SCIENCE

A WEEKLY JOURNAL DEVOTED TO THE ADVANCEMENT OF SCIENCE, PUBLISHING THE
OFFICIAL NOTICES AND PROCEEDINGS OF THE AMERICAN ASSOCIATION
FOR THE ADVANCEMENT OF SCIENCE.

FRIDAY, MARCH 18, 1904.

CONTENTS:

MSS. intended for publication and books, etc., intended for review should be sent to the Editor of SCIENCE, Garrison-on-Hudson, N. Y.

THE AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

SECTION C, CHEMISTRY.

THE joint meeting of Section C and of the American Chemical Society at St. Louis, December 28 to 31, 1903, was one of the most interesting in the history of the organization. Besides the usual technical papers were those of a physical chemical nature, with several of industrial and commercial value. The general order was varied by one whole session being devoted to a general discussion of valence.

The address of welcome was given by Dr. Frerichs, president of the St. Louis Chemical Society. The response was given by President J. H. Long of the Chemical Society. Dr. Long presided at the Chemical Society sessions and Vice-President Bancroft at the Section C sessions. The address of the retiring vice-president, Dr. Charles Baskerville, was delivered Monday afternoon, subject: 'The Elements: Verified and Unverified.' The address of the retiring president of the Chemical Society, J. H. Long, was delivered Wednesday evening, subject: 'Some Problems in Fermentation.'

The officers for the coming year are:

Vice-President—Wilder D. Bancroft, Cornell University.

Secretary—R. S. Curtiss, Union College.

Councilor—E. H. S. Bailey, University of Kansas.

Members of the Sectional Committee—E. C. Franklin, Leland Stanford; M. T. Bogert, Columbia University; L. P. Kinnicutt, Worcester; L. Kahlenberg, University of Wisconsin; G. B. Frankforter, University of Minnesota.

Member of General Committee—A. Springer.
Press Secretary—G. B. Frankforter.
Local Press Secretary—J. H. Knox.

The papers read were as follows:

The Ternary System, Benzene, Acetic Acid and Water: A. F. LINCOLN, University of Illinois, Urbana, Ill.

It was pointed out by Bancroft about ten years ago that the equilibria between two non-miscible liquids and a consulate liquid follow the mass law, and that there are only two sets of equilibria. The application of the law of mass action to the equilibria of these physical reactions has subsequently been demonstrated to hold very closely in the system, benzene, alcohol and water. Waddell concluded from his experiments that the system benzene, acetic acid and water does not conform to the mass law, and that the equilibria can not be represented by expotential formulas. The work on this system has been repeated by the author, who finds that one of the chief sources of error in a work of this kind is the ascertaining of the point of saturation, that is, of equilibrium. Values are given for temperatures 25° and 35°. The data show that the two equilibria can be represented by two expotential formulas and that, as in the case of chemical reactions, the exponent is not a function of the temperature. The conclusion is that for the system benzene, acetic acid and water, the equilibria do follow the law of mass action.

Thermometric Analysis of Solid Phases: WILDER D. BANCROFT, Cornell University, Ithaca, N. Y.

When two different solutions of a three-component system belong in the same field and reach the same boundary curve at the same point, the composition of the solid phase in that field can be deduced from the difference in the concentrations of the two solutions. This method has been applied to experiments of Heycock and Neville on gold and cadmium in tin and other solvents, published in 1891. It was shown that the compounds AuCd and $AuCd_3$ are formed. Reversing the process and assuming the existence of AuCd, it is possible to calculate the temperature measurements of Heycock and Neville. This work was done by Mr. E. S. Shepherd and will be published under his name in the February number of the *Journal of Physical Chemistry.*

A Method of Grading Soaps as to their Detergent Power: H. W. HILLYER, University of Wisconsin, Madison, Wis.

When a soap solution is caused to make drops beneath the surface of an oil, the number of drops formed by a given volume of the solution increases with the concentration of the solution. The increase in the number of drops with increase in concentration is a measure of the increased power of the solution to emulsify oily matter and consequently to cleanse. Advantage was taken of this connection between the number of drops and cleansing power, to work out a method of determining the cleansing power of commercial soaps. Certain soaps are efficient for use with cold water but not especially good for use with hot water. The reverse is also true. The method grades soaps for these two kinds of use. The cleansing agent is not the alkali of the soap, but the soap in its undecomposed form.

The Determination of Gliadin in Wheat Flour by Means of the Polariscope: HARRY SNYDER, Minnesota Experiment Station, St. Anthony Park, Minn.

The various proteids in wheat flour were briefly discussed and the desirability of a rapid and accurate method for the determination of gliadin noted. Methods based upon the use of the polariscope appeared to offer a satisfactory way for its determination. The quantity of optically active substances in wheat flour, as sucrose, invert sugar and the non-gliadin proteids soluble in alcohol, was found to be small, and if desired corrections could be made for these substances by precipitating the gliadin and polarizing the filtrate, the gliadin could be determined by difference. It was found that if 15.97 grams of flour were treated with 100 c.c. of 70 per cent. alcohol for 18 hours with occasional agitation, and the filtrate then polarized in a 220 mm. tube, the readings on the sugar scale ranged from —4 to —7 according to the amount of gliadin in the sample. It was also found that the polariscope readings multiplied by .2 gave results corresponding with the per cent. of gliadin nitrogen obtained by the usual process. When the results are substituted in the formula $(a)D = -a/PL$, the value obtained for the specific rotation of gliadin was found to be —90. Kjeldahl and Osborne obtained approximately —92. While only tentative standards could be formulated, on account of lack of sufficient data, it would appear from the results obtained that the polariscope offers a rapid and accurate method for the determination of gliadin in wheat.

Factors of Availability of Potash and Phosphoric Acid in Soils: G. S. FRAPS.

In the determination of plant food in soils, chemists have usually considered only that part which is soluble in the common solvents. Solubility is not, however, the only factor of fertility in the soil. The rate of decomposition or weathering of the soil is of great importance, as is also the power of the plants to assimilate. Weathering has received little or no attention. It is known to be of great importance with nitrogenous bodies, but in regard to phosphorus and potash no data can be given. Experiments show that there is a slight increase in both phosphoric acid and potash when the soil is kept moist and a great increase in potash when organic matter is present. This accounts for the necessity of vegetable matter in soils. Another factor is the difference in the solvent powers of plants. A soil may contain sufficient food for one plant, but not enough for another.

Thirty Years' Progress in Water Analysis: ELLEN H. RICHARDS, Massachusetts Institute of Technology, Boston, Mass.

It is hardly possible for the younger chemists to appreciate the benighted conditions in which the early '70's found us. Wanklyn's book, written in 1868, was the first book published on the subject of water analysis alone. Frankland and Armstrong, between 1866 and 1888, made critical examinations of methods, and reached important conclusions as to the meaning of the presence of the various substances in drinking-water.

During this time occurred a bitter controversy over the question whether the whole of the organic carbon and nitrogen or only a certain ratio of the total was important. It must be remembered that at this time chemistry was still young in this country. There were a few laboratories in the better scientific schools and there were a few strong men at work, yet chemistry in general, and water in particular, were far from satisfactory.

My note-book, dated 1872–73, contains, so far as my knowledge goes, the records of the earliest so-called sanitary analyses. About this time the method of reducing to grams was changed to milligrams, and when finally accepted produced astounding results.

The cause of the great discredit to water analysis in the '80's was due to the taking up of the quick and comparatively simple 'albuminoid ammonia' process by inexperienced chemists. Men with little or no training posed and advertised themselves as expert water analysts. What followed can easily be imagined. The public naturally became skeptical, and learned to discredit not only the work of these pseudo-chemists, but also the results of the experts. It was not an uncommon thing, as late as 1895, for samples of water to be sent to four or five different analysts in order to see how widely they differed in their opinions of the same sample. Of course, the fault lay largely with the analysts who assumed that their laboratory tests were all-sufficient.

Great good was accomplished along this line by the Massachusetts Legislature in 1886, resulting in a law entitled 'An Act to Protect the Purity of Inland Waters.' This organization included not only a chemical laboratory, but an engineering, biological and bacteriological staff as well, and the new idea of control of the watersheds and water supplies came to the front in order that selfishness of municipal disposal might be checked out of regard for the general good. This idea has been continued in the various state and municipal laboratories ever since.

At the present time the field of controversy has been somewhat shifted from organic matter to organisms whose pernicious activities are supposed to give rise to the most serious dangers.

A Study of the Nitrogenous Constituents of Meats: H. S. Grindley, University of Illinois, Urbana, Ill.

Object.—To increase by experimental study the present very limited knowledge of the proteids of flesh, in the condition in which they exist in meat as used for food.

Method.—Two samples of lean, raw beef flesh and one sample of cooked beef flesh were extracted successively with the following reagents: Cold water, 10 per cent.; sodium chloride solution, .15 per cent.; hydrochloric acid solution, .15 per cent; potassium hydroxide solution, and lastly hot water. The several forms of proteid and non-proteid nitrogen in each of these extracts were determined.

Results.—The detailed results are given in thirteen tables.

Conclusions.—1. Cooked meat is much less soluble in the above solvents than raw meat.

2. The acidity of a solution of flesh increases upon the coagulation of its proteids.

3. Cold water extracted 3.06 per cent. nitrogenous matter from raw meats and only .27 per cent. from boiled meat.

4. A 10 per cent. solution of sodium chloride extracted from raw meats 6.10 per cent. of proteid matter and only .5 per cent. from boiled meat.

5. A .15 per cent. solution of hydrochloric acid dissolved from raw meat 2.28 per cent. proteid and from boiled meat 2.30 per cent.

6. A .15 per cent. solution of potassium hydroxide extracted from raw meats 2.88 per cent. and from boiled meat 4.84 per cent. of proteid.

7. Hot water removed from raw meats .49 per cent. and from boiled meats 6.24 per cent. proteid matter.

8. Of the total proteid existing in the original raw meats 95.22 per cent. was dissolved by extracting successively with the above-named reagents, while only 50.59 per cent. of the total proteid of the boiled meat was thus made soluble.

Some Double Salts of Lead: John White, Rose Polytechnic, Terre Haute, Ind.

In 1863 the observation was made by Carius (*Liebig's Ann.*, 125, 87) that lead acetate is acted upon by alkyl haloids when heated with them in a sealed tube, using glacial acetic acid as the solvent, and that a class of compounds is obtained of the general type

$$Pb\left\{\begin{matrix} x \\ C_2H_3O_2 \end{matrix}\right.$$

where x is any halogen. These compounds he designated as the *acetines* of lead.

It is well known that lead sulphate is soluble in alkaline acetates, tartrates, etc., and experiment shows that the halogen salts of lead are also soluble under like conditions. It seems probable that these in passing into solution may form compounds of similar character to those mentioned above.

To test this, experiments were planned, whereby the products of the reaction might be collected and examined. Lead iodide was chosen for the preliminary experiments, because it was found that the products resulting from its solution in acetates and tartrates is white, hence the reaction could be followed by observing the change of color.

The following method of preparation of the salts was adopted: A very concentrated solution of the acetate to be used was first made in alcohol, the strength of which was adjusted for each case, varying from 50 to 95 per cent. To this a few drops of glacial acetic acid were added—otherwise the lead iodide is transformed almost entirely into the basic iodide—and then freshly precipitated lead iodide was brought into the hot solution until it was nearly saturated, the solution filtered and allowed to cool in a vacuum over sulphuric acid.

In each case, upon cooling, well-defined colorless crystals were obtained, which, after draining off and washing with a mixture of strong alcohol and ethyl acetate, were subjected to analysis. In no case, however, was the simple compound

$$Pb\left\{\begin{matrix} I \\ C_2H_3O_2 \end{matrix}\right.$$

corresponding to Carius's salt obtained; instead, the analyses showed that compounds were formed, which may be interpreted as a combination of this with the metallic acetate used. The following salts have so far been isolated and analyzed:

$$\text{I. } Pb\left\{\begin{matrix} I \\ C_2H_3O_2 + NaC_2H_3O_2 \cdot \frac{1}{2}C_2H_4O_2, \end{matrix}\right.$$
melting point (uncorr.) 124–125° C.

$$\text{II. } Pb\left\{\begin{matrix} I \\ C_2H_3O_2 + 3NaC_2H_3O_2 \cdot \frac{1}{2}C_2H_4O_2, \end{matrix}\right.$$
melting point undetermined.

$$\text{III. } Pb\left\{\begin{matrix} I \\ C_2H_3O_2 + KC_2H_3O_2, \end{matrix}\right.$$
melting point 208–208.5° C.

$$\text{IV. } Pb\left\{\begin{matrix} I \\ C_2H_3O_2 + NH_4C_2H_3O_2, \end{matrix}\right.$$
melting point 166–167° C.

$$\text{V. } Pb\left\{\begin{matrix} I \\ C_2H_3O_2 + Pb(C_2H_3O_2)_2 \cdot \frac{1}{2}C_2H_4O_2, \end{matrix}\right.$$
melting point 202–205° C.

They all (with the exception of II.) possess a characteristic crystal form and give fairly sharp melting points. It will be observed that some of them contain acetic acid of crystallization, while others do not, although they were all prepared in a similar manner. When dry they are quite stable, but are decomposed by water or moist air, forming first lead iodide, then the basic iodide. Organic solvents are without action. On account of the insolubility and general inactivity of these substances, it has not yet been possible to determine with positiveness their molecular structure. It is hoped that further investigation may throw additional light upon this point.

The Theory of Valence: G. B. FRANKFORTER, University of Minnesota, Minneapolis, Minn.

Valence followed, as a natural consequence, Dalton's atomic theory and the laws of definite and multiple proportion. The first real expression of the present valency theory was made by Frankland, followed by Kolbe and others, who showed the new idea was in close accord with facts. Notwithstanding the enormous amount of work and speculation of the past fifty years, the idea of valence remains as mysterious as ever. Whether valence represents certain lines of force as a result of some modified application of chemical affinity, or whether it represents certain electrical charges, remains for the future to determine. The electrolytic dissociation theory and the ionization theory would seem to point to the latter as one of the coming theories. Every one must admit that the present valence theory has been of inestimable value in the development of the science, yet none can doubt the fact that the foundation upon which the whole theory rests is by no means a firm one.

The Theory of Double Salts: James Locke, Massachusetts Institute of Technology, Boston, Mass.

The present theory of double salts is untenable. In the development of the double-salt theory during the past thirty or forty years, the tendency has been to represent even the most complex of these double compounds as if the valences of the respective elements were absolutely fixed. This condition of affairs has been brought about largely by the organic chemists who have carried the structural arrangement to the extreme, and many compounds are represented by definite fixed formulas without the slightest shade of reason. The salts of hydroferro and hydroferricyanic acids serve as excellent illustrations. The double salts of platinum, as represented by Remsen in his theoretical chemistry, also show the absurdity of the present theory. In fact, the present double-salt conception is without foundation and must sooner or later fall. The Werner theory comes nearer to a logical representation of the double salts than any theory which has yet been proposed.

Werner's Theory of Valence and the Constitution of Compounds: J. E. Teeple, Cornell University, Ithaca, N. Y.

The most common objection to Werner's theory is that it discards the present theory of valence, although Werner himself believes that it is only a logical outgrowth of the valence theory. The development of the present theory since the time of Frankland and Kekule may be summed up as follows: (1) A rise in the valence assigned to each element; (2) the increasing use of compact concentric formulas; (3) the common acceptance of the idea of varying valence; (4) the introduction of space relations in formulas, and (5) the growth of the idea of partial or residual valence. The results of the development along these five lines have been remarkable, notwithstanding the fact that no satisfactory explanations are offered for any of the complex compounds and especially the double salts. In fact, Werner's theory is the first to give a satisfactory explanation of the structural formulas as $CoCl_2 \cdot 6H_2O$, $CoCl_3 \cdot 3NH_3$, $CoCl_3 \cdot 4(NH_3)$, $Fe(CN)_6K_3$ and $Fe(CN)_6K_4$.

To understand Werner's theory three concepts are necessary: (1) Primary valence, (2) secondary valence and (3) coordinate number. By primary valence is understood the idea of valence in the ordinary sense as the power of holding together ions or radicals which usually unite with ions. Secondary valence, on the other hand, only combines substances which can not act as ions and are not equivalent to them. The coordinate number of an atom represents the maximum number of groups or atoms with which it may come into direct contact. This number is definite and unvarying for each element: four for carbon, six for cobalt and most of the metals. The number can easily be determined by its ammonia compounds or similar derivatives.

Following out these three concepts, we are able, for the first time, to express such compounds as $CoCl_3(NH_3)_6$ satisfactorily. Thus, around a central cobalt atom are arranged the six ammonia groups attached to the cobalt atom by secondary valences. They are in the first sphere of influence, and hence the whole complex $Co(NH_3)_6$ acts as a single ion. These six groups are probably regularly distributed around cobalt as the central atom and may, therefore, be represented by an octahedron with an ammonia group joined to each of the six vertices. In the second sphere, and not directly connected with the cobalt atom, lie the chlorine atoms. Being necessarily farther removed from the cobalt atom, we should expect more freedom of action for them than for the ammonia, that is, they would act as ions when the salt is in solution. All this may be briefly represented by the formula $Co(NH_3)_6Cl_3$. It has been experimentally proved that such complex ions as $Co(NH_3)_6$ do actually exist in solution and that, in this particular salt, all three chlorine atoms do act as ions.

Werner's theory also explains many hitherto inexplicable phenomena of the simpler compounds. Why does ammonium chloride, NH_4Cl, dissociate while the corresponding compound methyl chloride, CH_3Cl, its left-hand neighbor in the periodic system, does not? According to the idea given above, the hydrogen in the ammonium chloride would be in the first sphere of the nitrogen, the group NH_4 acting as an ion, while the chlorine would act in the second sphere. The compound should dissociate. It does. In the case of the methyl chloride, there is no dissociation because both the hydrogen and the chlorine are in the first sphere of influence and joined directly to the carbon atom. This same explanation also applies to the oxonium, sulphonium, phosphonium, iodonium and diazonium salts.

It is impossible to explain these molecular compounds by the old theory. The very term 'molecular compound' is proof that the old valence is insufficient.

Various attempts have been made to disprove Werner's theory, but in most cases experiments have proved rather than disproved the theory. This is especially true with regard to coordinate number, which gives to each element a fixed number and secondary valence which has a definite limit. It is not understood that this theory was designed to replace the old valence theory in cases of simpler compounds like sodium chloride or in any case where the present theory is satisfactory. It was only intended as an extension of the present theory.

Solubility of Gold in Certain Oxidizing Agents: VICTOR LENHER, University of Wisconsin, Madison, Wis.

Metallic gold is soluble in such inert acids as sulphuric and phosphoric when heated in the presence of such oxidizing agents as selenic, telluric, nitric and chromic acids, red lead, lead dioxide, nickelic oxide, manganese dioxide and the higher oxides of manganese. Anode oxygen will also readily cause solution of a gold electrode with electrolytes of either acids or alkali, most of the metal subsequently depositing on the cathode. In case of such salts as sodium sulphate or sodium nitrate, very little of the gold passes through or enters the electrolyte, and the gold anode is completely transformed into gold oxide.

On a Method for Preparing Salts with a Definite Number of Molecules of Water of Crystallization: LAUNCELOT W. ANDREWS, University of Iowa, Iowa City, Iowa.

Salts containing a maximum amount of water of crystallization when enclosed in a tight vessel with a large amount of the same salt in a more or less completely dehydrated condition are, when a condition of equilibrium is attained, converted with precision into a phase containing a definite amount of water greater by one step than that present in the salt used as desiccant. The employment of the method for the removal of mechanically adherent water from highly efflorescent salts, and for the preparation of compounds containing alcohol, benzene or acetic acid of crystallization was also referred to.

An Interesting Deposit from City Water Pipes: E. H. S. Bailey, University of Kansas, Lawrence, Kan.

The soft brown deposit, resembling peat, contained the following percentages: Silica, 13.20; water, 27.62; manganese oxide, Mn_3O_4, 34.07; ferric oxide, 8.04; alumina, 3.29, and therefore, resembles woad. The water itself only contained a minute trace of manganese.

A Method of Determining the Total Carbon of Coal, Soil, Etc.: S. W. Parr, University of Illinois, Urbana, Ill.

The substance is mixed with an excess of sodium peroxide and burnt in the well-known Parr calorimeter. The residue is then mixed with an excess of dilute sulphuric acid and the evolved carbon dioxide measured in a gas burette, the amount of carbon being calculated from the volume of the gas. The amount of carbon in the peroxide used is determined in a special blank experiment. The method gave good results for total carbon in iron, organic compounds, etc.

The Application of Physical Chemistry to the Study of Uric Acid in Urine: F. H. McCruden, Boston, Mass.

The greater solubility of uric acid in urine as compared with pure water is shown to be due to the establishment of an equilibrium between the uric acid and the acid phosphates. Hence the addition of even considerable amounts of alkalies, as compared with the uric acid, does not appreciably influence the solubility of the latter. The interesting details of this paper do not lend themselves to discussion in an abstract.

Investigation of the Bodies called Fiber and Carbohydrates in Feeding Stuffs, with a Tentative Determination of the Components of Each: P. Schweitzer.

The author presented in tabular form the results obtained by approximate methods of determination of 'pure fiber,' fibro-pentosan, pectose, pecto-pentosan, pentosan, sugar, starch and 'indefinite carbohydrates' in a large number of feeding stuffs.

The following papers were also read:

Herman Schlundt: 'The Dielectric Constants of some Inorganic Solvents.'

Hamilton P. Cady: 'Concentration Cells in Liquid Ammonia.'

James Locke: 'The Action of Ammonia upon Solutions of Copper Sulphate.'

Charles Baskerville: 'Phosphorescent Thorium Oxide.'

Charles Baskerville and George F. Kunz: 'On the Action of Radium Compounds on Rare Earth Oxides and the Preparation of Permanently Luminiferous Preparations by the Mixing of the Former with Powdered Substances.' By title.

Charles Baskerville: 'Action of Ultra-Violet Light on Rare Earth Oxides.'

W. D. Bigelow, H. C. Gore and B. J. Howard: 'The Ripening of Apples.'

John Uric Nef: 'Dissociation Phenomena of the Alkyle Haloids and of the Monatomic Alcohols.' Published in *Liebig's Annalen,* Vol. 318, p. 137.

Edward Bartow: 'Synthesis of the Quinoline Series.'

Arvid Nilson: 'The Life of a Barley Corn.'

G. B. Frankforter,
Secretary.