

# REVIEW OF AMERICAN CHEMICAL RESEARCH.

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ARTHUR A. NOYES, Editor.

REVIEWERS: Analytical Chemistry, H. P. Talbot and F. G. Moore; Biological Chemistry, A. G. Woodman; Carbohydrates, G. W. Rolfe; General Chemistry, A. A. Noyes; Geological and Mineralogical Chemistry, W. O. Crosby and C. H. Warren; Inorganic Chemistry, Henry Fay; Metallurgical Chemistry and Assaying, H. O. Hofman; Organic Chemistry, J. F. Norris; Physical Chemistry, H. M. Goodwin; Sanitary Chemistry, E. H. Richards; Industrial Chemistry, A. H. Gill and F. H. Thorp.

## GENERAL AND PHYSICAL CHEMISTRY.

A. A. NOYES, REVIEWER.

**The Precipitation of the Sulphides of Nickel and Cobalt in an Alkaline Tartrate Solution, together with an Investigation into the Nature of Certain Tartrates of these Metals.** BY O. F. TOWER. *J. Am. Chem. Soc.*, 22, 501-521.—The investigation is mainly a physico-chemical one. Nickel tartrate of the composition  $\text{NiC}_4\text{H}_6\text{O}_6$ , a solution of which is formed by digesting an excess of nickel hydroxide with cold dilute tartaric acid, was found, (1) by the freezing-point method, to have in 0.1 molar<sup>1</sup> solution a molecular weight nearly a third greater than that corresponding to the formula; (2) to have an exceptionally small electrical conductivity (at 0.01 molar concentration about one-third that of magnesium tartrate), which increases very rapidly with the dilution; and (3) to give rise, when nickel electrodes are placed in a 0.02 molar solution of it and a 0.1 molar one of nickel nitrate, to an electromotive force (0.048 volt), which corresponds to the presence of about 8 per cent. of the nickel in the form of its ions in the former solution. Corresponding measurements with potassium nickel tartrate, ( $\text{K}_2\text{NiC}_8\text{H}_8\text{O}_{12}$ ), made by digesting nickel tartrate at 40° with potassium hydrogen tartrate and in other ways, showed an apparent molecular weight about one-third of that corresponding to the formula just given, a conductivity not very different from that of a sodium tartrate solution containing an equivalent amount of the alkali metal, and an electromotive force corresponding to the presence of only 0.2-0.3 per cent. of nickel ions. All these facts are explained by the assumptions that the former salt exists largely as double molecules which are dissociated

<sup>1</sup> This word will be used in this Review, in accordance with the suggestion of Ostwald, to designate a concentration of one mol (one molecular weight in grams) per liter.

into  $\text{Ni}''$  and  $\text{O.CO.}(\text{CHOH})_2.\text{CO.O.Ni.O.CO.}(\text{CHOH})_2.\text{CO.O}''$  ions to a relatively small extent, and that the latter salt is almost completely dissociated into two K ions and this same complex nickel tartrate ion, this last ion being itself only very slightly dissociated at moderate dilutions, but appreciably so at very great dilutions. The author has also investigated the effect on the freezing-point of a neutral nickel tartrate solution of adding successive quantities of potassium hydroxide, but the results are so irregular, owing, perhaps, to the formation of a colloidal substance, which even separated as a jelly at one concentration, that the conclusions drawn from them in regard to intermediate compounds seem to the reviewer of little value. It may be mentioned, however, that when two mols of potassium hydroxide were added to one mol of  $\text{NiC}_4\text{H}_4\text{O}_6$ , the apparent molecular weight was found to be 185, while that corresponding to  $\text{K}_2\text{C}_4\text{H}_2\text{NiO}_6$  is 283, thus showing that the double molecules in the pure nickel tartrate solution are finally resolved by the potassium hydroxide, as might be expected, into single ones, and that these are considerably dissociated. Electromotive-force measurements showed that nickel ions were not present in appreciable quantities in this solution.—Freezing-point and conductivity measurements in the case of the various corresponding cobalt compounds, gave analogous results. The conductivity of neutral cobalt tartrate in 0.06–0.02 molar solution is, however, nearly one-half greater than that of the nickel compound. Finally, the author shows that in the solution prepared by adding an excess of sodium hydroxide to nickel tartrate solution and saturating with hydrogen sulphide, nickel sulphide is probably present in the colloidal condition; for the solution polarizes light, and nickel sulphide is precipitated from it by the addition of gum-arabic and alcohol. The different behavior of cobalt, which is precipitated by the hydrogen sulphide, therefore arises merely from the much smaller tendency of its sulphide to remain in the colloidal condition. Villiers' method of separation, which is based on this difference of behavior, is regarded by the author to be unsatisfactory for several reasons.

**The Relation between Structural and Magneto-optic Rotation.** BY A. W. WRIGHT AND D. A. KREIDER. *Am. J. Sci.*, 156, 416–427.—Experiments have been made by the authors to determine whether the molecular structure or aggregation to which optical activity is due is influenced by causing the chemical substance or crystals to be produced in a magnetic field, which itself, as is well known, imparts temporary activity to all substances. The results obtained were negative in all cases, it being found that *d*-tartaric acid was converted into the active forms at the same rate whether it was heated with water in a magnetic or in a neutral field, that racemic acid does not

become active when heated in a magnetic field, and that sodium chlorate does not show any increased tendency to crystallize in either the dextro- or laevorotatory form in a magnetic field. It was, however, found that both kinds of crystals of this substance, and that also crystals of ferrous sulphate have a marked tendency to form more abundantly in the strongest part of the field. It was also found, contrary to the previous experiments of Pope and Kipping (*Chem. News*, 75, 45), that the presence of an optically active substance (glucose) in the solution does not have any effect on the form of the sodium chlorate crystals produced.

**Toxic Action of Acid Sodium Salts on *Lupinus Albus*.** By LOUIS KAHLENBERG AND ROLLAN M. AUSTIN. *J. Phys. Chem.*, 4, 553-569.—It is found that the toxic effect of the acid sodium salts of oxalic, tartaric, malic, succinic, and citric acids, on seedlings of *Lupinus Albus*, increases with the extent of their dissociation into hydrogen ions, but is very far from proportional to the concentration of these, as is shown especially by a comparison with the effect of hydrochloric acid. As in the case of their sour taste (*this Rev.*, 6, 73), the physiological action of these salts is dependent, not only on the concentration of the hydrogen ions, but also on that of the salt as a whole.

**Relationships between Thermodynamic Fundamental Functions.** By J. E. TREVOR. *J. Phys. Chem.*, 4, 570-584.—The author derives a large number of equations expressing the relationships between the four fundamental functions, energy, free energy, the heat function, and the thermodynamic potential, both for the case of a system of definite masses and for the individual phases.

**The Boiling-points of Mixtures of Chloral and Water.** By JOSEPH C. CHRISTENSEN. *J. Phys. Chem.*, 4, 585-597.—It is found that the addition of 5 per cent. of water to pure chloral causes a depression of its boiling-point by about 2°; about 5 per cent. more water then raises it to its original value; after which further additions raise the boiling-point very gradually to that of pure water, which is about 3° higher than that of pure chloral.

**On the Emission and Absorption of Water Vapor by Colloidal Matter: Correction.** By P. DUHEM. *J. Phys. Chem.*, 4, 598.—Two equations in the previous article with the same title (*this Rev.*, 6, 74) are stated to be incorrect.

**On the Position of Helium, Argon, and Krypton in the Scheme of the Elements.** By WILLIAM CROOKES. *Am. J. Sci.*, 156, 189-192.—The author points out that in his earlier

proposed arrangement of the elements (*J. Chem. Soc.*, 53, 502, 1888) at equi-distant intervals on an ascending curve of figure-eight horizontal projection, vacant spaces exist into which the new elements, helium, neon, argon, metargon, and krypton, are, in consideration of their properties, appropriately inserted.

H. M. GOODWIN, REVIEWER.

**The Solution-tension of Zinc in Ethyl Alcohol.** BY HARRY C. JONES AND ARTHUR W. SMITH. *Am. Chem. J.*, 23, 397-403. —From Kahlenberg's value of the electromotive force (0.195 volt) of the cell: Zn, 0.1 n ZnCl<sub>2</sub> alcoholic, 0.1 n ZnCl aqueous, Zn (see *this Rev.*, 6, 11), the authors calculate the value of the electrolytic solution-pressure of zinc in alcohol to be  $1.9 \times 10^{10}$ . From the same investigator's measurement of the absolute potential difference between zinc and a 0.1 normal alcoholic ZnCl<sub>2</sub> solution, 0.327 volt, the value is of the same order of magnitude, namely,  $2.7 \times 10^{10}$ . These calculations are based on a determination of the dissociation of ZnCl<sub>2</sub> in alcohol by the boiling-point method, which gave 6.5 per cent. for a 0.1 normal solution. The electrolytic solution-tension of zinc in water, as computed by Ostwald, is  $10^{18}$ , thus about  $10^8$  times as great as the value in alcohol.

**The Conductivity Temperature Coefficient of some Liquid Ammonia Solutions.** BY EDWARD C. FRANKLIN AND CHAS. A. KRAUS. *Am. Chem. J.*, 24, 83-93. —Solutions of ammonium chloride, bromide, and iodide, of potassium iodide, of paranitrophenol, and of copper nitrate in liquid ammonia were sealed in thick-walled tubes provided with small platinum electrodes, and their molecular conductivity determined, over wide ranges of temperature. In all these cases, with rising temperature, the conductivity passed through a maximum. The same was found to be true for a solution of potassium iodide in methylamine. A solution of sulphur in ammonia showed a distinct conductivity at 139.5°, which is 6.5° above the critical temperature of ammonia. Solutions of potassium, sodium, and lithium in liquid ammonia have a positive temperature coefficient.

**On the Electrolytic Deposition of Metals from Non-aqueous Solutions.** BY LOUIS KAHLENBERG. *J. Phys. Chem.*, 4, 349-355. —Experiments were made on the deposition of silver from solutions of silver nitrate in pyridine, aniline, benzonitrile, quinoline, and acetone, and also on that of lead and antimony from non-aqueous solutions. Comparing the amount of silver deposited with that deposited in an ordinary silver voltameter connected in series with the electrolytic cell, it was found that the latter was uniformly higher, by nearly a per cent. in some cases. This discrepancy is

attributed to secondary reactions, as the silver-deposits from the non-aqueous solutions were usually discolored. It was found that silver could be completely separated electrolytically in compact form, from pyridine solutions, both pure and mixed with water. The work is stated to be only preliminary in character.

**On the Weston Cell.** BY H. T. BARNES. *J. Phys. Chem.*, **4**, 339-349.—The author has investigated a number of Weston cadmium cells of various construction with reference to the change in their temperature coefficients, which the experiments of Kohnstamm and Cohen on the inversion point of cadmium sulphate in the neighborhood of  $15^{\circ}$  would lead one to anticipate. Their experiments all show the temperature coefficient of these cells to agree remarkably well between  $15^{\circ}$  and  $40^{\circ}$ , and that they are expressed well by the formula  $E_t = E_{15} - 0.086(t - 15^{\circ})$ . Between  $0^{\circ}$  and  $15^{\circ}$  different cells behave quite differently however, some of them showing an abrupt change in their temperature coefficient at about  $2^{\circ}$ , others between  $8^{\circ}$  and  $15^{\circ}$ , while still others showed no sudden change at all. The values of the electromotive force for different cells at  $0^{\circ}$  varied as much as two millivolts. The mean corrected ratio of the electromotive force of the Clark cells at  $15^{\circ}$  to that of the cadmium cells at  $20^{\circ}$  was found to be 1.40658, while Kahle gives the nearly identical value 1.40663. The reviewer would mention in this connection that Jaeger and St. Lindeck, of the Reichsanstalt (*Ztschr. phys. Chem.*, **35**, 98), have found cadmium cells containing a 13 per cent. amalgam wholly reliable above  $10^{\circ}$ , while Cohen (*Ztschr. phys. Chem.*, **34**, 621) claims they are unreliable below  $23^{\circ}$ . The concentration of the amalgam appears to have a decided influence on the constancy of the cells.

**Electrolysis of Sodium Chloride.** BY C. G. L. WOLF. *J. Phys. Chem.*, **4**, 200-206.—The article describes a convenient apparatus for the electrolysis of solutions evolving gases at the electrodes, adapted for the laboratory and lecture room. The gases are separately collected, the apparatus kept at a uniform temperature in a thermostat, and the solution stirred. Its use is illustrated by an experiment on the electrolysis of sodium chloride.

**A Chromium Cell for the Rectification of Alternating Currents.** BY J. LIVINGSTON R. MORGAN AND W. A. DUFF. *J. Am. Chem. Soc.*, **22**, 331-334.—An electrolytic cell containing a ten per cent. sulphuric acid solution, a strip of platinum foil as cathode, and a fragment of metallic chromium as anode, was found to prevent the passage of a continuous current, if the external electromotive force was *gradually* increased, until the latter reached a value of 75 volts. The polarization is broken down at

this voltage and a current passes from chromium to platinum in the cell. The chromium electrode, however, then acquires the property of polarizing in the reverse direction; *i. e.*, a current in the reverse direction will now no longer traverse the cell from platinum to chromium until a certain voltage (which appears variable) is reached, when the cell is again broken down, a reversal takes place, and the chromium again becomes capable of opposing 75 volts when acting as anode. This remarkable behavior the authors attribute to the chromium passing from the "active" to the "inactive" state (Hittorf). The experiment is interesting in connection with the recent beautiful investigations of Ostwald on the periodic phenomena observed on dissolving chromium.

#### **Quantitative Lecture Experiments on Electrochemistry.**

BY W. LASH MILLER AND FRANK B. KENRICK. *J. Phys. Chem.*, 4, 599-618.—The authors describe in detail the construction of a lecture room galvanometer of the d'Arsonval type, and accessories, suitable for illustrating quantitatively numerous electrochemical relationships. The index of the galvanometer is so arranged that it closes a circuit through a relay, if deflected to either side of its zero position. The relay, in turn, is caused to alter a variable resistance in one arm of the Wheatstone bridge arrangement, until the adjustment for zero deflection is produced. The resistance thus automatically adjusted is recorded on a large dial, graduated to give directly in ohms the resistance of the substance measured. Fifteen quantitative lecture experiments are described, illustrating Faraday's Laws, molecular conductivity, Ostwald's dilution law, isohydric solutions, electromotive force, and polarization. (Compare also Noyes and Blanchard, *J. Am. Chem. Soc.*, 22, 726.)

#### **A New Bridge Arrangement for the Determination of Electromotive Force by Aid of the Lippmann Electrometer.**

BY J. LIVINGSTON R. MORGAN. *J. Am. Chem. Soc.*, 12, 202-204.—The arrangement consists in connecting a constant battery in series with a slide wire bridge and a resistance box containing thirteen coils each of the same resistance as the bridge wire, and balancing the unknown electromotive force against the drop in potential through a portion of the bridge coils and fraction (setting) of the bridge wire. This arrangement can hardly be designated as new.

#### **A New Electrolytic Cell for Rectifying Alternating Currents.**

BY W. L. HILDBURGH. *J. Am. Chem. Soc.*, 22, 300-304.—This is a very neat device by which one-half the wave of an alternating current can be repressed and the current thus rectified. It consists of a large platinum electrode covered with platinum black, partly immersed in a sulphuric acid solution, and partly exposed to an atmosphere of hydrogen. The other electrode

dipping in the same solution is a small platinum-wire point sealed into a glass tube. The best size for the electrodes varies with the current. The whole cell is enclosed in an atmosphere of hydrogen. When a current passes from the large to the small electrode through the liquid, hydrogen goes into solution at the large cathode and an equal quantity is liberated at the anode. On reversing the current, the small point-electrode becomes the anode and the oxygen polarization prevents the passage of the current, provided the impressed electromotive force is not too great; in the latter case several cells are connected in series.

**A Method for the Determination of Electrical Conductivity with Direct Current Instruments.** BY J. LIVINGSTON R. MORGAN AND W. L. HILDBURGH. *J. Am. Chem. Soc.*, 22, 304-307.—An alternating-current generator is connected in series with the electrolytic cell and a non-inductive resistance. Around the latter is shunted a galvanometer and a hydrogen cell for rectifying the alternating current (see preceding review). The deflection of the galvanometer is noted, and then a non-inductive resistance is substituted for the conductivity cell, and adjusted until the same deflection as before is indicated by the galvanometer. With the ordinary Kohlrausch electrolytic cell and an alternating voltage of two volts the authors state that the results agree satisfactorily with those obtained by the usual Kohlrausch method.

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## BIOLOGICAL CHEMISTRY.

A. G. WOODMAN, REVIEWER.

**The Proteids of the Egg Yolk.** BY THOMAS B. OSBORNE AND GEORGE F. CAMPBELL. *J. Am. Chem. Soc.*, 22, 413-422.—Salt solutions dissolve from egg yolk a mixture of protein compounds with lecithin, containing from 15 to 30 per cent. of lecithin. This lecithin is not removed by ether, but readily by alcohol. The resultant lecithin-free proteid obtained by fractional precipitation has a constant composition. The conclusion drawn is that the protein of egg yolk is principally a lecithin compound, soluble in salt solutions, and in its behavior resembling a globulin.

**The Protein Constituents of Egg White.** BY THOMAS B. OSBORNE AND GEORGE F. CAMPBELL. *J. Am. Chem. Soc.*, 22, 422-450.—In a previous paper (*this Rev.*, 5, 110) Osborne described preparations of crystallized egg albumin which indicated that with the substance ordinarily known as ovalbumin there are associated other protein bodies. The authors have since repeated the work on a larger scale, confirming the earlier observations, and are able to present a number of facts concerning these and other protein substances.