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WILLIAM A. NOYES, Editor.

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GENERAL AND PHYSICAL CHEMISTRY.

The Universally Exact Application of Faraday's Law. By THEODORE WILLIAM RICHARDS AND WILFRED NEWSOME STULL. *Proc. Am. Acad.*, 38, 409-413; *Ztschr. phys. Chem.*, 42, 621-625. —It is shown that an electric current deposits within 0.005 per cent. of the same amount of silver from a fused mixture of silver, sodium, and potassium nitrates at 250° as it does from an aqueous solution at 20° , thus furnishing the most accurate proof thus far brought forward of the validity of Faraday's Law for a fused electrolyte and at different temperatures. A. A. NOYES.

A Revision of the Atomic Weight of Caesium. By THEODORE WILLIAM RICHARDS AND EBENEZER HENRY ARCHIBALD. *Proc. Am. Acad.*, 38, 443-470. —Caesium chloride was purified by crystallizing repeatedly the dichloriodide, heating this, dissolving the residue, and precipitating the solution with hydrochloric acid. The ratios $\text{CsCl}:\text{AgCl}$ and $\text{CsCl}:\text{Ag}$ were determined from 25 analyses, and the atomic weight 132.877 was calculated therefrom. The corresponding ratios from six analyses of caesium bromide gave 132.880. The ratio $2\text{CsNO}_3:\text{Cs}_2\text{O}$ was also determined by heating the nitrate with pure silica, and from four such analyses the atomic weight 132.879 was calculated. This number is the final value adopted. To test the purity of the reagents and the accuracy of the method, entirely similar analyses were made with potassium chloride and nitrate; the results checked those of Stas almost completely, for they yielded 14.04 and 39.14 for the atomic weights of nitrogen and potassium. No evidence was found of the presence of any element of higher atomic weight, except a little thallium, in the original material used. The specific gravities of caesium chloride, bromide, and nitrate were found to be 3.972, 4.380, and 3.687, respectively, and the melting-point of the nitrate to be 414° . A. A. NOYES.

A New Method of Determining the Vapor Density of Metallic Vapors and an Experimental Application to the Cases of Sodium and Mercury. BY FRANK B. JEWETT. *Phil. Mag.*, (6), 4, 546-554.—The method is adapted only to saturated vapors, but can be used through a wide range of pressure and temperature. The apparatus consists of a two-liter hard-glass sphere to which are attached a capillary tube for exhausting the air and a larger ∇ -shaped tube in the sealed lower arm of which is placed the metal to be volatilized. The upper arm is then sealed, the bulb is filled with hydrogen or nitrogen and exhausted, the capillary sealed, and the whole heated in a special air-bath whose temperature, kept constant to 1° - 2° , is read from a platinum resistance thermometer. The bulb is then cooled, the ∇ -tube cut off, and the deposit of metal on the walls of the bulb dissolved off, and its amount determined analytically. In the case of sodium, it was dissolved in water, and the solution was then titrated with sulphuric acid. In the case of mercury the quantity vaporized was determined by measuring the decrease in height of the liquid mercury in the ∇ -tube, the latter being in this case of fine bore and carefully calibrated.

Results were obtained with sodium between 368° , where the absolute density was 9×10^{-8} , and 420° , where it was 750×10^{-8} . With mercury, the measurements extended from 40° to 325° , and the results agreed well with those of previous determinations by other methods. As no pressure measurements are communicated, the molecular weights cannot be calculated.

A. A. NOYES.

New Osmotic Membranes Prepared by the Electrolytic Process. BY H. N. MORSE. *Am. Chem. J.*, 29, 173-174.—The purpose of this preliminary note is to state that promising membranes consisting of zinc, cadmium, manganese, or uranyl ferrocyanide, of copper or uranyl phosphate, or of ferric or aluminum hydroxide have been prepared by the electrolytic process previously described (*this Rev.*, 7, 160; 8, 438).

A. A. NOYES.

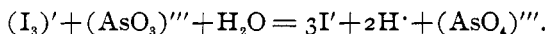
The Lowering of the Freezing-point of Aqueous Hydrogen Dioxide Produced by Certain Salts and Acids. BY HARRY C. JONES AND CHARLES G. CARROLL. *Am. Chem. J.*, 28, 284-291.—The results of Jones, Barnes, and Hyde (*this Rev.*, 8, 265) showing that salts lower the freezing-point of an approximately 5 per cent. solution of hydrogen dioxide to a less extent than they do that of pure water have been confirmed by a repetition of the experiments with potassium chloride and nitrate and by new ones with ammonium sulphate. It is suggested that this phenomenon may be due to a combination of the peroxide molecules with those of the salt. The effect lies in the opposite direction in the case of sulphuric and oxalic acids, the two acids investigated.

A. A. NOYES.

The Rate of the Reaction between Arsenious Acid and Iodine in Acid Solution; the Rate of the Reverse Reaction; and the Equilibrium between Them. BY J. A. ROEBUCK. *J. Phys. Chem.*, 6, 365-398.—The rate of the first-named reaction at 0° was found, both by following the course of the reaction with definite mixtures and by varying the initial concentrations, to be directly proportional to the concentration of the iodine or I_3' ions (C_A) and to that of the arsenious acid (C_B) and inversely proportional to that of the sulphuric acid present (C_D) and to the square of that of the iodine ions (C_C); that is, $dC/dT = k_1 C_A C_B / C_C^2 C_D$. This is shown to be in accord with the assumptions that the reaction which determines the rate is $(AsO_3)''' + HIO = (AsO_4)''' + H' + I'$, and that the equilibria of the reactions $(I_3)' = I_2 + I'$, and $(I_3)' + (OH)' = HIO + 2I'$ are established instantaneously.

The rate of the reverse reaction, the reduction of arsenic acid by hydriodic acid, was found to be proportional to the concentration of the arsenic acid (C_E), and to increase somewhat more rapidly than the concentration of the iodine ion (C_C) and much more rapidly than that of the sulphuric acid (C_D) when this is concentrated, but nearly in the same proportion when it is dilute. In dilute solution, therefore, the rate is approximately expressed by the equation $dC/dT = k_2 C_C C_D C_E$.

The equilibrium of the reaction was also determined at 0° with the help of a large number of experiments, and was found to be capable of close expression by means of the equation, $K = C_A C_B / C_C^3 C_D^2 C_E$, which is in correspondence with the ionic reaction that actually occurs:



The special aim of the investigation was to ascertain whether by equating the empirically found expressions for the rates of the two opposing reactions an expression identical in form with the equilibrium equation would result, as is required by the kinetic theory of chemical equilibrium. The results stated above strikingly show that this is the case. Moreover, the numerical value of the ratio of the two velocity-constants ($k_1/k_2 = 8.6 \times 10^5$) is of the same order of magnitude as the equilibrium-constant ($K = 1.5 \times 10^5$). Two experiments on the rates of the two reactions at 10° and one on their equilibrium at 20° showed that a rise of 10° multiplies the ratio k_1/k_2 by 1.6 and the equilibrium constant K by 1.4, thus by nearly the same amount.

The importance of these results makes it desirable that the investigation be continued with the aim of confirming them and of attaining a closer confirmation of the principles involved, which could probably be done by using the acids themselves (HI and As_2O_3) rather than their salts, by replacing the sulphuric acid by hydrochloric acid, whose dissociation relations are much simpler, and by experimenting only with dilute solutions. A. A. NOYES.

The Rate of Oxidation of Ferrous Salts by Chromic Acid.

By CLARA C. BENSON. *J. Phys. Chem.*, 7, 1-14.—The conclusions are reached that the rate is proportional to the square of the concentration, both of the ferrous salt and of the sulphuric acid, and that it is much reduced by the presence of ferric salts. Uncertain results were obtained as to the effect of the concentration the bichromate. The ferrous salt unoxidized at different periods of the reaction was determined by titrating with sodium arsenite the amount of iodine liberated (through the catalytic action of the ferrous salt) in four minutes after the addition of a potassium iodide solution to the reaction-mixture, comparative experiments being made under nearly the same conditions with known quantities of ferrous salt.

A. A. NOYES.

The Compensation Method of Determining the Rate of Oxidation of Hydrogen Iodide.

By JAMES M. BELL. *J. Phys. Chem.*, 7, 61-83.—The purpose of the work was to determine whether the addition of sodium thiosulphate to the reaction-mixture introduces an error into the determination of the rate of oxidation of hydriodic acid by various oxidizing agents. It was found that this was probably not the case with hydrogen peroxide. Chloric, bromic, and chromic acids, on the other hand, rapidly oxidize the thiosulphate, and, though the rate of this oxidation is less in the presence of iodide, the results obtained by the use of thiosulphate are seriously in error. A few measurements of the effect of varying the concentrations of the oxidizing agent and acid upon the rate of oxidation of the thiosulphate in the absence of iodide did not yield simple or uniform results.

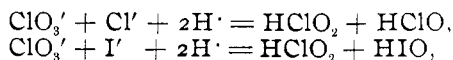
A. A. NOYES.

The Rate of Reaction in Solutions Containing Potassium Iodide, Potassium Chlorate, and Hydrochloric Acid.

By W. C. BRAY. *J. Phys. Chem.*, 7, 92-117.—It is found that the rate of this reaction can be approximately expressed by the equation

$$dC/dT = C_{I_2}^2 \times C_{ClO_3} \times (k_1 C_F + k_2 C_{Cl}),$$

provided the concentration of the acid (C_H) is between 0.5 and 2 normal and that of the iodide (C_I) is between 0.4 and 1 normal. This equation would result if the two following reactions take place simultaneously, and require time for their occurrence,



and if the iodide is then instantaneously oxidized by the $HClO_2$, $HClO$, or HIO . At smaller concentrations, however, especially of the iodide, this equation does not apply at all; when the concentration of the iodide is decreased from 0.025 to 0.006 normal the rate actually increases, according to the measurements presented.

Free iodine added even to saturation retarded the reaction only 15-20 per cent. On the other hand, the addition of only $\frac{1}{40}$ as much ferrous sulphate as there was chlorate present increased the rate in one case thirteenfold.

A. A. NOYES.

The Speed and Nature of the Action of Bromine on Oxalic Acid. BY THEODORE WILLIAM RICHARDS AND WILFRED NEW-SOME STULL. *Proc. Am. Acad.*, **38**, 321-337; *Ztschr. phys. Chem.*, **41**, 544-559.—It was found that the speed of the reaction (measured by the decrease in the bromine concentration) is scarcely affected by varying the oxalic acid concentration from 0.7 to 4 per cent., but that it is greatly increased by neutralization or the addition of a salt of a weak acid and decreased by all strong acids and in an especially high degree by hydrobromic acid. From these facts the authors conclude that it is the $C_2O_4^{--}$ ion which reacts with Br_2 molecules, and that the removal of the latter by combination with the hydrobromic acid (forming HBr_3) explains the great retardation caused by this acid.

A. A. NOYES.

The Relation between Negative Pressure and Osmotic Pressure. BY GEORGE A. HULETT. *Ztschr. phys. Chem.*, **42**, 353-368.—The author first reviews the experimental investigations on the negative pressure produced in liquid columns, and then discusses the theoretical considerations of Stefan and Tumlirz based on the kinetic theory of vaporization and Van der Waals' equation, from which he concludes that the tenacity of liquids, like alcohol and water, is such that they would withstand a negative pressure of 2,000 to 5,000 atmospheres, if it could be uniformly applied to them.

An experiment, analogous to previous ones by Askenasy, is then described, in which a funnel, whose top is closed with a porous porcelain plate having within it a copper ferrocyanide membrane, is joined to a tube two meters long, whose lower end after the whole is filled with water is dipped under mercury; upon standing, or more rapidly by drawing an air current over the porcelain plate to cause evaporation, the mercury column rose to a height of 1111 mm. or until a negative pressure of 377 mm. was produced. The rise of sap in trees is considered to be a phenomenon of the same kind, depending on the tenacity of the column of sap raised by the evaporation from the leaves and lenticels.

Since in a solution the osmotic pressure acts outwardly against its bounding surface and tends to increase its volume, it can be regarded as a negative pressure; and since it can be shown that submitting a liquid to a negative pressure must decrease its vapor pressure, it is seen why the vapor pressure of a solution is less than that of a pure solvent.

The author then considers the thermodynamic relation between the negative pressure on the liquid and its vapor-pressure, and owing to a minor error in the fourth step of his cyclical process and to his neglecting certain small terms, he obtains an approximate formula instead of the exact one previously derived by the reviewer (*Ztschr. phys. Chem.*, **35**, 714). Instead of then placing this negative pressure exactly equal to the osmotic pressure of a solution having the same vapor pressure (which is obviously correct since such a solution could be placed on the semi-permeable wall at A in the author's Fig. 3 without disturbing the equilibrium), the author follows the irrational procedure of the earlier deductions, which consists in placing the wall at the foot of the osmotic tube so that the osmotic pressure involved is that of a different solution (namely, a compressed one) from the solution whose vapor-pressure is considered. He therefore meets with the usual complications with reference to the volume term.

A. A. NOYES.

On the Iodides of Caesium. BY H. W. FOOTE. *Am. Chem. J.*, **29**, 203-212.—The author has proved that CsI_3 and CsI_5 are the only periodides of caesium capable of existing in contact with the aqueous solution either at its freezing-point or at 35.6° , for under this assumption the phase rule requires that there be three and only three constant values of the composition of the saturated solution, even though the excess of iodine over CsI in the solid phase may have any value whatever. These three solubility-values corresponding to the three pairs of solid phases (CsI and CsI_3 , CsI_3 and CsI_5 , and CsI_5 and I_2) were actually determined, and were proved to be constant when the proportions of the two solid phases were varied, thus showing the absence of intermediate compounds.

A mixture of solid caesium penta-iodide, iodine, and a little water were heated in a dilatometer: at 51.5° a large increase of volume occurred, corresponding to the formation of a new phase consisting of a heavy liquid. Above this temperature one of the two solid phases (CsI_5 or I_2) disappeared, according to which was present in smaller amount. The composition, both of the aqueous phase and of the heavy liquid, corresponding to the presence of each of these two solid phases was determined at 52.2° and 72.6° .

When dry caesium pentiodide and iodine are heated together, whatever may be their relative proportions, the mixture melts at 73° and the liquid produced has a constant composition, again proving the non-existence of higher periodides.

A. A. NOYES.

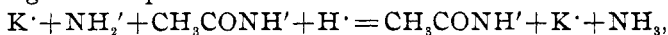
On Amorphous Sulphur. I. Influence of Amorphous Sulphur on the Freezing-point of Liquid Sulphur. BY ALEXANDER SMITH AND WILLIS B. HOLMES. *Decennial Publications, Univ. of Chicago*, **9**, 55-64; *Ztschr. phys. Chem.*, **42**, 469-480.—The au-

thors have determined by the Beckmann method the freezing-point of liquid sulphur containing various quantities of amorphous sulphur, which had been produced in it by previous heating of pure sulphur to temperatures above its melting-point. As soon as the freezing-point was obtained, the mass was poured into a cold porcelain dish, and, after standing till the following day to allow the amorphous sulphur present to solidify completely, 10 grams of the pulverized mass were extracted in a Soxhlet apparatus with cold carbon bisulphide which removed all the soluble sulphur, but dissolved of the amorphous sulphur only very small quantities, which were corrected for. Special experiments showed that no considerable conversion of amorphous to soluble sulphur took place during the cooling or subsequent standing.

The lowering of the freezing-point was found to be closely proportional to the quantity of amorphous sulphur present, showing that it forms a true solution. From the heat of fusion, the molar freezing-point lowering for sulphur as a solvent was calculated to be 328° , and with the help of this the molar weight of the amorphous sulphur was found to be 7.75×32 and therefore to correspond nearly to the formula S_8 . Hence amorphous sulphur has the same molecular formula as soluble sulphur when the latter is dissolved in various solvents. The melting-point of pure sulphur was found by extrapolation to be 119.25° and a sample was actually prepared so free from amorphous sulphur as to melt at 119.17° .

A. A. NOYES.

Reactions between Acid and Basic Amides in Liquid Ammonia. BY EDWARD C. FRANKLIN AND ORIN F. STAFFORD. *Am. Chem. J.*, **28**, 83-107.—In conformity with the previously established fact that both acid and basic amides are good conductors of electricity when dissolved in liquid ammonia, it is now shown that several of them react instantaneously with one another according to the equation



which is completely analogous to the neutralization of acids and bases in aqueous solution. The second hydrogen atom of the acid amides can also be replaced by a potassium atom by direct metathesis with potassium amide.

A. A. NOYES.

An Apparatus for Continuous Vacuum Distillation. BY CHARLES F. MABERY. *Proc. Am. Acad.*, **38**, 3-5; *Am. Chem. J.*, **29**, 171-173.—The convenient apparatus developed by the author in connection with his long series of investigations upon petroleum is described in detail. It cannot be briefly explained without the cut which accompanies the article.

A. A. NOYES.

Physico-Chemical Investigations in the Pyridine Series. BY E. J. CONSTAM AND JOHN WHITE. *Am. Chem. J.*, **29**, 1-49.—The following thermochemical constants expressed in small calories at 15° were determined:

Substance.	Molar heat of combustion.	Specific heat of vaporization (L).	Trouton constant (ML/T).	Molar boiling-point raising (0.02 T ² /L).	Heat of neutraliza- tion.
Pyridine.....	659,200	106.1	21.9	28.4°	4776
α -Picoline	816,100	93.3	21.5	34.6°	5980
β -Picoline	813,100	96.7	21.3	35.8°	5690
γ -Picoline	816,700

The heats of combustion and vaporization refer to constant pressure. The heats of neutralization were determined by neutralizing a 0.5 molar aqueous solution of the base with an equally concentrated one of hydrochloric acid. The specific heat capacities at t° were found to be $0.3915 + 0.000484 t$ for pyridine, and $0.3848 + 0.000774 t$ for both α - and β -picoline. Compare Ladenburg's results (*this Rev.*, 7, 151).

From these data the following conclusions are drawn. The heats of combustion of the three isomeric picolines are nearly identical, and their mean differs from the heat of combustion of pyridine by the same quantity (156,000 cal.) as do successive homologues in the methane and benzene series. The Trouton constant holds and has about the same value as with other compounds. The specific heat capacities are linear functions of the temperature, but the temperature-coefficients for pyridine and its homologues are not identical, as is approximately the case in other series.

Measurements are also given of the refractive power and density of the four bases. The results agree closely with those of Brühl.

The authors also determined the conductivities at 25° and at different dilutions, of the picrate of each of the four bases when dissolved in pure water and in solutions of the corresponding base (whereby hydrolysis was prevented). From the difference in conductivity the degree of hydrolysis was calculated with the help of the conductivity values for the picric and pyridine or picoline ions, which were themselves derived from new measurements with picric acid and sodium picrate and from those just referred to with pyridine or picoline picrate. The hydrolysis in $\frac{1}{256}$ molar solution was from 1 to 3 per cent. From the hydrolysis-value and the dissociation-constant of water the dissociation-constants of the bases were calculated by the equilibrium equation given by Arrhenius (*Ztschr. phys. Chem.*, 5, 17), and found to be 3×10^{-2} , 32×10^{-2} , 11×10^{-2} , and 11×10^{-2} for pyridine and for α -, β -, and γ -picoline, respectively. The values for pyridine and α -picoline agree fairly well with those found by Goldschmidt and Salcher (*Ztschr. phys. Chem.*, 29, 116) by a different method.

A. A. NOYES.

A Thermochemical Constant. BY F. W. CLARKE. *J. Am. Chem. Soc.*, 24, 882-892; *Ztschr. anorg. Chem.*, 33, 45-57.
A New Law in Thermochemistry. BY FRANK WIGGLESWORTH

CLARKE. *Proc. Washington Acad. of Science*, 5, 1-37.—The first of these articles was a preliminary one, and its substance together with much additional material is included in the second article. It is shown that the molar heat of combustion (K) (when both the hydrocarbon taken and the water formed are gaseous) of the 14 single, double, and triple bonded aliphatic hydrocarbons studied by Thomsen can be expressed by the equation $4K = \text{const.} \times (11c - 8n)$, where c is the number of oxygen molecules consumed in the combustion of 4 molecules, and n is the number of atomic unions in a single molecule (thus, with methane, $c = 8$ and $n = 4$; with acetylene, $c = 10$, $n = 3$). The deviations from the mean value of the constant (13,873) are not greater than 1.6 per cent. except in one case. This equation is interpreted as follows: $8n \times 13,800$ cal. represents the heat absorbed by the dissociation of 4 molecules into isolated carbon and hydrogen atoms, and $11c \times 13,800$ cal. represents the heat evolved by the combination of these atoms with molecular oxygen; consequently the validity of the equation involves that of the following principles: (1) the heat of formation of a fatty hydrocarbon from the isolated atoms is directly proportional to the number of atomic unions in the molecule and independent of the nature of the atoms; (2) the heat of combination of one isolated carbon atom with oxygen is identical with that of four hydrogen atoms with oxygen.

These principles are also shown to apply to the 20 halogen derivatives investigated by Thomsen, with the single exception of tetrachlormethane; for, in these cases hold true, as closely as before, the equations $4K = 13,800 (11c - 8n + h)$, $4K = 13,800 (11c - 8n + 2h_1)$, and $4K = 13,800 (11c - 8n + 4h_2)$, in which h , h_1 , and h_2 represent the number of chlorine, bromine, and iodine molecules, respectively, produced by the combustion of 4 molecules of the halogen compound. Hence, $13,800$, $2 \times 13,800$, and $4 \times 13,800$ calories represent the heat of formation of 1 mol of chlorine, bromine, and iodine from the isolated atoms.

The last-mentioned fact and the integral coefficients of the other quantities, n and c , indicate that 13,800 calories is a unit-quantity of heat, of which some small multiple is involved in every atomic union, and accordingly the author applies to it the special name of *henotherm* (from *ἐνώω*, unite). Thus, it follows from the above equations that the heat of union of an isolated carbon atom with an isolated hydrogen or halogen atom or with another carbon atom (whether singly, doubly, or trebly bonded is immaterial) is 2 henotherms.

A confirmation of these conclusions is furnished by the fact that the heat of addition of bromine in carbon tetrachloride solution to nine double-bonded compounds is 2 henotherms (4 in the case of diallyl), which is what is required by the author's conclusions, since two atomic unions (evolving 4 henotherms) and

the dissociation of one molecule of bromine (absorbing 2 henotherms) takes place; three complex oxygenated compounds give an abnormal heat-effect, however.

Furthermore, it follows that the heat of union of an isolated carbon atom or of four isolated hydrogen atoms with one oxygen molecule is 11 henotherms; this is, however, evidently a composite quantity equal to the difference of the heat of union of one carbon or four hydrogen atoms with isolated oxygen atoms, and the heat of dissociation of the oxygen molecule; and by making the somewhat arbitrary assumption that the latter heat is 1 henotherm, the author concludes that the former is 12 henotherms or 164,400 cal. The fact is also emphasized that the henotherm is nearly identical in value with the neutralization-constant (13,700 cal.) of strong acids and bases, which is the heat effect attending a very simple case of atomic union.

The heats of combustion of ten aliphatic amines are also expressed within 2 per cent. by a formula entirely analogous to that used for the halogen compounds, nine henotherms (123,300 cal.) being taken as the heat of dissociation of the nitrogen molecule. Ammonia forms an exception, so also do the four cyanogen compounds for which data exist, but the heats of combustion of these last can be correctly calculated, if a value of five, instead of two, henotherms be assigned to the union $C \equiv N$. Eight sulphur compounds conform to a formula like that used for the amines, a term being introduced to represent the heat of combustion of isolated sulphur atoms.

The simple and mixed ethers conform to the formula used for the hydrocarbons; the heat absorbed by the breaking of each of the unions in $C-O-C$, therefore, has the same value (2 henotherms) as in the groups $C-H$, $C-Cl$, $C-Br$, $C-I$, $C-C$, $C=C$, $C \equiv C$, $C-N$, and $C-S$. In the case of other oxygen compounds, however, and of the aromatic compounds, additional constants have to be introduced.

Finally it may be mentioned that the author finds that when his values for the dissociation of the chlorine, bromine, and iodine molecules are added to the heats of combination of the gaseous halogens with various metals and the heats of solution of the resulting salts in water, the sums have an almost identical value in the case of the three different halogens. Thus, the heat effect of these atomic unions is again constant, and the author's dissociation-heats for the three halogens are confirmed.

Whether these empirical formulas are merely mathematical fictions, or whether the author has succeeded in bringing to light real theoretical relationships, can be fully established only by an exhaustive study of the question whether the close agreement of the calculated and observed heat-effects could have arisen solely through the arbitrariness of the choice of even integral numbers of henotherms to represent the various elementary heat effects.

The argument of Loeben (*Ztschr. anorg. Chem.*, **34**, 179) that isomeric substances have somewhat different heats of combustion, proves, to be sure, that the author's principles can not alone furnish an exact explanation of the phenomena, but they may still represent the underlying causes upon which other secondary causes superpose their effects. It should be added that since this abstract was put into print, an article has also appeared by Thomsen (*Ztschr. phys. Chem.*, **43**, 487), in which the validity of the author's conclusions is denied.

A. A. NOYES.

References to Papers on Low Temperature Research. By J. S. SHEARER. *Phys. Rev.*, **15**, 243-254.—A list is given of the titles of the scientific articles published since 1890, describing low temperature work, together with the author's names and journal references. The titles are classified under seven general headings. Under "Chemical Phenomena" are found eight titles.

A. A. NOYES.

A Cell for Measuring the Electrical Resistance of Liquids. By W. WALTER DINWIDDIE. *Phys. Rev.*, **15**, 237-238.—The cell consists only of a straight, narrow, horizontal glass-tube just a meter long, whose ground ends are inserted by means of corks in much wider tubes in which the electrodes are placed. The mean cross-section of the tube is first determined by weighing it full of water. The cell is intended to enable students to make absolute resistance determinations.

A. A. NOYES.

The Electro-Affinity Theory of Abegg and Bodländer. By JAMES LOCKE. *Am. Chem. J.*, **28**, 403-410.—This article forms a continuation of the discussion of the justification and value of the theory named in the title (see *this Rev.*, **8**, 266, 446). The author reiterates and extends his previous objections to the theory, maintains that these were not removed by the recent reply of Abegg and Bodländer, and contends that these investigators have now admitted that other effects obscure the influence of electro-affinity in so many cases as to make its value as a new principle of chemical systematization very slight.

A. A. NOYES.

Action upon Metals of Solutions of Hydrochloric Acid in Various Solvents. By HARRISON EASTMAN PATTEN. *J. Phys. Chem.*, **7**, 153-189.—Qualitative statements are made in regard to the action upon twenty different metals of solutions of dry hydrogen chloride in anhydrous chloroform, carbon tetrachloride, ethyl chloride, benzene, silicon chloride, stannic chloride, phosphorus chloride, arsenious chloride, antimony chloride, sulphur chloride, and thionyl chloride. The conclusions drawn are that solutions that have a scarcely appreciable conductivity often act vigorously upon certain metals, especially upon zinc, magnesium, and aluminum, and that the phenomenon is of a highly specific character depending on chemical affinity, and apparently not related to the

electrical conductivity of the solution, to the heat of formation of the metallic chloride, or its solubility. Arguments are also presented against the assumption that ionization is an essential condition of chemical reactivity.

In a postscript the author defends the validity of his own results against the statement made by Professor Remsen in the discussion of the paper, that he had found that upon placing dry zinc in a dry solution of hydrogen chloride in benzene, only a slight evolution of hydrogen occurred and this ceased in less than two minutes, but began again on opening the tube and breathing into it. The author's contention is that the materials used by Professor Remsen, unlike his own, were not completely dry, and that a little water retards the action by hydrating and making pasty the film of zinc chloride upon the metal. He repeated his own experiment in the presence of witnesses with the same result as at first.

A. A. NOYES.

Solubility, Electrolytic Conductivity, and Chemical Action in Liquid Hydrocyanic Acid. BY LOUIS KAHLBERG AND HERMAN SCHLUNDT. *J. Phys. Chem.*, 6, 447-462.—The order of magnitude of the solubility and conductivity of about 150 organic and inorganic substances in liquid hydrocyanic acid is first stated. Quantitative data are presented for the conductivity, at 0° and at various concentrations, of 13 salts, 4 bases, and 7 acids, thus supplementing those of Centnerszwer (*Ztschr. phys. Chem.*, 39, 217). The six potassium salts investigated, and ammonium chloride, have a conductivity two or three times as great as that in aqueous solution under corresponding conditions, while that of silver nitrate is only about one-fourth as great as in aqueous solution. Bismuth and antimony chlorides, pyridine, and acetic, cyanacetic, trichloroacetic, and trichlorolactic acids have a conductivity less than 2 per cent. of that of the potassium salts. Hydrochloric and sulphuric acids, and amylamine, strychnine, and morphine are moderately good conductors, but these substances probably all reacted chemically with the solvent, as indeed some of the other substances may have done. In the case of almost all the substances, the molar conductivity increases rapidly with the dilution.

Qualitative statements are made in regard to the action of strong acids dissolved in liquid hydrocyanic acid upon various metals and upon carbonates.

A. A. NOYES.

A Study of the Conductivity of Certain Salts in Water, Methyl, Ethyl, and Propyl Alcohols, and in Mixtures of These Solvents. BY HARRY C. JONES AND CHARLES F. LINDSAY. *Am. Chem. J.*, 28, 329-370.—Systematic series of conductivity measurements in water, methyl alcohol, and ethyl alcohol, and mixtures of them were made both at 0° and 25° at dilutions of 32 or 64 to 1024 liters with potassium iodide, ammonium bromide,

strontium iodide, and lithium nitrate. A few measurements were also made with cadmium iodide and ferric chloride in these solvents and with strontium iodide in propyl alcohol and a 50 per cent. mixture of it with water.

In the case of all the salts except cadmium iodide, there is in the methyl alcohol-water mixtures a minimum conductivity. This is pronounced at both temperatures, but much more so at 0° than at 25° . Such a minimum is also shown in the ethyl alcohol-water mixtures at 0° , but not at 25° . The mixtures of methyl and ethyl alcohol do not exhibit this phenomenon, but the conductivity in a 50 per cent. mixture is less than the mean of those in the two pure solvents. It is suggested that assuming the correctness of the hypothesis of Dutoit and Aston, according to which the dissociating power of solvents increases with the association of their molecules, the decrease of conductivity may be due to a diminution of the molecular association of each solvent by the other. Since, however, even, at a dilution of 1024 liters, the maximum decrease of conductivity at 0° in the methyl alcohol-water mixtures is not far from 50 per cent. of the conductivity in pure water or methyl alcohol, the effect produced by mixing the solvents must be due mainly to a large decrease in the migration velocity rather than in the degree of dissociation. It is, to be sure, highly probable that the assumed change in molecular association of the solvents takes place and this is in some way related to the change in migration velocity.

Unfortunately, the authors have not discussed the significance of their valuable experimental material with respect to the two factors—dissociation and migration velocity—upon which conductivity depends, and it is to be hoped that they intend to supply this deficiency in a second paper. It is very important, in view of the present congestion of scientific data, that all investigators fully realize that their quantitative measurements, however carefully made, lose a large part of their scientific value unless the conclusions warranted by them are carefully studied and explicitly stated and summarized. It is also to be regretted that the authors have expressed their results in terms of the nearly obsolete Siemens unit.

A. A. NOYES.

On the Electrolytic Preparation of Iodoform from Acetone.

By HOWE ABBOTT. *J. Phys. Chem.*, 7, 84-91.—The authors have determined that the conditions under which the best yield of iodoform can be obtained by the electrolysis of an aqueous solution of acetone, potassium iodide, and sodium carbonate, are as follows: temperature, 75° ; current density, 0.9-1.35 amperes per sq. dm.; anode solution consisting of 6 grams Na_2CO_3 , and 10 grams KI in 100 cc. of water; addition of 5.5 cc. acetone in successive small portions of 0.5 cc. each. Under these conditions the yield was 60 per cent. referred to the electricity used, and 12.3 per cent. referred to the acetone. By reducing to one-fifth the

quantity of acetone, these two yields became 41 and 47 per cent. respectively.

A. A. NOYES.

On the Passage of a Direct Current through an Electrolytic Cell. BY S. L. BIGELOW. *J. Phys. Chem.*, 6, 603-629.—In this paper the old problem of continuous conduction through electrolytes at voltages below those requisite for electrochemical decomposition is considered. This question is one which has occupied the attention of physicists since the time of Faraday, the existence of a "metallic" conduction in electrolytes having been often asserted and as often denied. In the present paper the author, after discussing the various views advanced at different times, describes a number of experiments which show that a current will pass for weeks through an electrolyte below the decomposition voltage of water. This current depends upon the quantity of gas (oxygen, hydrogen) dissolved in the solution, and not upon the concentration of the electrolyte. He concludes, therefore, that the current observed is carried not by ions resulting from the dissociation of the electrolyte, but by a form of ions hitherto unrecognized due to the dissolved gases.

The following theory is suggested to explain the phenomenon. A dissolved gas is in a condition analogous to a rarefied gas, some of whose molecules are capable of carrying positive and others negative charges (Thomson). A hydrogen molecule plus a corpuscle of electricity is negatively charged and one minus such a corpuscle is positively charged, the process of solution being sufficient to occasion in some unknown way this ionized or electronized state. The very small current observed below the decomposition voltage of an electrolyte is conducted by these electrified molecules, while in ordinary electrolysis the current is conducted by the ordinary ions.

H. M. GOODWIN.

Electrolysis of Water. BY W. R. WHITNEY. *J. Phys. Chem.*, 7, 190-193.—The author maintains that Bigelow's hypothetical explanation (see the preceding abstract) of the passage of a current through water below the decomposition voltages is entirely unnecessary, since that phenomenon is fully accounted for by Helmholtz' principle, according to which the back electromotive force at the electrodes diminishes to the limit zero as the pressure of the hydrogen and oxygen gases in contact with them diminishes. Since, when their pressure is less than the external pressure, the hydrogen and oxygen deposited in the electrodes must be removed by the slow processes of diffusion and convection, the decomposition of the water cannot take place rapidly or with visible evolution of gas. The depolarization of the oxygen electrode by the dissolved hydrogen is also an important factor. The author also points out that the phenomenon is not in conflict with the laws of energetics, as Bigelow assumed, for the free energy, though not the total energy, of the gases decreases with their

pressure in the same proportion in which the electrical work required for their production decreases.

A. A. NOYES.

On the Inversion of Zinc Sulphate. BY H. T. BARNES AND H. L. COOKE. *J. Phys. Chem.*, **6**, 172-177.—In a previous paper (*this Rev.*, **6**, 79), it was shown that the inversion temperature of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ into $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ is considerably lower when determined by the electrical method than when determined by direct solubility measurements, the two values being 38.75° and 39.95° , respectively. As the former value has been confirmed by various other investigators, it was thought that the presence of mercurous sulphate in the Clark cell might account for the difference. Experiments show that the inversion temperatures determined with and without the presence of mercurous sulphate differ by a very slight amount, but the values obtained in both cases are less than that given by the solubility method: the difference cannot, therefore, be explained by the presence of this salt.

H. M. GOODWIN.

The Electromotive Force of Metals in Solutions of Cyanides. BY S. B. CHRISTY. *Am. Chem. J.*, **27**, 354-420.—This article, now published in a place more accessible to chemists, consists of the experimental part of the paper of the same title previously reviewed (*this Rev.*, **7**, 195).

H. M. GOODWIN.

Liquid Potentiometer: Determining Electrolytic Resistances with Direct Current Instruments. BY CARL HERING. *Western Electrician*, **30**, 411.—A method is described for measuring the conductivity of electrolytes with the ordinary Weston instruments with a precision sufficient for commercial work. The current flowing through the electrolyte, which is contained in a rectangular trough, is measured by an ammeter. Two auxiliary electrodes of gold are inserted at a measured distance apart, and the potential between them is balanced by an opposing one, the value of which is determined by a voltmeter. If the cross-section of the tank is also known, the specific resistance of the liquid can then be calculated.

H. M. GOODWIN.

On the Theory of the Electrolytic Rectifier. BY K. E. GÜTHE. *Phys. Rev.*, **15**, 327-335.—The author regards the well-known phenomenon at an aluminum anode as due not as usually assumed, to a high resistance film of aluminum hydroxide, but to the presence of a fluid layer, probably oxygen gas, held in a film of oxide or hydroxide. This layer prevents the passage of the negative ions from the solution of the electrode. This view is supported by a number of experiments: *First*, an increase in temperature increases the current through the electrode; *Second*, the concentration of the electrolyte is without effect; *Third*, the nature of the electrolyte is indifferent so long as the reactions at the anode are similar; thus two sets of observations on solutions

of alum, ferrocyanide of potassium, and zinc sulphate, and on solutions of alum, Rochelle's salt and copper sulphate gave nearly identical polarization curves. An aluminum anode in a chloride solution, however, behaves quite differently, the chlorine acting apparently like hydrogen (when the electrode is used as a cathode). These gases do not appear to be readily retained by the film and hence offer little opposition to the discharge of the ions in the solution.

The film is likened to a kind of semi-permeable membrane. A copper ferrocyanide membrane was shown to block out the current in one direction similar to the aluminum cell. It is suggested that ordinary polarization may also be due to a fluid membrane, consisting of pure water, between the solution and the electrode.

H. M. GOODWIN.

Influence of the Solvent in Electrolytic Conduction. By HARRISON EASTMAN PATTEN. *J. Phys. Chem.*, 6, 554-601.—This is a lengthy paper, in which the author considers the theory of Arrhenius so inadequate, and the concept of molecular conductivity so unwarranted, that he neither expresses his conductivity measurements on a number of mixed organic solvents in the usual way, nor discusses them from the dissociation point of view. The principal conclusions drawn from his experiments seem to be first, that the lowering of the specific conductivity of non-aqueous solutions by addition of a pure solvent is approximately proportional to the number of mols of solvent added, upon which result a new method of molecular weight determination may be based; second, Konowalow's conclusions (*Wied. Ann.*, 49, 733) that electrical conductivity increases with the heat effect of the chemical combination between solvent and solute and that the conductivity of aqueous solutions is related to the small molecular volume of water are regarded as untenable; and third, the conduction of electricity by a solvent depends upon the fact that a compound is formed by the solvent and solute when solution takes place, the degree of conductivity depending upon the constituents in this compound and possibly upon their arrangement. Reference must be made to the original paper for further details.

H. M. GOODWIN.

On the Relative Velocities of the Ions in Solutions of Silver Nitrate in Pyridine and Acetonitrile. By HERMAN SCHLUNDT. *J. Phys. Chem.*, 6, 159-172.—The transference numbers for silver in acetonitrile and pyridine solutions of silver nitrate were determined by the Nernst and Loeb method, at concentrations varying from one to one-fortieth molar. The values obtained were found to increase in both cases from 0.383 to 0.473, and from 0.326 to 0.440, respectively. The increase is thought to be an example of a general relation exhibited by salts which have a strong affinity for the solvent.

H. M. GOODWIN.

Experiments on the Electrolytic Reduction of Potassium Chlorate. BY G. H. BURROWS. *J. Phys. Chem.*, 6, 417-426.—Experiments are described on the effect of anode and cathode current densities, temperature, and duration of electrolysis on the reduction of potassium chlorate to chloride with copper electrodes. Calculating the electrical efficiency on the basis that 3×26.8 ampere-hours are required to reduce one mol of potassium chlorate, it was found that with both anode and cathode in the same compartment an efficiency approaching 200 per cent. could be obtained. This is true over quite a wide range of temperature and concentration, and is independent of cathode density. A high current density at the anode is desirable. Presence of free acid rapidly cuts down the efficiency.

To explain this abnormally high efficiency, experiments were carried out with the anode and cathode in separate compartments. A direct reduction of chlorate to chloride to the amount of 58 per cent. was found at the anode, cuprous chloride or copper oxide being formed. Little or no reduction occurred at the cathode, however. If, however, copper sulphate was added before the electrolysis to the cathode portion, a reduction of 91 per cent. was found. This result is in agreement with experiments of Binz on the effect of a zinc anode, or added zinc salt on the efficiency of the electrolytic reduction of indigo. The high efficiency obtained with a single compartment cell is therefore due to the presence at the cathode of copper dissolved at the anode.

H. M. GOODWIN.

Electrochemical Polarization. BY C. J. REED. *J. Franklin Inst.*, 153, 259.—A general discussion of the phenomena based on the following definition of polarization given by the author: "Polarization is a progressive change in the composition and electromotive force of an electrochemical system necessitated by the progressive exhaustion of one or more of the electrochemical reagents." The article contains nothing essentially new.

H. M. GOODWIN.

Electromotive Force of Alloys of Tin, Lead, and Bismuth. BY E. S. SHEPHERD. *J. Phys. Chem.*, 7, 15-17.—The author finds the electromotive force of alloys of tin and bismuth to be the same as that of tin. Mixtures of lead and bismuth, on the other hand, give an electromotive force which changes continuously as the percentage of bismuth changes from 0 to 10 and from 90 to 100, thus confirming the author's previous conclusion (*this Rev.*, 9, 106) that bismuth forms solid solutions with lead, but not with tin.

G. N. LEWIS.

Electrolytic Preparation of Sodium Amalgam. BY E. S. SHEPHERD. *J. Phys. Chem.*, 7, 29-30.—Sodium is deposited on a cathode consisting in a porous cup containing mercury, and

dipping in the electrolyte. The solid amalgam formed rises to the surface, leaving the path of the current unimpeded. An efficiency of 30–60 per cent. was found with 7 volts and 1 to 4 amperes.

G. N. LEWIS.

Reduction of Insoluble Cathodes. BY ALFRED T. WEIGHTMAN. *J. Phys. Chem.*, 7, 18–28.—The author discusses the technical reduction of lead sulphide at the cathode. The yield is good until 95 per cent. of the sulphide is reduced. The sulphides of copper, nickel, and iron give poor yields, as the current evolves hydrogen instead of reducing the ores. The difference is undoubtedly largely due to the high overvoltage of hydrogen on lead.

G. N. LEWIS.

The Transition Temperature of Sodid Sulphate Referred Anew to the International Standard. BY THEODORE WILLIAM RICHARDS AND ROGER CLARK WELLS. *Proc. Am. Acad.*, 38, 431–440.—By referring to three new thermometers standardized by the International Bureau, by eliminating the error due to the projecting mercury column and by using several new preparations of sodium sulphate, the authors obtain as the final value of the transition temperature on the hydrogen scale, $32.383^{\circ} \pm 0.001$. It is shown that as a fixed thermometric point this is at least as good as the freezing-point and better than the boiling-point of water. Since, moreover, it is nearer to the laboratory temperature than either of these points it bids fair to come into general use.

G. N. LEWIS.

An Apparatus for the Measurement of the Expansion of Gases by Heat under Constant Pressure. BY THEODORE WILLIAM RICHARDS AND KENNETH LAMARTINE MARK. *Proc. Am. Acad.*, 38, 417–428.—Former investigators have measured chiefly the change of pressure when a gas is heated at constant volume. The authors have constructed an apparatus in which the pressure is kept constant and the thermal expansion is observed. This apparatus consists essentially in a bulb containing the gas, a reservoir for maintaining constant pressure, and a pressure-gauge accurate to 0.01 mm. of mercury. The bulb in which the change of volume occurs is of peculiar construction and is totally immersed in the constant temperature bath. The volume readings are therefore made by electrical contact. The bath is filled with melting ice for the lower temperature, sodium sulphate in transition for the higher. The mean coefficient of expansion of hydrogen between 0° and 32.38° on the hydrogen scale is found to average 0.003659, which is probably accurate to one unit in the last place. The values for nitrogen and carbon dioxide are 0.003660 and 0.003727, respectively.

G. N. LEWIS.

A Method for Determining the Index of Refraction of Solid Hydrocarbons with the Pulfrich Refractometer. BY CHARLES

F. MABERY AND LEE SHEPHERD. *Proc. Am. Acad.*, **38**, 283-290; *Am. Chem. J.*, **29**, 274-281.—The solids were dissolved in a high boiling hydrocarbon and kept at a high constant temperature by coils of wire carrying a current. The refractive indices given by a number of purified paraffin hydrocarbons prepared from different sources were found to agree well with each other and with the theoretical values.

G. N. LEWIS.

The Density and Coefficient of Cubical Expansion of Ice. BY J. H. VINCENT. *Phys. Rev.*, **15**, 129-153.—This investigation was undertaken especially to throw light on the disputed question of the variability of the density of ice. The method is ingenious. A vessel full of mercury is closed except for a small hole in the bottom. Through this passes a wire connecting a weight pan below with an umbrella-shaped receptacle which holds the ice in the mercury. Water is frozen in this holder, balanced at several temperatures by weights in the pan below, and finally melted and balanced again. As coefficient of cubical expansion the author finds a mean of 0.000152. The mean of four experiments gave 0.9160 as the density of ice, with individual deviations of 0.06 per cent. The author judges that these deviations corroborate the conclusion of Nichols that different kinds of ice have different densities. Unfortunately the experiments seem inconclusive, since the author does not indicate in any way the deviations that may be caused by his method. One would be inclined to attribute the deviations to experimental error rather than to believe that two samples of ice produced under the same conditions differ in density by 0.1 per cent.

This question is of importance in its relation to the ice calorimeter, the accuracy of which, the author concludes from his data, cannot be greater than 0.1 per cent. As a matter of fact, however, since the change of volume on fusion is only about one-tenth of the total volume, a deviation of 0.1 per cent. in the density of the ice would make a difference of almost 1 per cent. in the reading of the calorimeter unless, indeed, the heat of fusion should happen to be less for ice of greater density.

G. N. LEWIS.

The Heat of Vaporization of Air. BY J. S. SHEARER. *Phys. Rev.*, **15**, 188-191.—By determining the change in the rate of vaporization of liquid air when a current is passed through an immersed coil, the author finds 50 small calories per gram as the heat of vaporization. This value increases with greater concentration of oxygen. From the equation of Clausius, the author calculates that the heat of vaporization is 45 cal., using the vapor pressure determinations of Olzewski and Baley, and 54 cal., using those of Estreicher.

G. N. LEWIS.

Some Optical Properties of Iodine. BY WILLIAM WEBER COBLENTZ. *Phys. Rev.*, **16**, 35-50, 72-93.—The author has compared the absorption spectra of solid iodine, liquid iodine, and iodine in carbon disulphide for visible and for ultra-red light. These spectra contain a number of pronounced bands, but no striking resemblances exist between the three. The pleochroism and abnormal dispersion of solid iodine are also investigated.

G. N. LEWIS.

Solubilities of Some Carbon Compounds and Densities of Their Solutions. BY CLARENCE L. SPEYERS. *Am. J. Sci.*, **164**, 293-302.—The author has determined the solubilities of a number of organic substances in water, methyl, ethyl, and propyl alcohols, toluene and chloroform, at different temperatures. The method is not such as to insure a very close approach to equilibrium between solid phase and solution. The densities of the solutions were also determined; and the author points out that the molecular volumes of all the solutes studied are greatest in water and are less in the other solvents in the order in which these are named above.

G. N. LEWIS.

An Experimental Investigation into the Existence of Free Ions in Aqueous Solutions of Electrolytes. BY JULIUS OLSEN. *Am. J. Sci.*, **164**, 237-248.—The author seems to have attempted to show a permanent heaping up of an excess of ions of one kind by a temporary electrostatic charge or by the application of an electromotive force less than the decomposition voltage. The paper contains many errors, and the results, which are purely qualitative, seem to the reviewer inconclusive.

G. N. LEWIS.

INORGANIC CHEMISTRY.

On Ceric Chromate. BY PHILIP E. BROWNING AND CHARLES P. FLORA. *Am. J. Sci.*, [4], **15**, 177-178.—Ceric chromate has the composition $\text{Ce}(\text{CrO}_4)_2 \cdot 2\text{H}_2\text{O}$. It forms bright scarlet crystals, stable, if dry, below 150° . It is soluble in dilute acids, but gives an orange-yellow basic salt when treated with water.

H. N. MCCOY.

On the Iodides of Caesium. BY H. W. FOOTE. *Am. Chem. J.*, **29**, 203-212.—The author determined the solubility of mixtures of the iodides of caesium in order to show that the only periodides capable of existence, at least within the range of temperatures investigated, are CsI_3 and CsI_5 . The composition of the solution, saturated at a fixed temperature, remained unchanged as long as the composition of the solid phases indicated a mixture of iodides containing more iodine than CsI and less than CsI_3 . Similarly the saturated solution in contact with mixtures of CsI_3