foil turned over the upper edge of the cup. The latter precaution is of course more necessary when acid vapors are emitted by crystals or mother liquor. The Gooch crucible, or the whole top of the cup, may be covered with a circular piece of platinum foil, the edges of which have been turned down to hold it in place. A hole in the bottom of the aluminum cup facilitates the removal of the vessel containing the mother liquor.

It is, of course, possible to make the apparatus more elaborate, for instance, by providing the aluminum cup with an especial porcelain or platinum lining. The system as described above, however, has the great advantage that it may be constructed with materials available in most laboratories. G. P. BAXTER.

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REVIEW.

RECENT PROGRESS IN PHYSICAL CHEMISTRY.

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The issuance by our Society this year of "Chemical Abstracts" has somewhat changed the requirements for the annual reviews of special topics. Heretofore their chief aim has been to present a brief synopsis of the more important foreign literature, to supplement the "Review of American Chemical Research" included in the monthly numbers of the Journal. Since, as far as collection of data is concerned, all of this field is now covered by the "Abstracts," the author has, in what follows, confined himself to the discussion of a few selected topics which have either attracted special attention of late or seem to open up or emphasize new or previously neglected fields of inquiry. In order to present some of these in their true perspective it has seemed necessary to trace the same line of thought back among the earlier workers, and in this respect there has been no attempt to limit the present article strictly to what has appeared during the past twelvemonth. As heretofore, the subject of radioactivity has been left for treatment in a separate article.

Perhaps the most significant trend of recent work is to be found in the concentration of effort toward narrowing the gap between molecular and molar phenomena. This field in which, among other important matters, the whole subject of colloids ultimately belongs, stands to-day in very much the same relation to physical chemistry and ordinary mechanics that physical chemistry stood to physics and chemistry twenty or thirty years ago. The classification of natural phenomena into sharply defined subjects may in most cases be interpreted simply as an admission that we are omitting a region between, in which, as we enter it from either side, the methods of treatment gradually fail us. Thus it was that the troublesome and outgrown distinction between chemical and physical combination was swept away by Gibbs, and under the broader conception of "phase" and "component" the two fields merged in one as far as heterogeneous equilibrium was concerned; but here Gibbs' definite contribution ended. The very conception of a "phase" in whatever words it is defined rests eventually upon the distinction between molecular and molar magnitudes. To emphasize this point of view we may frankly define a phase in the sense in which Gibbs uses the term, as a portion of matter homogeneous down to molecular magnitudes.

This gives us a perfectly sharp classification of systems until we reach the colloids. Then classification by its means ceases to be independent of theoretical assumptions, and depends upon where we arbitrarily draw the line between molecular and molar magnitudes in a series which passes through all possible values intermediate between the typical unquestioned extremes. It is this characteristic of a boundary or frontier region which has lent the subject of colloids much of its fascination for the investigator. Many, apparently overlooking the necessity that colloid phenomena must eventually furnish the connecting link between molar and molecular types, have striven to build up a new and entirely independent science on this foundation. This tendency has undoubtedly been greatly stimulated by the importance of colloids in biological problems. Where we may hope for the greatest permanent advances is, however, in the extension, with the necessary modification, of the well established notions from over both its border lines into the new field until they meet and merge in one more generalized set covering the whole extent. When, for instance, we are able to trace the phenomena of osmotic pressure up through the solutions of substances of large molecular weight such as the starches and simpler proteins on to the inorganic colloids and finally connect it with its equivalent in the unquestioned suspensions, we will have done much to realize Newton's dream of laws broad enough to embrace both chemistry and astronomy, stellar and atomic mechanics. Several recent papers in this direction deserve particular notice. Einstein (A. Einstein, *Ann. Physik* [4], **17**, 549–60 (1906); **19**, 289–306 (1906); **22**, 569–72 (1907)); with the aid of the molecular kinetic theory has developed the laws for "the osmotic pressure of suspended particles," also the "viscosity of a liquid holding in suspension a multitude of rigid spheres." The law of this generalized osmotic pressure, as we might style it, proves to be identical with that we have long been familar with in purely molecular phenomena, while the change in the apparent coefficient of viscosity of a liquid produced by the introduction of suspended particles is shown to be equal to the ratio of their total volume to that of the liquid, at least for small values of this ratio where the suspended particles are large compared with the molecules of the liquid.

From these two relations he then proceeds to calculate the rate of diffusion, in terms of the size of the particles and by comparing the results thus obtained with the values of molecular dimensions derived from other sources and the known diffusion coefficients of true solutions, shows the new formulae to agree with our present conceptions in those regions where the two overlap. A few of the most important formulae derived by Einstein, and the values of the symbols used are as follows

$$(1)\ P = \frac{RT}{V}\frac{n}{N} \qquad (3)\ D = \frac{RT}{N}\cdot\frac{1}{6\pi K r}$$

$$(2)\ \frac{K'}{K} = 1 + \phi \qquad (4)\ \lambda = \sqrt{2Dt} = \sqrt{\frac{RTt}{3N\pi K r}}$$

$$(5)\ Nr^3 = \frac{3}{4\pi c}\left(\frac{K'}{K} - 1\right) \qquad (6)\ Nr = \frac{RT}{6\pi K}\cdot\frac{1}{D}$$

P, V, R and T have the usual signification as in the gas laws.
N = number of molecules in a gram molecule.
n = number of suspended particles in volume V.
r = radius of suspended particles.
D = diffusion constant of suspended particles.
K = specific viscosity of pure liquid.
K' = specific viscosity of liquid with suspended particles.
ϕ = combined volume of suspended particles in unit volume of the liquid.
π = ratio of circumference to diameter of circle.
λ = mean displacement of a particle in a particular direction during time t.
c = molecular concentration of dissolved substance.

Perhaps it is only fair to point out that the weakest point in these papers as a whole lies in the author's tacit assumption in the original development that the suspended particles are large as compared with the structure of the liquid and then in subsequently applying the formulae to cases of typical solutions such as sugar in water where the question might be raised whether the sugar molecule in solution were large enough in comparison to the water molecule to justify this procedure. The author's determination of ϕ by equation (2) for a 1 per cent. sugar solution leads to a value four times that of the solid sugar, which he explains by each sugar molecule carrying an envelope of over 30 water molecules with it. These possible objections however lose significance entirely when we turn to suspended particles of relatively large dimensions, which are, after all, of chief interest to us in the present connection. Einstein suggests in passing that this opens the way to settling the disputed question as to the origin of the Brownian movements. What makes this work of particular significance at present is the surprising manner in which its predictions have been met by entirely independent experimental evidence from another quarter.

It is some years since Siedentopf and Zsigmondy brought out their "ultramiscroscope" which is simply an application to the study of excessively minute objects under the miscroscope, of a principle which has long been familiar to us in viewing excessively distant objects in the telescope; *viz.*, that an object which subtends thousands of times too small a visual angle to have its outlines seen, becomes visible as a point of light when strongly illuminated and viewed against a dark background, provided that the distance between such points is still perceptible in the ordinary sense. Thus by powerfully illuminating a submiscroscopic suspension of particles by a beam of light at right angles to the line of sight, we are able to perceive the position of each particle, although its shape is not merely far beyond our power of vision, but also beyond the theoretical limits of the miscroscope, which are set by the wave length of light itself. The relative sizes of the particles may be estimated roughly from their apparent brightness. The limits of ordinary miscroscopic vision may fairly be set at about 0.00025 mm. (*i. e.*, 250 $\mu\mu$) while the ultramiscroscope extends the limit of perception down to particles about 6 or 7 $\mu\mu$ in diameter. The closeness with which this approaches ordinary molecular dimensions may be judged by comparison with the values derived from the molecular kinetic theory. Thus Loby de Bruyn sets the diameter of molecules of soluble starch at 5 $\mu\mu$, Jäger those of chloroform at 0.8 $\mu\mu$ and O. E. Meyer the water molecule at 0.1 $\mu\mu$. A most excellent and conservative view of the progress made in this subject up to about two years ago is to be found in Zsigmondy's own book. (Zur Erkenntnis der Kolloide; R. Zsigmondy, Jena (1905), G. Fischer 186 pp.). Much valuable work has since appeared along the same lines, but we can consider here only one of the most recent developments which bears directly upon the theoretical matters pointed out above.

Svedberg (T. Svedberg, *Z. Elektrochem.*, **12**, 853–60, 909–10 (1906)) in working out the technique of the above method has devised a very ingenious scheme for observing and measuring the amplitude and period of vibration of colloid particles, and has applied this to the study of colloidal solutions of a number of metals including sodium, potassium and calcium in various organic solvents, the method of preparation of the alkali metal colloids being also due to Svedberg himself (T. Svedberg, *Ber.*, **38**, 3616–20 (1905); **39**, 1705–14 (1906)). The mode of operating consists essentially in allowing the colloid solution to flow through the field of the ultramiscroscope at a known speed. The motion of each individual particle due to the flow, compounded with that component of its vibratory motion at right angles to both this and the optical axis of the miscroscope produces a path closely resembling a sine curve which is traced so rapidly by the luminous point that it appears as a continuous line of light which allows of its dimensions being estimated with fair accuracy on an eye-piece micrometer. Svedberg finds that for particles of equal size and character in different liquids, the product of amplitude into the coefficient of viscosity of the liquid is a constant as required by Einstein's formula. The numerical value of the constants as derived from the observations is about six times that computed from Einstein's formula, but remembering that the theoretical formula contains two very uncertain quantities—diameter of the particle and number of molecules in a gram molecule—the agreement is astonishingly close, more especially as Svedberg's experimental data were published without knowledge of Einstein's work, only his last paper above referred to taking cognizance of the latter. What lends this kind of work special interest at present is the growing deadlock between what we may call the extreme thermodynamic school including such men as Mach and Ostwald on the one side and the extreme mechanists such as J. J. Thomson, Rutherford and Arrhenius on the other. The question is as to which represents the more fundamental conception of natural laws. Each form of treatment is applicable to the whole range of molar phenomena. It is only in case we come to deal experimentally with individual molecules that a choice between them becomes anything more than a matter of philosophic taste. If we do come to deal with individual molecules in the sense of the kinetic theory, Maxwell's Demon will have been realized and the limits of applicability of the second law of thermodynamics exceeded, and the old quest for perpetual motion of the second type once more reinstated among serious scientific pursuits. On the other hand, if thermodynamics, as far as the second law is concerned, succeeds throughout in its application to indefinitely small portions of matter, then the molecular theory, in its present form at least, must be given up as an objective conception of nature.

In this connection a remark of Ostwald's (*Z. physik. Chem.*, **57**, 383 (1907)) in reviewing Zsigmondy's book is significant as showing the effect that such recent work is having on even the most extreme representatives of the non-mechanistic school. He says "Von den vielen Eigentümlichkeiten sei in erster Linie die merkwürdige Eigenbewegung der submikroskopischen Teilchen erwähnt. die an die Brownsche Bewegung erinnert, aber von ihr verschieden ist. Der Berichterstatter muss bekennen, dass er noch nicht absehen kann, wie diese ausser Zweifel stehenden Tatsachen sich ungezwungen mit dem zweiten Hauptsatze werden vereinigen lassen. Hier scheinen Maxwell's Dämonen, die man im molekularen Gebiete als ungefährlich ansehen durfte, im Endlichen, ja Sichtbaren ein freies Feld für ihre experimentelle Widerlegung des zweiten Hauptsatzes zu haben." Svedberg has more recently (T. Svedberg, *Z. physik. Chem.*, **59**, 451–8 (1907)) contributed another article suggesting certain hypothetical mechanisms violating the second law.

It is probable that the wonderful success which mechanistic methods have met with in the field of radioactivity has had much to do with strengthening their position of late among chemists. To follow out this line would carry us too far afield, but it may be pointed out in passing that owing to the extreme delicacy of the methods of measurement the radioactive phenomena offer a promising field for the study of individual, atomic, and molecular phenomena, as illustrated for example in the spinthariscope and yet more quantitatively even in a recent paper by Kohlrausch (F. K. W. Kohlrausch, *Sitzb. Akad. Wiss. Wien.*, **115** [*2a*], 673–82 (1906); *Physik.-chem. Centr.*, **4**, 219) upon variations in the rate of radioactive change from the mean value.

Turning now from the progress made along molecular kinetic lines to the subject of thermodynamics proper, we meet a set of no less important advances from the chemist's standpoint. These run back genetically for several years and include contributions from a number of well-known workers, chief among whom may be mentioned, somewhat in chronological order, the names of: Lewis (*Proc. Am. Acad. Arts and Sci.*, **35**, 1–38 (1899); **36**, 145–68 (1900); also *Z. physik. Chem.*, **32**, 364–400; **35**, 343–68), Richards (*Proc. Am. Acad. Arts and Sci.*, **37**, 1–17 (1901); **37**, 399–411 (1902); **38**, 293–317 (1902)), Tammann (Krystallisieren und Schmelzen (1903) espec., p. 42), van't Hoff (Boltzmann Testschrift, p. 233–41 (1904)), Trevor (*J. Physic. Chem.*, **9**, 269–310 (1905)), Bell (*J. Physic. Chem.*, **9**, 381–91 (1905)), Haber (Thermodynamik technischer Gasreaktionen (Münich, 1905)), the whole as viewed at present seeming to have culminated in a most remarkable paper by Nernst (*Nachr. Ges. Wiss., Göttingen* (**1906**), [1], 1–40), published early last year and since brought more directly before American chemists by the Silliman lectures ("Experimental and Theoretical Applications of Thermodynamics to Chemistry," Chas. Scribner's Sons, New York, 1907, 123 pp.) given by Professor Nernst in New Haven, and of which it formed the basis.

It represents what promises to be the most important contribution of thermodynamics to chemistry since the work of Gibbs and Helmholtz, and forms a fine example of the magnificent results which the pure thermodynamical method is capable of accomplishing within its most fruitful field of application. The presentation in the original is already so compact and derives its individual steps from such diverse sources that it is impossible to give comprehensively even an outline of it here. (See Abstract by Abegg, *Z. Elektrochem.*, **12**, 738–43 (1906)). In as far as the outcome of such a thorough-going and detailed contribution as this can be reduced to epigrammatic statement we might perhaps say that it represents the amplification and correction of the old "law of maximum work" so as to cover changes in heat capacity and concentration in the reacting system, it being recognized that the disregard of these factors was what most seriously limited the applicability of the law as first advanced. Nernst points out that in its original form the law was true for all systems at absolute zero and very near the truth at higher temperatures for many changes involving only pure solids and liquids or at best concentrated solutions. He then introduces as his fundamental hypothesis the proposition that not only are the free and total energy of any system equal at absolute zero but their first derivatives with respect to temperature are also equal at this point. This necessitates specific heat being a strictly additive property at absolute zero and consequently the variation in heat of reaction with temperature depends solely on the temperature coefficient of specific heat. Starting now with the well-known van't Hoff equation for equilibrium

$$Q = RT^2 \frac{d \ln K}{dT},$$

assuming in the neighborhood of absolute zero a difference of 3.5 cal. between the molecular heat of the vapor at constant pressure and that of its corresponding solid or liquid, he deduces the working equation

$$\log K = -\frac{Q_0}{4.571T} + \Sigma\nu 1.75 \log T + \frac{\Sigma\nu\beta}{4.571} T + \Sigma\nu C$$

$Q_0 =$ heat of reaction for $T = 0$.

$\nu =$ number of molecules of each species counted positive on one side of equation and negative on the other.

$\beta =$ temperature coefficient of atomic heats.

$C =$ specific "chemical constant" for each molecular species.

The additive nature of these "chemical constants" is perhaps the most significant result of Nernst's development. This permits us to predict the true chemical equilibrium in any system from the heat of reaction and certain purely physical constants of the individual substances originally brought together, and since the purely physical phenomena of vaporization is merely a special case of equilibrium, the numerical value of C for each substance may be derived from a study of the temperature-vapor pressure curve for that pure substance. By a skilful use of a modified law of corresponding states, Nernst has even gone further and made it possible to calculate this constant C if we have an approximate value for the critical pressure of the substance and in addition know for some one temperature: (1) the vapor pressure, (2), the heat of vaporization, (3) the temperature coefficient of the latter. The value of these "chemical constants" seems to vary between relatively narrow limits. Of the twenty-three examples given, the lowest is hydrogen, 2.2 and the highest alcohol, 4.1. They rise fairly regularly with the boiling-point in the case of simple substances but are abnormally high in the case of polymerizing substances. For the application of the equation to actual cases, including a discussion of permissible simplifying assumptions, the original must be consulted. (See also K. G. Falk, THIS JOURNAL, **29**, 683–87 (1907)). Among the interesting consequences of the theory may be mentioned the deduction of a more exact form for Trouton's rule including a logarithmetric term, and the treatment of the question of the stability of chemical compounds from a perfectly general standpoint. This latter aspect has been developed at some length by Brill (*Z. physik. Chem.*, **57**, 721–38 (1907)) both for homogeneous and heterogeneous systems. For the case of a gaseous compound, each of whose molecules dissociates forming two new molecules, as, for example N_2O_4 into $2NO_2$, he deduces for a pressure of one atmosphere, the following table of approximate temperature (T) on the absolute scale, at which the dissociation will be one-half complete for reactions with a given heat of reaction (Q) at constant pressure and ordinary temperature, irrespective of the specific character of the substances involved.

Q.	T (absolute).
10,000 cal.	290°
15,000	405
20,000	525
30,000	780
50,000	1220
100,000	2350
200,000	4500

Leaving the subject of energetics and passing on to the properties of matter, we must place in the forefront Landolt's paper (H. Landolt, *Sitzb. Akad. Wiss. Berl.*, **8**, 262–98 (1906); *Z. physik. Chem.*, **55**, 589–621 (1906)) on the change in total weight during chemical reaction. This paper represents the result of years of patient work (H. Landolt, *Z. physik. Chem.*, **12**, 1–34 (1893)) in what to many must have appeared a hopeless, not to say thankless, cause. Step by step the accuracy of the experiments were increased until the probable error of a complete experiment had been forced down to so small a fraction of the minute changes which Landolt was here in search of, that he could be positive of the existence of new phenomena which all our work since Lavoisier had demonstrated to be undetectable. To summarize the actual results it may be said that out of the 14 reactions of various types studied, only two gave systematically a change in weight decidedly larger than the errors of observation. These were the reductions of silver sulphate or nitrate by ferrous sulphate and the reduction of iodic acid with hydriodic acid. The experiment involved a mass of reacting material of about 250–350 grams, the total experimental error determined from blank control experiments not exceeding 0.03 mg. Every one of nine separate experiments on each of the above reactions gave a loss in weight which ranged in the first reaction from 0.068 mg. to 0.119 mg. and in the second reaction from 0.047 to 0.177 mg. Out of the 75 experiments performed in all, 61 showed loss in weight and the greatest gain in weight in any experiment was 0.019 mg. or well within experimental error. From the data thus far obtained it does not seem possible to connect the type of reaction with the sign or magnitude of the changes in weight. In the paper the possibility is suggested that the loss in weight merely represents the escape of electrons. Landolt's transfer from the University to the Reichsanstalt temporarily interrupted this work but it is now reported that he has it actively under way again.

The relation of chemical constitution to crystal structures, although almost of necessity a close one, has been one of the least productive fields of inquiry either for the experimenter or the theorist. We have, to be sure, made some progress in the limited field where we have had the rotation of the plane of polarized light to help us, but this merely scratches the surface of the general problem, and leaves the most fundamental geometrical aspects of the question as obscure as ever. It is with all the more satisfaction, therefore, that we welcome the recent attempt of Pope and Barlow (*J. Chem. Soc.*, **89**, 1675–1744 (1906); *C. A.*, **1907**, 1809; see also Review in *Am. Chem. J.*, **37**, 638–54) to indicate a line of attack for this problem which really reaches the basic geometric principles in a perfectly concrete manner. The greatest stumbling block at the very outset has been the erratic way in which series of related compounds are distributed among the various crystallographic systems or classes of symmetry. Tutton's classic work (see *J. Chem. Soc.*, for past ten years) on isomorphic salt series has given us a fairly clear idea of the relations existing within these latter series. The present paper on the other hand derives much of its strength from its method being essentially independent of the distinction between even the crystal systems or classes of symmetry, the system of reference adopted being a modification of the topic axis idea in which the sum of the valencies of all atoms in the compound takes the place of the specific volume heretofore used in defining these axes. The physical hypotheses upon which the whole development is based are: (1) that crystal structure is determined by the arrangement of the atoms, or better their spheres of influence, in such wise as to present the closest possible packing of the assemblage and (2) that the volumes of the spheres of influence of the different atoms in a compound are directly proportional to the valencies of the atoms. Starting with these simple arbitrary hypotheses it is surprising what a vast mass of heretofore apparently unrelated chemical and crystallographic facts the authors are able to coördinate and explain. As many of them are cited in the abstract above referred to they need not be repeated here. It is interesting and suggestive to compare this theory of valence, derived as it is primarily from the crystallographic standpoint, with that of Abegg and Bodlander which had its origin in electrochemical phenomena and the closely related theory of Werner (see last year's review THIS JOURNAL, **27**, 908, also A. Werner, *Ber.*, **40**, 15–69 (1907)) which was purely chemical in origin. Perhaps the most fundamental difference between the present theory and its predecessors is its freedom from any assumption of intrisic polarity within the atoms themselves, the definite assignment of which forms so important a part in Abegg's scheme. Pope's conception of valence leads here to the admission that the valencies of different atoms need not necessarily bear exactly the simple ratio to one another that we are accustomed to assign. There is, to be sure, nothing in pure chemistry to contradict this, but such a condition of affairs would be hard to reconcile with Faraday's laws of electrochemical equivalents.

Traube, also (J. Traube, *Ber.*, **40**, 137–39 and 723–33 (1907)), has recently attempted to refer valence to atomic volume, basing his deduction, however, on the refractive index of isotropic substances with the aid of the electron theory and a number of rather specialized assumptions as to the division of the atomic volume among the essential parts of what may be termed the atom as a whole. Still another radically different view of valence based on an assumed eccentricity of the atomic nucleus in its ether envelope is presented by Ensrud (G. Ensrud, *Z. physik. Chem.*, **58**, 257–87 (1907)) and supported by evidence drawn from the specific heat of gases. Thus far our theories of valence have for the most part dealt only with the building up of atoms into molecules but the time seems fast approaching when they must also be made to connect with the theories concerning the structure of the atom itself which the study of radioactivity and related topics are fast forcing upon us. On the whole, the subject of valence seems to present just at present an exceptionally promising field for the chemist who can without prejudice freely correlate the partial truth evidently contained in each of the above rather specialized treatments of the general subject. We may, in passing, refer to a historical sketch of the conception of valence recently published by Herz (*Chem.-Ztg.*, **30**, 1273–5 and 1284–6 (1906)).

The subject of liquid crystals still continues to attract much interest, but thus far the work has been chiefly from the preparative side. Vorländer (D. Vorländer, *Z. physik. Chem.*, **57**, 357–64 (1907)) has described a number of very interesting and beautiful examples, chiefly azo compounds, which show not only one but two liquid crystal modifications and some which remain in the crystalline state over more than a hundred degrees of temperature. Under certain conditions he states that it is possible to obtain liquid crystals with well defined angles and straight edges. Lehmann (O. Lehmann, *Z. physik. Chem.*, **56**, 750–66 (1906), and Jaeger (F. M. Jaeger, *Rec. trav. chim.*, **25**, 334–51 (1906), and *Versl. Akad. Wet. Amsterdam*, **15**, 345–8; 389–401; 401–10 (1906)) have described a long series of esters of cholesterol and phytosterol, all of which show anisotropic liquid forms. According to Lehmann, every one of the cholesterol esters may be had in two anisotropic liquid forms although in most cases, one of these is labile while Jaeger claims a total of five possible, distinct, liquid phases, for the cinnamic acid ester. Double bonds and the presence of certain groups, such as the azo and azoxy, seem to favor greatly the appearance of these very soft crystals, which indeed is what they really are. What may seriously be called quantitative physical measurements on these crystals, have as yet scarcely been undertaken, but with the rapidly increasing list of substances now at our command to draw from, the opportunities here presented for fundamental work, the direct comparison of crystal building forces with surface tension and ordinary mechanical stresses, cannot long remain unappreciated by investigators. Merely by way of suggestive example may here be cited the work of Lehmann (O. Lehmann, *Ann. Physik*, **21**, 381–3 (1906)) on the relative orientation of the two forms of crystal as they pass over into each other at the transition point; also the fact that fluid crystals on glass surfaces seem always to orient themselves with their optic axes as nearly perpendicular to these surfaces as possible. Silver iodide seems to be practically the only typical electrolyte which has been shown to possess an appreciably fluid anisotropic form. Kohlrausch (W. Kohlrausch, *Wied. Ann.*, **17**, 642 (1882)) long ago showed that the electrolytic conductivity of this substance undergoes a tremendous change in passing from the hard to the soft crystalline state at 145°, but that the change from the soft or liquid crystal state to that of an isotropic liquid occasions scarcely a perceptible break in the temperature-conductivity curve. This, in the light of our present conception of liquid crystals, brings us face to face with the question of the degree of electrolytic dissociation in crystals of strong electrolytes. Lorenz (R. Lorenz, "Elektrolyze Geschmolzener Salze," Bd. III 297–311; *Monogr. über angew. Elektrochem.*, Bd. 22, Halle (1906)) has come out flatly in favor of the assumption of a high degree of electrolytic dissociation in solid crystalline salts, attributing their low conductivity in the solid state almost exclusively to the high internal friction. Much work has been done on metallic conductivity in different directions through the crystal, but a corresponding study in a thorough and systematic manner for electrolytic conductivity is still lacking, and although presenting many difficulties it promises very interesting results (Tegetmeier, *Wied. Ann.*, **41**, 18 (1890)).

The study of electrolytic dissociation in non-aqueous solutions has received its most important contributions of late from Walden in a continuation of the work already reported in last year's review (THIS JOURNAL, **28**, 905 (1906)). Nine articles in this series have now appeared, *viz*: I, General Introduction (P. Walden, *Z. physik. Chem.*, **46**, 103–88 (1903)); II, Electrical Conductivity (*Ibid*, **54**, 129–230 (1905)); III, Viscosity and its Relation to Conductivity (*Ibid.*, **55**, 207–49 (1906)); IV, Molecular Weight by Boiling-Point Method (*Ibid.*, **55**, 281–302 (1906)); V, Solubility (*Ibid.*, **55**, 683–720 (1906)); VI, Heat of Solution (*Ibid.*, **58**, 479–511 (1907)); VII, Heat of Dissociation and Heat of Solution (*Ibid.*, **59**, 192–211 (1907)); VIII, Relations of Refractive Index and Electrolytic Dissociation (*Ibid.*, **59**, 385–415 (1907)); IX, Electrostriction (*Ibid.*, 60, 87–100 (1907)). One of the most salient features of the work is the sharpness with which Walden has been able to separate the effects of changes in the degree of ionization from those due to the friction of the moving ions. The key to Walden's success is to be found in his systematic plan of campaign. He first worked over in a qualitative way a very wide range both of solvents and solutes and from these selected a working list of about fifty typical solvents and some four or five solutes. The strictly quantitative work was then chiefly confined to these substances and their mixtures. The solutes were for the most part iodides of organic ammonias, the most complete series of measurements being carried out upon solutions of tetraethyl ammonium iodide. The first important outcome of the work, as already noted in last year's review, was the giving of a quantitative form to the Nernst-Thomson relation between dissociating power and the dielectric constant of a solvent, Walden finding that if the same electrolyte were dissolved in two different solvents to such concentrations that its degree of dissociation was the same in each, then the volumes of the two solutions, for equal quantity of the solute, were inversely proportional to the cubes (in last year's review this was incorrectly stated as the first powers) of the dielectric constants of the solvents. He further established the fact that at complete dissociation and high dilution the molecular conductivity of the same electrolyte in different solutions is very nearly inversely proportional to the coefficient of viscosity of the pure solvent. Thirdly the heat of dissociation for a given electrolyte was found to be independent of the solvent. Many more interesting details are brought out in the papers, but the above are perhaps the most striking features on account of their simplicity and generality. This work is being continued and it will certainly take its place as one of the classics in this branch of inquiry. Bauer (E. Bauer, *Z. Elektrochem.*, **12**, 725–6 (1906)) points out that Walden's results support the prediction which both he and Malmström (R. Malmström, *Z. Elektrochem.*, **11**, 797–809 (1905); E. Bauer, *Z. Elektrochem.*, **11**, 936–38 (1905)) had previously made upon theoretical grounds, that the ionic concentrations of a binary electrolyte in two immiscible solvents after establishment of partition equilibrium between the two solutions should be in the ratio of the cube of the dielectric constants of the solvents. The same reasoning also requires that the solution pressure of a metal in different solvents be proportional to the cube of the dielectric constant of the solvent, and consequently, the order of elements in the absolute potential series should be independent of the solvent. Van Laar (J. J. van Laar, *Z. physik. Chem.*, **58**, 567–74 (1907): **59**, 212–17 (1907)) shows how Walden's results corroborate and explain the relation between solubility and dissociation empirically established by Abegg and Bodlander, and likewise the equation of Luther connecting distribution and dissociation equilibria. The high migration velocity of ions common to solute and solvent, first explained by Danneel (see THIS JOURNAL, **28**, 904) has been further studied by Hantzsch and Caldwell (A. Hantzsch and Kenneth S. Caldwell, *Z. physik. Chem.*, **58**, 575–84 (1907)) using formic and acetic acids and pyridine as solvents. In conformity with the theory advanced by Danneel, they find pyridinium salts in pyridine, formates in formic acid and acetates in acetic acid all show abnormally high migration velocities.

Another long and praiseworthy campaign which is at last bringing forth positive results of great importance is the direct measurements of osmotic pressure undertaken by Morse and Frazer with the help of their students (H. N. Morse, J. C. W. Frazer and students, *Am. Chem. J.*, **26**, 80–6; **28**, 1–23; **29**, 173–4; **32**, 93–119; **34**, 1–99; **36**, 1–39, 39–93; **37**, 324–60, 425–67, 558–95; **38**, 175–226). After several years' work devoted to perfecting the Pfeffer cell and auxiliary apparatus, the technique has been reduced to a certainty and a wonderfully high order of accuracy secured. In the past, the lack of this very technique has driven us, perhaps too willingly, to rely entirely upon the indirect method of measurement by freezing- and boiling-point displacements, vapor pressures and electrochemical measurements, and we have come to overlook the fact that these, though perhaps more convenient, are far less delicate measures of the quantities sought. For instance in aqueous solutions 1 mg. molecule of solute per liter produces only 0.0018° depression of the freezing-point but would still represent on an oil column manometer an osmotic pressure of 10 cm. We must look to direct osmotic pressure measurements to determine the very high molecular weights of colloids. This must eventually form another important link in the chain connecting typical solutions and suspensions referred to in an earlier portion of this article. In this same connection, reference should here be made to the work of Berkeley and Hartley (Earl of Berkeley and E. G. J. Hartley, *Proc. Roy. Soc., London, A*, **78**, 68; also *Phil. Trans.*, **206A**, 481–507 (1906)), who have succeeded in carrying the measurements for cane sugar solutions up to pressures of 135 atmospheres. Morse and Frazer have already published results obtained by their methods on a wide range of sugar solutions and still more data of a similar character are promised in the near future. One of the most interesting results of the measurements thus far published, at least from a theoretical standpoint, is the fact that it is apparently the volume of the pure solvent rather than that of the finished solution which must be multiplied by the osmotic pressure to give a constant; or as they express it, we should use the "weight normal" rather than the "volume normal." The molecular osmotic pressures which they have measured at 20° are some 2 to 4 per cent. greater than the corresponding molecular gas pressures, while at 0° they are from 6 to 11 per cent. higher. The authors carefully refrain, however, from drawing general conclusions until they shall have extended their measurements to a wider range of temperatures.

An attempt has been made by van Laar (J. J. van Laar, *Proc. Acad. Wet. Amsterdam*, **21**, 53–63 (1906); *Physik.-chem. Centr.*, **4**, 11) to establish the same "weight normal" relation from a thermodynamic standpoint, the theoretical values thus obtained agreeing well with Morse and Frazer's measurements. Another relation pointed out by van Laar is that we are led to expect that the divergence from the PV = RT law will be in opposite senses in the gas and osmotic pressures for most systems. Caldwell (R. J. Caldwell, *Proc. Roy. Soc.*, *A* **78**, 272–95 (1906)) in studying the effect of salts and non-electrolytes upon the inversion of cane sugar by acids also points out how much simpler relations are obtained by referring concentrations to equal quantities of solvent. This paper, together with one by Armstrong (H. E. Armstrong, *Proc. Roy. Soc.*, *A* **78**, 264–71 (1906)) dealing further with the same data, aims to establish the association of solvent and solute in contra-distinction to dissociation of the solute as a general explanation for the peculiarities of electrolytes. Both papers contain much very suggestive matter, however little one may agree with their main contention. The electrolytic dissociation theory in fact has been steadily absorbing of late many of the original concepts of its old opponent, the so-called hydrate theory. A good illustration of this is to be found in H. C. Jones's work on hydrates in solution which has recently been collected and published in book form by the Carnegie Institution of Washington. Another paper touching the same subject by Bousfield (W. R. Bousfield, *Proc. Roy. Soc.*, *A* **77**, 377 (1906) also *Phil. Trans.*, **206*A***, 101–59) presents experimental data in support of his formula (W. R. Bousfield, *Z. physik. Chem.*, **53**, 257–313 (1905)) for the diameter of the hydrated ion at different dilutions of the solution and shows how this may be directly connected with such properties as migration velocity, viscosity, degree of dissociation, density and refractive index.

The subject of photochemistry has come to stand further and further apart from the other divisions of physical chemistry chiefly because, in the latter, it has been the study of reversible processes which have served to bring out the logical connection between apparently unrelated phenomena, while in photochemistry until very recently such processes were almost unknown. In other words in the great majority of laboratory reactions brought about by the action of light, its function may be compared to that of a catalyzer, in that it removes passive resistances from reactions already potentially possible rather than making permanent contribution itself to the free energy of the system. When we stop to realize that the photochemistry of chlorophyll action, upon which the organic world absolutely depends, represents on the contrary an entirely different type of process, in which radiant energy is actually transformed into chemical energy and stored as such, the undeveloped possibilities of the subject are apparent. The first noteworthy study of such phenomena by Luther, Wiegert and Wilderman was cited in last year's review (THIS JOURNAL, **28**, 909 (1906)). Since then a growing interest in the subject has manifested itself. Luther and Wiegert have continued their work on anthracene and dianthracene (R. Luther and F. Wiegert, *Z. physik. Chem.*, **53**, 384–427 (1905)) and Wilderman (M. Wilderman, *Trans. Roy. Soc. London*, **206A**, 335–401; also *Z. physik. Chem.*, **59**, 553–81, 703–5 (1907)) has also published a second very extensive set of measurements on the action of light on a series of galvanic cells. Warburg (E. Warburg, *Ann. Physik*, **13**, 464–76 (1904)) pointed out some time ago that the formation of ozone by various forms of electric discharge was probably in the main a photochemical process due to the very high ultraviolet light thus produced. This has since been followed up in more detail and quite recently Regener (E. Regener, *Ann. Physik*, 20, 1033–46 (1906)) and Russ (F. Russ, *Z. Elektrochem.*, **12**, 409–12 (1906)) have shown that ultraviolet light of wave length 200–300$\mu\mu$ decomposes ozone into oxygen, while light of still shorter wave lengths brings about the reverse reaction. The simplicity of the substance here concerned coupled with this unique relation to the different portions of the spectrum, lend this reaction an exceptional importance. In this connection it may be noted in passing, that Ladenburg and Lehmann (E. Ladenburg and E. Lehmann, *Ann. Physik*, **21**, 305–18 (1906)) have recently observed certain transitory bands in the absorption spectrum of liquid ozone which they attribute to a still more unstable allotropic modification of oxygen. Among the most suggestive of recent contributions from the theoretical standpoint are two papers by Trautz (M. Trautz, *Z. wiss. Phot.*, **4**, 160–72, 351–59 (1906); also *Z. Elektrochem.*, **12**, 811 (1906)) in which he points out the close relation between reactions which produce luminescence and those whose velocity is affected by light. Any system in complete thermodynamic equilibrium must be radiating and absorbing as a "black body." If the system has not reached its chemical equilibrium, Trautz believes it highly probable that the radiation and absorption will not be that of the ideal black body. If this divergence from the black body spectrum for the temperature of observation becomes sufficiently great for us to detect, we have either a photochemical reaction or a case of chemical luminescence depending upon the sense in which the equilibrium between radiation and absorption is displaced. It is further pointed out under what restrictions thermodynamics may be applied to photochemical reactions and what types of reaction velocity may be expected, experimental evidence for some special cases being presented. The small temperature coefficient of the reaction velocity in photochemical reaction has often been pointed out, and Trautz's deductions make it probable that this quantity is larger the further toward the red end of the spectrum the region of photochemical sensitiveness lies. As experimental confirmation of the view, new data on the oxidation of alkaline pyrogallol solution are presented. In the dark this reaction produces a red luminescence, and it is powerfully accelerated by red light but very little, if at all, by violet. Its temperature coefficient is about 2.4 for 10°. Bancroft (W. D. Bancroft, *J. Physic. Chem.*, 10, 721–28 (1906)) has lately attacked the general problem of photochemistry from still another aspect, pointing out how by treating each active color of light as a new variable comparable with temperature and pressure, the phase rule may be generalized to include photochemical systems even though these merely represent stationary states and not true thermodynamic equilibria. In illustration and confirmation of this treatment one of his students (G. A. Rankin, *J. Physic. Chem.*, **11**, 1–8 (1907)) has studied the equilibrium of rhombic and amorphous sulphur in carbon bisulphide under the influence of light of varying intensity. Another reversible photochemical reaction has lately been reported by Dewar and Jones (J. Dewar and O. H. Jones, *Proc. Roy. Soc. Lond.*, **79***A*, 66–80 (1907)) in the case of iron tetra- and pentacarbonyls in presence of carbon monoxide. It appears, on the whole, to resemble closely the case of anthracene and dianthracene studied by Luther and Wiegert. In closing, we must not omit mention of the extremely interesting work of Usher and Priestley (F. L. Usher and J. H. Priestley, *Proc. Roy. Soc. Lond.*, **77***B*, 369 (1906), and **78***B*, 369 (1906)) on the primary reactions of the chlorophyll assimilation. They have apparently been able through very ingenious technique to experimentally realize outside of the plant the much looked-for lower aldehyde stage of the process. The importance of this question and the experimental difficulties are both so great that independent confirmation and extension of the experiments are much to be desired. The purely catalytic action of light has also been studied by itself of late by Wiegert (F. Wiegert, *Ann. Physik*, **24**, 55–67 and 243–66 (1907)), both from the theoretical and from the practical side. The reactions between chlorine, carbon monoxide and phosgene fall in this category. On the whole, it seems not too much to hope that we are rapidly approaching an epoch in photochemistry similar to that which electrochemistry passed through some twenty or thirty years ago when it was first really made an integral part of general physical chemistry. May it not be that in the process of this development, photochemistry, like electrochemistry, will furnish us with a new wealth of experimental and theoretical methods for attacking the old problems of general chemistry?

When we come to consider the results of the mere application of physicochemical principles and methods to other branches of chemistry we meet a mass of material which, to do justice to, would carry us far beyond the scope of the present review, but it may still not be out of place to note a few suggestive cases, although such a selection must of necessity be rather an arbitrary one. Toward the problem of protein synthesis Taylor (A. E. Taylor, *J. Biol. Chem.*, **3**, 87–94 (1907)) and Robertson (T. B. Robertson, *Ibid.*, **3**, 95–9 (1907)) have each contributed an example of the reversal of the process of protein digestion, the former working with protamine sulphate and trypsin from the liver of the clam, and the latter with certain stages in the digestion of casein by pepsin. It is instructive to note that both authors were led to their respective methods by purely physicochemical lines of reasoning. The first paper also contains a good set of references to earlier work on reversions of physiological interest. Still another instance of the reduction of a biochemical process to physicochemical control is offered by the work of Buchner, Meisenheimer and Shade (E. Buchner, J. Meisenheimer and H.

Shade, *Ber.*, **39**, 4217–31 (1906); also H. Shade, *Z. physik. Chem.*, **57**, 1–46, **60**, 110 (1907)) who have studied the fermentation of sugar by colloidal platinum solutions and shown that the progress of the reaction is entirely comparable to that of the ordinary yeast fermentation. From the dynamical treatment of the process they are further able to point out the probable type of the intermediate stages of the reactions. To the work on establishment of a convenient absolute scale of acidity and alkalinity by the use of indicators standardized by gas cell measurements, which was begun by Friedenthal (Friedenthal, *Z. Elektrochem.*, **10**, 114–9 (1904)) and Salm (E. Salm, *Ibid.*, **10**, 341–46 (1904); **12**, 99–101 (1906)) has been added a valuable set of data by Salm (E. Salm, *Z. physik. Chem.*, **57**, 471–501 (1906)) covering a wide range of indicators. A much needed thorough systematization of our knowledge of the constitution of alloys which was commenced by Tammann (G. Tammann, *Z. anorg. Chem.*, **37**, 303–13. The subsequent papers of this series have also appeared from time to time in the same journal) five years ago, now comprises over fifty papers by himself, assistants and students, covering a large number of the important binary systems, and similar systematic work is just beginning to be undertaken seriously in ternary systems (R. Sohmen and A. v. Vegesack, *Z. physik. Chem.*, **59**, 257–83; **60**, 507–9; also Jänecke, *Ibid.*, **59**, 697–702; **60**, 399–412 (1907)). Of course the systems having iron as one component have for some time past attracted much attention, but even here the individual workers have, for the most part, centered their activities on minutiae of special problems. A movement toward a broader treatment of the whole subject seems, however, to have set in and is being encouraged and supported by several of the leading institutions and societies concerned. Closely related to these metallurgical problems are the geological questions of rock formation, and here may be noted the work of the Geophysical Laboratory of the Carnegie Institution of Washington, some of whose results have already appeared in THIS JOURNAL (A. L. Day and E. S. Shepherd, THIS JOURNAL, **28**, 1089–1114 (1906)). In this work the phenomena of supersaturation, superfusion and vitrification greatly complicate the problems. These latter phenomena in themselves are beginning to receive more direct investigation. Young and Burke (S. W. Young and W. E. Burke, THIS JOURNAL, **28**, 315–47; **29**, 329–48)) already have reviewed the older work and pointed out some new relations. Miers and Isaac (H. A. Miers and Miss F. Isaac, *Proc. Roy. Soc. Lond.*, *A* **79**, 322–50 (1907)) working with mixtures of salol and betol have determined the condition for various labile and metastable eutectics between a pair of components, both of which show strong superfusion. They also discuss briefly the bearing of the work on interpretation of geological problems. In this connection for sake of completeness, mention may be made of the older work of Guertler on fusions of lead borates (W. Guertler, *Z. anorg. Chem.*, **40**, 225–53 (1904)), the general problem of devitrification (W. Guertler, *Ibid.*, **40**, 208–79 (1904)) and the melting-points of the alkaline earth borates (W. Guertler, *Ibid.*, **40**, 337–54); also that of Zschimmer's paper on the properties of various glasses (E. Zschimmer, *Z. Elektrochem.*, **11**, 629–38 (1905)) and Doelter's little book, "Petrogenesis" (Die Wissenschaft Sammlung Hft. 13, Braunschweig, Vieweg. (1906)).