ducted, and even then no satisfactory analysis could be secured, the results, however, indicating quite clearly that only one molecule of acetic anhydride had been added to the diquinazolyl.

HAVEMEYER LABORATORIES,
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# A REVIEW OF RECENT PROGRESS IN PHYSICAL CHEMISTRY.

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IT IS becoming more difficult year by year to make a satisfactory survey of any given field of scientific investigation. In the last year 1644 articles were classed as physico-chemical and abstracted in the Physikalisch-chemisches Centralblatt. To attempt anything like a summary of this enormous mass of literature would be absurd. I shall only try in a fragmentary way to touch upon some of the larger problems of general chemistry and a few of the more noteworthy contributions toward their solution. As is customary in these reviews I shall consider only the work done in foreign lands, and I shall further restrict the field by omitting any reference to the modern developments in radioactivity and the theory of electrons, for I fear that if I should embark upon this fascinating subject little space would be left for the older problems of our science.

In no other line of physico-chemical research during the past year has there been more satisfactory progress than in the determination of the so-called free energy of chemical reactions, nor is there any work of greater importance than this to be done. Complete tables for free energy such as we now have for the heat of chemical reactions would permit the technical chemist to calculate at once the maximum amount of work which he could hope to obtain from a given reaction or the minimum amount of work necessary to effect it. It would enable the student of pure chemistry to predict under given circumstances just what reactions could occur and how nearly they would run to an end. It would be the first step towards a fuller knowledge of chemical affinity.

Since mechanical power is now the most valuable of all commodities, the great technical problem of the day is to obtain from the combustion of coal the largest possible amount of available work. Many attempts have been made to construct a galvanic cell which will consume at one electrode the oxygen of the air, at the other some kind of fuel. Several of these attempts such as the carbon monoxide cell of Borchers and the coke cell of Jacques have at first appeared successful, but in every case it has been shown that the electromotive force obtained was the result either of thermal effects, or of some secondary reaction, and was not due to the combustion of the fuel. Haber and Moser (*Z. Elektrochem.* **11**, 593 (1905)) have now succeeded in measuring at 445° and at 518° the electromotive force of a cell in which carbon monoxide and oxygen combine reversibly to form carbon dioxide. Since the cell which they constructed is very polarizable, and gives its maximum electromotive force only when the feeblest currents are allowed to pass, it cannot be regarded as a very great step towards the perfect technical fuel cell. Still this work, together with previous data concerning the equilibria between carbon, oxygen, carbon monoxide and carbon dioxide, with which it stands in close agreement, and with the recent work of Löwenstein (*Z. physik. Chem.* **54**, 706 (1905)) on the dissociation of carbon dioxide between 1500° and 2000°, permits now a reliable calculation of the maximum work that we may hope to obtain, at any temperature, from the combustion either of coal or of carbon monoxide.

Hardly less important than the free energy of the formation of carbon dioxide is the free energy of formation of water. This is a quantity which until within a year has been regarded as known with fair accuracy. The hydrogen-oxygen cell, which was first studied by Grove in 1839, has since been the subject of numerous investigations. Its electromotive force was repeatedly found to lie between 1.08 and 1.12 volts. Very recently Westhaver (*Z. physik. Chem.* **51**, 65 (1905), using iridium electrodes instead of platinum, obtained a very well defined value of 1.06 volts. What the true significance of these values may be is a very interesting question, but it is now certain that they in no case represent the maximum electromotive force corresponding to the reversible union of oxygen and hydrogen to form water. The true value is undoubtedly a tenth of a volt higher than the highest of these. Nernst and von Wartenberg (*Göth. Nachr.* 1905, Heft 1), from the dissociation of water vapor at high temperatures, obtain 1.23 volts for the true electromotive force of the hydrogen-oxygen cell at 25°, while in this country the almost identical value, 1.22 volts, has been obtained by an entirely different method. The method of Nernst and von Wartenberg consisted in passing water vapor through a porcelain tube heated to a constant temperature between 1000° and 2000° and then through a capillary in which it was very rapidly cooled. From the quantity of hydrogen and oxygen left the dissociation of water vapor at the temperature of the hot tube was calculated. It amounted to about 0.02 per cent. at 1500° and 0.2 per cent. at 1800°. These values agree with others obtained with a different method by Löwenstein (*Z. physik. Chem.* **54**, 706 (1905)) who also worked in Nernst's laboratory. In order to calculate from the degree of dissociation at these high temperatures that at ordinary temperatures it is necessary to know not only the heat of formation of water at ordinary temperatures but also the specific heats of the reacting substances throughout the whole temperature range. The specific heats of gases at high temperatures have hitherto been only roughly determined through a study of the maximum pressure developed in explosions. This gap is now being filled. Holborn and Henning (*Ann. Physik.* [4] **18**, 739 (1905)), at the Reichsanstalt, have recently made a thorough series of calorimetric determinations of the specific heat of water vapor between 0° and 800°.

Another equilibrium of great importance both to technical and to theoretical chemistry has been very thoroughly studied during the past year. This is the equilibrium between sulphur trioxide on the one side and sulphur dioxide and oxygen on the other. Bodenstein and Pohl (*Z. Elektrochem.* **11**, 373 (1905)), in a very complete investigation, applied successfully both the mass law and the equation (isochore) of van't Hoff to this reaction between 500° and 900°. Their results have been further corroborated by the independent work of Lucas (*Z. Elektrochem.* **11**, 457 (1905)) and these two investigations taken with the earlier work of Knietsch (*Ber.* **34**, 4093 (1901)), Bodländer and Köpper (*Z. Elektrochem.* **9**, 789 (1903)), and Lunge and Pollit (*Z. angew. Chem.* **15**, 1105 (1902)), establish within a small margin of error the data which will be fundamental in computing the free energy of all the sulphates, and which at the same time are of the highest importance for the practical development of the sulphuric acid industry.

The commercial manufacture of ammonia from its elements appears now to be not only a possibility but a probability. The difficulty at present lies in the fact that at temperatures of 1000° or over, where equilibrium is quickly reached, the elements show but a slight tendency to combine and the yield of ammonia is small. On the other hand, at lower temperatures where the combination would progress much further, the reaction is exceedingly slow. The problem here is simply to find a catalyzing agent which will take the rôle that platinum takes in the oxidation of sulphur dioxide, and enable the reaction to take place rapidly at a temperature where the yield is large. Haber and van Oordt (*Z. anorg. Chem.* **43**, 111 and **44**, 341 (1905)), who have investigated fully the equilibrium between ammonia and its elements, have sought such a catalyzer in some metal which will unite rapidly with nitrogen to form the nitride but from which the nitrogen can be withdrawn by a current of hydrogen. They have so far investigated calcium and manganese but neither of these proves to be the right substance.

Much of our earlier knowledge of equilibria at high temperatures was obtained by analysis of the products of explosions. Nernst (*Z. anorg. Chem.* **45**, 126 (1905)) and Finckh (*Z. anorg. Chem.* **45**, 116 (1905)) have both shown the unreliability of this method. Its validity depends in fact upon the rather unlikely assumption that equilibrium is reached at the moment of maximum temperature and that it does not have time to change during the cooling that follows. Nernst shows, however, that by observing the maximum pressure produced by the explosion a knowledge of the equilibrium may frequently be obtained.

The whole subject of equilibria between gases at high temperatures has been most admirably presented by Haber ("Thermodynamik Technischer Gasreaktionen," R. Oldenberg, Munich and Berlin (1905)) in a treatise on "The Thermodynamics of Technical Gas-reactions." This book from an acknowledged master of both theoretical and applied chemistry contains a lucid exposition of the problems and recent developments in this important field. It is a pleasure to learn that a translation into English is soon to appear.

Of the investigations of free energy and chemical equilibrium at ordinary temperatures perhaps the most interesting is one by Luther and Sammet (*Z. Elektrochem.* **11**, 293 (1905)); (Sammet : *Z. physik. Chem.* **53**, 641 (1905)) concerning the reactions,

$$HIO_3 + 5HI \rightleftarrows 3I_2 + 3H_2O$$

and

$$HBrO_3 + 5HBr \rightleftarrows 3Br_2 + 3H_2O.$$

Both of these reactions run so nearly to an end that all the reacting substances cannot exist together at concentrations which can be determined by analytical methods, but it was found possible in the first case to determine the equilibrium by using as the source of iodide ion the difficultly soluble silver iodide whose solubility product is known. The iodide ion concentration was then so small that the remaining substances $(\overset{-}{IO_3},\overset{+}{H},I_2)$ taking part in the reaction existed in equilibrium in quantities sufficient for analytic determination. Equilibrium was reached at 25° in seven weeks, at 60° in four days. At each temperature the mass law was followed, according to the equation,

$$\frac{\overset{+}{H}{}^6)(\overset{-}{IO_3})(\overset{-}{I})^5}{(I_2)^3} = K,$$

and the values of K found for the two temperatures were consistent with the equation of van't Hoff. The same reaction was studied in an independent way by the determination of the electromotive force of the cell $Pt(\overset{-}{IO_3};\overset{+}{H};I_2)—(I_2;\overset{-}{I})Pt$. This was found by direct measurement to be 0.549 volt, while from the value of K the authors calculated likewise 0.549 volt, a remarkably good agreement. Furthermore, the electromotive force of this cell varied with varying concentrations of the different substances in good agreement with theory. Theory demands that the oxidation potential of any oxygen acid such as permanganic, chromic, etc., should depend upon the concentration of the hydrogen ion, but this is the first case in which it has been found possible to verify this theory and obtain a truly reversible potential. It is indeed the first time that any single reversible potential has been measured, which depends upon the concentration of three substances $(\overset{-}{IO_3};\overset{+}{H};I_2)$.

In the midst of this rapid progress toward a fuller knowledge of chemical affinity it is with something of a shock that we read (DeForcrand, *Compt. rend.* **139**, 906 (1904)) that Berthelot's principle of maximum work is the only sure guide to chemical affinity. In another article (*Compt. rend.* **139**, 908 (1904)) the same author (DeForcrand) admits that there are slight corrections to be applied in using this principle, but maintains that only from the heat of reaction can we predict whether or not a reaction will occur. There is something pathetic in this loyal allegiance to a lost cause. Experiments are now being extended to temperatures at which the principle of Berthelot can only be true in rare cases. Indeed at the temperature of the electric furnace it will probably be found a pretty general rule that *only those reactions occur which are accompanied by an absorption of heat.*

But while denying the factitious importance given to thermochemical data by the principle of Berthelot there is danger that we may underestimate their real value. In the future these data will be required especially in calculating the conditions of chemical equilibrium at one temperature from those at another, and there is even now an immediate need for an accurate revision of thermochemical measurements, for even such important data as the heat of formation of water and hydrochloric acid are known with little accuracy. That it is possible with methods now available to make much more accurate thermochemical measurements than the majority of those that are to be found in the literature is shown by an investigation of Wörmann (*Ann. Physik.* [4] **18**, 775 (1905), and Inaug. Dissert. Münster i. W. (1905)) upon the heat of neutralization of strong acids and bases and its change with the temperature, the latter being found to be almost exactly linear. The results obtained have furthermore an intrinsic value in that they permit the calculation of the degree of electrolytic dissociation of water at all temperatures from the degree of dissociation at any one temperature.

At the same time new improvements are constantly being made in calorimetric methods and new investigations on the fundamental units of energy. Dieterici (*Ann. Physik.* [4] **16**, 593 (1905)) and Behn (*Ann. Physik.* [4] **16**, 653 (1905)) have studied the ice calorimeter and have obtained independently almost identical values for its characteristic constant. They both determined also the ratio between the mean calorie and the

15° calorie and their results agree closely with each other and with the work of Barnes. Dieterici investigated the specific heat of liquid water throughout the whole range from 0° to 300°, and incidentally found a value for the mechanical equivalent of heat which agrees well with the best previous results and for which the author claims an accuracy within 0.05 per cent.

Dewar (*Proc. Roy. Soc.* **76** A, 325 (1905)) has continued his researches upon the liquid air and the liquid hydrogen calorimeters and shows that with the former it is possible to detect 0.02, with the latter 0.003 of a gram-calorie. With these calorimeters he has determined the specific heats of several substances at low temperatures. The value for diamond between —188° and —252.5°—namely, 0.0043—is the smallest that has been obtained for any solid substance. Dewar (*Proc. Roy. Soc.* **74** A, 122 (1904)) has also continued his investigations on the absorption of gases by charcoal at low temperatures, and finds that this absorption increases rapidly with decreasing temperature. The author might have predicted this thermodynamically for he has found that the absorption is always accompanied by a considerable evolution of heat; indeed, this heat in the case of hydrogen, nitrogen and oxygen is greater than the heat of liquefaction. This phenomenon is doubtless closely connected with the evolution of heat which has been observed at ordinary temperature when fine powders, such as silica or charcoal, are moistened with liquids.

Other interesting work at low temperatures has been done by Valentiner (*Ann. Physik.* [4] **15**, 74 (1904)), who has determined the ratio $C_p/C_v$ for nitrogen, at the temperature of liquid air, where it behaves like a pretty imperfect gas, and by Olszewski (*Ann. Physik.* [4] **17**, 986 and 994 (1905)) who attempted to liquefy helium by allowing it to cool by sudden expansion from 180 atmospheres at —259°. In this process the author estimates that the gas was cooled to within 1.7° of the absolute zero but no sign of liquefaction appeared.

Turning to the subject of reaction velocity, we find a large and rapidly accumulating mass of literature, much of which is of a character too detailed for discussion in a review of this kind; nor are there lacking articles in this field which contain speculations of such fantastic character that they threaten to retard rather than promote real progress.

An interesting point in the general theory of reaction velocity is raised by Brunner (*Z. physik. Chem.* **51**, 106 (1905)), who shows the untenability of the commonly accepted notion that the velocity is proportional to the quotient of the driving tendency of the reaction, as measured by its free energy, divided by a certain more or less constant chemical resistance. Brunner points out that at the beginning of a reaction, before any of the products are formed, the momentary tendency to react is infinite while the velocity is undoubtedly always finite.

The theory of Nernst (*Z. physik. Chem.* **47**, 52 (1904)) and Brunner (*Z. physik. Chem.* **47**, 56 (1904)), that the speed of every heterogeneous reaction is simply the speed of diffusion of the reacting substances toward the surface separating the two phases, has not been substantiated. Thus Goldschmidt (*Z. Elektrochem.* **11**, 430 (1905)), studying the speed of ester saponification in heterogeneous systems, finds several cases in which the reaction velocity in the homogeneous phase is the determining factor, and Brunner (*Z. physik. Chem.* **51**, 494 (1905)) himself finds in the solution of arsenic trioxide an example of a reaction whose velocity is determined by the speed of a chemical process in the surface film itself. Brunner here adheres to the theory in a modified form, but the modification consists practically in the denial of the original theory. The views of Nernst and Brunner have, however, helped to bring about a recognition of the real importance of processes of diffusion in heterogeneous reactions.

It is now generally admitted that most of the gaseous reactions which have been studied do not take place in the homogeneous gaseous phase, but upon the surface of the containing vessel. One of the most interesting cases of this kind has been studied by Bodenstein and Ohlmer (*Z. physik. Chem.* **53**, 166 (1905)) who, after showing that the union of carbon monoxide and oxygen occurred chiefly on the surface of the glass vessel in which they were contained, attempted to diminish this action of the walls by using tubes of fused quartz. Instead they found a much greater catalytic effect than before. In studying further this phenomenon the authors came to the very remarkable conclusion that the catalytic action of the silica is reduced by the presence of carbon monoxide and to a greater extent the greater the concentration of carbon monoxide. We have here therefore the curious case of a substance acting as a negative catalyzer to a reaction in which it itself takes part. This new phenomenon the authors term negative autocatalysis. It seems to me that their work may furnish a clue to one of the most mysterious of chemical phenomena. It was Davy who first noticed that phosphorus glows in air but not in pure oxygen, and in general that it glows more brightly the smaller the concentration of oxygen in contact with it. Since then the same phenomenon has been observed in the combustion of hydrogen phosphide, and in fact of most other gases. If now it can be shown that all these reactions take place only at the surface of some solid, and that the catalyzing action of the surface is reduced by the presence of oxygen, the phenomenon would be completely analogous to that observed by Bodenstein and Ohlmer.

An interesting case of catalysis has been observed by Bredig and Fraenkel (*Z. Elektrochem.* **11**, 525 (1905)) in the decomposition of ethyl diazoacetate. The rate of this decomposition is enormously affected by the presence of even very dilute acid.

The reaction therefore promises to be serviceable as an indicator by which small concentrations of hydrogen ions may be quantitatively determined as, for example, in estimating the degree of hydrolysis of slightly hydrolyzed salts.

Much attention has been given recently to the application of physico-chemical methods to the study of the dynamic isomers and their rates of transformation. Of especial interest to organic chemists is the work on the desmotropic compounds, carried on by Dimroth (*Ann.* **335**, 1 (1904) and **338**, 143 (1905); *Z. Elektrochem.* **11**, 30 (1905)), Brühl and Schroeder (*Z. physik. Chem.* **50**, 1 (1904); *Ber.* **37**, 3943 (1904)), Goldschmidt (*Z. Elektrochem.* **11**, 5 (1905)) and others.

It has been pointed out by LeBlanc (*Z. Elektrochem.* **11**, 9 (1905)) that the problem of the passive state of metals is essentially a problem in reaction velocity and that a metal is passive when the reaction by which the metal enters solution in the ionic condition is in some way greatly retarded. But what the nature of the resistance is which causes this retardation and why it suddenly appears and as suddenly disappears is still an unsolved problem. Much interest has lately been shown in this puzzling phenomenon. Müller (*Z. Elektrochem.* **11**, 755 (1905)) has studied passive zinc and manganese, Ruer (*Z. Elektrochem.* **11**, 661 (1905)), passive platinum, Baborovski (*Z. Elektrochem.* **11**, 465 (1905)) has published a very interesting article on passive magnesium, and Sackur (*Z. physik. Chem.* **54**, 641 (1905)) has even gone so far as to speak of passive hydrogen. It is doubtful whether in all these cases the phenomenon is really of the same character as that which is observed in the case of iron and chromium.

The use of a reversible iron electrode in the new Edison-Jungner storage cell seems at first sight inconsistent with the marked tendency of iron to assume the passive state, especially in alkaline solutions. This point led to an interesting discussion in the Bunsen *Gesellschaft* by Elbs (*Z. Elektrochem.* **11**, 734 (1905)), Foerster (*Z. Elektrochem.* **11**, 948 (1905)), Gräfenberg (*Z. Elektrochem.* **11**, 736 (1905)) and Müller (*Z. Elektrochem.* **11**, 949 (1905)). It was shown in fact that when the cell is filled, special precautions must be taken to make the iron active, and that the degeneration of the cell, which has sometimes been observed, is probably due to the gradual assumption of the passive state. This may be retarded by various devices, for example, a trace of mercury apparently acts catalytically to prevent passivity.

No entirely satisfactory theory of passivity has yet been advanced. The old oxide film theory still has its supporters although it has now been definitely shown that such a film must be a good electric conductor and must be so thin that the optical properties of the metallic surface remain unchanged. In connection with this theory it would be interesting to see if the phenomenon of passivity could be obtained in some solvent such as liquid ammonia, which contains no oxygen. Perhaps the most plausible among the various explanations of passivity is that offered by Kruger and Finkelstein (*Z. physik. Chem.* **39**, 91 (1902)). According to their idea a metal like iron contains both ferric and ferrous iron, is an alloy, as it were, of the two. In equilibrium there is a certain ratio between the quantities of the two, but when the equilibrium is once disturbed it is restored only with extreme slowness. When iron is acted on by an oxidizing agent only the ferrous portion dissolves, leaving a film of ferric iron, which behaves as a noble metal until more ferrous iron is produced from it, or until it is mechanically broken so that a new portion of metal is exposed. Müller (*Z. Elektrochem.* **11**, 823 (1905)) has recently proposed a new theory, based on the idea of electrons, which appears to be essentially a development of this theory of Kruger and Finkelstein.

Ruer (*Z. Elektrochem.* **11**, 661 (1905)) assumes passivity in platinum in order to explain the fact that platinum electrodes do not go into solution when made the anodes with a direct current, but are readily attacked by an alternating current. Presumably the platinum anode is soon rendered passive by the direct current and therefore ceases to dissolve, while with the alternating current each cathodic polarization restores the activity of the metal. This view is borne out by the fact that certain oxidizing agents have practically no action on platinum, but the platinum goes into solution when dipped alternately into the oxidizing agent and some reducing agent.

A good deal of work has been done recently upon electrolysis by the alternating current. Brochet and Petit (*Ann. chim. phys* [8] **3**, 433 (1904); *Compt. rend.* **139**, 855 (1904); *Z. Elektrochem.* **10**, 909 and 922 (1904) and **11**, 441 (1905)) have studied especially those reactions which may have a technical significance. LeBlanc *Z. Elektrochem.* **11**, 8 and 704 (1905)), by determining under what conditions a metal is dissolved during the passage of an alternating current, hopes to find evidence concerning the speed of formation of a complex ion from its constituents, for he argues that under ordinary circumstances a metal will dissolve during one phase of the alternating current, but redeposit in the same quantity during the reverse phase. If, however, the metallic ions formed during the first phase are removed— or example by the formation of a complex—before the phase changes, then the metal will fail to deposit and the total result will be the gradual solution of the metal. LeBlanc explains in this way the solution of copper by an alternating current in a solution of a substance like a cyanide which forms complexes with the copper ion. He hopes to be able to calculate the speed of formation of such a complex from the influence of the frequency of alternation of the current upon the amount of copper dissolved. It is doubtful, however, whether he has given sufficient consideration to other factors which enter into the problem.

This question of the speed of formation of a complex ion from its components, and *vice versa*, has been given prominence by an article of Haber (*Z. Elektrochem.* **10**, 433 and 773 (1904)). Electromotive force measurements show that the concentration of silver ion in a normal solution of potassium silver cyanide is about $10^{-23}$ normal, or perhaps half a dozen single ions in a liter. It has been supposed that such figures have a purely statistical significance, and mean not that half a dozen particular silver atoms exist continuously in the condition of simple ions while all the rest of the silver ions remain in the complex ions, but rather that all the silver atoms alternate, with unknown frequency, between the two conditions expressed by the symbols $\overset{+}{\mathrm{Ag}}$ and $\overset{-\,-}{\mathrm{Ag(CN)}}_3$ and that any one atom on the average remains in the $\overset{+}{\mathrm{Ag}}$ condition $10^{-23}$ part of the time. Now Haber doubts whether these small concentrations calculated by the Nernst equation have even so much meaning. His ingenious argument is somewhat as follows: When equilibrium is established in the system, $\overset{+}{\mathrm{Ag}}+3\overset{-}{\mathrm{CN}} \rightleftarrows \overset{-\,-}{\mathrm{Ag\ CN)}}_3$, the reaction velocities in both directions must be equal, although the substances on the left-hand side are present in extraordinarily small concentrations. Assuming that the velocity of their combination would increase with their concentration, according to the principle of Guldberg and Waage, Haber calculates that if a solution could be prepared normal both in silver and in cyanide ions they would unite $10^{23}$ times as fast as a normal solution of $\overset{-\,-}{\mathrm{Ag(CN)}}_3$ dissociates. Now the latter reaction has been generally assumed to be fairly rapid, since silver can be readily precipitated from the cyanide, either by a sulphide or by the electric current. Choosing for this rate what he considers a reasonable value, Haber obtains for the velocity of combination in the hypothetical normal solution of $\overset{+}{\mathrm{Ag}}$ and $\overset{-}{\mathrm{CN}}$ a velocity so great that to interpret the reaction in the usual way we should be obliged to conceive of the atoms moving together with a velocity millions of times greater than the velocity of light. We thus reach an absurd conclusion which apparently is based solely upon (1) the Nernst equation (2) the principle of Guldberg and Waage, and (3) the general atomistic conception. A lively discussion following the publication of this paradox was participated in by Danneel (*Z. Elektrochem.* **10**, 609 (1904)), Abegg (*Z. Elektrochem.* **10**, 607 (1904)) and Bodländer (*Z. Elektrochem.* **10**, 604 (1904)). The latter pointed out what appears to be the real solution of the problem. Haber's whole argument rests on the assumption that the complex silver cyanide ion dissociates with fair rapidity into its constituents, and this is in turn based solely on the fact that silver is readily precipitated from the cyanide solution. Obviously, the tacit assumption is here made that the complex ion can enter into no reaction without first splitting into its ions. If this entirely gratuitous assumption is omitted, the whole paradox disappears. The assumption that reactions in aqueous solution take place only between ions is itself one which I presume the majority of physical chemists have never adopted and which certainly has now been shown by the experiments of Kahlenberg and others to be directly opposed to all the evidence. Walker (*Trans. Chem. Soc.* **85**, 1082 (1904)) has also recently contributed a number of arguments in opposition to this view.

Much work remains to be done before we can form any adequate conception of the conditions that actually exist in an aqueous solution of an electrolyte. Walker (*Z. physik. Chem.* **51**, 706 (1905)) has shown that a considerable number of weak electrolytes which were formerly supposed to form exceptions to the mass law belong to the class of amphoteric electrolytes, that is, substances which are capable of yielding simultaneously hydrogen and hydroxyl ions. When this complication is taken into consideration all these substances are found to behave normally. On the other hand, no complete explanation has yet been offered for the deviation of strong electrolytes from the Ostwald dilution law, and it is still an open question whether this deviation is apparent or real. Jahn (*Z. physik. Chem.* **50**, 129 (1904)) adheres to his idea that the deviation is in the main apparent and caused by an increase in the velocity of the ions in strong solution, whereby their concentration as measured by the conductivity method appears greater than it really is. In support of this view he has recently made a number of freezing-point determinations of solutions of strong electrolytes and calculates from these the concentrations of the ions and of the undissociated salt. He shows that the values thus obtained agree with the (somewhat modified) dilution law. But there is some doubt as to whether freezing-point determinations are yet sufficiently accurate for this kind of calculation. Goebel (*Z. physik. Chem* **53**, 213 (1905)), for example, points out that the freezing-point law of van't Hoff is not quite true and that a correction should be made for the change in the heat of fusion of ice with the temperature. Applying this correction to existing data upon various salts he shows that they then become consistent with the mass law. Drucker (*Z. Elektrochem.* **11**, 904 (1905)), however, shows that Goebel made use of unreliable data for calculating the heat of fusion of ice. A a matter of fact the true correction is only about one-half of that used by Goebel, but is nevertheless large enough to be taken into consideration in exact work.

The method of Rothmund and Drucker for determining the degree of dissociation of strong acids, by studying their distribution between water and a non-miscible organic solvent, has been further employed by Drucker (*Z. physik. Chem.* **49**, 563 (1904)) and by Bogdan (*Z. Elektrochem.* **11**, 824 (1905)) with rather uncertain results.

A most interesting point, especially in its connection with the views of Jahn, has been raised by Danneel (*Z. Elektrochem.* **11**, 249 (1905)). It has often been noted as an interesting fact, that the two ions which move most rapidly in aqueous solution, hydrogen and hydroxyl, are the component ions of the water itself. Now it has been shown independently by Tijmstra (*Z. physik. Chem.* **49**, 345 (1904)) and by Dempwolff (*Physik. Z.* **5**, 637 (1904)) that in methyl alcohol the ion $\overline{CH_3O}$ travels with exceptional speed, and Danneel concludes that in general the ions of the solvent move faster than others and that this is due to their ability, so to speak, to go through a solvent molecule rather than around it. In other words, the neutral molecules play a rôle in the conduction similar to the one that was ascribed to them by the old Grotthus theory. If this view is correct, the ions of a salt should likewise move more rapidly in the presence of the neutral salt, that is, in concentrated solutions, as Jahn believes that they do. Why this same effect is not shown to an even greater extent in the case of the weak electrolytes, in which the proportion of the undissociated substance is much greater, Danneel does not attempt to explain. Whatever the probability may be of a material change in the ionic velocities at high concentrations, the best evidence seems to show that at least below concentrations of tenth-normal the electrical conductivity furnishes a good, at any rate the best, measure of the degree of dissociation, and that here there is a real deviation from the mass law. The idea seems to be gaining ground that this deviation is due to change in the dissociating power of the solvent caused by the addition of the electrolyte. All the recent views concerning the "Anomalies of Strong Electrolytes" have been brought together in an excellent monograph by Drucker "Die Anomalien der Starken Elektrolyte," Ahren's Sammlung X, 1 and 2, Enke, Stuttgart, (1905).

Continued investigation of conductivity in non-aqueous solutions, instead of bringing an answer to the problem of the real nature of electrolytic conductivity, serves rather to show how far we still are from the final solution of this question. Who would have thought a few years ago of classing ether as an electrolyte or as an electrolytic solvent? Yet Plotnikow (*J. Russ. physik. chem. Soc.* **36**, 1282 (1904)) has shown that a solution of phosphoric acid in ether conducts one-third as well as its solution in water, while Steele, McIntosh and Archibald (*Phil. Trans.* **205**

A, 99 (1905)) have found that ether dissolved in liquid hydrochloric acid is an excellent electrolyte.

One of the most extensive researches in this subject is by Walden (*Z. physik. Chem.* **54**, 129 (1906)) on organic solvents. His method of attack is unique, in that he chooses some particular solute, especially tetraethylammonium iodide, which he takes as "normal electrolyte" and studies its solution in a large number of solvents. In this way he has been led to several interesting generalizations, two of which may be mentioned here. The first concerns the relation between dielectric constant and dissociating power and may be stated as follows. If two solutions of the same electrolyte in different solvents are taken at such dilutions that the degree of dissociation is the same in both then $\frac{E_1}{E_2} = \frac{v_2}{v_1}$, or $Ev = \text{const.}$, where $E_1$ and $E_2$ represent the two dielectric constants, $v_1$ and $v_2$ the dilutions. This is only an approximate law but it is the first successful attempt to obtain any sort of quantitative relation between dielectric constant and dissociating power. The second purely empirical principle relates to the conductivity at infinite dilution. The smaller the value of this quantity is in a given solvent, the greater is its temperature coefficient. In other words, the values of the conductivity at infinite dilution in different solvents approach each other with increasing temperature.

Another paper deserving special mention is one by Steele, McIntosh and Archibald (*Phil. Trans.* **205** A, 99 (1905)) on hydrogen chloride, bromide, iodide, and sulphide as conducting solvents. The authors have made a very thorough study of the properties of these liquids, especially the first three, and they have determined the vapor-pressures, surface tensions, and densities of the pure solvents and the molecular weights, the transport numbers and the conductivity of their solutions. They obtain a remarkable result in determining the molecular weight of toluene in hydrochloric acid. The value found is 30, or about one-third of the normal molecular weight. Yet the solution is a non-conductor.

Hydrogen sulphide as a solvent has also been studied by Antony and Magri (*Gazz. chim. ital.* **35**, 208 (1905)). Schroeder (*Z. anorg. Chem.* **44**, 1 (1904)) has studied solutions in pyridine, and Walker and Johnson (*Trans. Chem. Soc.* **87**, 1597 (1905)) solutions in acetamide. Most of these observers have found numerous cases in which the molecular conductivity in dilute solutions increases with the concentration. Indeed, this behavior seems to be characteristic of a very large class of non-aqueous solutions. It is not improbable that this is an extreme manifestation of the same phenomenon that is responsible for the deviation from the mass law in aqueous solutions. In both cases the molecular conductivity at low concentrations is smaller than was to be predicted.

In many of the investigations that we have mentioned it has been shown that the solutes which give conducting solutions are able to form definite solid compounds with the solvent, thus indicating that probably in the solution, too, there is a union of solvent and solute. For example ether and toluene dissolved in hydrochloric acid differ in that the former is a conductor, the latter is not. Ether forms definite compounds with the solvent, while toluene does not. It now seems probable indeed that the formation of an electrolytic solution is usually, if not always, accompanied by "solvation." The belief is sometimes expressed that this solvation is the immediate cause of electrolytic dissociation. This view is discussed by Bousfield (*Z. physik. Chem.* **53**, 257 (1905)) who elaborates the idea of Kohlrausch (*Proc. Roy. Soc.* **71**, 338 (1903)) that each ion in aqueous solution is surrounded by an "atmosphere" of water molecules.

Domke and Bein (*Z. anorg. Chem.* **43**, 125 (1905)) have reopened a question which a few years ago was answered, rather too dogmatically, in the negative, namely, whether from the density and other physical properties of aqueous sulphuric acid it is possible to obtain evidence of the existence of definite hydrates in solution. They carried out, apparently with the highest accuracy, an exhaustive series of experiments upon the density and coefficient of expansion of sulphuric acid of different strengths. Although cautious about drawing conclusions from their data, they believe that their work taken in conjunction with the measurements of other physical properties by other experimentors furnishes strong grounds for the belief that a mixture containing sulphuric acid and water in equimolecular proportions consists almost entirely of the substance $H_2SO_4.H_2O$. As to the existence of other hydrates the evidence is less conclusive.

In the study of colloids little progress has been made since the very complete review of this subject by Professor Noyes, which recently appeared in this Journal (**27**, 85 (1905)). Billitzer's (*Z. physik. Chem.* **51**, 129 (1905)) theory of colloids will probably not find very wide acceptance until his experimental results have been better corroborated than they have been hitherto. Sutherland (*Phil. Mag.* [6] **9**, 781 (1905)) has worked out a theory of diffusion for non-electrolytes and applies it to a solution of egg albumen. From the rate of diffusion of this substance he obtains for it a molecular weight of 32,814 and gives it the formula $C_{1436}H_{2164}N_{35}O_{43}S_{15}$. The calculation rests, however, upon a pretty hypothetical basis.

Benedicks (*Z. physik. Chem.* **52**, 733 (1905)) believes that in one of the constituents of steel he has found a case of solid colloidal solution. Brown (*Ann. Physik.* [4] **16**, 166 (1905)) tries to show that the solutions of metals in liquid ammonia are colloidal in character. He would probably have considerable difficulty in reconciling his theory with the great lowering of the vapor-pressures which has been observed in these solutions by Franklin and Kraus, Joannis, and others.

The apparent success of the calculations of Arrhenius and Madsen upon the toxins, antitoxins, etc., have led some chemists to regard these substances as true solutions. Henri (*Z. physik. Chem.* **51**, 19 (1905)) has brought them back to what is undoubtedly their true place, under colloidal suspensions, in an important article entitled "Enzymes, Toxins, Antitoxins and Agglutinins."

While renewed interest in atomic weights has been aroused by several new and very accurate analyses, more recognition has also been given during the past year to the new physico-chemical methods of determining atomic weights. These methods all depend upon the assumption that every gas, as its pressure is diminished, approaches a perfect gas. In other words, the law of Avogadro, that under like conditions the molecular weights of gases are proportional to their densities, is a true limiting law for all gases as their pressure is indefinitely diminished. Therefore, if the density of any gas compared with oxygen is known, and the coefficient of compression of both gases between 0 and 1 atmosphere, the molecular weight of the gas can be exactly determined.

This method has been applied by Berthelot (*Z. Elektrochem.* **10**, 621 (1904)), Guye (*Compt. rend.* **140**, 1386 and 1241 (1905)), Leduc (*Compt. rend.* **140**, 717 (1905)), Rayleigh (*Proc. Roy. Soc.* **74**, 446 (1905); *Z. physik. Chem.* **52**, 705 (1905)), Jaquerod and Scheuer (*Compt. rend.* **140**, 1384 (1905)) and others. Guye, for example, obtained the following values $S = 32.065$, $C = 12.002$, $Cl = 35.476$, $Ar = 39.866$, all of which agree excellently with the atomic weights obtained by analytic methods. For nitrogen, on the other hand, the results obtained by this method are all lower than that found by Stas, 14.04. Thus the different investigators obtained the following results: Berthelot, 14.007; Leduc, 14.008; Rayleigh, 14.007; Guye, from the comparison of the four pairs of gases—$N_2,O_2$; $N_2,CO$; $N_2O,CO_2$; $NO,O_2$—finds 14.009, 14.006, 14.007, 14.008. Jaquerod and Perrot (*Compt. rend.* **140**, 1542 (1905)) determined the coefficients of expansion of several gases between 0° and 1067°, the melting-point of gold, and thus found the densities at the higher temperature. At this temperature Avogadro's law appears to hold even at atmospheric pressure. The atomic weight of nitrogen calculated from its density at this temperature is 14.008. From the remarkable agreement of all these values we may conclude that the true atomic weight of nitrogen is not far from 14.008. Guye (*Bull. oc. chim.* **33**, 1 (1905)) has in fact recently obtained the value 14.009 by an analytical method. Gray (*J. Chem. Soc.* **87**, 1601–1620) has also found the value 14.010 by an analytical method.

This work has also been of great importance in another way.

From the calculations used in getting the above results it is possible to determine the fundamental constants of a perfect gas. According to Berthelot the volume of 1 gram-molecule of a perfect gas at 0° and 760 mm. (latitude of 45°) is 22.412 liters, and the absolute zero of temperature on the perfect gas scale is —273.09° C.

The chief contributions made recently toward the solution of the problem of chemical valence have been by two men, Werner ("Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," Braunschweig, F. Vieweg and Son (1905)) and Abegg (*Z. anorg. Chem.* **39**, 330 (1904)). The appearance of Werner's book enables us for the first time to survey the whole of this author's extensive work, collected in a compact and systematic form. Werner has worked so independently and there have been so few points of contact between his work and the general development of theoretical chemistry, that it is difficult to find the right perspective for judging his views of chemical composition. No one can doubt the immense value of the great mass of experimental material which he has accumulated and it seems likely too that many of his theories, especially the idea of the coördination number, will in some form or other find a permanent place in chemistry; on the other hand, the treatment is unquestionably one-sided, and suffers from some apparent confusion between the concepts of affinity and valence and from a failure to give full recognition to the polar character of valence.

This idea of polarized valence, which is essentially the electrochemical theory, has been clearly stated by Abegg. Distinction must be made between positive and negative valence. Thus the valence of sulphur in sulphur trioxide is +6, that in hydrogen sulphide is —2. The difference between the two valences is 8 and not 4 as frequently stated. Thus it requires 8 units of an oxidizing substance, or 8 equivalents of an electric current to convert a sulphide into a sulphate. Likewise, the valence of nitrogen is —3 in ammonia, +5 in nitric acid; that of iodine is —1 in the iodides, +7 in the periodates. As in these cases so in general the difference between the extreme positive and the extreme negative valence which an element (especially a non-metallic element) can exhibit is usually eight and never more than eight. For the marked prominence of this number eight in the valence theory no explanation has been offered. Doubtless the natural arrangement of the elements in eight groups is a cognate fact.

An interesting question has been raised by LeBlanc (*Z. Elektrochem.* **11**, 813 (1905)), Can one element form both positive and negative ions? It appears from the experiments of LeBlanc as well as from those of Müller and Lucas (*Z. Elektrochem.* **11**, 521 (1905)), and Müller and Nowakowski (*Z. Elektrochem.* **11**, 931

(1905)), that tellurium, which lies on the border line between metals and non-metals, can go into electrolytic solution like any metal at the anode, and can also go into solution as $\overset{--}{\mathrm{Te}}$ at the cathode.

The correctness of Lehmann's views on the nature of liquid crystals may now be regarded as pretty definitely established. Tammann (*Z. Elektrochem.* **11**, 955 (1905)) still holds to the view that the so-called crystalline liquid is a suspension, not a homogeneous substance, but he not only has offered no explanation of why an emulsion should form when the solid crystals melt, but all attempts to separate the supposed emulsion into its components have been in vain. De Kock (*Z. physik. Chem.* **48**, 128 (1904)) repeats Tammann's own experiments and obtains results incompatible with the emulsion theory. Bredig and Schukowsky (*Ber.* **37**, 3419 (1904)) have subjected the liquids to cataphoresis without effecting any separation. Rotarski and Zemcuznyj (*Ann. Physik.* [4] **17**, 185 (1905)) have followed the cooling curve of azoxyanisol and azoxyphenetol from a higher temperature through the temperature at which the transition from the anisotropic to the crystalline liquid appears. A definite transition accompanied by a considerable heat change should produce a marked discontinuity in the cooling curve at the temperature of transition. As a matter of fact the curves of cooling showed only an extremely slight irregularity at the transition point. The authors believe that this is a strong argument against Lehmann's and for Tammann's theory, but it need not be so regarded, for Schenck (*Z. Elektrochem.* **11**, 951 (1905)) had already pointed out that the heat of transition from crystalline liquids to ordinary liquids must be very small, as evidenced by the very large change in transition point caused by impurities. A good summary of the arguments in favor of the Lehmann theory as well as of the recent developments in the study of mixed liquid crystals and other branches of the subject, is contained in a new book by Schenck ("Kristallinische Flüssigkeiten und flüssige Kristalle," W. Engelmann, Leipzig, (1905)).

The problems of photochemistry may be divided into those concerning the action of light upon chemical reactions and those which concern the absorption and emission of light by chemical substances. By far the most important recent investigation in the former field is one by Luther and Weigert (*Z. physik. Chem.* **51**, 297 (1905)). Luther studied for the first time a few years ago a case in which light affects not merely the speed of reaction but also the equilibrium of a chemical process. This was the decomposition of silver chloride to silver subchloride and chlorine. There has been some doubt, on account of the difficulty in determining the real nature of the solid phases concerned, as to whether this was a true reversible photochemical reaction. Now Luther and Weigert have found a homogeneous reaction, that between anthracene and dianthracene, which takes place in opposite directions in the light and in the dark. The formation of anthracene from dianthracene runs in the dark practically to an end, but in the light a certain amount of dianthracene is formed from the anthracene, and this is true whether the substance is in the solid, gaseous, or dissolved state. The system in the light is in a sort of dynamic equilibrium in which the percentage of dianthracene depends directly upon the amount of light which enters.

It is possible that in certain galvanic cells whose electromotive force changes in the light we have another instance of real displacement of equilibrium. A number of such cells has been studied by Wilderman (*Proc. Roy. Soc.* **74**, 369 (1905)).

In the domain of photography Sheppard and Mees (*Proc. Roy. Soc.* **74**, 447 (1905) and **76**, 217 (1905)) have elaborated a theory of the dynamics of photographic development which, if correct, possesses both theoretical and practical importance. A monograph by Luther ("Die Aufgaben der Photochemie," Antrittsvorlesung gehalten an der Univ. zu Leipzig, July (1905)) clearly outlines the present state of photography and its problems.

An exhaustive study of the emission of light by chemical substances and reactions, especially the phenomena known as chemiluminescence, triboluminescence and crystalloluminescence has been made by Trautz (*Z. physik. Chem.* **53**, 1 (1905)). Guinchant (*Rév. gén. sciences* **16**, 683 (1905)) has also published a review of the work that has been done in this comparatively unknown domain.

Fundamental work upon the phenomenon of phosphorescence has been done by Lenard and Klatt (*Ann. Physik.* [4] **15**, 225 and 425 and 633 (1904)), and by Waentig (*Z. physik. Chem.* **51**, 435 (1905)). The former investigators attempted to determine just what conditions are essential to phosphorescence in the case of the sulphides of the alkaline earths. They established the fact that the sulphide does not phosphoresce when pure and that, moreover, two impurities must be present, one a compound of a heavy metal, the other a compound of an alkali metal. Waentig believes that the phosphorescence is due to a slow reaction by which the system passes from an unstable to a stable condition. An argument in favor of this theory is that the power of phosphorescence disappears permanently when the substance is heated or subjected to heavy pressure.