SCIENCE

FRIDAY, AUGUST 17, 1906.

CONTENTS.

THE ITHACA MEETING OF THE AMERICAN CHEMICAL SOCIETY. I.

THE thirty-fourth general meeting of the American Chemical Society met in the chemical laboratory of Cornell University, at Ithaca, N. Y., on June 28–30. The society met partly in general session and partly in sections as follows:

Inorganic Chemistry: L. M. Dennis, chairman. Organic Chemistry: G. B. Frankforter, chairman.

Physical Chemistry: W. Lash Miller, chairman. Industrial Chemistry: J. D. Pennock, chairman. Biological Chemistry: Waldemar Koch, chairman.

Agricultural and Sanitary Chemistry: E. B. Voorhees, chairman.

On Thursday evening there was a complimentary smoker given to the society by the Town and Gown Club. On Friday afternoon the members of the society attended the dedication of the Rockefeller Physical Laboratory. Following this, they left for an excursion to a hotel on Cayuga Lake, where dinner was served at 7:30. On Saturday morning Dr. E. Haanel, of the Department of Mines, Ottawa, Canada, gave an address on 'Electric Smelting Experiments at Sault Ste. Marie.' One hundred and thirty-two members of the society were in attendance on the meeting, which was a most enjoyable and successful one. The following are abstracts of papers which were presented:

GENERAL SESSION.

AFTER a brief address of welcome by Dean T. F. Crane and a response by President W. F. Hillebrand for the society, the following addresses were given:

The Terpenes and Colophonium with Some of Their Industrial Chemical Problems: G. B. FRANKFORTER.

The author in cooperation with students has been studying the terpenes and colophonium for a number of years. The pine family of the north and west has been

studied both from the strictly chemical and from the industrial standpoints. Large numbers of analyses of the wood of the Norway pine and the Douglas fir as to the amount of both the terpenes and colophonium were made. The stumps and roots of these species were likewise exhaustively studied. A chemical examination of the terpenes indicated that the common terpene present differed from the pinene of the southern pine, the boiling-point being lower, the optical properties and the compounds formed being different. A new series of compounds, the chlor-hydrochlorides, has been made both from the terpenes above mentioned and from common pinene. The colophonium from both the Norway pine and the Douglas fir has been shown to consist of two different acids. These acids are being carefully studied.

Harcourt and Esson's Method in Chemical Mechanics: W. LASH MILLER.

As the rate of a chemical change in a homogeneous solution depends on the temperature and on the concentrations of the dissolved substances, measurements of the rate are best made in solutions whose temperatures are kept constant by means of a thermostat and in which the concentrations are kept constant by dissolving quantities large in comparison with those generated or destroyed during the reaction. In 1866 Harcourt and Esson measured rates of change in solutions containing a large excess of each of the reagents but one. Although they pointed out the advantages of this method of working, their example was not followed. Hood, in 1878, used in excess each but two of the reagents; van't Hoff ('Études,' 1884) used equivalent quantities and compared the results of experiments with different initial concentrations; while from 1885 to 1895 it was the custom to work with more or less equivalent concentrations and to deduce the 'order'

of the reaction from a series of analyses. By this time the method of Harcourt and Esson was forgotten. In 1895 A. A. Noyes resuscitated van't Hoff's method; in 1901 Ostwald proposed a method which somewhat resembles Harcourt's; and in the same year Harcourt and Esson's way of working was revived in the laboratory of the speaker, where the principles of the method have been extended (method of constant rates) and applied to the study of chemical equilibrium (arsenic and iodine). The power of Harcourt and Esson's method as a tool of research was illustrated by a number of examples.

Some Problems for Agricultural Chemists: E. B. VOORHEES.

This paper is historical and suggestive, rather than containing the results of definite experiments. It points out the conditions heretofore existing in this country, which have encouraged agricultural chemists to demonstrate the principles already understood, rather than to investigate. Notwithstanding the larger use of commercial fertilizers in the east, and better farming methods in the west, there is an apparent exhaustion of soils, which calls for scientific investigation of those problems connected with the soil and its fertility.

The nitrogen question is supreme, notwithstanding the discoveries that have recently been made, in reference to both the symbiotic appropriation of nitrogen, and its abstraction from the air by electric means.

The Occurrence of Boracic Acid in Death Valley, California, and in Tuscany: EDWARD HART.

This was a description of two trips, one to Death Valley in 1902–3 and one to the soffoni of Tuscany in May, 1906. The boric acid occurs near Daggett, California, as colemanite, $Ca_2B_6O_{11}$, and as calcium

borate in borate mud. The colemanite is sent to Bayonne, N. J., and converted into borax. The borate mud is treated at Daggett with sulphur dioxid and the boric acid crystallized out and shipped. In Tuscany the boric acid vapors are passed into water which is then evaporated. The vapors from driven wells have a pressure sometimes of nine atmospheres and after purification are used for driving steam-ngines. Nearly pure ammonium sulphate is also produced.

AGRICULTURAL AND SANITARY CHEMISTRY.

E. B. Voorhees, chairman.

The Improved Refractometer Slide Rule and its Application: ALBERT E. LEACH and HERMANN C. LYTHGOE.

The refractometer slide rule was first described in the *Jour. Am. Chem. Soc.,* in 1904. Since then it has been somewhat improved and is now on the market. It is designed for the use of oil and food chemists who have occasion to employ the butyro or the Abbé refractometer. It readily converts indices of refraction (which the Abbé instrument reads directly) into degrees on the butyro-refractometer, and *vice versa.* It also enables one to transfer scale readings or refractive indices taken at any temperature into their equivalent at any other, thus avoiding troublesome calculations.

Comparative Effect of Organic and Mineral Matter in Soil-extract Cultures: OSWALD SCHREINER.

A series of experiments with wheat and other seedlings is reported in which the effect of the organic and inorganic constituents of the soil solution and of organic manures are studied. It is shown that the toxic effect of certain soil extracts is not entirely overcome by fertilizer salts, but is more markedly affected by organic substances, such as pyrogallol, the organic matter from ordinary stable manure, etc., as well as by treatment with certain other non-nutrient substances, or even by mere boiling of the extract, indicating the presence of volatile or thermolabile organic substances. Results are obtained by separating the organic and inorganic portions of a stable manure extract and studying the effect of the various fractions on wheat seedlings. The results show that the organic substances play a very large part in the effectiveness of the extract, and more especially through an action other than that of nutrition.

Chemical and Bacteriological Factors in the Ammonification of Soil Nitrogen: JACOB G. LIPMAN.

It is well known that organic nitrogen, either as applied in manures and fertilizers, or as forming a part of the soil humus, is utilized to an unequal extent in different soils. Since the crops growing on any soil do not derive their nitrogen food directly from the nitrogenous organic compounds, but make use of them only after they are changed into more simple substances in the processes of decay, it follows that the unequal utilization of the organic nitrogen, in different soils, is intimately related to the quantitative and qualitative differences in the development of certain classes of soil organisms. On the other hand, the soil bacteria are themselves influenced in their growth by the chemical and physical constitution of the soil; and the simplification of organic compounds in arable lands is, therefore, a function of both chemical and bacteriological activities. It is shown that when 100 c.c. of a ten per cent. solution of peptone is inoculated with ten grams of fresh soil the rapid transformation of the peptone nitrogen takes place. On distillation with excess of magnesia a large portion of this peptone nitrogen distils over as ammonia.

The amount of ammonia depends on the nature of the soil. The question arises as to the reason why one soil will lead to the formation of more ammonia than another soil under the same conditions. Are the differences due to the numbers or kind of bacteria or are they due to variations in the chemical composition of the soil? Experiment has demonstrated that the bacteriological factor has been found to play the predominant rôle in the ammonification of soil nitrogen and that it is itself directly affected by the chemical composition of the soil.

The detailed results of these studies will be reported in the *Journal of the American Chemical Society.*

Composition of the Drainage Waters of Some Alkali Tracts: F. K. CAMERON.

It was shown how the analysis of a drainage water could be used in interpreting the changes taking place in alkali soils under drainage. Illustrations were given, on the one hand, showing that the same salts present in the soil remain, though the total amount had been diminished, and on the other hand, illustrations were given where not only the amount of salts, but the particular kinds of salts, had changed.

Nutrition Investigation of the Office of Experiment Stations, and the Results of Some Recent Work: C. F. LANGWORTHY.

The purpose and scope of the human nutrition investigation carried on under the auspices of the Office of Experiment Stations of the Department of Agriculture, were briefly outlined, particularly the work of the fiscal year 1905–6, and the results of some dietary studies with aged men and women were summarized. From the data presented and a summary of similar work, the factor nine tenths was proposed as representing the amount consumed by a man past middle life, as compared with a man in full vigor at moderate muscular work.

Keeping of Tobacco: J. M. BELL.

This article has been published in full in SCIENCE, June 16, 1906.

A Method for the Determination of the Lead Number in Maple Syrups and Maple Sugar: A. L. WINTON and J. LEHN KREIDER.

The method proposed is based on the well-known fact that lead subacetate produces a voluminous precipitate in genuine maple products, whereas in products adulterated with refined cane sugar the amount is deficient. A solution of 25 grams of the material is precipitated with 25 c.c. of standard lead subacetate, made up to 100 c.c., filtered, and the lead determined in 10 c.c. of the filtrate. The amount of lead consumed in forming the precipitate is found by difference. This expressed as per cent. of the material is the 'lead number.' The lead number in samples of maple syrups of known purity was not less than 1.20, but in adulterated samples it ranged from 0.02 to 0.92.

The Application of Colorimetric and Other Delicate Analytical Methods to the Study of Agricultural Problems: OSTWALD SCHREINER and J. F. BREAZEALE. (By title.)

Legume Bacteria and Soil Fertility: KARL KELLERMAN. (By title.)

Toxicity of Some Ammonium Salts on Wheat Seedlings in Solution Cultures: CHARLES A. JENSEN. (By title.)

A Preliminary Study of the Combinations of Acids with Casein as determined by Conductivity Measurements: L. L. VAN SLYKE.

For more than half a century there has been at issue a question as to whether or not the coagulum formed when milk sours or is acted on by acids is a combination of casein and acid. As the result of work carried on in the Geneva Station Labora-

tory by Mr. E. B. Hart and myself satisfactory evidence was produced to show that casein can and does combine with acids to form insoluble casein salts. An attempt was made to settle the quantitative side of the question by suspending free casein in a given amount of dilute acid of known strength, filtering and determining the amount of acid left uncombined. This method was found to be inadequate. It then occurred to the writer that results might be obtained by suspending free casein in dilute acid and then testing the filtrate for changes of electrical conductivity. This work is being done largely by Mr. Donald D. Van Slyke.

The conductivity method shows that the base-free casein forms an insoluble compound with dilute hydrochloric acid, which slowly combines with more acid forming a soluble compound. This soluble compound forms more readily with more concentrated acid and is unstable, being readily decomposed by bases with precipitation of a compound probably pure casein. Further the conductivity method shows that the amount of acid combined with casein is considerably in excess of that found by the method first used and that the low results are accounted for by the formation of this soluble compound.

The work is still unfinished and many other phases will be studied.

Movement of Water and Solutions in Soils: F. K. CAMERON and J. M. BELL.

It has been pointed out in Bulletin 30, Bureau of Soils, that the movement of water in capillary media is described by the empirical formula,

$$y^n = Kt.$$

Further experiments show that in case of the movement of water through a capillary tube n is equal to 2. A theoretical deduction of this formula has been given.

Relation of Sodium to Potassium in Soil and Solution Cultures: J. F. BREAZEALE. (By title.)

The Distribution of Soluble Bodies between Water and Soils, or other Finely-divided Solids: F. K. CAMERON and H. E. PATTEN.

It has been shown that the rate of absorption generally follows the law expressed by the equation

$$\frac{dy}{dt} = K(C - y),$$

which is the equation describing a reaction of the first order. The distribution of substances, both organic and inorganic, between a soil or other absorbing material and the solvent was studied, and it was found in a majority of cases that the curves were of a logarithmic character, which appears to be expressed by the empirical formula,

$$\log \frac{y}{C - y} = K_x.$$

Several cases were found, however, which were better expressed by a linear equation. It was shown that the soils and other absorbing media have a maximum saturation capacity, C in the above formula, which has an important significance from an agricultural point of view.

Abnormal Transpiration in relation to Growth in Wheat under Certain Conditions: OSWALD SCHREINER and CHARLES A. JENSEN. (By title.)

Superphosphates: F. K. CAMERON and J. M. BELL.

In the four-component system—lime, sulphuric acid, phosphoric acid, water, which are the essential constituents of superphosphates—five stable solids have been found at 25°, viz., monocalcium phosphate, dicalcium phosphate, anhydrite, gypsum and a series of solid solutions in phosphoric acid and lime. The inversion points and

the boundary lines of the fields have been determined. At 66°, however, the field for gypsum disappears. From these data there was shown the effect of leaching superphosphates by water at ordinary temperatures.

A Simple Fat-extraction Apparatus: G. S. FRAPS.

The apparatus uses a mercury joint, and is simple and cheap.

Flavoring Extracts, Natural and Artificial, in Food Products: EDWARD GUDEMAN. (By title.)

A Colorimetric Method for the Determination of Absorbed Oxygen in Water: G. B. FRANKFORTER and A. D. WILHOIT.

The importance attached to the amount of absorbed oxygen in a sanitary analysis of water led the authors to search for a colorimetric method which would be in line with sanitary methods in general, and which would at the same time be rapid and accurate. A method using cuprous ammonium chloride was finally adopted. The advantages of the method, however, are largely in the construction of the apparatus. After various oils and even perfect rubber stoppers were found to be inefficient in protecting the colorless cuprous ammonium chloride from oxidation by air, a special glass stopper was devised. This stopper with a siphon was fitted into the top of one of the Hehner cylinders so as to protect the water in the tube from the air and at the same time to be used as a colorimeter by making comparisons in the ordinary way. The manipulation is very simple. The glass cork is placed in the Hehner cylinder so that the lower end stands at 101 c.c. Then 100 c.c. of water under examination is allowed to flow in. By turning a three-way stop-cock 1 c.c. of cuprous ammonium chloride is added, when a blue color immediately appears depending in intensity upon the amount of free oxygen in the water. The color is matched in the second Hehner cylinder by cupric ammonium chloride of known strength and representing a known quantity of oxygen. With this apparatus very rapid and accurate determinations are possible.

The Estimation of Citral in Lemon Oil: E. MACKAY CHACE. (By title.)

ORGANIC CHEMISTRY.

G. B. Frankforter, chairman.

The Fruit of Smilacina racemosa and trifolia: NICHOLAS KNIGHT.

The purpose of the work was, as far as possible, to determine the composition of the fruit. The berries were gathered between August 15 and September 5, 1905, at Sylvan Beach, N. Y., on the shore of Oneida Lake. They were allowed to ripen in the house. At first they were green in color and the fruit of the *racemosa* were about the size of peas, the fruit of the *trifolia* being smaller. As they ripened both species became of a reddish color, resembling currants. The *racemosa* fruit contains free tartaric and a small quantity of citric acid, a red coloring matter and glucose. The nutlets or kernels were ground and digested with boiling alcohol, by which an oil or possibly two oils were received. These were investigated. The fruit of the *trifolia* showed a similar composition, the main difference being potassium tartrate in place of the free tartaric acid.

The Constitution of Paris Green and its Homologues: S. AVERY.

The writer shows by a review of the literature that great uncertainty exists in regard to the constitution of these substances. Many years ago Ehrmann found that a commercial sample of Paris green (Schweinfurt green) consisted of three molecules of copper meta-arsenite in chemical combination with one molecule of cop-

per acetate. Later Wöhler made a green starting with copper butyrate and found the ratio to be 2:1. The writer shows that Paris green and its homologues may be regarded as isomorphic crystalline mixtures in which the extreme limits of the ratio of copper arsenite to the copper organic acid salt lie between 3:1 and 2:1. This view is confirmed by the study of greens, samples of which have been made containing a great diversity of organic acids. It is further confirmed by a study of certain zinc arsenites.

A Chemical Study of Curare: G. B. FRANK-FORTER and H. M. NEWTON.

The authors have made an exhaustive examination of the various forms of curare, or arrow poison. It required several years to collect these samples in the crude form as prepared by the Indians. On one or two occasions the bulbs or original containers had been partly filled with sand by the Indians, only a small amount of the alkaloid having been placed on the top of the sand. The analyses of these samples varied widely in composition. The amount of inorganic matter varied from 15 to 68 per cent., and in one or two cases the substance was found to be perfectly inert, physiologically. Reactions indicated an alkaloid with marked basic properties. No crystallized compounds were made, but analyses of the base prepared from the platinum double salts indicated that the formula for the alkaloid, notwithstanding the fact that it is used extensively as a medicine at the present time, is still in doubt. The formula given for the free base by Sachs was obtained from an analysis of the platinum double salt. The formula of Preyer has been shown to be incorrect, as the material analyzed contains a large amount of inorganic matter. From the work already done, the authors conclude that the free base in curare or curarine is more complex than the formula given by Sachs.

PHYSICAL CHEMISTRY.

W. Lash Miller, chairman.

Cooperation in Physical Chemistry: W. D. BANCROFT.

We could be of more assistance to each other if we had a system of reports by which we knew what bits of research work the others were doing. Each one of us has stored away in his memory a number of generally unfamiliar facts which he has stumbled upon in his reading or in his laboratory. These may not be important enough to him to justify his doing enough work to get anything worth publishing, or he may have more important matters on hand and so lack the time. If now any one of us learns that any one of the others is doing a bit of investigation into which this, that, or the other fact fits nicely, the observation can at once be turned over to the man who can use it, much to the benefit of both parties.

It is probable that nobody goes to one of the meetings of the Chemical Society without getting a few suggestions of value to him. On the other hand, owing to the great distances and consequent expense, we do not get together as often as we should like. If we kept more in touch, we should be getting continually some of the advantages which we now get from the occasional meetings. The matter would not be difficult to arrange. In October and February each man could make out a list of the work planned or in operation. These reports could be manifolded and distributed. So far as I can see, the plan has practically no objectionable features and might be of great value. It seems therefore worth trying.

Uniformity in the Use of Algebraic Symbols: W. LASH MILLER.

The desirability of a uniform system of symbols for use in works on physical, chemical and engineering subjects has often been urged; and various systems have been suggested, one of them by a former president of this society.

The latest proposal, made by Linders in his pamphlet 'Die Formelzeichen,' Leipsic, 1905, is very ambitious, and involves the use of German and Russian type in addition to the Greek and Latin alphabets. Would it be more practical to divide the sciences into groups, and to fix on a uniform system of symbols for use in each group, without insisting that a letter to which one meaning has been assigned in geometry, for instance, should not be employed with another meaning in chemistry? Is it desirable to appoint a committee to consider the whole question and report at a subsequent meeting?

The Influence of Calcium on Iron: O. P. WATTS. (By title.)

The Electrical Conductivity of Solutions of the Alcohols in Liquid Hydrobromic Acids: E. H. ARCHIBALD.

Qualitative tests were first made to see what classes of the alcohols would dissolve in this solvent to give conducting solutions. The liquid acid is found to be very selective as regards the bodies which it will dissolve, being a solvent for one alcohol but not for another, although they differ but little in constitution. The conductivities of solutions of some fourteen of the alcohol bodies have been measured quantitatively over a considerable range of dilution. In the case of the greater number of the solutions the temperature coefficients have also been determined. The molecular conductivity in nearly all cases increases rapidly with the concentration. In a few instances for the more dilute solutions of the simpler alcohols the molecular conductivity either decreases slightly with the concentration or

remains practically constant. As far as these investigations have extended those bodies which dissolve conduct the electric current. The temperature coefficients are in some cases positive, in some cases negative.

The Electrical Conductivity of Solutions of the Organic Acids in Liquid Hydrobromic and Hydrochloric Acids: E. H. ARCHIBALD.

Qualitative tests of about twenty of the organic acids showed that quite a number would dissolve in both solvents to give conducting solutions. As far as can be ascertained those acids which dissolve to any extent give solutions which will conduct. The quantitative measurements show that the hydrochloric acid solutions have by far the greater conducting power, at least in the case of nearly all the bodies examined. The molecular conductivity for both solvents, except in a few cases for the very dilute solutions, increases with the concentration. The temperature coefficients in all the cases examined are positive.

The Identification of Insoluble Phases: L. F. HAWLEY.

By means of the solubility method the formula $2PbCO_3 . Pb(OH)_2$ for the basic carbonate of lead was confirmed. Mixtures of lead carbonate and oxide in varying proportions were treated with a 20 per cent. sodium acetate solution and the amount of lead dissolved in 50 c.c. was determined. The oxide was found to hydrate in the presence of the carbonate until sufficient hydroxide was formed to give $2PbCO_3 . Pb(OH)_2$. The solubility remained constant over a range of concentrations up to two molecules of the carbonate to one of the oxide, and with more than two of the carbonate to one of the oxide the solution was also constant, but at a lower value. This shows the presence of a compound with a formula corresponding to the

concentration at which the solubility changes.

Another method was used in the identification of the insoluble phases formed when thallium sulphide and stannic sulphide are precipitated together. Since the phases have different colors the appearance or disappearance of a phase can be readily observed under the microscope. From pure Tl_2S up to a concentration corresponding to Tl_4SnS_4 two phases can be distinguished, the black Tl_2S, and the red Tl_4SnS_4; from this point up to 76 per cent. SnS_2 two phases are present, the red Tl_4SnS_4 and a reddish yellow transparent phase, while beyond 76 per cent. SnS_2 all concentrations are homogeneous, showing a solid solution.

The Equilibrium between Ammonia and Hydrogen Sulphide: J. P. MAGNUSSON. The reaction

$$NH_3 + H_2S \rightleftarrows NH_4SH$$
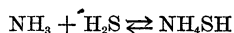
was studied at 20° over a range of 95 cm. partial pressure. The mass-law formula

$$p_{NH_3} \times p_{H_2S} = \text{const.}$$

describes this equilibrium over the pressure range studied if the pressure of the undissociated NH_4SH is neglected and if corrections are made for the deviations of the gases from Boyle's law. For hydrogen sulphide this deviation was found to be within the limit of experimental error over the pressure range studied, but for ammonia the deviation was considerable at the higher pressures. This was shown to be due to the adsorption of the gas on the glass surface of the measuring tube and on the NH_4SH crystals. The adsorption of gases on the walls of the containing vessel has an important bearing on our conception of the so-called imperfect gases.

The Precipitation of Lead Chromate: EDWARD E. FREE.

Precipitations were made from equivalent solutions of $Pb(NO_3)_2$ and K_2CrO_4 under as nearly as possible equal conditions. The rapidity of precipitation is greater from hot solutions and more concentrated ones. The crystals are large when the solutions are hot and dilute. The presence of glue greatly retards precipitation. The color is apparently the same under all conditions of precipitation, provided the solutions are neutral. Alkali will impart an orange tinge due to basic chromate. Minor accidental variations in the manner of precipitation have a great influence.

Solubility of the Phosphates of Magnesium: F. K. CAMERON and J. M. BELL.

The behavior of calcium phosphates in contact with water and with phosphoric acid solutions has already been studied in this laboratory by Cameron, Seidell and Bell. It was found that at 25° only two calcium phosphates exist in equilibrium with aqueous solutions. At the higher concentrations monocalcium phosphate is the stable solid phase, and at intermediate concentrations dicalcium phosphate is the solid phase. At very low concentrations there is at least one series of solid solutions. The behavior of magnesium phosphates in contact with water and with phosphoric acid solutions has been studied in a similar way at 25° C. Here there are but two magnesium phosphates, the monomagnesium phosphate, which exists in contact with solutions containing above 700 grams of P_2O_5 per liter; below that concentration the stable solid is dimagnesium phosphate. The solution in contact with the above phosphates of calcium contains about 320 grams of P_2O_5 per liter, while that in contact with the phosphates of magnesium contains over 700 grams of P_2O_5 per liter.

The System Water-Gypsum-Lime: F. K. CAMERON and J. M. BELL.

The mutual solubility of gypsum in lime solutions and of calcium hydroxide in gypsum solutions has been determined at

25° C. The solubility of gypsum in lime solutions is depressed with increasing amounts of lime, while the solubility of lime in gypsum solutions shows very slight increases. The solution in contact with both calcium hydroxide and gypsum contains 1.59 grams $CaSO_4$ per liter and 1.22 grams of calcium hydroxide per liter. A solution containing calcium hydroxide alone contains 1.17 grams per liter and a solution containing gypsum carries 2.13 grams of calcium sulphate per liter. There is no basic sulphate of calcium at this temperature.

The Solubility of Gypsum in Phosphoric Acid Solutions: W. C. TABER.

The solubility of gypsum in several acids, notably hydrochloric, nitric and sulphuric, has already been studied. In this investigation of its solubility in phosphoric acid it was found that at 25° C. small amounts of phosphoric acid increase the solubility of gypsum to a marked extent, the solubility being greater as the concentration of the acid increases. At about 230 grams of P_2O_5 per liter there is a maximum solubility of about four times that in pure water. Above this concentration the solubility decreases regularly with increase of the acid content. The results of these experiments are in accord with other work on the solubility of gypsum in solutions of electrolytes which contain no ion in common with gypsum.

The Phosphates of Iron and Aluminum: F. K. CAMERON and J. M. BELL.

Crystalline phosphates of iron and of aluminum have been found to exist in solutions which contain high percentages of phosphoric acid. At lower percentages the precipitates appear to be solid solutions.

The Solubility of Nitric Oxide and of Air in Sulphuric Acid: O. F. TOWER.

The method of Bunsen was used, which consists in shaking the respective gas with sulphuric acid in a eudiometer tube, which is standing in a mercury bath.

The following are the results obtained:

Concentration of Sulphuric Acid.	Coefficient of Solubility In Nitric Oxide.	In Air.
98 per cent.	No constant results obtained.	0.0173
90 per cent.	0.0193	0.0107
80 per cent.	0.0117	0.0069
70 per cent.	0.0113	0.0055
60 per cent.	0.0118	0.0059
50 per cent.	0.0120	0.0076

These numbers are so small that the solubility of these gases in sulphuric acid can cause no appreciable error in the determination of nitrates, nitrites or the oxides of nitrogen by Lunge's method, unless excessive quantities of sulphuric acid are employed.

The Basic Solutions of Beryllium Sulphate: CHAS. L. PARSONS and W. O. ROBINSON.

Solutions of the normal salts of beryllium have the property to an unusual degree of dissolving large amounts of their own hydroxide or carbonate. The present paper deals with such basic solutions of the sulphate. Freezing-point determinations, on both dilute and concentrated solutions, show that, per mol. of SO_3, any increase in basic ratio over the normal raises the freezing-point. The osmotic effect of the sulphate is, therefore, always decreased by dissolving in it its own hydroxide. The electrical conductivity of the basic solutions is less than that of normal solutions containing the same amount of SO_3. Migration experiments show that beryllium forms no part of the anion. The basic solutions are not precipitated by crystalloids; but on dialysis hydroxide is left on the membrane, and the dialyzed solution has a lower basic ratio.

Further Study of the Sulphates of Beryllium: CHAS. L. PARSONS and CARL T. FULLER.

In the earlier work of one of us, it was found impossible to procure crystals from solutions of the sulphate having a basic ratio greater than BeO/SO_3. Crystals have now been obtained from solutions with a ratio as high as $3BeO/2SO_3$. These crystals are in every case the normal tetrahydrate, and by their separation the mother-liquors are rendered more basic. Repeated attempts to obtain the hexa-hydrate described by Levi-Malvano (*Ztschr. anorg. Chemie,* **48**, 446) have resulted in failure. Although the conditions described by that author were faithfully followed and other methods used, the tetrahydrate invariably separated. A series of experiments on dialyzing the sulphate solutions of a basic nature showed a tendency for the solution to become much less basic by dialysis and the hydroxide was left behind.

The Theory of the Dissociation of Gases around Highly Heated Wires: IRVING LANGMUIR.

In a previous paper the author gave the results of experiments on the dissociation of water vapor and carbon dioxide, made by passing the gases over glowing platinum wires. The present paper shows that under ordinary conditions dissociation phenomena take place so close to the surface of the wire that convection currents do not influence the dissociation. The temperature of the gas near the wire is then calculated from the heat conductivity and the heat given off by the wire. Taking into account the diffusion and the variation of the dissociation constant and of the velocity coefficient with the temperature, a formula is derived which enables one to calculate the difference between the dissociation for equilibrium at the temperature of the wire and the dissociation actually observed after passing the gas over the wire. Applying the formula to the results of the experiments, it is shown that this difference can not exceed 10^{-10} per cent. or only 10^{-5} of the actual dissociation. Therefore the only remaining source of error in the experiments was in the determination of the temperature of the wire and in the analysis of the gases. The results for the dissociation may be considered quite accurate.

The Lime-Silica Series of Minerals: ARTHUR L. DAY and E. S. SHEPHERD.

There are two definite compounds of lime and silica which can exist in contact with the melt: (1) the pseudo-hexagonal metasilicate, melting at 1,512° and inverting to wollastonite at about 1,200°; (2) the orthosilicate of calcium, melting at 2,080° and possessing three polymorphic forms, which have been given the names a, β and γ, in the order of their formation. The a form is monoclinic, density 3.27, hardness 5; the β form is orthorhombic, with about the same density; the γ form has a density of 2.97 and also crystallizes in the monoclinic system. The inversion point a to β occurs at 1,415°; β to γ at 675°. There are three eutectics in the series, tridymite + metasilicate at 35 per cent. CaO, 1,417°; metasilicate + orthosilicate at 54 per cent. CaO, 1,430°; orthosilicate + lime at $67\frac{1}{2}$ per cent. CaO, 2,015°. The constants of the original components are these: pure fused lime has a density of 3.32, hardness 3 +. The fusion temperature is unknown. Lime crystallizes in the isometric system and no polymorphic forms were found. Silica melts very gradually, beginning at about 1,600°, to an ultraviscous liquid. The melting point, like those of albite and orthoclase, is, therefore, indeterminate. At all temperatures above 800° quartz changes to tridymite and quartz glass crystallizes as tridymite, so that above this temperature tridymite is unquestionably the stable phase. The density of pure artificial tridymite is 2.320 (25°); that of quartz glass, 2.213 (25°); the purest natural quartz

has a density of 2.654 (25°). Neither $Ca_2Si_3O_8$, $Ca_4Si_3O_{10}$ nor $3CaOSiO_2$ can exist in the two-component system.

The Effect of Acetone on the Transference Numbers of Sodium and Potassium Chlorides: H. F. LEWIS.

It has been found that in general a change of solvent has little or no effect on the transference number of a salt, but no experiments have been published in which acetone was used. In the present investigation the apparatus was a large inverted U tube, the legs of which dipped into large test tubes; by means of a small tube blown into the top or bend of the U tube it was possible to withdraw a sample of the middle portion for analysis. Although the apparatus is not at all adapted to very accurate work, it was shown by blank measurements and tests with indicators that the method was sufficiently good to guarantee that the large differences found are not due to errors. A silver voltameter was used to measure the total decomposition. The cathode portions were analyzed by titrating with deci-normal silver nitrate. The middle portion changed in almost all cases less than one per cent.

	Parts of Acetone.	H	No. of Exp.
NaCl	0	.59	1
	1/8	.55	2
	1/4	.52	2
	1/2	.38	2
	3/4	.38	2
KCl	0	.49	5
	1/8	.44	1
	1/4	.40	3
	1/2	.37	3
	3/4	.31	4

In the above table of results the first column gives the parts of acetone in one of solution; the second column gives the transference number of the chlorine, and the last column gives the number of independent experiments on which the result is based. The experiments were carried out at room temperature; and all the solutions were approximately deci-normal with respect to the salt.

The Electrode Capacity of Iron and its Bearing on Passivity: C. McC. GORDON and FRIEND E. CLARK.

The oldest and most commonly accepted explanation of the passivity of iron carries with it the idea that it is due to a very thin oxide sheet. In later years several other hypotheses have been suggested, which, while perhaps better fitted to explain many of the existing conditions, have not entirely displaced the oxide theory. In case we assume the oxide theory we might expect the so-called passive iron to act as an electric condenser; the conducting iron and the conducting solution being separated by insulating oxide, similar to films on aluminum anodes. Measurements of this capacity—comparing it on the Wheatstone bridge with a metallic condenser of known capacity—have been made for iron electrodes in various solutions, with the following results:

(1) Passive iron (electrodes) acts as if covered with a sheet of oxide, as is evidenced by the following facts: (*a*) The electrodes have a capacity easily measured while active electrodes (that is, iron in dilute nitric acid or freshly deposited electrolytic iron) show no signs of such capacities. (*b*) The capacity values are about of the same order of magnitude as those of aluminum, where we certainly know there is such capacity. (*c*) Electrodes oxidized in a Bunsen burner flame give a similar capacity. The oxidized sheet, so formed, appears to be five or six times as thick as that of the electrodes made passive by the concentrated nitric acid. It is notably different, too, in that it has a small resistance. It acts like a leaky condenser, or a condenser in parallel with a resistance. (2) Iron transferred from the air to neu-

tral solutions behaves qualitatively exactly like iron oxidized in the flame. Its capacity, however, is somewhat larger than that of the passive iron, indicating a thin film or sheet. The resistance of this sheet is relatively smaller, due, as we suppose, to small holes or crevasses in the sheet.

The Electrical Conductivity of Tungstate Solutions: ROGER CLARK WELLS.

A study of the conductivity of various tungstates showed that in the case of sodium metatungstate and ammonium paratungstate a partial transposition begins to take place as soon as those salts are dissolved in water. Although the rate of this transformation is very slow at 25°, it increases rapidly with rising temperature. This discovery will undoubtedly explain the queer solubility determinations which several investigators have found for these salts without considering the time factor.

Freezing-point Measurements: W. G. SMEATON.

The author takes up a consideration of the difficulties encountered in freezing-point determinations and then proposes a method which is a modification of the Raoult method. This modification is based on the fact that, although cryohydrates are theoretically ideal cooling baths, in practise their use necessitates the introduction of the Nernst and Newton constants. The use of these constants is made necessary because the temperature of the cooling bath can not be regulated to produce a temperature equilibrium in the freezing-point vessel at the apparent freezing-point of the solution in all cases. In applying the modification it is most convenient to use a mixture of ice and salt. An auxiliary cooling bath permits rapid determinations. The apparent freezing-point is first determined rapidly in the auxiliary cooling bath. Then the temperature of the cooling bath is regulated to give temperature equi-

librium at the apparent freezing-point. In the meantime the ice has been thawed out of the freezing-point vessel which is undercooled in the auxiliary bath and then is transferred to the other bath. Inoculation is made when the temperature begins to rise uniformly. Thus the degree of undercooling is determined with the maximum of accuracy. Ice formation is prevented during undercooling by vigorous hand stirring. The method is rapid, easily manipulated, and gives accurate determinations with very small volumes of solution. The only correction to be applied arises from the change in concentration of the solution through the ice separated. The factor to be applied is a constant for a given apparatus under uniform conditions.

On Amorphous Sulphur; IV. Precipitated Sulphur: ALEXANDER SMITH and R. H. BROWNLEE.

This investigation deals with the proportions of amorphous sulphur ('supercooled $S\mu$') contained in sulphur which has been precipitated (1) from sodium polysulphide by the action of acids and of iodine, and (2) from sodium thiosulphate by the action of equivalent and excessive amounts of acids. The sulphur from polysulphides —so-called 'amorphous sulphur'—is almost wholly crystalline soluble sulphur. When the thiosulphate is used, different acids in equivalent concentrations give different proportions of amorphous sulphur. For a single acid the proportion increases more rapidly than the concentration of the acid. The proportion of insoluble sulphur seems to be greater the more rapid the action (due to high concentration of the acid), and therefore the smaller the droplets and the quicker the hardening of the precipitated liquid $S\mu$. Higher temperatures up to 25° hasten the action, and therefore give larger proportions of amorphous sulphur; but at 40° the tendency of $S\mu$ to revert to

Sλ asserts itself and the proportions are smaller.

On Amorphous Sulphur; V. Further Study of the Two Forms of Liquid Sulphur as Dynamic Isomers: ALEXANDER SMITH and C. M. CARSON.

This investigation deals with (1) measurements of the rate of transformation Sλ = Sμ in presence of different catalyzers; (2) study of the influence of iodine, a second component; (3) investigation of freezing-point phenomena of Sλ and determination of the 'natural' freezing-point (114.5°); (4) thermal effects when liquid sulphur is heated rapidly; (5) measurements of concentrations of Sμ when equilibrium has been reached at temperatures between 155° and 165°; (6) measurements of concentrations of Sμ when liquid sulphur is being heated rapidly; (7) relations of viscosity to preceding results; (8) discussion of causes of the thermal effects and of the whole problem in the light of these results.

G. R. WHITE,
Press Secretary.

(*To be concluded.*)

DOCTORATES CONFERRED BY AMERICAN UNIVERSITIES.

THE degree of doctor of philosophy or doctor of science has this year been conferred, as shown in the accompanying table, on 325 students by institutions competent to award these degrees. The number in 1906 is exactly the same as in 1905, but these two years represent an advance over any preceding year, bringing the number of doctorates conferred during the last nine years to 2,387. These figures do not include those who have received the degree or its equivalent from foreign universities. No statistics are at hand in regard to these students, but the number is probably in the neighborhood of fifty annually. We have not the information that would enable us to say what percentage of those who take

TABLE I.

DOCTORATES CONFERRED.

	1898	1899	1900	1901	1902	1903	1904	1905	1906	Total
Harvard	26	24	36	29	31	28	46	38	46	304
Chicago	36	24	37	36	27	32	36	44	31	303
Yale	34	30	26	39	29	36	39	34	29	296
Columbia	22	33	21	25	32	39	29	38	42	281
Johns Hopkins	33	38	33	30	17	23	31	35	32	272
Pennsylvania	24	20	15	25	14	29	18	26	28	199
Cornell	19	7	19	21	23	20	13	21	19	162
Clark	12	5	9	7	1	4	10	18	13	79
Wisconsin	5	6	5	6	11	4	12	9	9	67
Michigan	7	4	5	3	10	10	8	7	8	62
New York	5	9	7	6	4	4	9	7	9	60
Boston	0	0	0	0	0	4	7	14	10	35
California	1	3	2	2	1	3	3	4	9	28
Virginia	0	2	2	8	6	3	1	1	0	23
George Wash	1	0	5	3	2	4	3	3	2	23
Princeton	0	3	3	3	1	1	2	5	5	23
Minnesota	1	2	3	2	3	3	3	3	2	22
Bryn Mawr	3	3	1	2	2	0	5	2	2	20
Brown	1	3	3	2	2	5	0	2	1	19
Nebraska	2	1	1	1	0	0	2	3	7	17
Catholic	1	0	0	0	2	2	5	1	5	16
Stanford	2	0	2	2	2	1	1	1	2	13
Iowa	0	0	0	0	0	2	0	2	5	9
Washington	0	2	0	1	0	1	1	0	2	7
Georgetown	0	0	0	0	0	3	1	2	0	6
Vanderbilt	0	0	3	1	0	0	0	0	1	5
Colorado	0	1	0	0	0	0	2	0	2	5
North Carolina	0	0	0	0	2	1	0	1	0	4
Illinois	0	0	0	0	0	0	0	1	3	4
Cincinnati	0	0	0	0	0	1	1	1	0	3
Kansas	0	1	0	0	0	2	0	0	0	3
Lafayette	0	0	0	0	0	3	0	0	0	3
Missouri	0	1	0	0	0	0	0	2	0	3
Northwestern	1	1	0	1	0	0	0	0	0	3
Wash. and Lee	0	0	0	0	1	0	1	0	1	3
Lehigh	0	0	0	0	0	2	0	0	0	2
Syracuse	0	1	0	0	1	0	0	0	0	2
Tulane	0	0	1	0	0	0	0	0	0	1
	236	224	239	255	224	270	289	325	325	2387

the doctor's degree continues to engage in research work and productive scholarship, but probably not more than one third. Neither are there any data showing what percentage of those who are engaged in the advancement of science and learning holds the doctor's degree, but it may be estimated at about half. In so far as these estimates are correct, there would be about 250 men a year added to those who will hereafter devote themselves with some success to research work, and of these about half will work in the exact and natural sciences.

It must be confessed that this number is disappointingly small when the population and wealth of the country are considered. Dr. W. T. Harris, in the last report of the