

THE AMERICAN CHEMICAL SOCIETY

DIVISION OF PHYSICAL AND INORGANIC CHEMISTRY

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The use of radon in studying radio-chemical problems: S. C. LIND.

The determination by a chemical method of the mean effective path of alpha-particles in small spheres: S. C. LIND and D. C. BARDWELL. The mean linear path of alpha-particles in a gas contained in a sphere depends on the point of origin of the particle. If from the wall, it is $0.5 \times$ the radius of the sphere; if from the gas itself, it is $0.75 \times$ the radius. In order to determine the exact value under the experimental conditions in gas reactions, two series of measurements were made of the rate of combination of electrolytic hydrogen and oxygen: (1) with radon confined at the center of the reaction sphere, (2) with it mixed with the gases. The ratio of the velocity in (2) to that in (1) is, after suitable correction, that fraction of r sought. The value obtained is $0.61 \times r$. A possible interpretation in terms of diffusion of active deposit is presented.

Revision of the chemical effect of recoil atoms: S. C. LIND and D. C. BARDWELL. The experiments on the effect of recoil atoms in contributing to the chemical effects of radon in hydrogen and oxygen electrolytic mixture have been repeated under somewhat more favorable conditions than those originally employed in part II. The results confirm the earlier experimental ones satisfactorily. Certain apparent discrepancies between the inverse square of the diameter law and the recoil atom effect are removed.

Oxidation, reduction and decomposition of the oxides of carbon: S. C. LIND and D. C. BARDWELL. The rate of the following gas reactions have been studied kinetically when produced at ordinary temperature by radon: The decomposition of CO and of CO₂ (no reaction); reduction of CO by O₂; reduction of CO and of CO₂ by H₂. All of the rates are relatively rapid except that of decomposition of CO₂. The M/N values are mainly those to be expected on the theory of active gas ions forming addition products with one or two neutral molecules. The theory is advanced that the CO₂ ion reacts with neutral CO₂ to form an addition product (just as in the case of CO), but that this complex again decomposes into CO₂, giving no resultant reaction. This is supported by the evidence obtained by introducing H₂ as an acceptor for the CO₂ ions which is found to lead to rapid reduction of CO₂. It is shown that it is not merely a matter of the action of active hydrogen on neutral CO₂. The products of all the reactions have been analyzed, but owing to the small quantities of gases being dealt with, some of the results are not yet regarded as final.

A method for photographing the disintegration of atoms, and photographs of single and double atomic collisions, and a new type of rays: WILLIAM D. HARKINS and E. W. RYAN. In the collision of an alpha particle or helium nucleus with the nucleus of an atom of air three tracks are seen to radiate from a point. If a fourth track is present it represents either (1) the dis-

integration of the bombarded nucleus, or (2) a double collision. In a simple collision momentum is conserved, and all of the tracks lie in one plane. In a disintegration or a double collision momentum should be conserved if all of the tracks are considered, but, unless by accident, all of the tracks will not be coplanar. By taking 41,000 photographs of alpha ray tracks in air, argon and other gases the writers have obtained two photographs which represent either double collisions, a very improbable event, or an atomic disintegration. One of these was obtained in air, the other in argon. The photograph in argon gives the appearance to be expected if the helium nucleus first hit an argon nucleus and the argon nucleus, within a distance of $\frac{1}{2}$ mm, hit a second argon nucleus. A double collision of this kind is very much more improbable in air than in argon, and the photograph secured in air seems to indicate that a double collision did not occur. A new kind of rays, called zeta rays, have been found.

Reactions in phosgene solution. I: ALBERT F. O. GERMANN. Liquid COCl₂ does not react with metals nor is it in general a solvent for metallic salts (Beckmann and Junker). It dissolves AlCl₃ readily, forming phosgenates (Baud). Potassium, distilled in vacuo, covered with liquid COCl₂, shows no tarnish after a year; this is typical of the inactivity of the metals towards this solvent. However, covered with COCl₂ and exposed to the sunlight in ordinary soft glass tubes, potassium becomes coated with a violet deposit, which has the appearance of finely divided potassium; copper and zinc are corroded; and aluminium dissolves as AlCl₃, producing a yellow solution, which soon develops enough color to stop the reaction by absorbing the active wave lengths; in each case a gas (carbon monoxide) is evolved during isolation; magnesium is not attacked. Amalgamation makes Al active towards liquid phosgene, but has no effect in the case of Zn and Cu, whose chlorides are insoluble. Chlorine dissolved in COCl₂ attacks Al and Hg, but does not attack Mg. COCl₂ containing dissolved AlCl₃ attacks potassium, producing a rather voluminous precipitate and evolving a gas. The behavior of COCl₂ towards the metals in the presence of AlCl₃ is so unusual that this type of reactions has been given special study, the results of which are presented in another paper. Liquid COCl₂ converts KI into KCl and I₂, crystals of iodine separating from the solution as the reaction proceeds; CNI is more slowly decomposed; the usefulness of KI + Na₂S₂O₃ to separate Cl₂ from COCl₂ is thus brought into question.

Reactions in phosgene solution. II. The reaction of calcium with phosgene: ALBERT F. O. GERMANN and KENNETH A. GAGOS. It has been shown that, while metals in general do not react with COCl₂, a reaction may take place in the presence of AlCl₃, which is very soluble. In a preliminary survey, magnesium, calcium, zinc and cadmium, as well as potassium (as indicated in a previous paper) were found to yield a gas, shown to be carbon monoxide, with COCl₂ in the presence of AlCl₃. The compound with magnesium is liquid at ordinary temperatures, becomes very viscous when cooled, and yields a two layer system with COCl₂. This compound is under investigation. The compound with cadmium is

solid, and appears to be very soluble, but the reaction is slow; other methods of preparing it are being worked out. Calcium and magnesium react with great readiness, so that the reaction comes to completion in a relatively short time. It was found that the amount of action was proportional to the amount of AlCl_3 present, provided metal and COCl_2 are in excess. By saturating solutions containing weighed amounts of AlCl_3 , and dephosgenating the salt formed, residues of constant composition were formed, whose analysis led to the formula $\text{CaCl}_2 \cdot 2\text{AlCl}_3$. Vapor tension-composition measurements at 19.5°C . showed that the crystals separating from the solution contain two molecules of phosgene, so that their formula is $\text{CaCl}_2 \cdot 2\text{AlCl}_3 \cdot 2\text{COCl}_2$. The vapor tension of the compound at this temperature is about 25 mm.

The critical temperature and pressure of phosgene: ALBERT F. O. GERMANN and QUIMBY W. TAYLOR. Measurements have been made of the critical temperature of COCl_2 , but as far as we are aware, the critical pressure has not been measured. The COCl_2 used in this investigation was a technical sample obtained from the Chemical Warfare Service, and was purified by passing the gas over the usual absorbents for impurities, and by repeated fractional distillation under diminished pressure, until the vapor pressure at zero became constant. It was found impossible to prepare pure COCl_2 in this way (see also SCIENCE, 57, 564), as not one sample examined showed monovariance when liquefied at higher temperatures. The value obtained for the critical pressure, $P_c = 65 \text{ atm.}$, is therefore probably somewhat too high. The value obtained for the critical temperature, $T_c = 273 + 182$, is one degree below that obtained by Hackspill and Mathieu, and five degrees below that obtained by Paterno and Mazzuchelli.

The measurement of the heat of adsorption of gases by catalysts: R. A. BEEBE and H. S. TAYLOR. A method has been devised for the direct measurement of heats of adsorption. It consists in determining the temperature rise produced in the mass of a given catalyst when the gas to be studied is introduced into the system. The catalyst material is contained in a special vacuum vessel to facilitate thermal insulation. The heat capacity of the system is determined by liberating into the system a measured amount of electrical energy, using a resistance wire distributed throughout, but insulated from, the catalyst. The heats of adsorption of hydrogen on nickel and on copper have been determined as 14,000–20,000 calories and 9,600 calories respectively per mol of adsorbed gas. These values are markedly higher than the heat of vaporization (450 calories approx.). The measurements are being extended to other gases, other catalysts, and other preparations of the above catalysts, since the values obtained depend in part on the characteristics of the adsorbant.

Studies on solubility. The ideal activity coefficient of strong electrolytes in the presence of mixed electrolytes: J. N. BRÖNSTED and V. K. LAMER.

Overvoltage: WILLIAM D. HARKINS and H. S. ADAMS. The hydrogen overvoltage of mercury is found to be a linear function of the logarithm of the current density over a very extensive range if the cathode is carefully

pre-polarized; it decreases 2 millivolts per degree of rise of temperature, and remains constant as the pressure is varied between 14 and 2,300 mm. Stirring the electrolyte by a stirrer or by bubbling gas through it decreases the overvoltage of a number of metals, especially for those of high overvoltages at low current densities. A superimposed alternating current lowers the overvoltage in most cases but increases that of copper except at very low current densities, whether the copper is smooth or rough. The overvoltage of 12 metals at 25°C . was determined over a considerable range of current density. In agreement with the early observations of Harkins overvoltage is found to be related to the position of the element in the periodic system. Rough cathodes were found to give lower overvoltages than smooth ones. Overvoltage increases with time.

Two types of overvoltage: L. J. BIRCHER, WILLIAM D. HARKINS and GERHARD DIETRICHSON. Opposite opinions concerning the characteristics of overvoltage have arisen through the failure to recognize that there are overvoltages of two types. What we will designate as type A overvoltage is peculiar to active metals, has a positive temperature coefficient and its value corresponds closely to the single potential exhibited by the metal. This type of overvoltage persists in certain instances even though the current density is quite high. Certain recent investigations have given incorrect indications as to the characteristics of ordinary overvoltage by carrying out the work in a range in which overvoltage of type A is partly in effect. Ordinary or type B overvoltage has a negative temperature coefficient which for the current densities investigated, is 2 mv per degree for mercury, gold and copper; so thus far it has been found to be independent of the metal.

Effect of pressure upon overvoltage: In 1914 Harkins and Adams found that the hydrogen overvoltage of mercury remains practically constant between 14 and 2,300 mm, and Newbury found oxygen overvoltage to be constant between 1 and 100 atmospheres. Later work by other investigators indicates that on the contrary hydrogen overvoltage, at least for mercury, lead and nickel, increases with extreme rapidity as the pressure is lowered below 300 mm. The present investigation shows that the apparent great increase is fictitious, and is probably due to the failure of the comparison hydrogen electrode, used also as an anode, to function properly at low pressures. The present work indicates that in the cases of mercury, lead, and nickel at least, the potential of the cathode remains constant as the pressure is lowered to 11 mm, so the increase of overvoltage is very slight, being equal only to the small decrease of the potential of the hydrogen electrode. These results were obtained by using the mercurous sulphate electrode, instead of the hydrogen electrode, as the direct standard of reference, and by a comparison of the hydrogen and mercurous sulphate electrodes at different pressures.

Adsorption by precipitates VI; the adsorption of precipitating ions from mixtures of electrolytes: HARRY B. WEISER. The precipitation value for colloids of mixtures of electrolytes is influenced by the so-called antagonistic action of the precipitating ions and by the stabilizing

action of the ions having the same charge as the colloid. In cases where the influence of the stabilizing ion is slight, the precipitation values of mixtures show an approximately additive relationship since the antagonistic action of ions even of varying valence is not so marked as usually supposed in the region below the precipitation concentration of each. On the contrary, the antagonistic action is frequently so slight that the precipitating effect of mixtures of ions of the same or varying valence is less instead of greater than the additive value because of relatively greater adsorption of each at concentrations considerably below their precipitation value. Investigations on the hydrous oxides of iron, chromium and tin with precipitating ions showing a wide variation in their degree of hydration, disprove Freundlich's view that the hydration of a colloid and of the precipitating ions determines whether coagulation takes place at a higher concentration with mixtures than with a single electrolyte. The precipitation value of mixtures is higher than that of a single electrolyte in case an ion having the same charge as the colloid is so strongly adsorbed within certain concentrations that it opposes the action of the precipitating ions.

Adsorption of dyes by gels under a varying pH: R. E. MARKER and NEIL E. GORDON. Solutions of acid and basic dyes of a varying hydrogen ion concentration were shaken with silica, alumina and ferric oxide gels until equilibrium was established. The adsorption of dyes was then determined when it was found that the amount adsorbed by the ferric oxide and alumina gel in most cases was a function of the hydrogen ion concentration, while the change of adsorption with hydrogen ion was small in most cases with the silica gel.

Adsorption of dyes by gels under a varying pH in the presence of inorganic salts: C. E. WHITE and NEIL E. GORDON. The adsorption of acid and basic dyes was tried with silica, alumina and ferric oxide gels, while the hydrogen ion was changed within such limits as were possible under the conditions of the experiment, and while some inorganic salts of a definite concentration (usual .05N) was present. The inorganic salts cut down the adsorption in most cases.

Adsorption by activated sugar charcoal: ELROY J. MILLER. Evidence is presented to prove that adsorption of electrolytes from solution is accompanied by hydrolysis. Solutions of a number of salts when treated with pure, ash and nitrogen-free, activated sugar charcoal became alkaline, indicating that some hydrolysis had taken place with subsequent adsorption of the acid. By suitable means these adsorbed acids were recovered from the charcoal, identified and found to be equivalent in amount to the bases set free. This is in accord with the results obtained by Bartell and Miller (*J. Amer. Chem. Soc.*, 44, 1966 [1922], 45, 1106 [1923]) and in disagreement with the views of Michaelis and Rona (*Biochem. Zeit.*, 97, 57 [1919]), and Odén and Anderson (*J. Phys. Chem.*, 25, 311 [1921]), who maintain that hydrolytic adsorption does not take place.

Adsorption of inorganic salts by alumina gel under a varying hydrogen ion concentration: E. B. STARKEY and NEIL E. GORDON. .05N solutions of potassium nitrate,

potassium sulfate, potassium acid phosphate and the same salts of calcium, each having a varying hydrogen-ion concentration, were shaken with alumina gel until equilibrium was established. The adsorption of the different ions was determined. It was found that the hydrogen-ion concentration had marked effect on the amount of adsorption of the respective radicals.

The rôle of hydrogen ion concentration in the precipitation of colloids: H. V. TARTAR. A study has been made of the effect of hydrogen-ion concentration (pH) on the precipitation of mastic, gamboge, arsenious sulfide and aluminium hydroxide with electrolytes. Each of the negatively charged colloids is precipitated by acids at a given hydrogen-ion concentration regardless of the concentration of the sol. Different bases precipitate aluminium hydroxide sols of varying concentrations at the same pH. With salts, equal concentrations of ions of the valence are required to precipitate a given sol at the same pH and in nearly all cases the ion bearing a charge similar to that of the colloid particle is without effect. The efficiency of ions in precipitation is not absolute but must be considered with reference to the hydrogen-ion concentration.

Effect of light and H-ion concentration on the formation of colloidal gold in silicic acid gel. Rhythmic bands of purple of Cassius: EARL C. H. DAVIES. Experiments show that with silicic acid, gold chloride gels some remarkable effects of light are evident and that it is the light of short wave lengths which functions, if H_2SO_4 is present. The experiments remove W. D. Bancroft's objection to H. H. Holmes' diffusion theory of Liesegang band formation. A series of experiments shows that there is a distinct relation between H-ion concentration and the size of the "pockets" in which the gold is formed. A striking lecture experiment shows the influence of light on reduction. Purple of Cassius was obtained in true Liesegang bands.

The effect of hydrophillic colloids on the size and distribution of particles in electrolytic precipitation. I. Gelatin and basic lead carbonate: DORMAN MCBURNEY and W. G. FRANCE. The analogy between the effect of gelatin on the character of the deposit in the electro-deposition of metals and the electro-precipitation of salts is suggested. The effect of gelatin on the size and distribution of particles in the electro-precipitation of basic lead carbonate at $20^\circ + 1^\circ$ was studied. Photomicrographs of the product were taken and the size and distribution of particles determined by the method of Green. The data indicate that the presence of gelatin in concentrations from 0.013 per cent. to 1 per cent. is accompanied by a marked decrease in the average size of the particles of basic lead carbonate. A product of much greater uniformity in particle size is obtained in the presence of gelatin than in its absence.

Sol stability under centrifugation: W. G. FRANCE. The relative stability of a number of sols under centrifugation has been determined by observing the time required for the precipitation when definite volumes of sols are acted upon by known centrifugal forces. The sols investigated were $Fe(OH)_3$; Sb_2S_3 ; gold prepared by three different methods; and an ethyl alcohol gold sol

prepared by the Bredig method. The decreasing order of relative stability was found to be $\text{Fe}(\text{OH})_3$; Sb_2S_3 ; gold by Bredig method; gold by Tannin reduction; gold by formaldehyde reduction; and gold ethyl alcohol sol by Bredig method. It was further observed that, on standing after precipitation, the precipitated phase gradually diffused back into the dispersion medium in all cases except that of the ethyl alcohol, provided that centrifugation had not been carried on too long after precipitation. It is suggested that the stability may in part be accounted for on the assumption that a protective action is exerted by adsorbed films of the dispersion media, the nature of which are influenced by the methods of preparation of the sols.

A theory of emulsions and the inversion of emulsions: WILLIAM D. HARKINS. In 1917 the writer proposed a theory according to which the stability of emulsions, of the type produced by soaps, is dependent upon the existence, around the droplets, of a film of molecules, with the polar ends oriented toward the water, and the non-polar end toward the oil. A second, and independent, part of the theory considered the molecules as capable of representation as the frustra of cones (or in a plane as wedges). With sodium oleate drops of oil form inside the water. By a change from sodium to magnesium or calcium oleate the cross section of the polar or water-like end of the molecule is not greatly changed, but the substitution of two paraffin hydrocarbon chains for one increases the cross-section of the non-polar or oil-like end by about 42 per cent. Thus the polar end of the molecule becomes the smaller end of the frustrum; so the emulsion is inverted and the water drops become the inside phase. Naturally the size of the polar end of the molecule is also of importance. The paper will present evidence in favor of the theory.

A method for the study of rapid adsorption of gases in liquids: P. G. LEDIG and H. E. WEAVER. An apparatus is described which gives a photographic record of the course of absorption of a CO_2 bubble in a stream of hydroxide solution. From this photographic record the rate of absorption over the period of the absorption can be determined. A number of figures are presented showing the effect of concentration, bubble volume and other variables upon the rate of absorption.

The free energy of mercurides: ROSCOE H. GERKE. Alloys and metallic compounds are important classes of substances for which there are few free energy data. It is the purpose of this paper to collect available data on metallic compounds and solid solutions containing mercury, and, incidentally, point out that the method of calculating these quantities involves the use of partial molal free energy. Hitherto, the concept of partial molal free energy has not been used to split up the free energy of formation of a compound from its constituent elements into two parts, as has been done in this paper. In the case of the mercurides, and other metallic compounds, it will be seen that the free energy of formation of the compound from its elements is equal to the sum of the separate free energy changes which the elements undergo in the formation of the compound.

The conventions have been such that the free energy of

formation, ΔF (25 degrees) = -18,351 calories, means that there has been a decrease at 25 degrees and 1 atm. of free energy attending the formation of one mol of NaHg , from one atom of Na and 5 atoms of Hg. This decrease has been divided between the decrease for the sodium and the mercury respectively, such that F_2 equals -18,046 calories and F_1 equals 61 calories per atom. It is to be noted that the more electropositive the metal, the greater is the free energy change, except for the case of lithium.

The most striking and unexpected conclusion which can be drawn from these data is that the mercury does not greatly change in free energy, when it enters into chemical combination with a more electropositive metal. In other words, the vapor pressure of pure liquid mercury is only very slightly greater than the partial pressure of mercury from an amalgam saturated with a mercuride. On the other hand, the electropositive metal decreases in free energy more than the mercury in the formation of the compounds.

Although the free energy of other metallic compounds and also compounds of the type represented by iodine chloride can be calculated by the above method, it does not seem feasible to make similar measurements for a simple compound such as sodium chloride, since it is not possible to have solid sodium chloride in equilibrium with its solution of sodium in liquid chlorine.

In conclusion, it may be stated that, if mercury reacts with a more electropositive metal to form a mercuride, the change in free energy for the mercury is small compared with that of the more electropositive metal.

A relation between energy of reaction between atoms and electron affinity of electronegative atoms: ROSCOE H. GERKE. The energy of formation of halides from monoatomic elements in the gaseous state has been found to give an approximately constant value. In the case of KCl , NaCl , HCl , TlCl and AgCl , the values are respectively, 124.4, 115.3, 109.5, 108.3, 98.0 Kg. cal. The average energy of formation is 111.1 Kg. cal., which is in close agreement with the value, 111.0 Kg. cal., for the electron affinity of chlorine. In the case of bromides and iodides the agreement is not so close. These rough agreements seem to indicate that the energetics for these simple chemical reactions are accounted for by the differences in energy level of electrons in the atoms before and after the reaction. Also, the order of electropositive elements in the electromotive series seems to be governed by the heats of evaporation of the electropositive elements and the heats of sublimation of their compounds.

Relations involving the disintegration of atoms: WILLIAM D. HARKINS. The paper shows that the work of Rutherford on the disintegration of light atoms directly confirms the first definite theory of the composition of the light atoms, that of Harkins and Wilson. Thus, atoms in which the hydrogen is bound in the form of alpha particles have in no case given off hydrogen when bombarded by swift alpha particles. Also atoms in which the theory indicates that the part or parts of the nucleus which contains hydrogen not bound into alpha particles has the formula pe or $(pe)_2$, have not disintegrated to give long range hydrogen particles. Thus, as

indicated by one of the corollaries of the theory proposed by Harkins, hydrogen is found to be in unstable combination only when the part of the nucleus which does not consist of alpha particles contains more protons than electrons. This correspondence between the experimental facts and the theory was noticed independently by Fajans and the writer.

Characteristics of the alpha-ray bulb as a source of ionization: D. C. BARDWELL and H. A. DOERNER. For the corrections involved in Part III, a knowledge of the characteristics of the alpha-ray bulb as a radiator, as affected by the tip and neck, by the thickness of the wall and obliquity of passage of alpha-particles through it, and by the diameter of the bulb (reducing it to zero dimensions in order to afford radiation from a point source) is necessary. In addition, the other corrections applying to the outer sphere itself are treated, such as the dead-arm correction and the change of ionization intensity with the pressure. The recoil atom effect as revised in paper V is also used as a correction for the results, to reduce them to the same conditions as those obtaining outside the alpha-ray bulb, through which recoil atoms cannot penetrate.

A study of the factors influencing the velocity of crystallization (V. C.) of substances from supersaturated solutions: JOHN D. JENKINS and JAMES H. WALTON. An apparatus for the determination of very rapid crystallizations by following the process with a dipping refractometer immersed directly in the crystallizing solution has been devised and described, and a large number of runs made to determine the effect of the addition of various substances upon the V. C. of naphthalene and urea from their solutions in methyl alcohol. The results of those runs have been tabulated. The ability of a substance to affect the V. C. seems to be a very specific property. A thermometric method of measuring the V. C. of substances in various solvents has also been worked out and the apparatus and method described. It consists in inoculating a supersaturated solution with a known weight of standard seed crystals and measuring the rate of rise of temperature of the rapidly stirred solution in a thermally isolated cell. The constants are calculated from the curve this obtained after correction for radiation and heating due to the stirring of the solution.

Measurements of the V. C. of three solutes, urea, acetanilid and ammonium nitrate have been made by this method in various solvents and mixtures. The results of this investigation show that the important factor in the V. C. of these substances from such solvents and mixtures is the viscosity of the medium. The relation between the velocity constant, K , and viscosity is given by the equation— $KS = A/\eta$, where $0.57 - \eta$ is the viscosity of the solution, A is an arbitrary constant depending upon the solute, and S is the surface area of the crystals per unit volume of solution. The results of these experiments have been discussed in relation to some of the present theories and the inadequacies of some of these pointed out. Berthoud's formula— $dc/dt = (DS)/(\delta + D/K)$ ($C_0 - C$)—was shown to fit the facts better than any of the others. The temperature coefficient of the V. C. of acetanilid in several solvents has been deter-

mined and found to be due only to the decrease in viscosity of the medium at the higher temperature.

Heterogeneous Catalysis. I. The selective action of catalytic nickel in the hydrogenation of certain vegetable oils: A. S. RICHARDSON, C. A. KNUTH and C. H. MILLIGAN. The previous literature on selective hydrogenation is reviewed, and new data are presented to show that the hydrogenation of cottonseed, peanut and soya bean oils with use of nicked catalyst is characterized by the preferential conversion of linolic acid to oleic acid and its isomers. The selective character of the hydrogenation of these oils appears to be more marked with use of increasing amounts of catalyst and with increasing temperature up to an optimum in the neighborhood of 200 degrees C. The experimental results favor the view that intermediate adsorption compounds are formed between catalyst and unsaturated components. The nature of these adsorption compounds is discussed.

The catalytic activity of certain metals prepared by the reducing action of adsorbed hydrogen: L. H. REYERSON and KIRK THOMAS. Hydrogen, adsorbed by porous substances such as silica gel, reduced to the metallic state ions of the following metals, silver, gold, copper, platinum and palladium. Of these platinum, palladium and copper, supported by the silica gel, showed marked activity as catalysts in hydrogenation. At 0 degrees C. the palladium catalyst converted 95 per cent. of the ethylene used to ethane. At the same temperature the platinum catalyst converted 65 per cent. of the ethylene and at room temperature the copper catalyst converted 5 per cent. of the ethylene. These values represent averages, and they were obtained on passing the mixed gases through the catalyst once at a moderate rate.

Concerning zinc perchlorate: D. L. RANDALL. This salt, which was first mentioned by Serullas in 1831, has been little described in the literature. It was prepared by treating zinc carbonate with perchloric acid. On evaporation and cooling in a desiccator over fused calcium chlorid long needle-like crystals were formed. On analysis the results indicated the formation of the hexahydrate. The salt which is very soluble will deliquesce in a moist atmosphere but in a dry atmosphere will return to its crystalline form.

A further study of the sulfides and selenides of ammonium: A. S. KING and C. R. McCROSKY.

Fluosilicic acid III, titration and properties: C. JACOBSON. Schucht and Möller's (ber. 39, 3693, 1906) method has been improved. The acid is titrated with normal NaOH in two stages, by first adding an excess of a neutral salt like NaCl. The first stage titration takes place at five degrees or below, in concentrated solution, using methyl orange as indicator and may be represented by the following equations: $H_2SiF_6 + 2NaCl = Na_2SiF_6 + 2HCl$, $2HCl + 2NaOH = 2NaCl + 2H_2O$. The second stage titration serves as a check upon the first and is represented as follows: $Na_2SiF_6 + 4NaOH = 6NaF + H_4SiO_4$. The results are consistent and satisfactory. The properties such as specific gravity, index of refraction, odor, taste, stability, chemical activity, etc., of a 60 per cent. solution of fluosilicic acid have been recorded.

Solubilities of yttrium salts: B. S. HOPKINS, M. C.

CREW and HILDUR E. STEINERT. The salts used were prepared from the yttrium material purified in the investigation which gave the present accepted atomic weight value of yttrium. A saturated solution was prepared in a thermostat, definite portions withdrawn and the solution weighed in a crucible inclosed in glass stoppered weighing bottle. The amount of yttrium oxide was determined by igniting to the oxide and weighing. From these values the amount of anhydrous yttrium salt in solution in 100 grams of water was calculated. Values were obtained for the chloride, bromide, nitrate and sulfate of yttrium at temperatures ranging from 0 degrees to 95 degrees. The curves were all regular, showing for the chloride a slight increase of solubility with rise of temperature; for the bromide and nitrate somewhat greater increase in solubility and for the sulfate a regular decrease in solubility with rise of temperature. Dilatometer tests showed no change in hydration within the temperatures used.

Electrometric titration of iodate, bromate, chlorate, ferricyanide with titanous salt: W. S. HENDRIXSON. The results show that the halogen oxy-acids can be accurately determined at room temperature, and stopping at the end points; that is, without adding an excess of titanium and titrating back with another oxidizing agent. In the presence of sulfuric acid iodate and bromate show two sharp falls in potential, the first marking the complete destruction of the oxidizing acid and the second the reduction of the free halogen. All these acids give large, sharp rises in potential on adding a few drops of titanous solution at the beginning of the titrations.

The influence of gelatin on the transference numbers of hydrochloric acid: W. H. MORAN and W. G. FRANCE. The transference numbers were measured by the concentration cell method using M/10 and M/100 HCl at 25 degrees. The value for the anion was found to be 0.1699. The addition of gelatin over a concentration range of 0 to 20 per cent. resulted in a change in the value of the anion transference number from 0.1699 to 0.7772. Conductivity measurements of M/10 and M/100 HCl were made over the same gelatin concentration range. In both cases the conductivity was so reduced as to indicate that HCl was removed as a whole from the solutions by the gelatin. The results obtained are in agreement with the prediction previously made by one of us in collaboration with A. L. Ferguson (A. L. Ferguson and W. G. France, *J. Am. Chem. Soc.*, 43, 2161, 1921), in which it was stated that in acids the presence of the gelatin would result in an increase in the transference number of the anion.

The setting of plaster of Paris and its acceleration: HARVEY A. NEVILLE. The setting of plaster of Paris is accelerated by solutions of inorganic compounds and retarded by certain organic substances. The explanation of this as due to the increase (or decrease) in the solubility of CaSO_4 by the dissolved substance is unsatisfactory. The acceleration may be considered an example of "catalysis in hydration." The stages in the setting of plaster of Paris are apparently: (1) Absorption by the plaster of all the water in amounts up to four times its weight. A stiff gel is formed and a very slight tem-

perature effect is noted; (2) the gel breaks to form gypsum and free water, most of which gradually evaporates from the pores. Considerable heat is evolved in this stage due to the reaction: $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} + 1\frac{1}{2}\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 3900$ calories. Both the formation and the breaking of the gel are accelerated by inorganic compounds. The retarders act as protective colloids.

Chloroform hydrate and its transition point: ARTHUR E. HILL. The existence of the compound $\text{CHCl}_3 \cdot 18\text{H}_2\text{O}$, discovered by Chancel and Parmentier, has been confirmed. The compound can be formed by cooling the two components until ice appears, at -0.1 degree; in the absence of ice no compound is formed even on long contact. It is formed only at the interface between chloroform and water, and can not be obtained from either of the saturated liquids alone; the rate of formation is very low. In order to purify it for analysis, it is placed in a desiccator over ice, and maintained at 0 degrees or below; the excess liquid evaporates, forms compound on the ice in the lower part of the desiccator and leaves the stable system, compound-ice-vapor. The compound has a transition temperature into the two nearly insoluble liquids, chloroform and water, at $+1.45$ degrees. On warming, however, it shows suspended transformation into the liquids, and may be heated at least as high as 6 degrees before total disappearance. The possibility of superheating depends upon the slowness with which equilibrium is attained in the liquid state, the reactions being first the dissociation of fused compound into its components and second the separation of the liquid into two liquid layers. The phase-rule diagram shows that the compound must possess a metastable congruent melting-point which falls within the two-liquid area. Suspended transformation in a system of this character has not previously been noticed.

The rôle of pectin in gel formation: HARRY N. HOLMES and HARRIET A. HOWE. It seems probable that partial dehydration of hydrated pectin explains the formation of fruit jellies. The sugar acts as a dehydrating agent and the hydrogen ions are probably adsorbed with an influence on hydration. Alcohols take up part of the water from a pectin solution with formation of gels. Glacial acetic acid also takes up water from a pectin solution with formation of gels. So does the proper concentration of phosphoric acid and of hydrochloric acid and of sulfuric acid. A one per cent. solution of pure pectin in hot 0.1 N NaOH gels on standing. Perhaps pectin is a weak acid and forms sodium pectate, well hydrated. Ammonium and barium pectates have similar properties. Barium chloride solutions produce no gels with pectin solution but if a sodium pectate is first formed addition of any soluble salt forms a gel. So does direct addition of barium hydroxide to a pectin solution.

Gel structure: WILLIAM C. ARSEM. The viewpoint presented is that a gel is an intimate mixture of two phases, one solid and the other liquid. The solid phase is pseudo-crystalline. It forms a molecular lattice which differs from a perfect crystalline lattice in that it is greatly expanded and the atoms are not connected at all possible points. A large proportion of the auxiliary

valences are not brought into play except as they may function in holding molecules of the liquid phase. There are thus a great many voids of approximately molecular dimensions which are filled with the liquid phase. A discussion is given of the mutual relations of the sol, gel and crystal states and the conditions for their formation, together with explanations of some colloid phenomena such as swelling and syneresis.

Films: benzene derivatives: WILLIAM D. HARKINS and ELVAH GRAFTON. On account of the fact that the structure of benzene is unknown and since compounds of benzene are in general much more difficult to work with in films on water than the derivatives of the paraffins, practically no experimental work has been done with benzene derivatives. Using as a basis the orientation theory of surfaces, and the plane formula of benzene, Harkins, Davies and Clark in 1917 considered that the area per molecule should increase in the order pyrocatechol, resorcinol and hydroquinone. This is here confirmed experimentally. The area per molecule in square Angstrom units is found to be phenol, 36.6, pyrogallol, 42.7; pyrocatechol, 55.3; resorcinol, 96; hydroquinone (185). The value for hydroquinol is not comparable with the others, since the molecules in the film were not in contact. The surface polarity of these compounds increases in the order; phenol, pyrocatechol, resorcinol, pyrogallol and hydroquinol, and thus increases as the distance between the hydroxyl groups around the ring in the plane formula.

Preparation of manganates and permanganates in liquid ammonia and water systems: H. B. SIEMS.

A method of determination of the solubility of hydrocarbons in water and the solubility of a few cyclic hydrocarbons at 25° C.: ERNEST BATEMAN and CARLETON HENNINGSEN. A method is described for determining the solubility of hydrocarbons in water with an accuracy of at least ± 5 per cent. The method consists essentially of aeration of the saturation solution at elevated temperatures and passing the air and hydrocarbon through a combustion furnace. The solubility of a few cyclic hydrocarbons in water at 25° C. is given as follows: Benzene, 0.190 gms; cyclohexene, 0.020 gms; cyclohexane, 0.0050 gms; toluene, 0.057 gms; mesitylene, 0.0056 gms; durene, 0.0015 gms; and diphenyl, 0.00041 gms per 100 cc solution.

The solubility of some amino and nitro derivatives of benzene in water at 25° C.: ERNEST BATEMAN and ROY BAECHLER. The paper shows that nitro derivatives of benzene can be reduced to amino compounds up to the limit of their solubility in water. The amino group can then be determined by the usual Kjeldahl method. The solubility in water at 25° C. for nitrobenzene, m-dinitrobenzene, sym-trinitrobenzene, o-nitrochlorbenzene, p-nitrotoluene, o-nitrophenol, p-nitrophenol, o-aminophenol, p-chloraniline and m-nitroaniline are given.

The autoxidation of hydroquinone and the stability of the quinhydrone electrode: V. K. LAMER and ERIC K. RIDEAL.

Studies in photographic sensitivity III. Effect of oxidizers on the sensitivity and on the latent image: E. P. WIGHTMAN, A. P. H. TRIVELLI, S. E. SHEPPARD. Photo-

graphic one-grain-layer plates treated with copper sulfate solution before exposure are desensitized by increasing the "gamma" or slope of the normal exposure portion of their characteristic density-log exposure curves, maximum density being reached at approximately the same exposure for both treated and untreated plates. This is contrary to the effect on the original ordinary commercial plates in which the whole curve is shifted by the CuSO_4 treatment. The mechanism of the action in each case is probably dissimilar from the action of chromic acid and other oxidizing agents. The former is likely one of adsorption, the latter an oxidation effect. Some experiments on ordinary Graflex plates, treating the latent image with chromic acid for various lengths of time (exposure time constant) showed a gradual increase in destruction of the latent image, until very little remained on 16 hours treatment. Increasing exposures enormously does not increase materially the densities produced. The results are in agreement with previous work on desensitizing with oxidizing agents.

The size-frequency distribution of grains of silver halide in photographic emulsions and its relation to sensitometric characteristics VI. Photographic densities derived from size-frequency data: E. P. WIGHTMAN, A. P. H. TRIVELLI, S. E. SHEPPARD. A method of deriving experimentally the densities for any given exposure, in the characteristic H. and D. (density-log exposure) curve of a simple photographic emulsion from its grain size-frequency distribution has been investigated and briefly is as follows: (1) The size-frequency distribution of the grains per unit area (1 cm^2) is obtained; (2) the area-distribution of the different sizes of grains are calculated from this; (3) the area-distribution of residual grains after exposure and development is then found in the same way; (4) from (2) and (3) is then calculated the area-distribution of the developable grains; (5) the expansion ratio of developed to developable grains is found and (6) by means of this the area-distribution of developed grains is obtained; (7) the density for any given exposure and class-size of grains is calculated from the formula $D = \log 1/1 - r\bar{n}\bar{x}$, where r is the expansion ratio, n the number of developable grains of average size $\bar{x}$; (8) a composite density is obtained from the formula $D = \log 1/1 - (r_1 n_1 \bar{x}_1 \div r_2 n_2 \bar{x}_2 \div \dots \div r_n n_n \bar{x}_n$ and not by simply adding the densities for each class size.

The absorption spectra of 2(phenylazo) phenol and its derivatives: JOEL B. PETERSON, C. E. BOORD and A. W. SMITH. Twenty-four derivatives of the "orthohydroxy-azobenzene" type were prepared and their absorption spectra photographed in M/15,000 molar solution in 95 per cent. alcohol. The free dyes show a very persistent band in the region 280-380 which is prolonged on the red side almost to 500 for the lower intensities. The p-m-o order of displacement for the mono substituted phenyl derivatives is not evident in this dilution, except for the p-nitro phenyl derivative, which is markedly displaced toward the red. The phenyl, p-chlorophenyl, p-bromophenyl and p-iodophenyl series of derivatives show increasing displacement toward the red in the order given due to the weighing effect. The presence of alkali tends

to suppress the more persistent portion of the band characteristic of the free dye and to develop a new band in the region between 400 and 500. The order of suppression produced by ten moles of alkali per mole of dye is p-m-o for the mono substituted phenyl derivatives, the para derivative being suppressed the least and the ortho derivative the most.

The absorption spectra of phenylazodimethylaniline and its derivatives: DONALD M. COULTER, C. E. BOORD and A. W. SMITH. Twenty derivatives of the phenylazodimethylaniline type were prepared and their absorption spectra measured by the photographic method. The free dyes show a broad band in the general region 520-350 when photographed in M/15,000 molar solutions in 95 per cent. alcohol. The p-m-o order of displacement for substituents in the phenyl nucleus is not evident in this dilution. The absorption bands of the p-nitrophenyl and p-idiophenyl derivatives are markedly displaced toward the red. The presence of acid in the solution tends to broaden and split this band into two narrower bands occupying positions at 280-380 and 420-600 respectively. The band of shorter wave length is suppressed and the one of longer wave length intensified by increasing concentration of acid. The p-m-o order now appears in the intensity or persistence of the bands. In the shorter wave length band the ortho derivative is the most persistent and the para derivative the least. In the longer wave length band the reverse is true. The diethylaniline derivatives show less sensitiveness to acid than the corresponding dimethyl aniline derivative. When the p-methoxyphenyl and p-ethoxyphenyl derivatives are compared the reverse effect is noted.

Azido-dithiocarbonic acid. II. Determination of the acid and its salts: G. B. L. SMITH and A. W. BROWNE. Free azido-dithiocarbonic acid, HSCSN_3 , may be determined quantitatively by titration with a standard alkali, using methyl red as indicator. The use of methyl orange introduces a slight error in very dilute solutions. The acid and its soluble salts may be determined by titration with silver nitrate, using either the Gay Lussac or a modified Volhard procedure. An alternative method consists in weighing the silver azido-dithiocarbonate with due precautions to avoid explosion, or in determining the silver content of the precipitate by conversion to silver chloride. In the presence of chlorides, bromides, iodides, thiocyanates and cyanides, the azido-dithiocarbonate radical may be determined under suitable conditions by titration with an alcoholic solution of iodine.

Azido-dithiocarbonic acid. III. Electrometric titration. Equivalent conductivity: G. B. L. SMITH and G. H. BRANDES with A. W. BROWNE. Electrometric titration shows that azido-dithiocarbonic acid is comparable in strength with hydrochloric acid. An indicator changing at $\text{pH} = 5$ is ideal for use in its titration. Conductivity measurements reveal the fact that it is strongly ionized. The equivalent conductivity of the SCSN_3 ion at 25 degrees is about 40 as determined by measurements upon the sodium and the potassium salt.

Electrochemical change solutions (by title): HENRY E. ARMSTRONG.

Preparation of manganates and permanganates in

liquid ammonia and water systems: H. B. SIEMS. If a permanganate is treated with a strong base in aqueous solution it is reduced to a manganate. Since metallic amides are the bases of the liquid ammonia system, one might expect them to reduce permanganates to manganates. Experimentally, it was demonstrated that all prepared permanganates are soluble in liquid ammonia, and all available manganates are very insoluble in liquid ammonia. Organic and inorganic permanganates were reduced with corresponding amides, using anhydrous ammonia as a solvent. Lithium manganate, which Abegg considered as not capable of existence, was prepared in an aqueous solution. A solution of metallic potassium in liquid ammonia reacted with potassium permanganate to give the manganate. An excess of potassium solution gave manganese dioxide. Permanganates in contact with liquid ammonia undergo decomposition. Anhydrous lithium permanganate in anhydrous liquid ammonia decomposes almost instantly with liberation of heat.

The potential between tri and bivalent titanium: GEORGE SHANNON FORBES and LAWRENCE PERCIVAL HALL. A mixture of TiCl_3 and TiCl_2 was obtained by heating Ti, 99.9 per cent. pure, in HCl for 15 hours, first at 250°, then at 350°. Excluding air with pure CO_2 , it was dissolved and filtered into the cell. $\text{Hg}-\text{TiCl}_3, \text{TiCl}_2, \text{HCl } 4n \text{ KCl HCl } 0.1n \text{ Hg}^+$. All operations were at 0° C. The E. M. F. rose in 18 hours or less to a maximum, constant for several hours. Total Ti was determined gravimetrically and total reducing power by electrometric titration, giving TiCl_3 and TiCl_2 . Eight cells when recalculated by the logarithmic formula to equal or molar concentrations of TiCl_3 and TiCl_2 averaged 0.698 ± 0.005 volt. The normal potential, referred to the normal hydrogen electrode at 0° through the temperature coefficients of Lewis and Randall is 0.366 volt when HCl averages 0.05 M and decreases slightly as this increases, probably due to more rapid decomposition of TiCl_3 .

The effect of water vapor on systems of chlorine-solid potassium iodide and chlorine-solid potassium bromide: L. B. PARSONS and JAMES H. WALTON. When dry potassium iodide or potassium bromide is allowed to stand in contact with dry chlorine gas, no reaction takes place even after several hours. In the presence of water vapor a reaction takes place, the extent of which depends upon the concentration of water in the system. An apparatus was constructed for the study of the effect of different concentrations of water vapor on the reactions between solid potassium bromide and solid potassium iodide with chlorine. With potassium bromide the effect of temperature was also studied. It was found that for each temperature there is a minimum partial pressure of water vapor which must be reached before any considerable reaction takes place between the chlorine and the potassium halide. This minimum effective concentration of water vapor has been shown to correspond to the vapor pressure of a saturated solution of the various constituents of the system.

GRAHAM EDGAR,
Secretary