REVIEW.

RECENT PROGRESS IN PHYSICAL CHEMISTRY.

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In this review as in previous years the aim has not been to catalogue the literature of the period but merely to cite briefly a few of the more significant developments as characterizing the present spirit and aims of the frontier of the subject thus suggesting to some extent in what directions visible progress may reasonably be expected in the immediate future. The subject of radioactivity has been left for separate treatment elsewhere.

In the more purely systematic and descriptive side of the subject the most noteworthy contributions have undoubtedly concerned themselves with the metallic alloys. Tammann's systematic application of thermal analysis and metallographic examination of the binary alloys referred to in last year's review is still continuing, and the results thus far collected have recently been compared by N. Guerter (*Z. anorg. Chem.*, **51,** 397–44 and **54,** 58–88; *Jahrb. Radioakt. u. Elektronik.*, **5,** 17–81; *Physik. Z.*, **9,** 29–36), with the mass of previously well nigh unintelligible data which we possess relative to the electrical conductivity of alloys, with the result that certain strikingly simple relations now appear which may be summarized as follows: (1) The curve of specific conductivity plotted against composition has the same form as that of the temperature coefficient of conductivity, *e. g.*, a decrease in conductivity being accompanied by a corresponding decrease in its temperature coefficient. (2) A definite chemical compound of two metals has a lower conductivity and temperature coefficient than the pure metals (all of which have essentially the same coefficient). its resistance not disappearing as the absolute zero of temperature is approached. (3) Over any range of concentration representing a single series of mixed crystals whether between pure metals or compounds or both a very rapid fall in conductivity is found near both pure compounds of the series, which rapidly flattens into a broad minimum in the middle of the series. (4) Over ranges of concentration representing mechanical mixtures of two phases, whether either or both of these be the pure metals, compounds or saturated solid solutions, we find the simple "mixture law," referred to the two phases present, to hold both as regards conductivity and its temperature coefficient. (5) The difference between observed resistance of a homogeneous isomorphic mixture and that calculated from the simple "mixture law" referred to its two isomorphic components is independent of temperature, *i. e.*, its temperature coefficient is zero and it further follows from (3) that its value varies with concentration from zero for either extreme of the isomorphic series to a maximum at its middle.

A very close parallelism between the electrical resistance and the mechanical hardness of these series of isomorphic crystals has recently been pointed out and discussed by N. S. Kurnakov and S. F. Zhemchuzhnuii (*Z. anorg. Chem.*, 60, 1–37), but a theoretical explanation is yet entirely wanting.

In a brief but very suggestive paper by F. Skaupy (*Z. physik. Chem.*, **58,** 560–66), the experiment is tried of applying the Ostwald dilution law to the conductivity of metals dissolved in mercury, *i. e.*, the increase in conductivity of the pure mercury due to addition of the small amount of another metal. A remarkable agreement with the formula was found except in the case of zinc and cadmium, which latter may be due to the close relation of these metals to the mercury itself in the periodic system. Thus the more dilute the amalgam the greater is the apparent conductivity of a given weight of dissolved metal. The author interprets this as due to a progressive dissociation between the metal atoms and their electrons quite analogous to ordinary electrolytic dissociation, and further pointing out that this leads us to the view that metals are simply those substances whose atoms have weak affinity for combination with electrons while non-metallic atoms have a strong affinity; electrolytes are substances some of whose atoms or radicals have weak and others have strong affinity for electrons and non-electrolytes are substances all of whose radicals have strong affinity. The author shows that this view enables one to calculate the migration velocity of the free electrons in metals which is found to be of the order of a centimeter per second for a potential gradient of one volt per centimeter.

These results are of special interest in connection with the recent work of Kraus (THIS JOURNAL, **30,** 1197–1218 and 1323–43) upon the blue solutions of sodium and potassium in liquid ammonia. Here, too, both molecular weight determinations by vapor pressure measurements as well as the migration phenomena lead to the conclusion that we are dealing with a dissociation between atom and electron, but in this latter case it is supposed that the electron is associated with molecules of the solvent. Kraus believes the sodium or potassium ion formed in these solutions by the loss of an electron from the corresponding neutral atom to be identical with the positive ion in ordinary solutions of sodium or potassium salts. As to whether the blue color is to be attributed to the neutral atoms or molecules of the metal or to the combination of the electron with the solvent he does not as yet commit himself.

Nernst's recent generalization of chemical equilibria which was treated at some length in last year's review (THIS JOURNAL, **30,** 292–4) has attracted a great deal of attention during the past year and on the whole has met with very encouraging support. Among the tests thus far given it are the work of M. Trautz (*Z. Elektrochem.*, **14,** 271–80 and 534–44) on the equilibrium of $SO_2 + Cl_2 \rightleftarrows SO_2Cl_2$ and that of Bodenstein and Dumond (*Z. physik. Chem.*, **61,** 437–46) on formation of $COCl_2$ at 500–600°. For both of these reactions the Nernst equations were found in good accord with the facts. M. Pier (*Z. physik. Chem.*, **62,** 385–419) has also applied it to the dissociation of the chlorine molecule. Discrepancies between theory and practice in the case of the dissociation of a number of metallic oxides, hydroxides and carbonates have been pointed out in THIS JOURNAL (**30,** 1354–65) by Foote, Smith, Walden, and Johnson. Perhaps the most interesting case of all is that of the equilibrium of ammonia with its elements. At the time Nernst first put forward his equations the experimental data available on this reaction, notably those of Haber and van Oordt (*Z. anorg. Chem.*, **44,** 341–78 (1905)) were found to diverge widely from the theoretical predictions, and this has led to redeterminations of the experimental values, both by Haber and LeRossignol (*Ber.*, 40, 2144–54 and *Z. Elektrochem.*, **14,** 181–96), and by Jost (*Z. anorg. Chem.*, **57,** 414–30). In both cases electric furnaces were developed capable of withstanding high gas pressures and the accuracy of the determinations thus greatly increased. The new values show throughout a smaller synthesis of ammonia than the older data, those of Jost being practically in agreement with the Nernst formula but those of Haber and LeRossignol still showing some 25–50 per cent. greater amounts of ammonia formed. But even this degree of approximation may be considered as a fair agreement when we stop to consider the extremely general form of the equations and the uncertainty attending the determinations of some of the constants. It is interesting to notice in this case that in Jost's experiments the highest conversion of the nitrogen and hydrogen into ammonia was about 0.9 per cent. at 685° and a pressure of 50 atmospheres using manganese as a catalyzer. With lower pressures and higher temperature this rapidly decreased. An interesting application of the Nernst equation to general metallurgical problems is presented by W. Stahl (*Metallurgie*, **4**, 682–90 (1907)), including extended tables of results. On the whole it may be said that this still promises to be one of the most important tools in the development of our physicochemical formulae, although it must of course be frankly admitted that like all other purely thermodynamical methods it does not pretend in any way to explain the mechanism of the changes which it mathematically describes.

It is an encouraging sign to see an ever-increasing recognition of the fact that permanent progress in the study of colloids is to be measured by the extent to which we are able to generalize our conceptions of chemical, molecular-kinetic and molar forces so that they may all be collectively applied to one and the same particle irrespective of its size. A series of articles by B. H. Buxton and O. Teague (*Z. physik. Chem.*, **57**, 47–89; **60**, 469–504; and **62**, 287–307), chiefly concerned with the behavior of a number of aniline dyes of high molecular weight, has recently furnished us with one of the best series of graduated colloidal properties among substances of definite chemical composition as yet studied. The characteristic colors of the individual substances greatly facilitate and simplify the technique and increase our confidence in the results as compared with so much of the earlier work which has been based on animal and vegetable products of very uncertain constitution and homogeneity. The authors find that all the chief phenomena of agglutination and mutual precipitation between colloids may be duplicated with these substances and traced very directly to typical chemical reactions. The phenomenon of an increasing combination in stages preceding precipitation recently pointed out by Arrhenius (THIS JOURNAL, **30**, 1382–8) in the case of agglutination of bacteria and blood corpuscles is also clearly demonstrable with these dyes. Thus the basic and acid dyes migrate under the influence of the electric current in opposite directions and precipitation only occurs when those of opposite sign are mixed with one another and then only within certain limiting proportions, but even outside of this zone of precipitation it is found that in the mixed solution the dye which is then in excess will carry a large portion of the other with it in its migration.

In a discussion of the mechanism of the so-called adsorption phenomena which have been made a sort of scapegoat for so many of the apparent anomalies of colloidal systems, T. B. Robertson (*Z. Chem. Ind.*

Kolloide, **3**, 49–76) takes occasion to point out how indefinite and arbitrary the physical concepts at present comprised under this head have become and how these may be rendered more precise and at the same time brought into a more natural relation to ordinary chemical combination by the application of the mass law of Guldberg and Waage if we provide an additional term representing surface energy in the latter and take account of the extent of the surface of contact of different phases, or what amounts to the same thing, the size of the discrete particles concerned in the equilibrium as compared to molecular dimensions. This term practically disappears when the suspended particles become of the size of molecules on the one hand or of ordinary molar dimensions on the other, but in the mid-ground between these extremes we have the colloids and here the term is of finite magnitude and accounts for the otherwise anomalous behavior. While the paper does not pretend to be more than a mere outline it undoubtedly does clearly point out the line of attack along which we may most confidently look for permanent progress in this subject. It has been pointed out by Rothmund (*Z. physik. Chem.*, **63**, 54–82) that the very stable and definite opalescence that appears in liquids just before reaching their critical temperature and in liquid mixtures before reaching their critical solution point is probably due to a state identical with ordinary colloid solutions. On account of the extreme simplicity of the molecules which are here available for experiment and the certainty and rapidity with which equilibrium is established, this would seem a promising point of attack for many of the problems connected with what we are accustomed to think of as more typical colloidal systems.

Landolt has recently given us (*Ber. Berlin Akad.*, **1908**, p. 354) the last chapter of the painstaking work on change of weight during chemical reactions, which must, in time to come, be reckoned among our scientific classics. After reviewing all the sources of error and the magnitude of the difference found he concludes that these latter (see last year's review, THIS JOURNAL, **30**, 294) after all do not exceed the total probable errors of experiment and consequently we still have no real experimental evidence of a change in total weight during any chemical reaction. In this connection a paper of G. N. Lewis (*Tech. Quart.*, **21**, 212–25) may be cited where a "non-Newtonian" theory of matter and energy is developed whose only point of contact as yet with direct experiment is to be seen in the field of electron velocity. One of the consequences of this theory would be that for every gram calorie of energy lost by a system its weight should decrease by 4.6×10^{-14} grams or an amount far beyond the delicacy of our means of observation to detect even for the most violent chemical reactions. In his Adamson lectures (University of Manchester, Nov. 7, 1907, March University Press, 1908) J. J. Thomson presents this whole subject in a popular and entirely non-mathematical form, pointing out that while in the case of the combination of hydrogen and oxygen to form water the change in weight should be of the order of $^1/_3$ of a milligram per metric ton, in the case of the decomposition of radium the change may be as great as $^1/_8$ of a milligram per gram of radium and suggests that it may be possible by observation of a pendulum made of uranium to detect variations in the proportion between mass and weight.

The fundamental contributions to photochemistry, noted in last year's review have, as predicted, served as a nucleus for a very energetic and promising awakening of interest in these problems. A. Byk (*Z. physik. Chem.*, **62**, 454–92), F. Weigert (*Z. physik. Chem.*, **63**, 458–66), E. Warburg (*Ber. physik. Ges.*, **5**, 753–7), M. Trautz (*Z. wiss. Photog.*, **6**, 169–94, 270–3 and 331–6, also *Z. Elektrochem.*, **14**, 454–60) and E. Baur (*Z. physik. Chem.*, **63**, 683–710) have each discussed the energetics of photochemical equilibrium from a different standpoint. Thus Byk starting from the electromagnetic theory treats the action of light as an electrochemical phenomenon and attempts to picture the behavior of the electrons within the molecule under the action of the high frequency alternating displacement currents which constitute what we call light waves, taking as concrete example the anthracene-dianthracene reaction, for which he also works out in careful detail the purely thermodynamic treatment and gives an interesting discussion of the two methods and their mutual relationships. He points to the electrochemical conception as alone furnishing a satisfactory explanation for certain observed discrepancies between theory and practice which Luther and Weigert attempted to account for by a hypothetical intermediate compound. The paper by Weigert above cited is a reply to this, in which he abandons the intermediate compound hypothesis but shows that the purely thermodynamical treatment of the phenomena is capable of taking care of all the observations within the limits of experimental error if due regard is had for the usual divergences from the simple gas laws in the case of concentrated solutions. The two papers taken together furnish an admirable survey of the subject from the ordinary thermodynamic standpoint.

The papers by Warburg and by Trautz above cited have also for their central idea the bringing of photochemistry within the scope of thermodynamics, but by a very different and, if successful, more fundamental line of attack. The application of the second law of thermodynamics to radiant energy requires that by no system of lenses or mirrors can light be so focused on any body as to raise the temperature of the latter above that of the source emitting the light. Thus independent of its color and intensity (*i. e.*, the length and amplitude of its waves) every beam of light must have another intrinsic property depending upon the temperature of the source from which it came, irrespective of the distance which it may have traveled. This is represented by what has been termed the "radiation temperature" of the light and may perhaps best be thought of as a relation between the convergence (or divergence) of the rays of the beam and its intensity per unit area of cross section, which does not vary no matter how far the light travels or how it is reflected or refracted. Warburg points out the possible significance of this conception to photochemistry by raising the question whether the radiation temperature of the light entering and leaving the system are not to be considered as the analogues of the temperatures of the "source" and "receiver" of heat in our thermodynamic "cyclic" for ordinary thermochemical equilibria. Trautz adopting this suggestion weaves it into his former treatment of photochemical sensitiveness and chemical luminescence as the reciprocal processes of complete photochemical equilibrium (last year's review, THIS JOURNAL, **30**, 300) and with its aid develops and discusses equations defining the latter state and very closely resembling in form those we are familiar with for ordinary thermal equilibrium.

Experimentally the question resolves itself, as both authors point out, into setting up two sources of radiation at very different temperatures, selecting the same portion of the spectrum of each, then diaphragming down the hotter or moving it further away until the energy per unit area in the two beams is the same, and finally testing their relative photochemical activity. If a difference is found it can only be due to difference in radiation temperature and would be of special interest as justifying this purely empirical extrapolation of the second law, which may, fairly, be considered as the most severe direct experimental test that has ever been asked of it. It is only recently that several satisfactory red-sensitive photochemical reactions have been worked out which make the experimental verification over a wide enough range of temperature possible, and the numerical results promised in the near future will be awaited with keen interest.

Coming, lastly, to the paper of Baur above cited we find another attempt to connect photo- and electrochemistry, not as in Byk's through the electromagnetic theory of light but by direct experiment with galvanic cells whose electromotive force varies with the illumination, somewhat along the line of the work of M. Wildermann (see last year's review, THIS JOURNAL, **30,** 300 and the conclusion of the work, *Z. physik. Chem.*, **60,** 70–86) but representing a more careful working out in a few related points rather than the collection of a large mass of miscellaneous experimental data. The most interesting electrode examined consisted of platinized platinum in a mixture of the sulphates of tetra- and hexavalent uranium. This shifted its otherwise very constant potential when illuminated by sunlight some 0.03 volt, the metal becoming more negative with respect to the solution, and returned to its old value again in the dark; but the establishment of equilibrium in either direction required some minutes which the author interprets as due to accumulation and dissipation by the electrolyte of a certain portion of the energy of the light. This leads him to introduce and discuss as a new photochemical quantity the "light content (Lichtinhalt) of the system, which may be defined as that portion of the radiant energy which has been absorbed by the system but not yet converted into heat. This is probably so small a quantity in most cases as to easily escape detection except where a special search is instituted, and this it is now purposed to do systematically. In this connection an important relation pointed out in the paper by Byk should be cited: *viz.*, that the idea generally held that photochemical sensitiveness and light absorption are primarily related is after all only a secondary and approximate consequence, the direct associate of sensitiveness being not the strong absorption but the high refractive index as indicating a responsive condition of the electrons within a molecule as regards the particular color of the light. In support of this it is pointed out that while absorption is always associated with photochemical sensitiveness the reverse is by no means the rule, and that as far as measurements are at present available the point in the spectrum for maximum sensitiveness seldom if ever coincides with the maximum absorption but comes nearer the point of maximum refractive index, especially where anomalous dispersion occurs. If we accept and combine the views of Byk and Baur on this point we conceive the light to be always first absorbed as internal energy of the molecules (electron vibrations) which may then undergo one of two transformations, either into heat (vibration of the molecule as a whole) or into chemical potential (internal rearrangement or else disruption of the molecule or molecules).

In this same paper Baur puts forward as a very suggestive inorganic model or analogue of chlorophyll action the following set of reactions, discussing the conditions under which they might be realized:

$$4AgCl + H_2O \text{ (in light) } \longrightarrow 2Ag_2Cl + 2HCl + O \longrightarrow$$

$$2Ag_2Cl + 2FeCl_3 \longrightarrow 2AgCl + 2FeCl_2$$

$$2FeCl_2 + 2H_3Fe(C_2O_4)_3 + 2HCl \longrightarrow 2FeCl_3 + 2H_2Fe(C_2O_4)_2 + 2H_2C_2O_4$$

$$2H_2Fe(C_2O_4)_2 + H_2C_2O_4 + 2CO_2 \longrightarrow 2H_3Fe(C_2O_4)_3$$

which taken as a whole are equal to

$$H_2O + 2CO_2 = H_2C_2O_4 + O$$

which may be followed by the oxalic acid twice splitting spontaneously into a higher and lower stage of oxidation, a process analogous to fermentation of sugar,

$$H_2C_2O_4 \longrightarrow HCOOH + CO_2$$

$$2HCOOH \longrightarrow COH_2 + CO_2 + H_2O$$

thus reaching the formaldehyde stage which has been experimentally demonstrated (see last year's review, THIS JOURNAL, **30**, 301). It is further pointed out that even in the plant it is very probable that the photochemical reaction proper only carries the reduction to the oxalate stage which represents a considerably lower chemical potential than formaldehyde, the energy required to raise part of the oxalate to the latter stage being derived from the descent of another portion of oxalate back to water and carbon dioxide.

While thus outlining the study of reactions in which radiant energy actually displaces a true equilibrium it may be as well to discuss at greater length a series of investigations by Weigert on the purely catalytic action of light, the beginnings of which were merely mentioned in last year's review (*Ann. Physik.*, **4**, **24**, 55–67 and 243–66; and *Z. Elektrochem.*, **16**, 591–598). As is well known, free chlorine enters many reactions much more vigorously under the action of light. In the particular case $Cl_2 + CO \rightleftarrows COCl_2$ Weigert has experimentally demonstrated that although the reactions in both directions are greatly accelerated by light the final condition of equilibrium is not in the least affected. He offers as an explanation the formation of molecular aggregates in the body of gas, analogous to the fog nuclei produced by ionization, these acting then catalytically upon the chemical reaction in a manner analogous to colloidal platinum. The reaction really observed is thus not itself photochemically sensitive at all but simply catalyzed by a minute quantity, of a substance produced photochemically. If, as suggested, this catalyzer is in the form of nongaseous particles the velocity of the reaction might well be determined by the rate of diffusion, which would help to account for the predominance of first order reactions as well as the small temperature coefficients met with in photochemistry. In the last of the papers above cited it is shown that the decomposition of ozone, which is not ordinarily accelerated by rays of the visible spectrum, becomes powerfully so when chlorine is added, the effect being proportional to the quantity of light absorbed by the chlorine and, what is perhaps most noteworthy, independent of the ozone concentration. This last fact, which at first sight seems to contradict the theory of nuclei, may be explained on the assumption that in this case the latter are rapidly destroyed again by the reaction they catalyze; at all events the work has opened up a most interesting new field and through all of this can be seen how rapidly chemistry and physics are again converging on the new ground of the electron theory. It bids fair to usher in a distinctly new epoch even wider in its scope if not more fruitful than that of the dissociation theory which in its present form one is often tempted to believe has been worked pretty well to its dregs except as an aid to the purely systematic and descriptive side of our subject.

In chemical kinetics the highest order of reaction yet reported has been the fifth and this was represented by only one example, the reaction being potassium iodide and potassium ferricyanide studied by Donnan and Le Rossignol (*Trans. Chem. Soc.*, **83**, 703–716 (1903)). This reaction has lately been very thoroughly studied by Just (*Z. physik. Chem.*, **63**, 513–578) with the result that although confirming Donnan and Le Rossignol's observations, he shows they were too hasty in classing it as of the fifth order, their criteria being insufficient and their result depending to some extent upon the particular conditions of their experiments. Extending the determinations over a wider range of conditions, particularly as regards temperature, he shows the reaction to be bimolecular with respect to the iodide and unimolecular with respect to the ferricyanide or of the third order as a whole. We thus have no experimental evidence at present for any fifth order reactions.

The question as to whether or not there is such a thing as a measurable velocity of crystallization independent from diffusion and heat conduction has received an affirmative answer from R. Marc (*Z. physik. Chem.*, **61**, 385–398) who finds the crystallization of slightly supersaturated solution of potassium sulphate when vigorously stirred with a considerable amount of fine uniform crystals of the same salt to obey the law of a second order reaction and have a temperature coefficient of velocity of about 1.6 for 10°. The velocity was found to be independent of the rate of stirring after the latter had reached a certain point. This is the most positive evidence we have had yet on this interesting question and continuation of the work is promised.

During the year several phenomena have been reported which appear entirely at variance with our present conceptions, and whose further control and explanation will be watched with interest; thus R. Abegg and F. M. G. Johnson (*Z. physik. Chem.*, **61**, 455–63) have followed up Baker's observation (*Trans. Chem. Soc.*, **65**, 611–24 (1894)) that perfectly dry ammonium chloride does not appreciably dissociate upon volatilization, whereas if the least trace of moisture is present the dissociation into ammonia and hydrochloric acid is practically complete. A set of very careful measurements by Johnson confirms Baker's determinations of gas density both for the ordinary and the perfectly dry salt, and to this data he adds exact determinations of the vapor pressure of the solid in both the ordinary and the perfectly dry states, which prove to be identical over the whole range of temperature measured. That is, we are presented with the anomaly of two systems, in each of which we have a solid apparently in equilibrium with its own gaseous molecules (*i. e.*, partial pressure of undissociated NH_4Cl) at two different pressures, one of which is many times as great as the other. We have become so used to explaining the facts of heterogeneous equilibrium upon the hypothesis that the ratio of concentrations of a given molecular species in two adjacent phases are independent of other species present that this comes as a rather severe shock. J. J. van Laar (*Z. physik. Chem.*, **62**, 194–8) has questioned the establishment of a true equilibrium in this system but Abegg (*Z. physik. Chem.*, **62**, 607–8) maintains that its establishment from both directions is adequate proof of its reality.

In this connection an article by J. Stieglitz (THIS JOURNAL, **30**, 946–54) may be recalled in which he shows that in a saturated solution of a salt the concentration of undissociated molecules is not always constant as usually assumed in developing the conception of "solubility product." However, in this latter case the discrepancies are less while the presence of a solvent as well as the less direct line of attack make the finding of an alternative explanation much easier.

Another interesting anomaly is presented by Ernst Cohen and J. W. Commelin (*Z. physik. Chem.*, **64**, 1–52) who have taken up L. Kahlenberg's (*J. Physic. Chem.*, **10**, 141–209 (1906)) direct measurements of osmotic pressure in pyridine solutions with sheet rubber as a semi-permeable membrane and shown that the erratic results obtained, and which Kahlenberg urged as evidence against the validity of the gas laws for solutions, are in all probability referable to traces of water in the pyridines which in some unknown way prevent the establishment of equilibrium. The apparent observations awaiting satisfactory explanation are: (*a*) water alone as solution in pyridine shows no pressure in the osmometer; (*b*) even traces of water in a solution of sugar in pyridine may increase the maximum pressure shown by this in the instrument nearly fourfold; (*c*) the pressure after having reached a maximum falls again to zero although only insignificant quantities of solute have escaped through the membrane, and the cell as a whole is still intact as shown by repetition of the experiment with fresh portions of solution and solvent. The authors promise further work upon the problem. We are also indebted to them through this article for the best concise summary of previous work on direct osmotic pressure measurements as yet published.

The old question as to whether the ions of an electrolyte are themselves hydrated has lately received from E. W. Washburn (*Tech. Quart.*, **21**, 164–320 (1908)) the most thorough and painstaking experimental investigation yet accorded it. His method is essentially that of the former workers, depending on measurement of the change in the concentration of the water with reference to some inert non-electrolyte added to the solution. The method, of course, only gives the difference of hydration between anion and cathion but for the chlorides this was found to be in favor of the cathion throughout and on the average 0.3 molecule H_2O per atom for H, 1.3 for K, and 2.0 for Na, and 4.7 for Li. Correcting our accepted transport numbers for this displacement of the solvent they are found to become almost independent of concentration and to agree then with those determined by the method of moving boundaries worked out by Denison and Steele (*Trans. Chem. Soc.*, **89**, 999–1013; *Z. physik. Chem.*, **57**, 110–27). The author points out that inversely a comparison of results by the two methods may be used to determine the degree of hydration.

On July 10th, last, H. Kamerlingh Onnes finally succeeded in liquefying helium at the cryogenic laboratory of the University of Leiden (*Akad. Welten. Amsterdam*, pp. 163–79 (1908), and *Comm. Phys. Lab. Leiden*, No. 108). The method used was the counterpart of that already employed for hydrogen. The helium compressed to 50 to 100 atm. was percooled to 15° absolute by liquid hydrogen evaporating under a pressure of 6 cm. of mercury and then allowed to expand in a small liquefier of the Hampson type. The liquid is so light (sp. gr. 0.15) that its liquefaction and separation from the gas was at first overlooked. Working with 200 l. of gas in the circulating system some 60 cc. of liquid were prepared. Its boiling point is about 4.3° absolute. Placed under a vacuum of 1 mm. of mercury no solidification or appreciable increase in viscosity took place, although the temperature of 3° absolute was probably reached. How much lower we may go by increasing the degree of vacuum is yet an open question, but the author points out that should helium behave like pentane it would not become viscous above 1.5° nor solid until 1.0° absolute was reached. The critical temperature is estimated at not much above 5° absolute and the critical pressure between 2 and 3 atmospheres.

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THE EFFECT OF NEUTRAL SALTS ON HYDROLYSIS BY WATER.

BY DAVID R. KELLOGG.

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[PRELIMINARY PAPER.]

It has long been known that when an ester undergoes hydrolysis in the presence of an acid, the addition of a neutral salt of the acid used, if the acid is a "strong" one, greatly increases the rate at which the reaction takes place. This was shown by Arrhenius,[1] Euler,[2] Spohr,[3] and many others. In every case they found that the effect of the salt is greater the more dilute the acid. The question then arose as to the effect when the concentration of the acid is zero, *i. e.*, in a neutral solution. The only work that has been discovered along this line was done by W. A. Smith.[4] In his work on "The Progressive Dissociation of Organic Dibasic Acids," he determined the extent of dissociation by measuring the rate at which the acids inverted cane sugar. It occurred to him to investigate the effect of neutral salts on the rate of inversion in the absence of acid. Accordingly he tried solutions of sodium succinate, sodium oxalate, sodium sulphate, potassium chloride, and sodium carbonate, the solutions being 1/64 normal. He found that salts of weak acids had almost no effect, while potassium chloride and sodium sulphate, which belong to the class of the most nearly neutral salts, had a large effect. The results for pure water and for potassium chloride he plotted on a time-per cent. inversion diagram—duplicate determinations varying for the potassium chloride,

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[1] *Z. physik. Chem.*, **4**, 237.

[2] *Ibid.*, **32**, 348.

[3] *J. prakt. Chem.*, **33**, 270.

[4] *Z. physik. Chem.*, **25**, 410.