GENERAL AND PHYSICAL CHEMISTRY.

A. A. NOYES, REVIEWER.

Lecture Experiments. Reversible Chemical Reactions. By W. LASH MILLER AND F. B. KENRICK. *J. Am. Chem. Soc.*, 22, 291–300.—The mass-action law is qualitatively illustrated by six groups of experiments on the equilibrium of reactions familiar to students of elementary inorganic chemistry. The manipulation is decribed in detail; but in several instances it is not clear what the experiment is intended to illustrate; thus it is not apparent that the mass-action law requires that dilution with water should cause precipitation of silver bromide or of cupric hydroxide from their ammoniacal solutions, nor that the former salt should be precipitated by silver nitrate and potassium bromide, except through a consideration of the electrolytic dissociation theory, to which no reference is made by the authors.

Notes on Lecture Experiments to Illustrate Equilibrium and Dissociation. By JULIUS STIEGLITZ. *Am. Chem. J.*, 23, 404–408.—The first experiment described consists in sealing 0.029 gram bromine, in glass tubes of 40 cc. capacity, in one case with an equal molecular quantity of phosphorus tribromide (or trichloride), and in another case with nine (or six) times as much of these substances, and heating the tubes side by side in a beaker of water to 80°–90° (or 40°–55°). The brown color of the bromine vapor is much deeper in the tubes containing no excess of the phosphorus compound. The other experiments relate to electrolytic dissociation, and consist in showing that the color produced by adding a little ammonia to phenolphthalein or litmus solution is greatly weakened by the addition of concentrated ammonium chloride solution, owing to the reduction of the dissociation of the ammonium hydroxide.

On a Minimum in the Molecular Lowering of the Freezing-Point of Water, Produced by Certain Acids and Salts. By VICTOR J. CHAMBERS AND JOSEPH C. W. FRAZER. *Am. Chem. J.*, 23, 512–520.—The investigation is a continuation of that of Jones and Chambers (*this Rev.*, 6, 72), and the results obtained are entirely similar. The substances investigated cryoscopically were copper sulphate, phosphoric acid, hydrochloric acid, sodium acetate, cadmium iodide, strontium iodide, and zinc chloride. All of them except the first show a marked minimum in the molecular lowering at concentrations between 0.05 and 0.5 mol per liter. The authors consider that the results further confirm the explanation, previously offered, that the quantity of solvent is reduced by the combination of it with the dissolved substance to form a hydrate.

On the Freezing-Points of Aqueous Solutions of Non-Electrolytes. BY E. H. LOOMIS. *Phys. Rev.*, **9**, 257–287.—The method is essentially the same as that used by the author in his previous work (*this Rev.*, **3**, 23), but an error due to a variation in the temperature of the stem of the thermometer is now eliminated. It is shown that no appreciable error is involved in the author's method by reason of a difference between the convergence temperature (Nernst and Abegg, *Ztschr. phys. Chem.*, **15**, 681), and the true freezing-point, inasmuch as this difference was found by direct experiment to amount to only 0.004°. The molecular lowerings (calculated for 1 mol in a *liter* of *solution*) found by the author are given in the following table.

Solute.	Concentration in mols per liter.						
	0.01	0.02	0.05	0.10	0.20	0.50	1.00
Methyl alcohol	1.83	1.81	1.82	1.82	1.83	...	...
Ethyl alcohol	1.81	1.84	1.84	1.85	1.85	...	...
n-Propyl alcohol	1.89	1.86	1.87	1.86	1.86	...	...
n-Butyl alcohol	1.89	1.84	1.85	1.86	1.86	...	...
Amyl alcohol	1.85	1.86	1.85	1.845	...	...	...
Glycerine	1.86	1.86	1.86	1.87	1.88	...	...
Dextrose	1.88	1.84	1.86	1.88	1.90	...	...
Cane-sugar	1.87	1.89	1.89	1.92	1.98	...	...
Mannite	1.85	1.86	1.86	1.87	1.90	1.97	...
Acetone	1.85	1.86	1.86	1.85	1.85	...	1.91
Chloral hydrate	1.86	1.87	1.85	1.87	1.88	...	2.05
Aniline	1.85	1.86	1.83	1.81	1.77	...	...
Ether	1.62	1.68	1.71	1.73	1.73	...	...

From plotting the results the author concludes that all the investigated substances exhibit at extreme dilution a constant molecular lowering of the value 1.86°, with the exception of the three substances methyl alcohol, ethyl alcohol, and ether, for which the extrapolated values are 1.82°, 1.84°, and 1.50° respectively. The author suggests that these apparent exceptions may arise from an error consisting in the evaporation of these volatile solutes out of their aqueous solutions during the experiment, but he has not adequately tested this explanation, which seems an entirely reasonable one, especially in the case of ether, which exhibits the most serious anomaly. Nevertheless, the investigation as a whole furnishes a comprehensive and most exact verification of the Raoult-van't Hoff principle and of van't Hoff's thermodynamical formula, by which the molecular freezing-point lowering for water is calculated to be 1.87°. Finally it is worthy of note that the deviations from this value rarely exceed about 1 per cent. even in solutions containing as much as 0.1 mol per liter.

A Revision of the Atomic Weight of Iron. By THEODORE WILLIAM RICHARDS AND GREGORY PAUL BAXTER. *Proc. Am. Acad.*, **35**, 253–260.—Ferric oxide made in two different ways, was ignited at 900° in a current of air, weighed, and then reduced in a current of electrolytic hydrogen at 900°. Two determinations with oxide prepared from precipitated ferric hydroxide gave 55.900 as the mean value of the atomic weight, and five determinations with oxide made from ferric nitrate gave on the average 55.883, the last value being considered nearest the truth. Experiments are described which prove that the ferric oxide occludes no appreciable amount of gas, and the same had been previously shown to be true of iron ignited in hydrogen. Previous determinations are criticized at the close of the article ; and the errors which led to the higher value (56.0) commonly adopted are suggested.

On the Determination of Sulphuric Acid in the Presence of Iron : A Note on Solid Solutions. By THEODORE WILLIAM RICHARDS. *Proc. Am. Acad.*, **35**, 377–383.—The author maintains, on the basis of the previously published experiments, that the precipitation of iron with barium sulphate is due to the occlusion, at the moment of the separation of the precipitate, of a complex basic compound of iron and sulphuric acid analogous to the well-known compound of chromium, and that the amount occluded will be dependent upon the amount of the complex salt present in the solution, in accordance with the distribution law.

The Driving Tendency of Physico-Chemical Reaction and Its Temperature Coefficient. By THEODORE WILLIAM RICHARDS. *J. Phys. Chem.*, **4**, 383–393 ; *Proc. Am. Acad.*, **35**, 471–480.—The author first discusses the relations between the two familiar van 't Hoff equations :

$$\frac{d}{dt} \, ln \, \frac{c_1^{n_1} c_1'^{n_1'} \cdots}{c_2^{n_2} c_2'^{n_2'} \cdots} = \frac{U}{RT^2} \text{ and } \frac{d}{dt} \, ln \frac{p_1^{n_1} p_1'^{n_1'} \cdots}{p_2^{n_2} p_2'^{u_2'} \cdots} = \frac{-\lambda}{RT^2}.$$

He emphasizes the advantages of the latter, designating it the reaction isobar, since λ represents the absorption of heat when the reaction takes place under constant external pressure. A further equation, designated the reaction metatherm, is derived, which includes both the case of a reaction at constant pressure and that of one at constant volume. In the latter part of the article it is suggested that there may be theoretical advantages in considering the equilibrium ratio, or constant (k) resolved into separate constant factors ($z_1, z_1' \cdots$) characteristic of each of the reacting substances, of whose reciprocals the constant shall be the same function as it is of the partial pressures ; that is

$$k = ln\frac{p_1{}^{n_1}p_1{}^{'n_1'}\cdots}{p_2{}^{n_2}p_2{}^{'n_2'}\cdots} = ln\frac{z_2{}^{n_2}z_2{}^{'n_2'}\cdots}{z_1{}^{n_1}z_1{}^{'n_1'}\cdots}.$$

The factors $z_1, z_1' \cdots$ are designated "single physico-chemical potentials," and the constant k is called "the driving tendency of the reaction," since it is regarded "as an opposing pressure tendency just equal to the ratio of the pressures actually observed."

A Table of Atomic Weights of Seventy-four Elements.

By THEODORE WILLIAM RICHARDS. *Proc. Am. Acad.*, **35**, 621.— The only changes, aside from the number of figures retained, from the table published by the same author two years ago (*this Rev.*, **4**, 119), and the only important differences from the values recently adopted by Clarke (*this Rev.*, **6**, 72), are shown below :

	1898.	1900.		Richards.	Clarke.
Boron	10.95	11.0	Antimony	120.0	120.4
Calcium	40.0	40.1	Cerium	140.	139.0
Iron	56.0	55.9	Iron	55.9	56.0
Selenium	79.0	79.2	Magnesium	24.36	24.3
Tungsten	184.4	184.	Palladium	106.5	107.0
			Strontium	87.68	87.60

A Preliminary Investigation of the Conditions which Determine the Stability of Irreversible Hydrosols.

By W. B. HARDY. *J. Phys. Chem.*, **4**, 235–253.—The author has shown that the particles of heat-modified proteid or egg-white in the form of a hydrosol (that is, in the form of an aqueous colloidal solution) are electropositively or electronegatively charged and move towards the one electrode or the other when subjected to the influence of a high difference of potential, according as the solution is acid or alkaline ; and that in neutral solution the electric field has no influence, in which case the particles and the fluids are said to be isoelectric. The isoelectric point is of great importance since it is also the point of minimum stability or of most ready coagulation of the hydrosol, this principle being generally applicable to hydrosols, in spite of the great differences in stability towards chemical agents which different ones exhibit. The article is, however, mainly devoted to the effect of various salts, acids, and alkalies in coagulating hydrosols. The author derives from his experiments the new principle that the coagulation is determined by that one of the two ions which has an electric charge opposite in sign to that of the colloidal particle ; and confirms the conclusion previously drawn by others that bivalent ions are enormously more active in causing coagulation than univalent ones, and that trivalent ions again are far more active than bivalent ions. In proof of this principle it is

shown that dialyzed silica, proteid in presence of a trace of alkali, dialyzed mastic, and colloidal gold, whose particles are all electronegative, are coagulated at once or in a relatively short time by aluminum sulphate, copper sulphate, or chloride, cadmium nitrate, barium chloride, and magnesium sulphate, but are not coagulated by equivalent solutions of potassium or sodium sulphate or of sodium chloride ; while proteid in the presence of a trace of acid and dialyzed ferric hydrate, whose particles are electropositive, are coagulated at once by all the sulphates investigated, namely those of aluminum, copper, magnesium, potassium and sodium, but not by the chlorides of copper, barium, or sodium, nor by the nitrate of cadmium. The salt concentration necessary to coagulate ferric hydrate was found to be $1/4000$ mol per liter in the cases of potassium and magnesium sulphate, but $1/10$ to $1/50$ mol in the cases of the chlorides of sodium and barium and the nitrate of cadmium ; similar concentration results are given also in the case of gum mastic and of colloidal gold. In accordance with the author's principle is also the behavior of acids and alkalies, for the concentration necessary for the coagulation of negative colloid particles by acids or of positive particles by bases is shown to be that at which the various acids or bases have the same specific conductivities and, therefore, approximately the same concentration of hydrogen or hydroxyl ions. On the other hand, the effect of acids on positive particles or of bases on negative particles, though somewhat irregular, is clearly dependent on the valence of the negative and positive ions respectively. A series of experiments is also given on the concentration of potassium sulphate necessary to produce coagulation of colloidal gold in solutions containing acetic acid or ammonia in various amounts. The article closes with a summarized statement of results, interspersed with hypothetical considerations.

On the Mechanism of Gelation in Reversible Colloidal Systems. By W. B. HARDY. *J. Phys. Chem.*, 4, 254–273.—From a study of gelatine-water-alcohol and agar-water mixtures it is concluded that, in accordance with the view of van Bemmelen (*Ztschr. anorg. Chem.*, 18, 20), the jellies or gels produced by cooling consist of a framework of solid material within which is enclosed a fluid. Further details of the structure are also described. The solid can be separated from the fluid by gentle pressure. The composition of the two phases was determined in the case of the agar-water mixture for different proportions of the components and for different temperatures, and was found to vary with both of these conditions, a fact seemingly inconsistent with the phase rule, to account for which hypotheses are sug-

gested by the author. The composition of the phases was also found to depend greatly on whether the final temperature was reached from a higher or lower temperature, there being a marked lagging effect.

Vapor-Pressure Relations in Mixtures of Two Liquids, I and II. By A. ERNEST TAYLOR. *J. Phys. Chem.*, 4, 290–305 ; 355–369.

—These papers describe an experimental investigation of the vapor-pressure of mixtures of acetone and water at various temperatures, and of the composition of the vapor from such mixtures. Part I is devoted to a description of the apparatus and methods employed. The main feature of the vapor-pressure method, which consisted in determining the boiling-point under measured pressures, is considered to be the arrangements for the avoidance of superheating ; a large quantity of a mixture of garnets with scrap platinum or with silver tetrahedra was placed in the boiling vessel, and this was submerged, up to the level of the liquid within, in a water-bath kept 8° above the boiling-point. The composition of the vapor was determined in a separate operation by distilling off 20 cc. from a 220 cc. portion of the mixture, and determining the boiling-point of this distillate under atmospheric pressure. Part II contains the experimental results together with their graphical representations and reductions of them for even temperatures and pressures. The boiling-points of pure water and acetone and of mixtures of them varying successively by 10 per cent. in composition, were determined at a large number of different pressures lying between 115 mm. and 715 mm. The composition of the distillate was determined for each mixture at two pressures, 200–250 mm. and 740 mm. The discussion of the results is reserved for a third paper.

On the Determination of Transition Temperatures. By H. M. DAWSON AND P. WILLIAMS. *J. Phys. Chem.*, 4, 370–382.—

In order to determine the transition temperature of hydrated salts, the authors have measured in the neighborhood of the temperature, instead of the composition, the *density* and *electrical conductivity* of solutions saturated with each of two solid phases, and by plotting the results have tried to locate the point of intersection of the two curves. The property of density was shown to give entirely satisfactory results with sodium sulphate ; but this was not true of the electrical conductivity, for in such concentrated solutions this property changes very slowly with the concentration. This gives good results with less soluble salts, however ; as was shown by experiments with sodium sulphate. Incidentally an apparatus is sketched and described for the determination of the conductivity of hot saturated solutions; and

the transition temperatures of $Na_2SO_4.10H_2O$, $MnCl_2.4H_2O$, and $Th(SO_4)_2.9H_2O$ are determined to be $32.38°$, $58°-59°$, and $47°-48°$.

The Allotropic Forms of Selenium. BY A. P. SAUNDERS. *J. Phys. Chem.*, **4**, 423–513.—The larger part of this lengthy paper is devoted to a list of references to previous articles relating to the properties of the various forms of the element selenium, and to abstracts of those articles. The author concludes from his investigation that selenium exists in three distinct forms, the liquid (including vitreous, amorphous, and soluble selenium), the red crystalline form, and the gray crystalline or metallic form. The new experiments described consist first of a large number of dilatometric measurements, by which it is shown that the metallic form is the stable one up to 220°, where it melts, it showing no tendency below that temperature to go over into any other form; and that vitreous selenium remains for years unaltered at the ordinary temperature, but goes over into the metallic form at 60°–80°, though occasionally it may, by rapid heating, be brought to 180° before changing. The results are then given of qualitative experiments on the effect of a large number of liquids on amorphous selenium, one group of them transforming it into the red crystalline form, another group, composed exclusively of nitrogen compounds, changing it into the metallic form, and the third group, consisting of water and aqueous solutions, having no influence. Experiments are also described which make it probable that the red crystals have an instable melting-point at 170°–180°. Finally a critical consideration of previous results and of some experiments of his own leads the author to adopt as the most probable specific gravity values, 4.26 for the amorphous, 4.28 for the vitreous, 4.47 for the red crystalline, and 4.80 for the metallic form.

An Exposition of the Entropy Theory. BY J. E. TREVOR. *J. Phys. Chem.*, **4**, 514–528.—The author claims to have given a rigorous mathematical deduction of the entropy principle without any reference to the properties of gases.

Entropy and Heat Capacity. BY J. E. TREVOR. *J. Phys. Chem.*, **4**, 529–532.—The conclusion is reached that "a system's entropy, plus its heat capacity with reference to any reversible path, is equal to the change per degree, on the same path, of the system's store of heat."

The Relation of the Taste of the Acid Salts to Their Degree of Dissociation, II. BY LOUIS KAHLENBERG. *J. Phys. Chem.*, **4**, 533–537.—The author attempts to confute the explanation

advanced by Richards (*this Rev.*, 6, 121) and the reviewer (*this Rev.*, 6, 73) of the fact that the sour taste of acids and acid salts is not proportional to the concentration of the hydrogen ions in their solutions. That the author has entirely failed to understand that explanation will be evident when it is stated that the experiment which he brings forward to disprove it consists in causing a hydrochloric acid solution, so weak as not to taste sour when tasted in the ordinary manner, to remain long in motion in contact with the tongue, with the result that no sour taste is thereby developed.

The Eighth Group of the Periodic System and Some of Its Problems. BY JAMES LEWIS HOWE. *Proc. Am. Assoc. Advancement Sci.*, 49 ; *Science,* 12, 20–34.—This paper is a vice-presidential address in which the history of our knowledge of the platinum metals and their compounds is briefly presented.