general, to completely classify valence, both the polar (or submerged polar) and the non-polar valence and the kernel charge and the number of electrons in the sheath must be given. No line of demarcation between primary and secondary valence can be found, but it is believed that the valence of each atom in all compounds with determinable molecular weight can be classified if we will admit that in exceptional cases single electrons and triplets and even quintuplets can be held in common in the sheaths of two atoms.

The preparation of hydrogen electrodes: GERHARD DIETRICHSON and C. N. SHAH. An extensive study was first made of the various methods described in the literature for the preparation of hydrogen electrodes. The difficulties encountered in connection with each of these were carefully noted. Following this the necessary conditions for the electrodeposition of platinum from solutions of pure chloroplatinic acid were determined. This involved in particular a proper control of the concentration and the current density relations. The character of the base on which the platinum was deposited was also found to be important. Hydrogen electrodes prepared by this method were found to give on the whole very satisfactory results.

Diurnal bands of platinum and stability of gold and platinum oxalates in silica gels: EARL C. H. DAVIES. (1) Diurnal bands of colloidal platinum have been made by diffusion, in periodic light, of oxalates into an acid silica gel containing platinic chloride. (2) Laboratory directions are given for making silica gels containing oxalates and either platinum or gold chloride with no red or blue gold or black platinum appearing, except by exposure to light. (3) Conditions are described for producing, alternately, red and blue bands of any desired width and at any distance apart, without having any diffusion of oxalates into the silica gel. (4) A photochemical after-effect is found in the reduction of gold oxalate in a silica gel. (5) A study has been made of the effect of aging on the reduction, in dark and in light, of gold oxalate in silica gels.

Further studies in luminescent Grignard compounds: W. V. EVANS and EDW. DIEPENHORST. Twenty new luminescent Grignard compounds are reported. The observation is made that apparently all Grignard compounds give luminescence on oxidation if the group combined to the magnesium is heavier than an ethyl group. The luminescence from the aliphatic compounds, however, is as a rule not as brilliant as from the aromatic. Luminescent Grignards have been made in fourteen different solvents and the effect of these solvents on the luminescence noted. A method for making Grignards in sealed tubes is suggested. The para-position is much the best position for producing this light and its intensity increases with the weight of the organic radical in the para-position. The spectrograms of four new compounds have been secured and the observation made that the spectra of the different compounds seem to occupy the same position on the plate, that is, between 447 $\mu\mu$ and 518 $\mu\mu$.

The constricted arc as a light source for photochemical work: GEORGE SHANNON FORBES and GEORGE R. HARRISON. The intensity, steadiness, economy, convenience, efficiency and life of the constricted column mercury vapor lamp are discussed in comparison and contrast with the standard sealed-electrode commercial lamp 8 mm in diameter. The best electrical and cooling conditions for emphasizing each of these factors are given, together with the best conditions for average operation. By absolute measurements it is shown that the constricted arc can be made to give about three times the visible and ultraviolet radiation given by the commercial arc per square millimeter of slit with the same power input, and that from ten to thirty times as much light can be obtained by making a sacrifice in the life of the lamp, which is largely offset by the ease and cheapness of renewal.

Studies in photographic sensitivity. VII. The action of hydrogen peroxide on single-layer silver halide plates: E. P. WIGHTMAN, A. P. H. TRIVELLI and S. E. SHEPPARD. Single-grain-layer silver halide plates are only very slightly affected by hydrogen peroxide, no matter what the concentration of H_2O_2 or time of treatment, unless they have been given a previous light exposure. In this case the number of grains showing developability seems to be greater than the sum of those produced by light and hydrogen peroxide separately. The reason suggested for this is that not only developable latent image but also undevelopable image is produced by light and that the hydrogen peroxide carries this over into developable latent image as well as makes its own proportion of grains developable. It is shown that Clark's hypotheses (a) that the so-called sensitivity of specks consists of silver oxide or hydroxide (b) that the action of hydrogen peroxide is a purely chemical one on this oxide or hydroxide, reducing this to silver which then makes the plate developable, and (c) that reversal is due to peptization of the silver by the hydrogen peroxide, are all untenable, not being supported by experimental facts. It is further shown that while our original hypothesis that the action of H_2O_2 is one of chemiluminescence is not completely substantiated it is at least not strongly controverted except by one fact, namely, that acid H_2O_2 seems to be slightly more effective than alkaline H_2O_2 in producing a latent image.

On the other hand, alkaline H_2O_2 may cause peptization of the sensitivity specks and hence work against the formation of developable centers.

The effect of solvents on the absorption spectrum of a simple dye: WALLACE R. BRODE. The absorption spectrum of benzeneazophenol dissolved in thirty organic solvents and in mixtures of some of them was measured in the visible and ultra-violet. No definite relation was found between the frequency of the absorption bands and either the refractive indices or the dielectric constants of the solvents, except for solvents of the same homologous series. When dissolved in a mixture of two solvents, the absorption band is that given by the dye dissolved in the most polar solvent even if only 1 per cent. of this solvent is present in the mixture. The absorption limits of the solvents for a layer 1 cm thick were measured and form a gradual series of radiation filters between a frequency of 850 and 1,350.

The cathodic deposition of metals: K. FRÖLICH and GEO. L. CLARK. *I. Theory of the mechanism:* 1. There is no evidence of an intermediate state in the electrodeposition of metals. The discharge of a metallic cation and the subsequent crystallization of the atom thus liberated are two phenomena so intimately connected that they must be considered one process. (2) In the deposition of the metals of the iron group a resistance has to be overcome which can not be traced back to specific properties of the electrolyte. A closer examination shows that the same type of resistance is encountered in the deposition of most metals and gives rise to what is termed the "true metal overvoltage." (3) The true metal overvoltage is highest for metals giving low hydrogen overvoltage and *vice versa.* By discussing this phenomenon in view of the hydride theory of hydrogen overvoltage, the conclusion is arrived at that the true metal overvoltage is caused by the interference of hydrogen with the process of building up the normal space lattice of the metal, while the discharge reaction itself is a reversible reaction for all metals. (4) The relation between metal overvoltage and hydrogen overvoltage appears to be very helpful in explaining the cathodic crystal formation of the individual metals.

II. A preliminary experimental X-ray study of electrodeposited nickel: (1) Thirty Laue, monochromatic pinhole and powder diffraction photographs have been taken of nickel films electrodeposited on platinum and on aluminum, the films being split off in the latter case. These specimens were deposited from chloride, sulfate, sulfate containing gelatine, complex oxalate and complex ammonium electrolytes. With the sulfate electrolyte the anode metal, temperature, concentration and current density were varied. (2) The structure of the platinum foil is derived from the well-defined figures characteristic of a strongly rolled metal. (3) The metal deposits of nickel all show the tendency of the crystals to orient themselves with the 100 planes parallel to the electrode surface, though under a condition of strain. Powder diffraction spectra characteristic of random orientation were obtained only with the high temperature electrolyte. With current densities as low as 0.10 amps./cm^2 the orientation is maintained. Complex ammonia electrolytes give best orientation which must be connected with the vigorous hydrogen evolution and hydride formation. Other deposits are compared. A deposit from sulfate electrolyte split from an aluminum electrode produced a single broad diffraction ring with Mo K alpha rays, thus indicating the extremely small size of the crystals. (4) Copper deposited on platinum at high current densities shows orientation of crystals contrary to other work. (5) The experimental results are interpreted to support in general the theory of the mechanism of electrodeposition presented in the first paper of this series.

On the photochemistry of fluorescent dyes: PHILIP SUBKOW. It is shown that the action of light on the solutions of the alkali salts of eosin and fluorescein causes a photochemical reaction to accompany the fluorescence such that the alkali salt is hydrolized and a colloidal solution of the acid dye is formed. Accompanying this reaction is a photochemical precipitation of the colloid. Ozone or certain oxides in the presence of light apparently aid this reaction. That this reaction does not seem to obey the Einstein photochemical law or the Bunsen-Roscoe law in Wood's experiments is explained by the absorptive effect of the colloidal dye on the incident radiation and effects of convective currents. Further, the so-called protective action is explained as due to the absorption of light by the colloid formed by the temperature hydrolysis of the salt.

Note on the radiation theory of chemical reactions: PHILIP SUBKOW. Applying the Gibbs equation to Baly's theory of stationary states and phase quanta, it is shown that the absorption regions of N_2O_5 as calculated from the velocity of decomposition of N_2O_5 corresponds to those actually observed.

The versatility of ferrous hydroxide: PETER FIREMAN. Freshly precipitated ferrous hydroxide, in undergoing oxidation through the action of the air, gives rise to the formation of a long series of well-defined colored pigments, in dependence on slight changes in the composition and conditions of the mother liquor. Black ferro-ferric oxide, yellows of the composition $Fe_2O_3 . H_2O$ and browns of the composition Fe_2O_3 are briefly described and the broad conclusion is drawn that the oxidation at low temperatures leads to the formation of hydrated oxides of iron yellow in color while the oxidation at higher temperatures leads to the formation of anhydrous oxides of iron.

The catalytic synthesis of water vapor in presence of metallic nickel: ARTHUR F. BENTON and PAUL H. EMMETT. A study of the catalytic combination of hydrogen and oxygen over metallic nickel has shown that the water formation is accompanied by superficial oxidation of the catalyst. When the surface has become completely covered with oxide the rate of catalysis suddenly decreases to a small value. The reduction of such a completely oxidized surface by pure hydrogen exhibits autocatalysis, but even the maximum reduction rates so obtained are small in comparison with the rates of hydro-oxygen combination at the same temperature. The evidence indicates, however, that the interface area, on which the rate of reduction depends, is much greater in the catalytic process than in the reduction. The conclusion is reached that the catalysis can be largely and perhaps entirely accounted for on the theory of successive oxidation and reduction of the catalyst.

The preparation of phosgene-salts: ALBERT F. O. GERMANN and CHARLES RUSSELL TIMPANY. In pursuit of the study of phosgene solutions, the ordinary methods of preparing salts were found to be inadequate in the preparation of phosgene-salts. To carry out these preparations, an apparatus has been devised in which 100 grams of crude salt may be prepared and purified by recrystallization and washing in phosgene solution without contact with the atmosphere, by a reaction in which metallic chlorides are neutralized by a phosgeno-acid, as follows: $CoAl_2Cl_8 + CaCl_2 = CaAl_2Cl_8 + CoCl_2$. A method of analysis of the product, which carries phosgene of crystallization, is given. The vapor tension and solubility of the salt in phosgene at 25° are given.

A general theory of solvent systems: ALBERT F. O. GERMANN. Based on the well-known behavior of water and of ammonia solutions, it would seem plausible to expect the typical ions of acids to deviate from the familiar H^+ type, just as the typical ion of bases is known to deviate from the OH^- type, when a wide variety of solvents is investigated. The term ''parent solvent'' is defined, and its relation to a system of related acids, bases and salts outlined. Application of these ideas is made to phosgene, which is shown to yield an acid in which CO^{++} replaces H^- of the familiar acids. Reactions of this acid in phosgene solution parallel the reactions of familiar acids in water solution. Applications to other solvents are suggested.

Note on some properties of some soluble borates: F. P. DUNNINGTON. When lithium carbonate in excess is boiled with boracic acid solution, there is formed lithium di-meta-borate. This is very soluble in cold water and may be concentrated to a syrupy consistency, while the corresponding sodium salt, borax, is little soluble. Potassium di-meta-borate, made by mixture of molecular weights of potassium hydrate and boracic acid, is soluble in about four parts of water. Solutions of lithium, sodium and potassium di-meta-borate are alkaline to litmus and to phenol phthalein. If each of these in solution is titrated with boracic acid until neutral to phenol phthalein, it will in each case require exactly one more molecule of boracic acid and so form the tetra-meta-borate. The sodium tetra-meta-borate is soluble in about four parts of water. The stronger water solutions of borates present the antiseptic properties of boracic acid in a more concentrated form than has heretofore been employed in surgery.

Emulsification: BRIAN MEAD. Some unusual results have been obtained, using sodium oleate and sodium stearate as emulsifying agents. Sodium oleate can, under certain conditions, be made to give water in oil emulsions by exposure of its solution to air. Sodium stearate, under certain conditions, will dissolve in oil and will then act as an emulsifying agent for water in oil. The significance of these results is discussed.

The oxidation of benzaldehyde: BRIAN MEAD and J. D. COCHRANE, JR. Benzaldehyde, which is usually considered to be an example of an autoxidizable substance, has been found not to be so. The amount of oxidation which takes place (as measured by the actual absorption of oxygen) is found to depend entirely on the intensity of the light to which the benzaldehyde is subjected. If the source of light be cut off, when the oxidation is proceeding, the reaction ceases after a very short interval. It will proceed at the same rate if the benzaldehyde is again illuminated. Preliminary results with X-rays shows that these do not cause the reaction to proceed at all.

The partial molal heat content of ammonia solutions: GERHARD DIETRICHSON, R. T. LESLIE and J. E. WHITTENBERG. The partial molal heat content of ammonia solutions has been determined at 25° C. over a range of concentrations from 0.1 to 0.7 mol-fraction of ammonia. This was done by means of an adiabatic calorimeter involving a distillation process. The amount of electrical energy required to vaporize definite quantities of water and ammonia from solutions of different concentrations was first determined. The heats of vaporization so obtained were plotted against the corresponding mol-fractions. The partial molal heat contents were in turn obtained by making use of the method of intercepts. The experiments carried out on ammonia solutions represent an attempt to supply some of the thermal data that are needed in connection with the absorption refrigeration process.

The mechanism of the fixation of nitrogen as sodium cyanide: E. W. GUERNSEY and M. E. SHERMAN. It has been found that the formation of sodium cyanide in a heated mixture of sodium carbonate, carbon and iron proceeds by the following steps: Sodium carbonate is reduced to give metallic sodium, metallic sodium reacts with carbon to form sodium carbide and sodium carbide absorbs nitrogen to form sodium cyanide, this latter reaction occurring in the gas phase. Each of these steps has been carried out, and it has been shown to be improbable that there is an appreciable amount of cyanide formed except through this series of reactions. Both the formation of sodium carbide from the elements and the absorption of nitrogen by the carbide are distinctly reversible reactions. Iron appears to exert marked catalytic action only on the final reaction, the formation of cyanide from carbide and nitrogen.

ARTHUR E. HILL
Chairman