Anonyme. The Journal of physical chemistry. Published at Cornell university [puis Published under the auspices of the American chemical society, the Chemical society and the Faraday society]. 1896 [I]-. 1901.

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GAS-POLARIZATION IN LEAD ACCUMULATORS

BY C. J. REED

Nernst and Dolezalek have published in Zeitschrift für Elektrochemie of May 10, 1900, a discussion of the "Gas-Polarization of Lead Accumulators". The conclusions arrived at and the interpretations given to certain experimental results do not seem to be tenable. Some of the statements as to experimental facts also appear on investigation to be not well founded. The preliminary statement is made that the *electrolysis of dilute sulphuric acid between lead electrodes does not take place with an electromotive force of less than about two volts; that the products of electrolysis are not hydrogen and oxygen, but lead and lead peroxide; that gas is generated only when the electromotive force is increased to about 2.3 volts.*

On the strength of these statements alone it is assumed that the *formation of lead and lead peroxide from lead sulphate in a lead accumulator takes place at an electromotive force less than that required to decompose water, and that, therefore, there results from electrolysis, not the reaction absorbing the least energy, but a reaction absorbing considerably more energy, namely, the formation of lead and lead peroxide, instead of hydrogen and oxygen.*

Influenced by these assumptions and the conclusions deduced therefrom, the authors have built up an explanation of a supposed anomaly, which really does not exist. The specific problem proposed by the authors for explanation was, *why can a lead accumulator with an aqueous electrolyte and an electromotive force exceeding two volts exist, since the electrolyte is decomposed rapidly between platinum plates when the electromotive force reaches 1.7 volts?*

The rational solution of this question and the rational accounting for all of the changes in energy and matter may or may not be difficult when the facts have been correctly ascertained and stated. But the theory advocated in the paper referred to above is somewhat startling. This theory is that the liberation of hydrogen from a given combination and condition does not require the absorption of a fixed quantity of energy, but a variable quantity, the value of which depends upon the occluding or absorbing capacity of an adjacent body — not upon the energy evolved or absorbed in occlusion, but merely upon the relative mass or volume of hydrogen that a unit of the adjacent body is capable of occluding. They assume that greater energy is required to liberate hydrogen in contact with lead than is required to liberate it in contact with platinum, simply because the platinum has a greater occluding capacity for hydrogen than for lead.

The results which would follow from such a theory, if it could be established, are so momentous, and the sponsors who stand for the theory are of such eminent authority, that I shall consider it unnecessary to apologize for going rather minutely into the details of the experimental facts and arguments, which seem to entirely refute it.

In order that there may be no misunderstanding, it will be necessary to quote at some length the statements of Nernst and Dolezalek. They say :

"The explanation of this abnormal property of lead, through which, evidently, is furnished the possibility of making an accumulator of two volts, may easily be derived from the recently announced theory concerning the generation of hydrogen in contact with metals, which was demonstrated by the experiments of Caspari.

"According to this [theory][1] there is to be added to the

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[1] Reference is cited by the authors to Caspari's paper "Ueber Wasserstoffentwicklung", Ztschr. phys. Chem. 30, H. I., 89. But an examination of the paper reveals the fact that the proof referred to is only the supposition of Caspari, and is not at all warranted by the experiments he describes. He

minimum electromotive force of decomposition of an electrolyte (free formation energy) a term which takes into consideration a specific property of the electrode material, and which, as the experiments make probable, is inversely proportional to the absorbing capacity of the electrode metal for hydrogen. It seems, therefore, that the work, which is required for the formation of hydrogen bubbles on a metallic surface, decreases exceedingly with the [increasing] occluding capacity".

From this assumption the authors have concluded that, since the occluding capacity of lead for hydrogen is very small in comparison with the occluding capacity of platinum, the energy required to form hydrogen "bubbles" on a lead plate is, therefore, greater than that required with a platinum plate and greater than the formation energy of the decomposed compound. In other words, it is assumed that the quantity of energy required to electrolytically separate hydrogen gas from a specific combination and condition is not constant, but depends upon a physical property of an adjacent body. They also assume, incidentally, that the liberation of hydrogen with lead electrodes is a secondary reaction, the decomposition of $PbSO_4$ being the primary, that is, the electrochemical reaction.

Against these assertions and assumptions I wish to place the following statements, which are held to be capable of experimental demonstration:

1. Hydrogen gas is evolved electrolytically in unlimited quantities from dilute sulfuric acid with electrodes of pure metallic lead when the electromotive force is less than 0.5 volt.

2. The electromotive force required to maintain a steady current between electrodes of metallic lead is less than 0.01 volt.

3. This occurs without the agency or presence of lead sulphate in the solution or on the cathode.

4. The electromotive force required to charge an accumula-

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entirely ignored the electrochemical reactions taking place and the electromotive forces due to the corresponding energy changes. His inferences, therefore, cannot be called proof.

tor is in no way dependent upon or related to the evolution of hydrogen or oxygen on a lead electrode, nor is it dependent upon the occluding capacity of lead.

The experimental demonstration of the first two of these propositions is of the utmost importance, as it leaves the entire theory of Nernst and Dolezalek, not only without facts to stand on, but without any object or anomaly to explain.

In order to prove that with lead electrodes hydrogen is evolved with less than 0.5 volt, it is only necessary to provide for a continuation of the reaction between *lead* electrodes long enough to study the reaction and to measure the electromotive force. This requires a rather large anode surface, because the electrochemical action rapidly changes the lead anode into an anode of lead sulphate. This change results in an entirely different electrochemical reaction as soon as the entire available or exposed surface of the lead anode has been converted into sulphate. A large mass of small, bright lead wire may be used satisfactorily as an anode and a small, bright lead wire as a cathode.

The amount of lead sulphate formed on the surface of the anode by a given current is, according to Faraday's law, proportional to the time the reaction continues. As the lead sulphate must cover the entire exposed surface of the anode to a certain depth before the reaction is interrupted or superseded by a different reaction, we have, evidently, only to provide a sufficiently large area of anode surface, in order to continue the reaction at a fixed rate for any desired period of time.

The evolution of hydrogen may be observed for a few seconds in considerable volume at 0.5 volt with an anode of lead having an area of only twenty-five square centimeters, if the lead cathode is reduced to a small sharp point. The most convenient and obvious method, however, of prolonging the reaction is to use as an anode, lead in a state of molecular or very minute division, subdivided chemically or electrolytically, such as is readily obtained in a charged negative accumulator plate, or in an electrolytically deposited "lead tree". By using such an anode and a clean strip of sheet lead as a cathode, we are enabled to prolong the demonstration as long as there remains any available metallic lead in the anode, or, in other words, until the accumulator plate is "sulphated" or discharged.

In all of the various experimental investigations referred to in the paper under consideration no attempt appears to have been made to really ascertain and to consider the chemical changes successively produced by the current, nor the energy changes, which must necessarily accompany those chemical changes. For example, electrodes of lead were interchanged with electrodes of lead sulphate or of platinum without considering that such a change would entirely alter the chemical reactions. One important consideration, which was entirely ignored, is the fact that an electric current passing between lead electrodes in pure, dilute sulphuric acid can produce at the cathode, hydrogen only, and at the anode, lead sulphate only. Consequently, the experiments of these investigators were not conducted under conditions which would enable them to detect these facts. If copper electrodes had been substituted for the lead electrodes, they would have noticed at once that the only products are copper sulphate at the anode and hydrogen at the cathode. With lead electrodes the reaction is similar, except that lead sulphate, instead of copper sulphate, is necessarily formed at the anode. Of course, the lead sulphate is much more insoluble than the copper sulphate and, in a very thin layer, is less evident to the unaided eye on account of being uncolored, but these well-known facts afford no ground for supposing that the lead sulphate is not formed under those conditions. On the contrary, we have abundant proof of the formation of lead sulphate under these identical conditions in the discharge of an ordinary lead accumulator. The available or exposed metallic lead (in spongy form) of the negative plate of an accumulator acts as an anode during discharge and is thereby converted directly, without the formation of any gas, into lead sulphate. This was proved many years ago by Gladstone and Tribe, and has been corroborated by all subsequent investigations.

When all of the exposed metallic lead of such an accumulator plate has been converted into lead sulphate, there is no longer any contact between the lead and the electrolyte. Metallic lead is no longer the electrode. The conversion of the lead electrode into lead sulphate has produced a new apparatus, new conditions, and a new reaction must occur, if the current is continued. An anode of lead sulphate has been substituted for an anode of lead, the mass of lead which remains unsulphated acting only as a conductor and helping to complete the circuit. Any electrochemical action which now takes place at the anode can affect only the lead sulphate or the electrolyte, the metallic lead having been entirely removed from the sphere of action. This change in the anode from lead to lead sulphate is very rapid and is completed in a fraction of a second with a small current, when the exposed surface is small, owing to the insolubility of the lead sulphate, which limits the reaction to a very thin, almost molecular external layer. But when the lead is minutely powdered, so as to expose to the electrolyte a large proportion of its mass, as in the ordinary accumulator plate, the time and current required to complete the change are proportionately greater.

If, after this change has been completed, the current be continued in the same direction, any one of several electrochemical reactions may occur, including the following:

1. The lead sulphate at the anode may be converted by oxidation into lead peroxide, PbO_2, or into lead persulphate, $Pb(SO_4)_2$.

2. After the anode has been converted wholly or partly into lead peroxide the electrolyte may be decomposed with the formation of any of several oxidation products, including oxygen, hydrogen peroxide, ozone, and persulphuric acid.

For each of these chemical changes there is an evolution or absorption of a definite quantity of chemical energy. The chemical energy of an electrochemical change is always added to or taken from the electrical energy of the circuit and either increases or diminishes the electromotive force between the electrodes, depending upon whether the chemical energy of the reaction is exothermic or endothermic. An attempt, therefore, to determine the electromotive force required to liberate hydrogen by measuring the potential difference between a lead cathode and an anode which changes from metallic lead, firstly to lead sulphate and then to lead peroxide, without considering the energy of these changes or determining which change is taking place at the time of the measurement, would appear to be the height of absurdity. Neither concentrations, osmotic pressures, nor mathematical formulæ can assist in such an undertaking.

It is evident from their results, as well as their statements, that no measurements were made by Nernst and Dolezalek or by Caspari of the electromotive force required to liberate hydrogen with *lead electrodes*, that no measurements were commenced until after the anode had ceased to be an anode of lead. Caspari states, for example, that he waited until the current became constant at a definite value before making his measurements, that is, until his anode was thoroughly converted into lead peroxide.

The fact that in their experiments the electromotive force required to evolve hydrogen was low during a brief initial period seems to have been noticed, but purposely ignored by all of the investigators, as though it were too insignificant a matter to be worthy of any serious consideration. Yet it was during this brief period only that the electrodes consisted of lead and it was the electromotive force between electrodes of lead that formed the subject of their investigations.

The electrochemical reaction between electrodes of metallic lead, which results in the formation of lead sulphate, is a reaction evolving very great energy (more than that required to liberate hydrogen), but all of the reactions occurring after the anode has been converted into lead sulphate or lead peroxide, absorb energy. Hence, the electromotive force required to produce a current will be different in the different cases, whether any hydrogen is liberated or not. The energy required to liberate hydrogen from a given chemical combination under given conditions evidently corresponds to a fixed electrochemical electromotive force. But the electromotive force found experimentally between two electrodes, at one of which hydrogen is evolved electrolytically, is merely the sum of this and all other electromotive forces included in the circuit between the two electrodes. This observed electromotive force between the electrodes is not, therefore, a measure of the electromotive force required to liberate hydrogen. No method has yet been found of eliminating experimentally the electromotive force at the other terminal of the electrolyte. The electromotive force between an electrolyte and a single electrode has never been measured and we have no positive experimental evidence that any such electromotive force exists. The use of a so-called "normal electrode" does not help us in the least. We are still measuring only the electromotive force between two electrodes.

The only known sources of electromotive force (positive or negative) between two electrodes emersed in an electrolyte are the electrochemical, the Joule, the Thomson (Kelvin), and the Peltier effects. The electromotive forces caused by the Joule, Thomson, and Peltier effects are due to energy introduced into or eliminated from the circuit in the form of heat. The Joule effect acts only in opposing an equal or greater electromotive force.

When the temperature of the system is maintained constant and uniform, the intensities of these thermo-electromotive forces are proportional to the strength of the electric current. They are, therefore, entirely eliminated when the temperature is constant and uniform and the current is zero. The electromotive force caused by the electrochemical effect is, however, not dependent upon the strength of the electric current, but depends only upon the chemical energy of one univalent electrochemical equivalent of the reacting substances. It follows, therefore, that, when the temperature of an electrochemical system is uniform and constant and the current zero, the measured electromotive force is that due solely to the electrochemical effect.

In the electrolysis of dilute sulphuric acid between electrodes of lead the electrochemical reaction results in the forma- of lead sulphate at the anode and hydrogen at the cathode, the complete electrochemical change being represented by the equation,

$$Pb + H_2SO_4Aq = PbSO_4 + 2H + Aq \quad \ldots\ldots\ldots\ldots (1).$$

The energy evolved by this reaction is, expressed as the equivalent in the form of heat, 215,700 — 210,100 = 5,600 (Berthelot) calories. The chemical affinity tending to cause this change to take place at either electrode is equivalent to an electromotive force of $\frac{5,600}{2 \times 23,240} = 0.12$ volt. As this affinity exists at each electrode, the electrochemical electromotive forces balance and can cause no current in either direction. The system cannot of itself produce an electric current through an external circuit. If, however, the slightest electromotive force be impressed upon the system from an external source in either direction through a closed circuit, the current can flow, producing lead sulphate at the anode and hydrogen at the cathode.

In the experiments performed by the writer, 0.38 volt was the lowest external electromotive force, with which an evolution of hydrogen was observed, but it was found that an electromotive force of 0.01 volt was sufficient to maintain a steady current. The source of the electromotive force used was a separately excited dynamo.

When the anode has been converted into lead sulphate and the cathode remains metallic lead, the next reaction forms lead peroxide, hydrogen, and sulphuric acid as follows:

$$PbSO_4 + H_2SO_4Aq = 2H + PbO_2 + 2SO_3Aq \quad \ldots\ldots (2).$$

This reaction absorbs an electromotive force equivalent to

$$\frac{215,700 + 210,100 - (63,400 + 2 \times 141,100)}{2 \times 23,240} = 1.73 \text{ volts.}$$

Ozone, O_3, will also be simultaneously formed by the independent electrolytic decomposition of the electrolyte between the PbO_2 anode thus formed and the lead cathode according to the equation,

$$3H_2SO_4Aq = 6H + O_3 + 3SO_3Aq \quad \ldots\ldots\ldots\ldots (3).$$

The electromotive force absorbed is equivalent to

$$\frac{630{,}300 - (-30{,}700 + 3 \times 141{,}100)}{6 \times 23{,}240} = 1.70 \text{ volts.}$$

As the electromotive force required to form ozone is 0.03 volt less than that required to form lead peroxide, there will always be some ozone formed as soon as there is any lead peroxide to act as an anode, that is, as soon as any current has passed. In practice it is found that the lead peroxide and the ozone always appear simultaneously when the operation is conducted at ordinary temperatures.

With an anode of lead peroxide and a cathode of metallic lead we may have the formation of either lead persulphate, $Pb(SO_4)_2$, hydrogen peroxide, H_2O_2, or persulphuric acid, HSO_4, at the anode and hydrogen at the cathode. The formation of the lead persulphate is represented by the equation,

$$PbSO_4 + H_2SO_4Aq = Pb(SO_4)_2 + 2H + Aq \cdots\cdots (4).$$

The formation energy of $Pb(SO_4)_2$ does not appear to have been published.

The formation of hydrogen peroxide with an anode of lead peroxide and a cathode of metallic lead is according to the equation,

$$2H_2SO_4Aq = 2H + H_2O_2Aq + 2SO_3Aq \cdots\cdots\cdots (5).$$

This absorbs on electromotive force equivalent to

$$\frac{2 \times 210{,}100 - (47{,}300 + 2 \times 141{,}100)}{2 \times 23{,}240} = 1.95 \text{ volts.}$$

The formation of persulphuric acid with an anode of lead peroxide and a cathode of metallic lead is represented by the equation,

$$2H_2SO_4Aq = 2HSO_4Aq + 2H \cdots\cdots\cdots\cdots (6).$$

The absorption is

$$\frac{2 \times 210{,}100 - 2 \times 158{,}200}{2 \times 23{,}240} = 2.23 \text{ volts.}$$

Reactions (1), (2), (3), (5), and (6) are known to occur, while (4) is known not to occur to any appreciable extent, since lead persulphate is very soluble and its formation would carry the lead into solution, where it would be precipitated as lead sulphate, leaving persulphuric acid in solution.

In all of the cases cited above the cathode is of metallic lead. If, instead of metallic lead, we use a cathode of lead sulphate and an anode of lead sulphate or lead peroxide, such as we have in the charging of a discharged accumulator, no current can pass without the reduction of the lead sulphate of the cathode to metallic lead and the oxidation of the lead sulphate of the anode to lead peroxide, the reaction being,

$$Aq + 2PbSO_4 = PbO_2 + Pb + 2SO_3Aq \cdots\cdots\cdots (7).$$

The absorption is

$$\frac{2 \times 215{,}700 - (63{,}400 + 2 \times 141{,}100)}{2 \times 23{,}240} = 1.845 \text{ volts.}$$

With the formation of lead and persulphuric acid from a cathode of lead sulphate and an anode of lead peroxide we have

$$H_2SO_4Aq + PbSO_4 = Pb + 2HSO_4Aq \cdots\cdots\cdots (8).$$

The absorption is

$$\frac{215{,}700 + 210{,}100 - 2 \times 158{,}200}{2 \times 23{,}240} = 2.36 \text{ volts.}$$

In the reaction forming ozone and metallic lead from a cathode of lead sulphate and an anode of lead peroxide we have

$$Aq + 3PbSO_4 = 3Pb + 3SO_3Aq + O_3 \cdots\cdots\cdots\cdots (9).$$

The absorption is

$$\frac{3 \times 215{,}700 - (3 \times 141{,}100 - 30{,}700)}{6 \times 23{,}240} = 1.82 \text{ volts.}$$

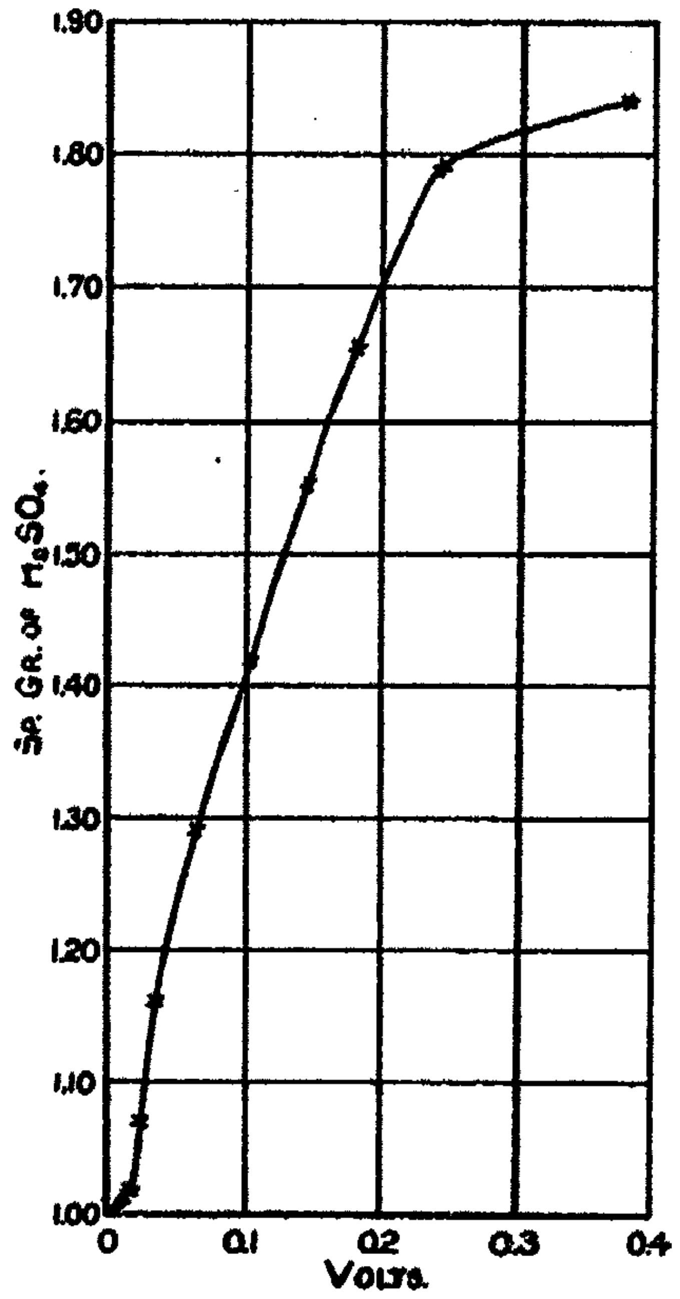
In the reaction forming hydrogen peroxide and metallic lead, we have

$$PbSO_4 + H_2SO_4Aq = Pb + H_2O_2Aq + 2SO_3Aq \cdots\cdots (10).$$

The absorption is

$$\frac{215{,}700 + 210{,}100 - (47{,}300 + 2 \times 141{,}100)}{2 \times 23{,}240} = 2.07 \text{ volts.}$$

In the above reactions it has been assumed that the sulphuric acid liberated from lead sulphate is always liberated as SO_3Aq, that is, as *very dilute* acid. In ordinary practice with lead accumulators this assumption is not correct, as the acid used in the accumulator is not very dilute and the dilution of the electrolytically liberated acid cannot exceed the dilution of the acid into which it is liberated. The acid set free will, as a matter of fact, always be considerably stronger than the solution constituting the electrolyte, particularly in the interior of a spongy electrode. A correction must, therefore, be added to the above results, which is the equivalent of the additional energy required to liberate the stronger acid. The total energy required to concentrate the most dilute acid to its maximum density (specific gravity of 1.842) is 17,850 calories per equivalent (bivalent), corresponding to an electromotive force of $\frac{17{,}850}{2 \times 23{,}240}$ $= 0.38$ volt. The necessary correction cannot, therefore, exceed this value. For any particular density of acid the corresponding dilution heat expressed in calories and the equivalent correction expressed in volts may be taken directly from the accompanying curve. The proper correction corresponding to the density of the acid used must be added once if the reaction liberates free acid at only one electrode, as in equation (2), and must be added twice when the acid is liberated at both electrodes, as in equation (7).



Assuming that in an accumulator the density of the electrolyte is 1.20, the strength of the acid liberated will be at least 1.20 and will probably be at least 1.30 or 1.35 at the point where it is liberated, that is, in the pores of the spongy electrodes. The correction corresponding to acid of this density is found from the curve to be 0.08 volt.

Applying this correction to the above reactions, we obtain in equation

(2) $1.73 + 0.08 = 1.81$ volts.
(3) $1.70 + 0.08 = 1.78$ "
(5) $1.95 + 0.08 = 2.03$ "
(7) $1.845 + 2 \times 0.08 = 2.00$ "
(8) $2.36 + 0.08 = 2.44$ "
(9) $1.82 + 2 \times 0.08 = 1.98$ "
(10) $2.07 + 2 \times 0.08 = 2.23$ "

The formation heats used in these calculations were mostly made at a temperature of about 15° C, and the electromotive forces are, therefore, correct for an electrochemical system maintained at that temperature when the circuit is open or when the current is very minute. It is scarcely necessary to add that they are entirely in accord with those universally obtained in practice. The increase in the strength of the acid in the pores of the active material and the consequent formation of persulphuric acid at the end of the charge accounts satisfactorily for the high electromotive force required.

When the electrodes of an electrochemical system constitute also the electrochemical reagents, as is the case with the lead sulphate, lead peroxide, and metallic lead of an accumulator, the decomposition tension of the intervening electrolyte is not necessarily a factor in determining the electromotive force between the electrodes. It will usually be a factor if the constituents of the electrolyte are actually set free. But it cannot be a factor if none of the constituents of the electrolyte are liberated by the electrochemical action, because the decomposition cannot then cause the absorption or evolution of the formation energy. The energy required to evolve the actual products formed by electrochemical action at the electrodes is always a measure of the electromotive force necessary to do the work of chemical separation (or combination) resulting in those products. If, for example, there were a dozen electrolytes intervening in series (separated by porous diaphragms) between the electrodes, the passage of the current through the series would cause decomposition (interchange of bases and acid radicles) at both terminals of each intervening electrolyte; but, as the constituents of these intermediate electrolytes are not set free, the electromotive force required for such liberation is not imposed upon the circuit. The same is true of a single electrolyte, such as dilute sulphuric acid, intervening between two electrodes, such as lead sulphate, which furnish the liberated products of electrochemical action. In this case the products liberated are lead, lead peroxide, and sulphuric acid, and the electromotive force required for the passage of the current is that which corresponds to the energy required to separate these bodies only, and is in no way dependent upon the electromotive force required to decompose any electrolyte or electrolytes that may intervene.

The chemical changes at the two electrodes occur in series and the current can reach the electrolyte only by passing into and out of the lead sulphate electrodes and decomposing this substance at both places. If the current could have access to the electrolyte without passing in series through the electrodes and decomposing them (as would be the case with platinum electrodes), the constituents of the electrolyte would be liberated and the electromotive force required would correspond to the energy of such liberation. But the current must cross the junctions between the electrolyte and the electrodes in series, and when these electrodes are of lead sulphate, they must undergo electrochemical decomposition.

When all available lead sulphate on both electrodes of an accumulator has been converted into the products, lead, lead peroxide, and sulphuric acid, the electrodes can no longer supply the products of electrochemical action and they must be supplied by the electrolyte. Oxygen, hydrogen, ozone, hydrogen peroxide, and pursulphuric acid then appear in quantities corresponding to the total current. But these products can then be liberated only by the passage of the current, and no current can pass without an electromotive force exceeding the counter-electromotive force of the charged accumulator with all of the products that have been formed. We might as well expect a boat to move against the current of a river when its velocity is less than that of the stream.

To prove that the liberation of hydrogen on a lead cathode is not due to the primary reduction of lead sulphate by the current and the secondary chemical action of the reduced lead on the water or acid present, it will be sufficient to show that the hydrogen is liberated in the same manner whether lead sulphate is present or not. This may be shown by electrolyzing with an anode of platinum and a cathode of clean, bright, metallic lead a solution of pure dilute sulphuric acid. Although there is no lead sulphate present, either on the cathode or in the solution, the passage of the current causes an instantaneous evolution of hydrogen as soon as the lead cathode touches the solution, the quantity being limited only by the current. It cannot be supposed that the action of the current at the cathode is to form and then reduce lead sulphate. As there is no other possible source of lead sulphate, there cannot be any present either before or during the passage of the current. Furthermore, an examination of the acid surrounding the cathode immediately afterwards shows no trace of lead sulphate or any other impurities, the acid evaporating without residue, though several hundred cubic centimeters of hydrogen may have been liberated.

This may be accomplished under practically the same conditions with both electrodes of lead and an electromotive force of 0.5 volt by using an anode of finely divided lead and surrounding the cathode with a porous cup containing the pure acid.

If the liberation of hydrogen is a secondary action, that is, the chemical action of reduced metallic lead on the water or dilute acid, it is difficult to see how this secondary reaction can depend upon either the electromotive force or the current. Such a secondary reaction must depend only upon the presence of the reacting materials, that is, upon the presence of the reduced lead and the solution. These are always present in an accumulator and ready to produce any possible secondary reaction as soon as the charging current flows, and they remain present after the charging current stops. The evolution of hydrogen, however, does not depend upon the presence of reduced lead in the solution, but upon the current, stopping when the current stops and commencing when the current begins, although there may remain at all times an abundance of reduced lead. While it is undoubtedly true that reduced lead does act slowly on dilute sulphuric acid, evolving hydrogen and gradually discharging the charged accumulator, it is equally certain that the evolution of hydrogen at a lead cathode during electrolysis does not depend upon the presence of lead sulphate, any more than the evolution of hydrogen at a platinum cathode depends upon the presence of platinum sulphate.

TWO DEVICES FOR CIRCULATING LIQUIDS AT CONSTANT TEMPERATURE

BY IRA H. DERBY

It has frequently been found necessary in this laboratory to obtain a constant temperature by means of a circulating liquid. Working with different methods, we found that any circulatory apparatus should be considered in respect to the following points:

(1) Rapidity of circulation;
(2) Ease of construction;
(3) Economy of operation;
(4) Rapidity of adjusting and maintaining the temperature;
(5) Usefulness over a great range of temperature.

One method which has hitherto been employed was that of Cady, the apparatus for which in construction and operation is apparently the ideal of simplicity. It was found, however, that the apparatus was somewhat difficult to regulate in consequence of the liquid having the tendency to siphon out when the speed of the motor was not well regulated. Another objection was that it was necessary to maintain the level of the liquid in the bath constant.

Another apparatus which we have employed, consists of a force pump, driven by an electric motor. Although this form of apparatus produces an excellent circulation and steady uniform flow of liquid through the constant temperature chamber, the initial expense and the power required to operate it preclude its use except in a few isolated cases. Moreover the expansion of the metal when heated to a higher temperature, makes it impossible to obtain a stuffing-box which is tight. One has, therefore, to resort to glass apparatus, and adopt principles quite different from those employed in the force-pump.

The first form which has been used for the circulation of liquids from a thermostat to the apparatus whose temperature is to be kept constant is shown in Fig. 1. In this diagram B represents the bath, A the jacket of constant temperature which has two side arms, C and D. Of these, the upper dips below the level of the liquid in the bath, while D is attached by glass connections to the tube E, which in our experiments was 2.5 cm. in diameter. To fill A with liquid, suction is applied at F, after which F is closed by a clamp. The tube E is set in the bath so that the upper rim of the tube is just below the surface of the liquid. In this cup is rotated, at high speed, a closely-fitting screw propeller W, which is attached to a shaft driven by an electric motor. The revolution of the wheel gives motion and direction to the liquid in contact with the wheel, and since DACB

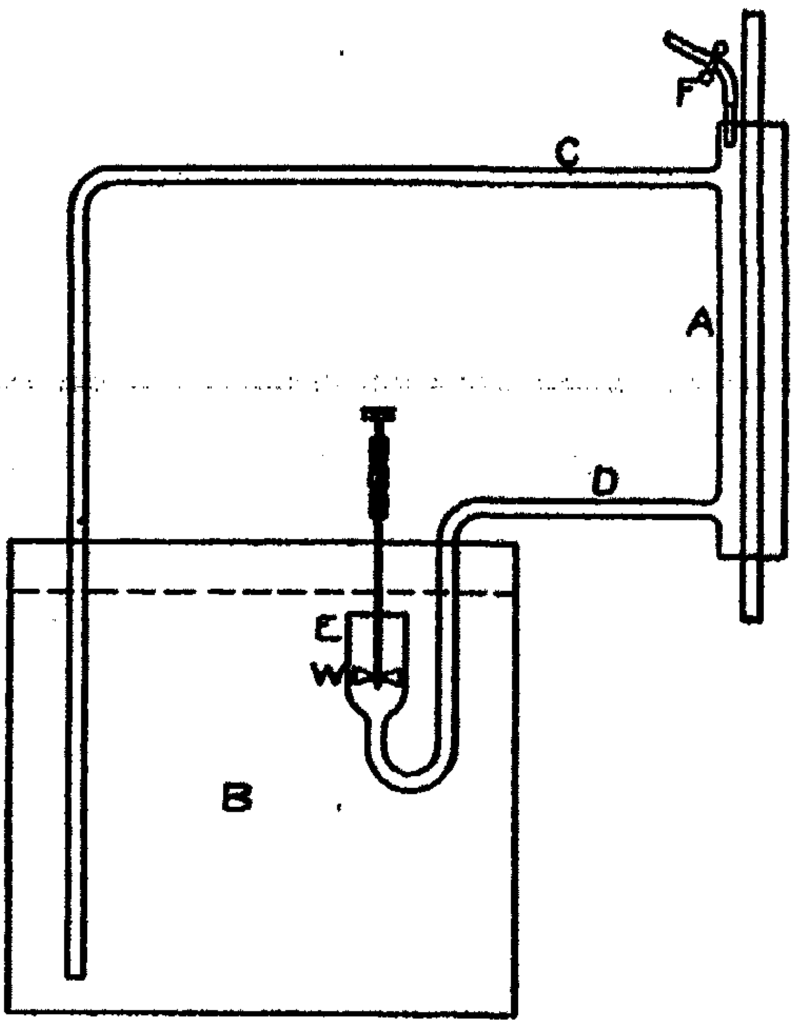


Fig. 1

forms a closed system, the rotation of the propeller must continually force liquid into and through the jacket at a rate which is a function of the speed of rotation and the size and length of the tubes C and D.

By use of this apparatus, which is extremely easy to make and to manipulate, very efficient circulation is obtained. It is absolutely necessary, however, to provide a stirrer for the bath B. To obviate the use of the circulating and stirring apparatus in separate parts, the second method was devised.

This is illustrated by Fig. 2. As in the previous case, B is the bath, A is the jacket, C and D are the outlet and inlet tubes, both of which pass below the surface of the liquid in the bath. The tube C is encircled by a loosely-fitting glass tube E, the lower end of which is blown to a bulb of diameter about 7 cm. In this bulb are blown two holes, H, of the diameter of 1 cm. To the shaft E is attached a driving wheel G, which is connected

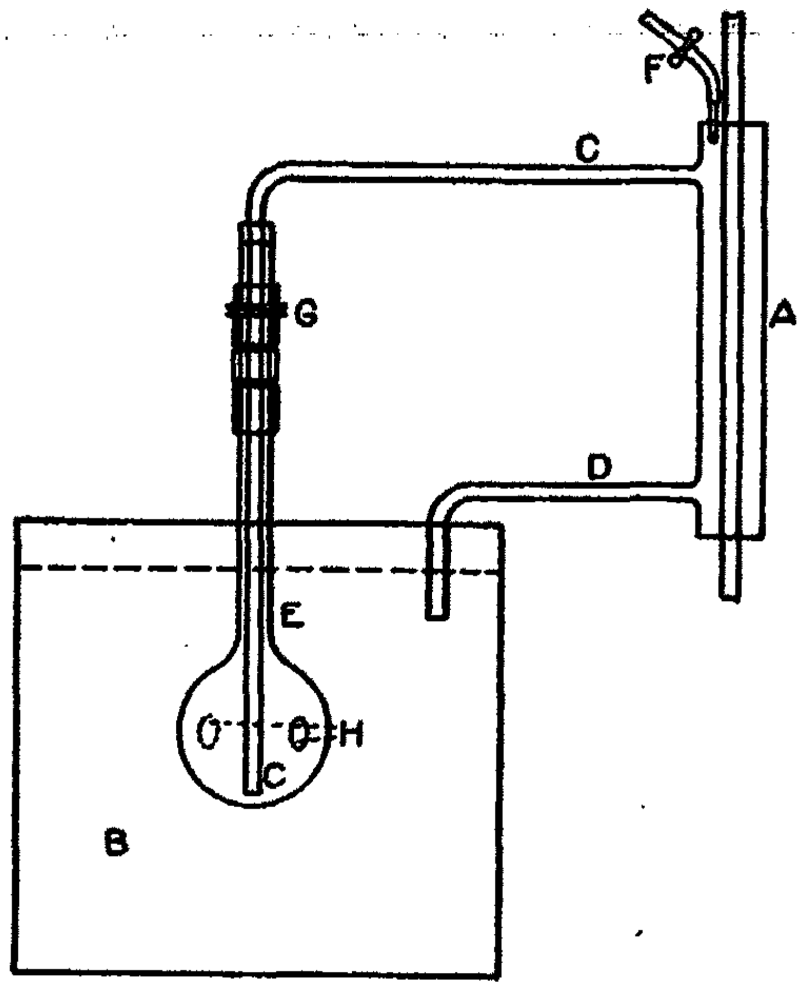


Fig. 2

to an electric motor by means of a belt. By means of suction applied at F, as in the preceding case, A, C, and D are filled with liquid. By now rotating GE rapidly, the liquid is by centrifugal action thrown away from CC, passes out through the holes H and causes the liquid to flow in the direction DACC (siphon action). This form of pump also acts as a very efficient stirrer, since the liquid thrown out of the holes in the bulb is scattered in the form of a fine spray through the liquid in the bath. This was proved in preliminary experiments by rotating a stirrer of this general form, but provided with a small hold in the bottom, in a two liquid layer system of sulfuric acid and toluene, when the acid was thrown in a very fine spray through the toluene. Additional proof was shown in a very pretty manner by the use of a colored solution in the tube CC.

By means of this apparatus, it was found possible to keep the temperature of the jacket A constant within a fraction of a degree at 90°. There is always a slight difference between the temperature of the bath and that of the jacket, depending on the amount of surface exposed to the air. But this is so constant that it causes little or no trouble.

This apparatus obviates the objections which we have found in Cady's; if the connection at F is tight, there is no tendency for the liquid to siphon out of the jacket, nor is it necessary to keep the level of the bath constant. The method has been subjected to a number of tests in circulating liquid in baths for vapor-density, gas volume, and other work, and so far as the five points mentioned above are concerned, it has been found very satisfactory.

Cornell University,
June, 1900.

ON THE EQUILIBRIUM OF CHEMICAL SYSTEMS[1]

BY PAUL SAUREL

INTRODUCTION

Among the many theorems which Gibbs has given in his famous memoir: On the Equilibrium of Heterogeneous Substances,[2] one of the most important for physical chemistry, if indeed not the most important, is the theorem which goes by the name of the phase rule. This theorem can be stated as follows: If a heterogeneous system consisting of r homogeneous phases formed by means of n independent components be in equilibrium, there exist between the temperature, the pressure and the nr concentrations, $nr + r - n$ equations, so that, if $n - r + 2$ of these variables be given the values of the others will be fixed.

This theorem allows us to classify chemical systems according to the value of the number $n - r + 2$, which has been called the variance of the system. In accordance with Trevor's nomenclature a system is said to be invariant, univariant, bivariant, trivariant, etc., according as the variance is equal to zero, to one, to two, to three, etc.; when the variance exceeds two the system is said to be multivariant.

Gibbs' theorem, however, does not furnish all the information which is necessary to characterize the state of equilibrium of a heterogeneous substance. Duhem[3] has completed it by

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[1] This article is a translation of the more important parts of a thesis Sur l'équilibre des systèmes chimiques, which was presented to the Faculté des Sciences of Bordeaux in April, 1900.

[2] Transactions of the Connecticut Academy of Arts and Sciences, 3, Part I, 1876; 3, Part II, 1878. J. Willard Gibbs. Thermodynamische Studien. Translated by W. Ostwald, Leipzig, 1892. J. W. Gibbs. Équilibre des systèmes chimiques. Translated by H. Le Châtelier, Paris, 1899.

[3] Jour. Phys. Chem. 2, 38, 103 (1898). Traité élémentaire de Mécanique chimique, 4, 294, 351.

showing that if the equations which connect the masses of the phases with the masses of the independent components and the volume of the system be taken into account, the equilibrium of a chemical system can be completely discussed. The results which are obtained in this way, when the masses of the independent components are given, are the following:

An invariant system can be in equilibrium only at a definite temperature, under a definite pressure and for definite values of the concentrations. At the equilibrium temperature and under the equilibrium pressure, the system admits of a continuous series of states of equilibrium in which the masses of the phases vary while the concentrations remain constant. The state of equilibrium of the system is completely determined if the values of two other variables be given, for example, the masses of two of the phases or the mass of one phase and the volume of the system, or again the volume and the entropy of the system.

A univariant system can be in equilibrium at an infinity of temperatures, but to each temperature there corresponds an equilibrium pressure and equilibrium concentrations. At a given temperature and under the equilibrium pressure which corresponds to that temperature, the system admits of a continuous series of states of equilibrium in which the masses of the phases vary while the concentrations remain constant. The state of equilibrium is completely determined if the value of one other variable be given, for example the mass of one phase or the volume of the system.

A bivariant or multivariant system can be in equilibrium at an infinity of temperatures and at each of these temperatures under an infinity of pressures. At a given temperature and under a given pressure the concentrations and the masses of the phases are determinate; the state of equilibrium is accordingly completely determined.

Duhem has gone further and has shown that, if the masses of the independent components of a bivariant system be suitably chosen, the system behaves like a univariant system, that is to say, to a given temperature there correspond an equilibrium pressure and equilibrium concentrations, and, at the given temperature and under the corresponding pressure, the system admits of a continuous series of states of equilibrium in which the masses of the phases vary while the concentrations remain constant. Duhem has given the name of *indifferent point* of a bivariant system to a state of equilibrium in which the system possesses the above mentioned properties of a univariant system.

It is natural to ask if the notion of indifferent point can be extended to multivariant systems. We have found that such an extension is indeed possible; if the masses of the independent components be suitably chosen, the multivariant system behaves like a univariant system. This result completes the discussion of the equilibrium of a heterogeneous system.

The theorems which we have just recalled relate to the equilibrium of a system; there is another series of important theorems which relate to the displacement of this equilibrium. In the first place there is a theorem which applies to univariant systems, viz.: Clapeyron's equation, which connects the simultaneous variations of the temperature and the equilibrium pressure. Gibbs[1] has shown that at an indifferent point of a bivariant system, formed by means of two components, the same equation holds; it is thus natural to ask if the application of this equation can be extended to the indifferent points of bivariant or multivariant systems formed by means of any number of independent components. We have found that such an extension is indeed possible.

For bivariant systems Gibbs[2] has given the following two theorems, of which the first has been independently rediscovered by Konowalow:[3]

If we consider, at a constant temperature, a bivariant system whose mass can be varied, the pressure of the system at the indifferent point which corresponds to the given temperature is, in general, a maximum or a minimum of the pressures possible

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[1] On the Equilibrium of Heterogeneous Substances, p. 155.

[2] Ibid. p. 155.

[3] Wied. Ann. 14, 48 (1881).

at the given temperature. Similarly, if we consider a bivariant system under a constant pressure, the temperature of the system at the indifferent point which corresponds to the given pressure is, in general, a maximum or a minimum of the temperatures possible under the given pressure.

Gibbs' demonstration is capable of immediate extension to the indifferent points of multivariant systems.

There remain to be mentioned two other important theorems which apply to bivariant and to multivariant systems, viz.: Le Châtelier's theorem on the displacement of equilibrium by variation of pressure[1] and van 't Hoff's theorem on the displacement of equilibrium by variation of temperature.[2] The first general demonstration of these theorems is due to Duhem.[3]

To establish the various theorems on the displacement of equilibrium which we have just recalled, demonstrations have been given which can not be easily connected; accordingly, it seemed desirable to deduce them all from a single formula. Planck[4] has given a general formula for the displacement of equilibrium, and he has made use of it to deduce Clapeyron's formula for univariant systems. Starting with Planck's formula we have been able to establish without difficulty the various theorems on the displacement of equilibrium, viz.: Clapeyron's equation for univariant systems and for the indifferent points of bivariant and multivariant systems, the theorems of Gibbs and Konowalow on indifferent points and finally the theorems of Le Châtelier and van 't Hoff.

We must now indicate the plan of this article.

In the first chapter we begin by recalling the criterium of equilibrium which is used in what follows. This criterium is the one that makes use of Gibbs' ζ-function. Duhem has given to this function the name total thermodynamic potential under constant pressure, and he has shown its great importance and usefulness in the study of the equilibrium of chemical systems.

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[1] Compt. rend. 99, 786 (1884).

[2] Études de Dynamique chimique, p. 161; Amsterdam, 1884.

[3] Annales de la Faculté de Toulouse, 4, N. (1890).

[4] Vorlesungen über Thermodynamik, p. 176; Leipzig, 1897.

We then give a demonstration of the phase rule which, in substance, is identical with the demonstrations of Gibbs and of Duhem, but which, in form, contains some simplifications.

In the second chapter we establish the conditions for the existence of an indifferent point in a bivariant system and in a multivariant system. These conditions enable us to give demonstrations of Clapeyron's theorems and of the theorems of Gibbs and Konowalow.

Finally, in the third chapter, starting with Planck's equation, we deduce the various theorems on the displacement of equilibrium: the theorems of Clapeyron, of Gibbs and Konowalow, of Le Châtelier, and of van 't Hoff.

The object we have had in view has been to put the theory of the equilibrium of heterogeneous systems into as compact and as simple a form as possible and, at the same time, to fill in some gaps in the theory.

This paper was written at the University of Bordeaux in the spring of 1900, and I wish to express here my gratitude to Professor P. Duhem of that University, for his unfailing kindness to me, and for the interest with which he followed the progress of my work.

CHAPTER I.

THE EQUILIBRIUM OF HETEROGENEOUS SYSTEMS

§ 1. The Phase Rule

Let us consider a heterogeneous system of r phases formed by means of n independent components whose masses are $\mathfrak{M}_1, \mathfrak{M}_2, \ldots, \mathfrak{M}_n$. By independent components of the system we mean substances, simple or otherwise, such that every system similar to the given system can be formed by taking suitable masses of these substances. Thus, for example, we say that the system which is formed by the dissociation of a mass of calcium carbonate into quicklime and carbon dioxide, is formed by means of the two independent components CaO and CO_2. For, although the system considered has been formed from a single mass of $CaCO_3$, we can obtain similar systems by adding an excess of CaO or of CO_2.

If we denote by E, H, and V the energy, the entropy and the volume of the heterogeneous system, and by T and Π its temperature and its pressure, the total thermodynamic potential Φ of the system is defined by the equation

$$\Phi = E - TH + \Pi V. \tag{1}$$

Similarly, if we denote by E_i, H_i and V_i the energy, the entropy and the volume of the *i*-th phase, the total thermodynamic potential Φ_i of that phase is defined by the equation

$$\Phi_i = E_i - TH_i + \Pi V_i. \tag{2}$$

Now it is evident that

$$V = \sum_{i=1}^{r} V_i; \tag{3}$$

if then we admit that

$$E = \sum_{i=1}^{r} E_i, \qquad H = \sum_{i=1}^{r} H_i, \tag{4}$$

it follows that

$$\Phi = \sum_{i=1}^{r} \Phi_i. \tag{5}$$

From the definition of Φ it can be shown that it is a homogeneous function of the first degree in the masses of the independent components. If, moreover, we admit that Φ is a function of the temperature and the pressure, it can be shown that when the system is in equilibrium

$$\frac{\partial \Phi}{\partial T} = -H, \qquad \frac{\partial \Phi}{\partial \Pi} = V. \tag{6}$$

In like manner, we shall admit that the total thermodynamic potential of the *i*-th phase is a function of the temperature and the pressure, and it can then be shown that when the phase is in equilibrium

$$\frac{\partial \Phi_i}{\partial T} = -H_i, \qquad \frac{\partial \Phi}{\partial \Pi} = V_i. \tag{7}$$

Moreover, if we denote by M_{ij} the mass of the j-th component which enters into the i-th phase, Φ_i will be a homogeneous function of the first degree in $M_{i1}, M_{i2}, \ldots, M_{in}$. We can therefore write

$$\Phi_i = \sum_{j=1}^{n} \frac{\partial \Phi_i}{\partial M_{ij}} M_{ij}. \tag{8}$$

We shall also write the formula which gives the variation of the total potential Φ_i, when the phase undergoes a virtual change which leaves the temperature and the pressure unaltered. The variation in question is given by the equation

$$\delta \Phi_i = \sum_{j=1}^{n} \frac{\partial \Phi_i}{\partial M_{ij}} \delta M_{ij}. \tag{9}$$

The partial derivatives which appear in equations 8 and 9 are homogeneous functions of the degree zero in $M_{i1}, M_{i2}, \ldots, M_{in}$; in other words, they are functions of the ratios of these masses. If, then, we denote by m_{ij} the mass of the j-th component which enters into the unit of mass of the i-th phase, the derivatives in question will be functions of $m_{i1}, m_{i2}, \ldots, m_{in}, T, \Pi$.

If the j-th component of the system is one of the independent components of the i-th phase, we shall write

$$F_{ij} = \frac{\partial \Phi_i}{\partial M_{ij}}. \tag{10}$$

If the independent components of the system are not independent components of the i-th phase, the masses $M_{i1}, M_{i2}, \ldots, M_{in}$ satisfy a certain number of conditions of the form

$$M_{ij} = \lambda M_{ik}, \quad M_{ij} = \mu M_{il}, \quad \ldots, \tag{11}$$

in which $\lambda, \mu, \ldots,$ are constants. As a consequence of these equations we shall have

$$\delta M_{ij} = \lambda \delta M_{ik}, \quad \delta M_{ij} = \mu \delta M_{il}, \quad \ldots . \tag{12}$$

But then, in the expressions for Φ_i and $\delta\Phi_i$, we may replace the terms

$$\frac{\partial \Phi_i}{\partial M_{ij}} M_{ij} + \frac{\partial \Phi_i}{\partial M_{ik}} M_{ik} + \frac{\partial \Phi_i}{\partial M_{il}} M_{il} + \cdots,$$

$$\frac{\partial \Phi_i}{\partial M_{ij}} \delta M_{ij} + \frac{\partial \Phi_i}{\partial M_{ik}} \delta M_{ik} + \frac{\partial \Phi_i}{\partial M_{il}} \delta M_{il} + \cdots,$$

by the terms

$$\left(\frac{\partial \Phi_i}{\partial M_{ij}} + f + g + \cdots\right) M_{ij} + \left(\frac{\partial \Phi_i}{\partial M_{ik}} - \lambda f\right) M_{ik} + \left(\frac{\partial \Phi_i}{\partial M_{il}} - \mu g\right) M_{il} + \cdots,$$

$$\left(\frac{\partial \Phi_i}{\partial M_{ij}} + f + g + \cdots\right) \delta M_{ij} + \left(\frac{\partial \Phi_i}{\partial M_{ik}} - \lambda f\right) \delta M_{ik} + \left(\frac{\partial \Phi_i}{\partial M_{il}} - \mu g\right) \delta M_{il} + \cdots,$$

f, g, ... being arbitrary functions. We shall then write

$$F_{ij} = \frac{\partial \Phi_i}{\partial M_{ij}} + f + g + \cdots,$$

$$F_{ik} = \frac{\partial \Phi_i}{\partial M_{ik}} - \lambda f,$$

$$F_{il} = \frac{\partial \Phi_i}{\partial M_{il}} - \mu g,$$

$$\vdots \quad \vdots \quad \vdots,$$

f, g, ... being arbitrary functions whose number is the same as that of the equations of condition 11.

If the j-th component does not enter into the i-th phase, that is to say if

$$M_{ij} = 0, \tag{13}$$

$$\delta M_{ij} = 0, \tag{14}$$

the derivative $\frac{\partial\Phi_i}{\partial M_{ij}}$ will be equal to zero and will disappear from equations 8 and 9. In that case we shall put

$$F_{ij}=0.$$

Then instead of equations 8 and 9 we may write

$$\Phi_i=\sum_{j=1}^{n}F_{ij}M_{ij}, \tag{15}$$

$$\delta\Phi_i=\sum_{j=1}^{n}F_{ij}\delta M_{ij}. \tag{16}$$

The thermodynamic potential of the system of r phases is accordingly given by the equation

$$\Phi=\sum_{i=1}^{r}\sum_{j=1}^{n}F_{ij}M_{ij}, \tag{17}$$

and the variation of this potential during a virtual change which leaves the temperature and the pressure unaltered is given by the equation

$$\delta\Phi=\sum_{i=1}^{r}\sum_{j=1}^{n}F_{ij}\delta M_{ij}. \tag{18}$$

Let us suppose that, for the system of r phases, there are p conditions of the form 13 and q conditions of the form 11. Then p of the quantities F_{ij} are identically equal to zero and disappear from equations 17 and 18. In the quantities F_{ij} which remain there appear q arbitrary functions which we may choose in any way that is convenient.

The variations δM_{ij} which appear in equation 18 are not all independent. In the first place, the definition of the masses M_{ij} shows that they satisfy the n equations

$$\sum_{i=1}^{r}M_{ij}=\mathfrak{M}_j, \qquad j=1, 2, \ldots, n. \tag{19}$$

In a change which leaves the total mass of each component unaltered, the variations δM_{ij} must accordingly satisfy the n equations

$$\sum_{i=1}^{r} \delta M_{ij} = 0, \qquad j = 1, 2, \ldots, n. \tag{20}$$

Moreover, these variations must satisfy p conditions of the form 14,

$$\delta M_{ij} = 0, \tag{21}$$

and q conditions of the form 12

$$\delta M_{ij} = \lambda \delta M_{hk}. \tag{22}$$

Among the nr quantities δM_{ij}, there are thus only $nr - n - p - q$ which are independent.

These preliminaries being established we can now apply the criterium of equilibrium. The system will be in equilibrium if, for every virtual change which leaves the temperature, the pressure and the masses of the components unaltered, we have

$$\delta \Phi \geqq 0.$$

If we suppose that no new phase can be formed, and that each phase actually contains a mass of each of its components, all the virtual changes will be revertible, and the preceding condition will reduce to

$$\delta \Phi = 0.$$

Thus the system will be in equilibrium if

$$\sum_{i=1}^{r} \sum_{j=1}^{n} F_{ij} \delta M_{ij} = 0, \tag{23}$$

for all the variations δM_{ij} which satisfy equations 20, 21 and 22.

If we multiply equations 20 by the arbitrary quantities F_1, F_2, ..., F_n, and if we subtract the results from equation 23, the condition of equilibrium will become

$$\sum_{i=1}^{r} \sum_{j=1}^{n} (F_{ij} - F_j) \delta M_{ij} = 0. \tag{24}$$

In this equation there are p terms which are identically equal to zero, namely, the terms which correspond to the p equations 21. Let us take F_j equal to one of the functions F_{1j}, F_{2j}, ..., F_{rj}, which is not identically equal to zero; on account of this choice n more terms disappear from the equation. Finally, let us choose the q arbitrary functions $f, g, \dots$, which appear in certain of the functions F_{ij}, in such a way that the coefficients of the q variations, such as δM_{ik} of equation 22, shall be identically equal to zero. There will then remain in equation 24 only the terms containing the $nr - n - p - q$ independent variations; we must then equate the coefficients of these variations to zero.

The conditions which we obtain in this way may be written in the form

$$F_{1j} = F_{2j} = \dots = F_{rj}, \qquad j = 1, 2, \dots, n, \tag{25}$$

if we agree not to write the p functions F_{ij} which are identically equal to zero. Because of this convention, the number of equations 25 is only $n(r-1) - p$. But we must observe that the choice which we made of the q arbitrary functions $f, g, \dots$ which appeared in certain of the functions F_{ij}, is such that q of the equations 25 are identities. The number of conditions 25 is thus only $nr - n - p - q$.

Equations 25 thus furnish $nr - n - p - q$ relations between the $nr + 2$ quantities m_{ij}, T, Π. To these equations we must add the r equations

$$\sum_{j=1}^{n} m_{ij} = 1, \qquad i = 1, 2, \dots, r, \tag{26}$$

which follow at once from the definition of the quantities m_{ij}, the p equations

$$m_{ij} = 0, \tag{27}$$

which correspond to the p equations 13, and the q equations

$$m_{ij} = \lambda m_{ik}, \tag{28}$$

which correspond to the q equations 11. Thus, between the temperature T, the pressure Π and the nr concentrations m_{ij}, there exist $nr - n - p - q + r + p + q$ relations; there are then only $n - r + 2$ of these variables which are independent. This theorem of Gibbs'[1] is known as the phase rule.

§ 2. Classification of Heterogeneous Systems

As Duhem has shown,[2] we can complete the study of the equilibrium of a heterogenous system, if we take into account the relations which exist between the masses of the phases and the masses of the components.

Let us denote by M_i the mass of the i-th phase; then

$$M_{ij} = m_{ij} M_i, \tag{29}$$

and equations 19 become

$$\sum_{i=1}^{r} m_{ij} M_i = \mathfrak{M}_j, \qquad j = 1, 2, \dots, n. \tag{30}$$

Moreover, if we denote by v_i the volume of the unit of mass of the i-th phase, we shall have

$$V_i = v_i M_i, \tag{31}$$

and

$$\sum_{i=1}^{r} v_i M_i = V. \tag{32}$$

When the system is in equilibrium, the specific volume v_i can be obtained from the thermodynamic potential of the unit of mass of the i-th phase by means of a formula similar to the one by which the volume of the system is obtained from the thermodynamic potential of the system; this specific volume is thus a function of $m_{i1}, m_{i2}, \dots, m_{in}$, T, Π.

The number $n - r + 2$ is called the variance of the system. If $r = n + 2$, the variance is equal to zero, and the system is called an invariant system. In this case, the variables T, Π, m_{ij}

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[1] On the Equilibrium of Heterogeneous Substances, p. 152.

[2] Jour. Phys. Chem. 2, 38, 103 (1898). Traité élémentaire de Mécanique chimique, 4, 294, 351.

have determinate values. Let us suppose that the masses $\mathfrak{M}_j$ are given; then if we choose arbitrarily the masses of two of the phases, the n equations 30 will determine the masses of the $r - 2$ remaining phases. Thus, if the masses of the components of an invariant system are given, the equilibrium of the system is indifferent.

If we know not only the masses of the components, but also the volume V of the system, then we can choose arbitrarily the mass of only one phase; the $n + 1$ equations 30 and 32 will determine the masses of the $r - 1$ remaining phases. The equilibrium of the system is still indifferent.

If $r = n + 1$, the variance of the system is equal to one and the system is called a univariant system. In this case we may choose arbitrarily one of the variables T, Π, m_{ij}; the others are then determinate. Let us suppose that the masses $\mathfrak{M}_j$ are given; then, if we choose arbitrarily the mass of one of the phases, the n equations 30 will determine the masses of the remaining $r - 1$ phases. Thus, the masses of the components being given, if we know also the temperature or the pressure, the equilibrium of the univariant system is indifferent.

If, in addition to the masses of the components, the volume of the system be given, the $n + 1$ equations 30 and 32 will determine the masses of the r phases. Thus, the masses of the components being given, if we know also the temperature and the volume or the pressure and the volume, the state of equilibrium of the univariant system is determined.

If $r = n$, the variance of the system is equal to two, and the system is called a bivariant system. In this case, we may choose arbitrarily two of the variables T, Π, m_{ij}; the others are then determinate. If the masses $\mathfrak{M}_j$ are given, the n equations 30 will determine the masses of the r phases. Thus, the masses of the components being given, if we know also the temperature and the pressure, the state of equilibrium of the bivariant system is determined.

Suppose that we know not only the masses of the components but also the volume of the system. The n equations 30 determine the masses of the r phases in terms of the concentrations m_{ij}. If we substitute these values of the masses M_i in equation 32, we shall have a new relation between the variables T, Π, m_{ij}. There is then but one of these variables which can be chosen arbitrarily. Thus, the masses of the components being given, the state of equilibrium of the bivariant system will be determined if the temperature and the volume or the pressure and the volume be given. The state of equilibrium of a bivariant system is thus, in general, determined if we know the masses of the components and two of the three variables: temperature, pressure and volume.

When the variance exceeds two, the system is called a multivariant system. If $r = n - p$, the variance of the system is equal to $p + 2$. In this case $p + 2$ of the variables m_{ij}, T, Π are independent. If the masses $\mathfrak{M}_j$ are given, $n - p$ of the equations 30 will determine the masses of the r phases in terms of the concentrations m_{ij}. If we substitute these values of the masses in the p remaining equation 30, we shall obtain p new relations between the concentrations. We can then choose arbitrarily only two of the quantities T, Π, m_{ij}. Thus the state of equilibrium of a multivariant system is determined if the masses of the components, the temperature and the pressure are given.

Suppose that we know not only the masses of the components, but also the volume of the multivariant system. From $n - p$ of the equations 30 we can determine the masses of the r phases in terms of the concentrations. If we substitute these values of the masses in the p remaining equations 30 and in equation 32, we shall obtain $p + 1$ new relations between the variables T, Π, m_{ij}. We can thus choose arbitrarily only one of these quantities. Thus the state of equilibrium of a multivariant system is determined if, in addition to the masses of the components, the temperature and the volume or the pressure and the volume are given. The state of equilibrium is thus, in general, determined if we know the masses of the components and two of the three variables: temperature, pressure and volume.

From the preceding discussion it follows that the state of equilibrium of any system is, in general, determined if we know the masses of the components and the values of two other variables. In an invariant system we can take, as independent variables, the masses of two phases or the volume of the system and the mass of one phase. In a univariant system we can choose the temperature or the pressure as one variable, and the volume of the system or the mass of one phase as the second variable. Finally, in a bivariant or multivariant system we can take any two of the three variables: temperature, pressure and volume.

CHAPTER II.

INDIFFERENT POINTS

§1. Indifferent Points of Bivariant Systems

In the last chapter we have shown that for a bivariant or multivariant system we may choose arbitrarily the temperature and the pressure and that then, if the masses of the components are given, the state of equilibrium of the system is, in general, determinate. There exist however exceptional states for which this proposition is no longer true and in which the bivariant or multivariant system behaves like a univariant system, that is to say, the temperature and the equilibrium pressure are connected by an equation, and, the masses of the components being given, at a given temperature or under a given pressure, the system admits of a continuous series of states of equilibrium. We shall give the name of indifferent point of a bivariant or multivariant system to a state of equilibrium of the system in which it possesses the properties of a univariant system which we have just recalled.

Consider a bivariant system and write the equations 30 which correspond to that case:

$$\sum_{i=1}^{n} m_{ij} \mathrm{M}_i = \mathfrak{M}_j, \qquad j = 1, 2, \ldots, n. \tag{33}$$

Let us write

$$\begin{vmatrix} m_{11}, & m_{21}, & \ldots, & m_{n1} \\ m_{12}, & m_{22}, & \ldots, & m_{n2} \\ \vdots & \vdots & & \vdots \\ m_{1n}, & m_{2n}, & \ldots, & m_{nn} \end{vmatrix} = \mathrm{A}, \tag{34}$$

and let us denote by A_{ij} the minor of this determinant which corresponds to the element m_{ij}. Then multiplying equations 33 by $\mathrm{A}_{i1}, \mathrm{A}_{i2}, \ldots, \mathrm{A}_{in}$ and adding, we obtain the following equations which must be satisfied by all the values of the quantities M_i which satisfy equations 33:

$$\mathrm{M}_i \mathrm{A} = \sum_{j=1}^{n} \mathfrak{M}_j \mathrm{A}_{ij}, \qquad i = 1, 2, \ldots, n. \tag{35}$$

As is well known, these equations give, in general, the values of the quantities M_i which satisfy equations 33. But if

$$\mathrm{A} = 0, \tag{36}$$

this is no longer the case. However, as the equations 35 must be satisfied by all the values M_i which satisfy equations 33, if we suppose that there are finite values of the masses M_i which satisfy these equations, we must also have

$$\sum_{j=1}^{n} \mathfrak{M}_j \mathrm{A}_{ij} = 0, \qquad i = 1, 2, \ldots, n. \tag{37}$$

The masses $\mathfrak{M}_j$ must accordingly satisfy the n homogeneous equations 37. The necessary and sufficient condition for this is that the determinant of these equations should be equal to zero. But this condition is satisfied, for

$$\begin{vmatrix} \mathrm{A}_{11}, & \mathrm{A}_{12}, & \ldots, & \mathrm{A}_{1n} \\ \mathrm{A}_{21}, & \mathrm{A}_{22}, & \ldots, & \mathrm{A}_{2n} \\ \vdots & \vdots & & \vdots \\ \mathrm{A}_{n1}, & \mathrm{A}_{n2}, & \ldots, & \mathrm{A}_{nn} \end{vmatrix} = \mathrm{A}^{n-1} = 0.$$

Suppose then that the condition 36 is satisfied and that the masses $\mathfrak{M}_j$ have been so chosen as to satsify equations 37. This choice can be made in an infinite number of ways since equations 37 determine only the ratios of the quantities $\mathfrak{M}_j$. Under these conditions, if we choose arbitrarily the mass of one of the phases, M_1 for example, the other masses will be determined by equations 33. To show this, let us, for the moment, disregard the first of equations 33 and let us write the others in the form

$$\sum_{i=2}^{n} m_{ij} M_i = \mathfrak{M}_j - m_{1j} M_1, \qquad j = 2, 3, \cdots, n. \tag{38}$$

Let us write

$$\begin{vmatrix} m_{22}, & m_{32}, & \cdots, & m_{n2} \\ m_{23}, & m_{33}, & \cdots, & m_{n3} \\ \vdots & \vdots & & \vdots \\ m_{2n}, & m_{3n}, & \cdots, & m_{nn} \end{vmatrix} = B,$$

and let us denote by B_{ij} the minor of this determinant which corresponds to the element m_{ij}. We shall suppose that the determinant B is not equal to zero.

Multiplying equations 38 by $B_{i2}, B_{i3}, \ldots, B_{in}$ and adding we obtain

$$M_i B = \sum_{j=2}^{n} \mathfrak{M}_j B_{ij} - M_1 \sum_{j=2}^{n} m_{1j} B_{ij}, \qquad i = 2, 3, \cdots, n. \tag{39}$$

If we give to M_1 any value whatever, these equations determine values of $M_2, M_3, \ldots, M_n$, and the values of $M_1, M_2, \ldots, M_n$ thus determined, will satisfy equations 33. To show this, let us multiply equations 39 by $m_{2k}, m_{3k}, \ldots, m_{nk}$, k being one of the numbers 1, 2, ..., n and add. We obtain

$$B \sum_{i=2}^{n} m_{ik} M_i = \sum_{j=2}^{n} \mathfrak{M}_j \sum_{i=2}^{n} m_{ik} B_{ij} - M_1 \sum_{j=2}^{n} \sum_{i=2}^{n} m_{ik} m_{1j} B_{ij},$$

$$k = 1, 2, \cdots, n,$$

or, by adding $Bm_{1k}M_1$ to each side of the equation,

$$B\sum_{i=1}^{n} m_{ik}M_i = \sum_{j=2}^{n}\mathfrak{M}_j\sum_{i=2}^{n} m_{ik}B_{ij} + M_1\left(Bm_{1k} - \sum_{j=2}^{n}\sum_{i=2}^{n} m_{ik}m_{1j}B_{ij}\right),$$

$$k = 1, 2, \ldots, n. \qquad (40)$$

The coefficient of M_1 in the second member of this equation can be written in the form

$$\begin{vmatrix} m_{1k}, & m_{2k}, & m_{3k}, & \ldots, & m_{nk} \\ m_{12}, & m_{22}, & m_{32}, & \ldots, & m_{n2} \\ \vdots & \vdots & \vdots & & \vdots \\ m_{1n}, & m_{2n}, & m_{3n}, & \ldots, & m_{nn} \end{vmatrix}.$$

If $k = 1$, this determinant reduces to the determinant A which, by hypothesis, is equal to zero; and if $k = 2, 3, \ldots, n$, the elements of two lines become identical, and the determinant again reduces to zero. Thus, for all values of k, the coefficient of M_1 is equal to zero.

Further, if $k = 2, 3, \ldots, n$, the coefficient of $\mathfrak{M}_j$:

$$\sum_{i=2}^{n} m_{ik}B_{ij},$$

is equal to zero unless j is equal to k, in which case this coefficient is equal to B. Accordingly we have

$$B\sum_{i=1}^{n} m_{ik}M_i = B\mathfrak{M}_k, \qquad k = 2, 3, \ldots n, \qquad (41)$$

If $k = 1$, we shall write the second member of equation 40 in the form

$$B\mathfrak{M}_1 - \left(\mathfrak{M}_1 B - \sum_{j=2}^{n}\sum_{i=2}^{n}\mathfrak{M}_j m_{i1}B_{ij}\right).$$

The quantity within the parenthesis can be written in the determinant form

$$\begin{vmatrix} \mathfrak{M}_1, & m_{21}, & m_{31}, & \dots, & m_{n1} \\ \mathfrak{M}_2, & m_{22}, & m_{32}, & \dots, & m_{n2} \\ \mathfrak{M}_3, & m_{23}, & m_{33}, & \dots, & m_{n3} \\ \vdots & \vdots & \vdots & & \vdots \\ \mathfrak{M}_n, & m_{2n}, & m_{3n}, & \dots, & m_{nn} \end{vmatrix},$$

and this is equal to zero in virtue of the first of equations 37. We have accordingly

$$B\sum_{i=1}^{n} m_{i1}M_i = B\mathfrak{M}_1. \tag{42}$$

As we have supposed that B is not equal to zero, we may divide equations 41 and 42 by that quantity and we obtain equations 33. Thus the values of $M_1, M_2, \dots, M_n$ which are given by equations 39 do satisfy equations 33.

When the conditions 36 and 37 are satisfied, the system behaves like a univariant system and we have an indifferent point of the bivariant system. To show this, we recall that, for a bivariant system, two of the quantities T, Π, m_{ij} can be chosen arbitrarily; but as equation 36 furnishes a new relation between these quantities, there is now only one which is arbitrary. Moreover, the masses $\mathfrak{M}_j$ having been chosen so as to satisfy equations 37, we can choose the mass M_1 of one of the phases arbitrarily and equations 39 determine the masses of the remaining phases. Thus, at a given temperature and under the corresponding pressure, the equilibrium of the bivariant system is indifferent.

§ 2. Indifferent Points of Trivariant Systems

Let us consider next a trivariant system, that is, a system for which $r = n - 1$, and let us write equations 30 for this case:

$$\sum_{i=1}^{n-1} m_{ij}M_i = \mathfrak{M}_j, \qquad j = 1, 2, \dots, n. \tag{43}$$

For the moment, disregard the first of these equations and consider the $n-1$ others:

$$\sum_{i=1}^{n-1} m_{ij} M_i = \mathfrak{M}_j, \qquad j = 2, 3, \ldots, n. \qquad (44)$$

Let us write

$$\begin{vmatrix} m_{12}, & m_{22}, & \ldots, & m_{n-1,2} \\ m_{13}, & m_{23}, & \ldots, & m_{n-1,3} \\ \vdots & \vdots & & \vdots \\ m_{1n}, & m_{2n}, & \ldots, & m_{n-1,n} \end{vmatrix} = C, \qquad (45)$$

and let us denote by C_{ij} the minor which corresponds to the element m_{ij}. Multiplying equations 44 by C_{i2}, C_{i3}, ..., C_{in} and adding, we find

$$M_i C = \sum_{j=2}^{n} \mathfrak{M}_j C_{ij}, \qquad i = 1, 2, \ldots, n-1. \qquad (46)$$

Suppose that

$$C = 0. \qquad (47)$$

Then if equations 46 are to be satisfied we must also have

$$\sum_{j=2}^{n} \mathfrak{M}_j C_{ij} = 0, \qquad i = 1, 2, \ldots, n-1. \qquad (48)$$

These $n-1$ equations are compatible, for we have

$$\begin{vmatrix} C_{12}, & C_{13}, & \ldots, & C_{1n} \\ C_{22}, & C_{23}, & \ldots, & C_{2n} \\ \vdots & \vdots & & \vdots \\ C_{n-1,2}, & C_{n-1,3}, & \ldots, & C_{n-1,n} \end{vmatrix} = C^{n-2} = 0.$$

Accordingly let us suppose that equation 47 is satisfied and that the masses $\mathfrak{M}_2$, $\mathfrak{M}_3$, ..., $\mathfrak{M}_n$ have been chosen so as to satisfy equations 48. This can be done in an infinite number of ways since equations 48 determine only the ratios of the masses

$\mathfrak{M}_2, \mathfrak{M}_3, \ldots, \mathfrak{M}_n$. Let us disregard the first of equations 44 and let us write the others in the form:

$$\sum_{i=2}^{n-1} m_{ij}M_i = \mathfrak{M}_j - m_{1j}M_1, \qquad j = 3, 4, \cdots, n. \tag{49}$$

Let us write

$$\begin{vmatrix} m_{23}, & m_{33}, & \cdots, & m_{n-1,3} \\ m_{24}, & m_{34}, & \cdots, & m_{n-1,4} \\ \vdots & \vdots & & \vdots \\ m_{2n}, & m_{3n}, & \cdots, & m_{n-1,n} \end{vmatrix} = D,$$

and let us denote by D_{ij} the minor which corresponds to m_{ij}. We shall suppose that the determinant D is not equal to zero. Then multiplying equations 49 by $D_{i3}, D_{i4}, \ldots, D_{in}$ and adding, we get

$$M_iD = \sum_{j=3}^{n} \mathfrak{M}_j D_{ij} - M_1 \sum_{j=3}^{n} m_{1j}D_{ij}, \qquad i = 2, 3, \cdots, n-1. \tag{50}$$

If we give to M_1 any value whatever, these equations will determine the corresponding values of $M_2, M_3, \ldots, M_{n-1}$.

Let us see now under what conditions these values of M_1, $M_2, \ldots, M_{n-1}$ will satisfy equations 43. Multiply equations 50 by $m_{2k}, m_{3k}, m_{n-1,k}$, k being one of the numbers 1, 2, ..., n, and add. We get

$$D\sum_{i=2}^{n-1} m_{ik}M_i = \sum_{j=3}^{n} \mathfrak{M}_j \sum_{i=2}^{n-1} m_{ik}D_{ij} - M_1 \sum_{j=3}^{n} \sum_{i=2}^{n-1} m_{1j}m_{ik}D_{ij},$$

$$k = 1, 2, \cdots, n,$$

or, adding $Dm_{1k}M_1$ to each side of the equation,

$$D\sum_{i=1}^{n-1} m_{ik}M_i = \sum_{j=3}^{n} \mathfrak{M}_j \sum_{i=2}^{n-1} m_{ik}D_{ij} + M_1 \left(m_{1k}D - \sum_{j=3}^{n} \sum_{i=2}^{n-1} m_{1j}m_{ik}D_{ij} \right),$$

$$k = 1, 2, \cdots, n. \tag{51}$$

The coefficient of M_1 in the second member of this equation can be put into the determinant form

$$\begin{vmatrix} m_{1k}, & m_{2k}, & m_{3k}, & \cdots, & m_{n-1,k} \\ m_{13}, & m_{23}, & m_{33}, & \cdots, & m_{n-1,3} \\ m_{14}, & m_{24}, & m_{34}, & \cdots, & m_{n-1,4} \\ \vdots & \vdots & \vdots & & \vdots \\ m_{1n}, & m_{2n}, & m_{3n}, & \cdots, & m_{n-1,n} \end{vmatrix}.$$

Now, if $k = 3, 4, \ldots, n$, the elements of two lines of this determinant become identical and the determinant reduces to zero. If $k = 2$, this determinant is the determinant C which, by hypothesis, is equal to zero. If $k = 1$, we shall have a determinant different from C, but which we shall also suppose to be equal to zero. We thus introduce the new condition

$$\begin{vmatrix} m_{11}, & m_{21}, & \cdots, & m_{n-1,1} \\ m_{13}, & m_{23}, & \cdots, & m_{n-1,3} \\ \vdots & \vdots & & \vdots \\ m_{1n}, & m_{2n}, & \cdots, & m_{n-1,n} \end{vmatrix} = 0. \qquad (52)$$

Thus for all the values of k, the term in M_1 disappears from the second member of equation 51.

The coefficient of $\mathfrak{M}_j$:

$$\sum_{i=2}^{n-1} m_{ik} D_{ij},$$

will be equal to zero for $k = 3, 4, \ldots, n$, except when j is equal to k, in which case it is equal to D. We have thus

$$D \sum_{i=1}^{n-1} m_{ik} M_i = D\mathfrak{M}_k, \qquad k = 3, 4, \cdots, n. \qquad (53)$$

When $k = 2$, we shall write the second member of equation 51 in the form

$$D\mathfrak{M}_2 - \left(\mathfrak{M}_2 D - \sum_{j=3}^{n} \sum_{i=2}^{n-1} \mathfrak{M}_j m_{i2} D_{ij}\right).$$

The quantity within the parenthesis can be written in the determinant form

$$\begin{vmatrix} \mathfrak{M}_2, & m_{22}, & m_{32}, & \dots, & m_{n-1,2} \\ \mathfrak{M}_3, & m_{23}, & m_{33}, & \dots, & m_{n-1,3} \\ \mathfrak{M}_4, & m_{24}, & m_{34}, & \dots, & m_{n-1,4} \\ \vdots & \vdots & \vdots & & \vdots \\ \mathfrak{M}_n, & m_{2n}, & m_{3n}, & \dots, & m_{n-1,n} \end{vmatrix},$$

and the first of equations 48 shows that this determinant is equal to zero. We have thus

$$D\sum_{i=1}^{n-1} m_{i2} M_i = D\mathfrak{M}_2. \qquad (54)$$

Similarly, when $k = 1$, we can write the second member of equation 51 in the form

$$D\mathfrak{M}_1 - \begin{vmatrix} \mathfrak{M}_1, & m_{21}, & m_{31}, & \dots, & m_{n-1,1} \\ \mathfrak{M}_3, & m_{23}, & m_{33}, & \dots, & m_{n-1,3} \\ \vdots & \vdots & \vdots & & \vdots \\ \mathfrak{M}_n, & m_{2n}, & m_{3n}, & \dots, & m_{n-1,n} \end{vmatrix}.$$

If then, we choose the mass $\mathfrak{M}_2$ so that

$$\begin{vmatrix} \mathfrak{M}_1, & m_{21}, & m_{31}, & \dots, & m_{n-1,1} \\ \mathfrak{M}_3, & m_{23}, & m_{33}, & \dots, & m_{n-1,3} \\ \vdots & \vdots & \vdots & & \vdots \\ \mathfrak{M}_n, & m_{2n}, & m_{3n}, & \dots, & m_{n-1,n} \end{vmatrix} = 0, \qquad (55)$$

we shall have

$$D\sum_{i=1}^{n-1} m_{i1} M_i = D\mathfrak{M}_1. \qquad (56)$$

As D is not equal to zero, we may divide equations 53, 54 and 56 by that quantity; we thus obtain equations 43. Thus the values of $M_1, M_2, \ldots, M_{n-1}$, which are given by equations 50, do satisfy equations 43.

The trivariant system now behaves like a univariant system. To show this, we observe that for a trivariant system three of the variables T, Π, m_{ij} are independent. But we have just imposed upon those variables the two new conditions 47 and 52; there is thus but one which is independent. Further, the masses of the components having been chosen so as to satisfy equations 48 and 55, we can choose the mass M_1 arbitrarily and the masses of the other phases will be determined by equations 50. Thus, whenever the conditions 47, 52, 48 and 55 are satisfied we shall have an indifferent point of the trivariant system.

Equations 47, 52, 48 and 55 have as consequences certain other equations which will enable us to write the conditions for an indifferent point in a symmetric form. To show this, let us denote the determinant that appears in equation 52 by C′, and by C'_{ij}, the minor which corresponds to the element m_{ij}, and let us consider the equations which we obtain by omitting the second of equations 43:

$$\sum_{i=1}^{n-1} m_{ij} M_i = \mathfrak{M}_j, \qquad j = 1, 3, \ldots, n. \qquad (57)$$

Multiplying these equations by $C'_{i1}, C'_{i3}, \ldots, C'_{in}$ and adding, we find

$$M_i C' = \sum_{j=1,3}^{n} \mathfrak{M}_j C'_{ij} = 0, \qquad i = 1, 2, \ldots, n-1. \qquad (58)$$

As C′ is equal to zero, it follows that we must have also

$$\sum_{j=1,3}^{n} \mathfrak{M}_j C'_{ij} = 0, \qquad i = 1, 2, \ldots, n-1. \qquad (59)$$

The first of these equations is equation 55.

In like manner let us consider the equations which we obtain by omitting the third of equations 43:

$$\sum_{i=1}^{n-1} m_{ij}M_i = \mathfrak{M}_j, \qquad j = 1,\ 2,\ 4,\ \cdots, n. \tag{60}$$

Let us write

$$\begin{vmatrix} m_{11}, & m_{21}, & \cdots, & m_{n-1,1} \\ m_{12}, & m_{22}, & \cdots, & m_{n-1,2} \\ m_{14}, & m_{21}, & \cdots, & m_{n-1,4} \\ \vdots & \vdots & & \vdots \\ m_{1n}, & m_{2n}, & \cdots, & m_{n-1,n} \end{vmatrix} = C'', \tag{61}$$

and let us denote by C''_{ij} the minor which corresponds to the element m_{ij}. Multiplying equations 60 by C''_{i1}, C''_{i2}, C''_{i4}, $\ldots$, C''_{in} and adding, we obtain

$$M_iC'' = \sum_{j=1,2,4}^{n} \mathfrak{M}_jC''_{ij}, \qquad i = 1,\ 2,\ \ldots,\ n-1. \tag{62}$$

As M_i admits of an infinite number of values it follows that we must have

$$C'' = 0, \tag{63}$$

and

$$\sum_{j=1,2,4}^{n} \mathfrak{M}_jC''_{ij} = 0, \qquad i = 1,\ 2,\ \ldots,\ n-1. \tag{64}$$

By continuing this reasoning, we see that whenever the trivariant system is in a state of indifferent equilibrium, all the determinants of order $n-1$ which can be formed from the following matrix:

$$\begin{matrix} \mathfrak{M}_1, & m_{11}, & m_{21}, & \cdots, & m_{n-1,1} \\ \mathfrak{M}_2, & m_{12}, & m_{22}, & \cdots, & m_{n-1,2} \\ \vdots & \vdots & \vdots & & \vdots \\ \mathfrak{M}_n, & m_{1n}, & m_{2n}, & \cdots, & m_{n-1,n} \end{matrix} \tag{65}$$

are equal to zero.

§ 3. Indifferent Points of Systems of Variance p + 2.

Let us consider now a multivariant system of variance, $p+2$, that is, a system for which $r = n - p$. By reasoning similar to that used in discussing trivariant systems, we can show that we shall have an indifferent point of the system whenever the concentrations satisfy the $p + 1$ equations:

$$\begin{vmatrix} m_{1j}, & m_{2j}, & \cdots, & m_{n-p,j} \\ m_{1,p+2}, & m_{2,p+2}, & \cdots, & m_{n-p,p+2} \\ \vdots & \vdots & & \vdots \\ m_{1n}, & m_{2n}, & \cdots, & m_{n-p,n} \end{vmatrix} = 0, \; j = 1, 2, \cdots, p+1, \quad (66)$$

and the masses of the components satisfy the equations:

$$\begin{vmatrix} \mathfrak{M}_{p+1}, & m_{2,p+1}, & \cdots, & m_{n-p,p+1} \\ \mathfrak{M}_{p+2}, & m_{2,p+2}, & \cdots, & m_{n-p,p+2} \\ \vdots & \vdots & & \vdots \\ \mathfrak{M}_{n}, & m_{2n}, & \cdots, & m_{n-p,n} \end{vmatrix} = 0,$$

$$\begin{vmatrix} m_{1,p+1}, & \mathfrak{M}_{p+1}, & \cdots, & m_{n-p,p+1} \\ m_{1,p+2}, & \mathfrak{M}_{p+2}, & \cdots, & m_{n-p,p+2} \\ \vdots & \vdots & & \vdots \\ m_{1n}, & \mathfrak{M}_{n}, & \cdots, & m_{n-p,n} \end{vmatrix} = 0,$$

$$\cdots\cdots\cdots\cdots\cdots$$

$$\begin{vmatrix} m_{1,p+1}, & m_{2,p+1}, & \cdots, & \mathfrak{M}_{p+1} \\ m_{1,p+2}, & m_{2,p+2}, & \cdots, & \mathfrak{M}_{p+2} \\ \vdots & \vdots & & \vdots \\ m_{1n}, & m_{2n}, & \cdots, & \mathfrak{M}_{n} \end{vmatrix} = 0, \quad (67)$$

$$\begin{vmatrix} \mathfrak{M}_{j}, & m_{2j}, & \cdots, & m_{n-p,j} \\ \mathfrak{M}_{p+2} & m_{2,p+2} & \cdots, & m_{n-p,p+2} \\ \vdots & \vdots & & \vdots \\ \mathfrak{M}_{n}, & m_{2n} & \cdots, & m_{n-p,n} \end{vmatrix} = 0, \qquad j = 1, 2, \cdots p.$$

When $p = 0$, these conditions reduce to conditions 36 and 37, which we have found for bivariant systems, and when $p = 1$, they reduce to the conditions 47, 52, 48 and 55 of trivariant systems.

Further, by reasoning similar to that used for trivariant systems, we can show that, whenever the multivariant system is in a state of indifferent equilibrium, all the determinants of order $n-p$ that can be formed from the matrix

$$\begin{array}{lllll} \mathfrak{M}_1, & m_{11}, & m_{21}, & \ldots, & m_{n-p,1} \\ \mathfrak{M}_2, & m_{12}, & m_{22}, & \ldots, & m_{n-p,2} \\ \vdots & \vdots & \vdots & & \vdots \\ \mathfrak{M}_n, & m_{1n}, & m_{2n}, & \ldots, & m_{n-p,n} \end{array} \qquad (68)$$

are equal to zero.

If the temperature or the pressure of a bivariant or multivariant system be given, and if the variables T, Π, m_{ij} satisfy conditions 66 and the masses of the components satisfy conditions 67, the equilibrium of the bivariant or multivariant system will be indifferent and the mass of one of the phases can be chosen arbitrarily. If the volume of the system be also given, equation 32 shows that the masses of all the phases will be determined; the equilibrium will no longer be indifferent. Thus the state of equilibrium of a bivariant or multivariant system at an indifferent point will be completely determined if the temperature and the volume or the pressure and the volume are known.

It follows from this discussion and from that given at the end of the last chapter that, with the exception of invariant systems, the state of equilibrium of every other system is determined when the temperature and the volume or the pressure and the volume are known.

There is a property of indifferent points which should be mentioned here. Let us consider a multivariant system of r phases formed by means of n independent components. If the system is at an indifferent point, we know that all the determinants of order r that can be formed from the matrix

$$\begin{matrix} \mathfrak{M}_1, & m_{11}, & \ldots, & m_{r1} \\ \mathfrak{M}_2, & m_{12}, & \ldots, & m_{r2} \\ \vdots & \vdots & & \vdots \\ \mathfrak{M}_n, & m_{1n}, & \ldots, & m_{rn} \end{matrix}$$

are equal to zero. Consider now a second system which differs from the system of r phases, in indifferent equilibrium, by the addition of a new phase formed from the same components. The equilibrium of the new system, if it be possible, will be indifferent. For this to be so, we know that all the determinants of order $r+1$ which can be formed from the matrix

$$\begin{matrix} \mathfrak{M}_1, & m_{11}, & \ldots, & m_{r1}, & m_{r+1,1} \\ \mathfrak{M}_2, & m_{12}, & \ldots, & m_{r2}, & m_{r+1,2} \\ \vdots & \vdots & & \vdots & \vdots \\ \mathfrak{M}_n, & m_{1n}, & \ldots, & m_{rn}, & m_{r+1,n} \end{matrix}$$

must be equal to zero. But it is easy to see that all these determinants reduce to zero, for each determinant of order $r+1$ can be developed into a sum of determinants of order r, each of which is, by hypothesis, equal to zero. Thus the indifferent points of a multivariant system of r phases are also indifferent points of a bivariant or multivariant system of $r+1$ phases.

§ 4. Clapeyron's Equation

The total thermodynamic potential of the i-th phase is given by the equation

$$\Phi_i = \sum_{j=1}^{n} F_{ij} M_{ij},$$

and we know that, when the system is in equilibrium,

$$\frac{\partial \Phi_i}{\partial T} = -H_i, \qquad \frac{\partial \Phi_i}{\partial \Pi} = V_i.$$

Consider an infinitesimal reversible change of the i-th phase, that is, consider two adjacent states of equilibrium. The change which the potential of the phase undergoes can be written in the following ways:

$$d\Phi_i = \frac{\partial \Phi_i}{\partial T} dT + \frac{\partial \Phi_i}{\partial \Pi} d\Pi + \sum_{j=1}^{n} \frac{\partial \Phi_i}{\partial M_{ij}} dM_{ij}$$

$$= -H_i dT + V_i d\Pi + \sum_{j=1}^{n} F_{ij} dM_{ij}, \qquad (69)$$

$$d\Phi_i = \sum_{j=1}^{n} F_{ij} dM_{ij} + \sum_{j=1}^{n} M_{ij} dF_{ij}. \qquad (70)$$

The comparison of equations 69 and 70 yields at once the equation

$$V_i d\Pi = H_i dT + \sum_{j=1}^{n} M_{ij} dF_{ij}.$$

Let us divide this equation by the mass M_i and let us denote by v_i and η_i the volume and the entropy of the unit of mass of the i-th phase; we thus obtain

$$v_i d\Pi = \eta_i dT + \sum_{j=1}^{n} m_{ij} dF_{ij}. \qquad (71)$$

When the system of r phases is in equilibrium, conditions 25 are satisfied. We may write them in the form

$$F_{1j} = F_{2j} = \ldots = F_{rj} = F_j, \qquad j = 1, 2, \ldots, n, \qquad (72)$$

in which F_j denotes the common value of the functions F_{ij} which correspond to the j-th component. In a reversible change, equations 72 are constantly satisfied; accordingly, for an infinitesimal reversible change we shall have

$$dF_{1j} = dF_{2j} = \ldots = dF_{rj} = dF_j, \qquad j = 1, 2, \ldots, n, \qquad (73)$$

and we can write equations 71 in the form

$$v_i d\Pi = \eta_i dT + \sum_{j=1}^{n} m_{ij} dF_j, \qquad i = 1, 2, \ldots, r. \qquad (74)$$

If the system under consideration is invariant, dT, $d\Pi$ and dF_j are equal to zero and all the terms of equation 74 vanish. In every other case, however, we can eliminate, from the r equations 74, $r - 1$ of the quantities $d\Pi$, dT, dF_j. If the system is univariant, r is equal to $n + 1$, and we can eliminate the n quantities dF_j. We thus obtain

$$\begin{vmatrix} v_1, & m_{11}, & m_{12}, & \dots, & m_{1n} \\ v_2, & m_{21}, & m_{22}, & \dots, & m_{2n} \\ \vdots & \vdots & \vdots & & \vdots \\ v_{n+1}, & m_{n+1,1}, & m_{n+1,2}, & \dots, & m_{n+1,n} \end{vmatrix} d\Pi$$

$$= \begin{vmatrix} \eta_1, & m_{11}, & m_{12}, & \dots, & m_{1n} \\ \eta_2, & m_{21}, & m_{22}, & \dots, & m_{2n} \\ \vdots & \vdots & \vdots & & \vdots \\ \eta_{n+1}, & m_{n+1,1}, & m_{n+1,2}, & \dots, & m_{n+1,n} \end{vmatrix} dT. \qquad (75)$$

If the system is bivariant, r is equal to n, and we can eliminate $n - 1$ of the quantities dF_j, for example dF_2, dF_3, $\dots$, dF_n. We thus obtain

$$\begin{vmatrix} v_1, & m_{12}, & m_{13}, & \dots, & m_{1n} \\ v_2, & m_{22}, & m_{23}, & \dots, & m_{2n} \\ \vdots & \vdots & \vdots & & \vdots \\ v_n, & m_{n2}, & m_{n3}, & \dots, & m_{nn} \end{vmatrix} d\Pi = \begin{vmatrix} \eta_1, & m_{12}, & m_{13}, & \dots, & m_{1n} \\ \eta_2, & m_{22}, & m_{23}, & \dots, & m_{2n} \\ \vdots & \vdots & \vdots & & \vdots \\ \eta_n, & m_{n2}, & m_{n3}, & \dots, & m_{nn} \end{vmatrix} dT$$

$$+ \begin{vmatrix} m_{11}, & m_{12}, & \dots, & m_{1n} \\ m_{21}, & m_{22}, & \dots, & m_{2n} \\ \vdots & \vdots & & \vdots \\ m_{n1}, & m_{n2}, & \dots, & m_{nn} \end{vmatrix} dF_1. \qquad (76)$$

Finally, for a multivariant system of variance $p + 2$, r is equal to $n - p$. Eliminating the $n - p - 1$ quantities dF_{p+2}, dF_{p+3}, $\dots$, dF_n, we find

$$\begin{vmatrix} v_1, & m_{1,p+2}, & \ldots, & m_{1n} \\ v_2, & m_{2,p+2}, & \ldots, & m_{2n} \\ \vdots & \vdots & & \vdots \\ v_{n-p}, & m_{n-p,p+2}, & \ldots, & m_{n-p,n} \end{vmatrix} d\Pi$$

$$= \begin{vmatrix} \eta_1, & m_{1,p+2}, & \ldots, & m_{1n} \\ \eta_2, & m_{2,p+2}, & \ldots, & m_{2n} \\ \vdots & \vdots & & \vdots \\ \eta_{n-p}, & m_{n-p,p+2}, & \ldots, & m_{n-p,n} \end{vmatrix} dT$$

$$+ \sum_{j=1}^{p+1} \begin{vmatrix} m_{1j}, & m_{1,p+2}, & \ldots, & m_{1n} \\ m_{2j}, & m_{2,p+2}, & \ldots, & m_{2n} \\ \vdots & \vdots & & \vdots \\ m_{n-p\,j}, & m_{n-p,p+2}, & \ldots, & m_{n-p,n} \end{vmatrix} dF_j. \qquad (77)$$

When $p = 0$, equation 77 reduces to equation 76.

Gibbs has shown,[1] in the particular case of a univariant system formed from one component, that equation 75 can be put into the form of Clapeyron's equation, and that at an indifferent point of a bivariant system, formed by means of two components, equation 76 can be written in the same form. We shall now show that, for any univariant system, it is possible to write equation 75 in the form of Clapeyron's equation, and that for any bivariant or multivariant system at an indifferent point, equation 77 can be written in the same form.

Consider first a univariant system. At a given temperature and under the corresponding pressure, the system admits of a continuous series of states of equilibrium in which the masses of the phases vary while the concentrations remain unchanged. Let us denote by M'_i and M_i the mass of the i-th phase, in two of these states of equilibrium, and by V′ and V, H′ and H, the volume and the entropy of the system in these two states. If the masses of the components remain unchanged, equations 30 show that we may write

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[1] On the Equilibrium of Heterogeneous Substances, p. 155.

$$\sum_{i=1}^{n+1} m_{ij}(M'_i - M_i) = 0, \qquad j = 1, 2, \ldots, n. \qquad (78)$$

In like manner the consideration of equation 32 and of the analogous equation

$$H = \sum_{i=1}^{n+1} H_i = \sum_{i=1}^{n+1} \eta_i M_i, \qquad (79)$$

shows that we may write

$$\sum_{i=1}^{n+1} v_i(M'_i - M_i) = V' - V, \qquad (80)$$

$$\sum_{i=1}^{n+1} \eta_i(M'_i - M_i) = H' - H. \qquad (81)$$

If, from the $n+2$ equations 78, 80 and 81 we eliminate the $n+1$ quantities $M'_i - M_i$, we obtain

$$\begin{vmatrix} H' - H, & V' - V, & 0, & 0, & \ldots, & 0 \\ \eta_1, & v_1, & m_{11}, & m_{12}, & \ldots, & m_{1n} \\ \eta_2, & v_2, & m_{21}, & m_{22}, & \ldots, & m_{2n} \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \eta_{n+1}, & v_{n+1}, & m_{n+1,1}, & m_{n+1,2}, & \ldots, & m_{n+1,n} \end{vmatrix} = 0, \qquad (82)$$

or by developing,

$$(H' - H) \begin{vmatrix} v_1, & m_{11}, & \ldots, & m_{1n} \\ v_2, & m_{21}, & \ldots, & m_{2n} \\ \vdots & \vdots & & \vdots \\ v_{n+1}, & m_{n+1,1}, & \ldots, & m_{n+1,n} \end{vmatrix}$$

$$= (V' - V) \begin{vmatrix} \eta_1, & m_{11}, & \ldots, & m_{1n} \\ \eta_2, & m_{21}, & \ldots, & m_{2n} \\ \vdots & \vdots & & \vdots \\ \eta_{n+1}, & m_{n+1,1}, & \ldots, & m_{n+1,n} \end{vmatrix}. \qquad (83)$$

If we compare this equation with equation 75, we get at once

$$\frac{d\Pi}{dT} = \frac{H' - H}{V' - V}. \tag{84}$$

If we denote by Q the quantity of heat which the system absorbs in passing from the state H, V to the state H′, V′, we have

$$Q = T(H' - H), \tag{85}$$

and equation 84 takes the well-known form

$$\frac{d\Pi}{dT} = \frac{Q}{T(V' - V)}. \tag{86}$$

Consider now a bivariant or multivariant system at an indifferent point. At a given temperature and under the pressure which corresponds to the indifferent point, the system admits of a continuous series of states of equilibrium in which the masses of the phases vary while the concentrations remain unchanged. If the variance is equal to $p + 2$, we can write the following equations analogous to 78, 80 and 81,

$$\sum_{i=1}^{n-p} m_{ij}(M'_i - M_i) = 0, \qquad j = 1, 2, \ldots, n, \tag{87}$$

$$\sum_{i=1}^{n-p} v_i(M'_i - M_i) = V' - V, \tag{88}$$

$$\sum_{i=1}^{n-p} \eta_i(M'_i - M_i) = H' - H. \tag{89}$$

Then, disregarding the $p + 1$ equations 87 which correspond to $j = 1, 2, \ldots, p + 1$, we can eliminate from the $n - p - 1$ remaining equations 87 and equations 88 and 89, the $n - p$ quantities $M'_i - M_i$. We thus obtain

$$\begin{array}{llllll} H' - H, & V' - V, & 0, & 0, & \ldots, & 0, \\ \eta_1, & v_1, & m_{1,p+2}, & m_{1,p+3}, & \ldots, & m_{1n} \\ \eta_2, & v_2, & m_{2,p+2}, & m_{2,p+3}, & \ldots, & m_{2n} \\ \vdots & \vdots & \vdots & \vdots & & \vdots \\ \eta_{n-p}, & v_{n-p}, & m_{n-p,p+2}, & m_{n-p,p+3}, & \ldots, & m_{n-p,n} \end{array} = 0, \tag{90}$$

or, developing,

$$(H'-H)\begin{vmatrix} v_1, & m_{1,p+2}, & \dots, & m_{1n} \\ v_2, & m_{2,p+2}, & \dots, & m_{2n} \\ \vdots & \vdots & & \vdots \\ v_{n-p}, & m_{n-p,p+2}, & \dots, & m_{n-p,n} \end{vmatrix}$$

$$= (V'-V)\begin{vmatrix} \eta_1, & m_{1,p+2}, & \dots, & m_{1n} \\ \eta_2, & m_{2,p+2}, & \dots, & m_{2n} \\ \vdots & \vdots & & \vdots \\ \eta_{n-p}, & m_{n-p,p+2}, & \dots, & m_{n-p,n} \end{vmatrix}. \quad (91)$$

Comparing this equation with equation 77 and noticing that at an indifferent point the terms in dF_j vanish in virtue of conditions 66, we see at once that

$$\frac{d\Pi}{dT} = \frac{H'-H}{V'-V}. \quad (92)$$

If we denote by Q the quantity of heat which the system absorbs during the reversible change from the state H, V, to the state H′, V′, we have

$$Q = T(H'-H), \quad (93)$$

and equation 92 takes the form of Clapeyron's equation :

$$\frac{d\Pi}{dT} = \frac{Q}{T(V'-V)}. \quad (94)$$

Equation 94 completes the analogy which exists between a univariant system and a bivariant or multivariant system at an indifferent point. In both cases, the temperature and the pressure are connected by an equation and the derivative of the pressure with respect to the temperature is given by Clapeyron's formula. Moreover, at a given temperature and under the corresponding pressure, each of the systems admits of a continuous series of states of equilibrium in which the masses of the phases vary while the concentrations remain unchanged.

§ 5. The Theorems of Gibbs and Konowalow

Equation 77 furnishes two more important theorems. Consider a reversible isothermal change of a bivariant or multivariant system. $d\mathrm{T}$ being equal to zero, the first term of the second member of equation 77 disappears from the equation. If the system passes through an indifferent point, the coefficients of the terms in $d\mathrm{F}_i$ will reduce to zero in virtue of conditions 66. If we suppose that the coefficient of $d\Pi$ is not equal to zero, which, by equation 91, is equivalent to the supposition that $\mathrm{V}' - \mathrm{V}$ is not equal to zero, we shall have

$$d\Pi = 0.$$

This means, in general, that the pressure passes through a maximum or a minimum of the values which are possible at the given temperature. Thus, at a given temperature, the pressure of a bivariant or multivariant system at the indifferent point which corresponds to that temperature, will be, in general, a maximum or a minimum of the pressures possible at the given temperature.

In like manner, it can be shown that, under a given pressure, the temperature of a bivariant or multivariant system at the indifferent point which corresponds to that pressure, will be, in general, a maximum or a minimum of the temperatures possible under the given pressure. The demonstration requires the coefficient of $d\mathrm{T}$ to be different from zero, which, by equation 91, is equivalent to the supposition that $\mathrm{H}' - \mathrm{H}$ is not equal to zero.

Gibbs has established[1] these two theorems in the case of a bivariant system, and we have simply reproduced his demonstration, applying it, however, to the general equation 77 instead of restricting it to equation 76. Konowalow has rediscovered[2] the first of Gibbs's theorems in the particular case of a bivariant system formed by means of two independent components.

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[1] On the Equilibrium of Heterogeneous Substances, p. 155.

[2] Wied. Ann. 14, 48 (1881).

CHAPTER III.

THE DISPLACEMENT OF EQUILIBRIUM

In the last chapter we have established several theorems relating to the displacement of equilibrium, namely, the theorems of Clapeyron and of Gibbs. We shall now treat the question of the displacement of equilibrium in a more general manner and shall show how, from one and the same formula can be deduced the principal theorems relating to the displacement of equilibrium, namely, the theorems of Clapeyron, of Gibbs, of Le Châtelier and of van 't Hoff.

Let us consider a system of r phases formed by means of n independent components. The total thermodynamic potential of the i-th phase satisfies the equation :

$$\Phi_i = \sum_{j=1}^{n} \frac{\partial \Phi'}{\partial M_{ij}} M_{ij}.$$

If we adopt a notation slightly different from that employed in the preceding chapters and write

$$F_{ij} = \frac{\partial \Phi_i}{\partial M_{ij}},$$

we shall have for the total potential of the i-th phase :

$$\Phi_i = \sum_{j=1}^{n} F_{ij} M_{ij},$$

and for the total potential of the system

$$\Phi = \sum_{i=1}^{r} \sum_{j=1}^{n} F_{ij} M_{ij}.$$

The system will be in stable equilibrium, if, for every virtual change which leaves the temperature, the pressure and the mass of the system unchanged, the total potential of the system increases. If for certain virtual changes the total potential remains constant while for all the others it increases the system will be in a state of indifferent equilibrium. Let us impose upon the system a virtual change which leaves the temperature, the pressure and the mass of the system unchanged; if we neglect terms of orders higher than the second, the total potential of the system will become:

$$\Phi + \sum_{i=1}^{r} \sum_{j=1}^{n} F_{ij}\delta M_{ij} + \tfrac{1}{2} \sum_{i=1}^{r} \sum_{j=1}^{n} \sum_{k=1}^{n} \frac{\partial F_{i}}{\partial M_{ik}} \delta M_{ij}\delta M_{ik}.$$

The system will accordingly be in stable equilibrium if we have:

$$\sum_{i=1}^{r} \sum_{j=1}^{n} F_{ij}\delta M_{ij} + \tfrac{1}{2} \sum_{i=1}^{r} \sum_{j=1}^{n} \sum_{k=1}^{n} \frac{\partial F_{ij}}{\partial M_{ik}} \delta M_{ij}\delta M_{ik} > 0$$

for all the virtual changes. If this inequality is satisfied and if all the virtual changes are revertible, we may also write the following inequality:

$$-\sum_{i=1}^{r} \sum_{j=1}^{n} F_{ij}\delta M_{ij} + \tfrac{1}{2} \sum_{i=1}^{r} \sum_{j=1}^{n} \sum_{k=1}^{n} \frac{\partial F_{ij}}{\partial M_{ik}} \delta M_{ij}\delta M_{ik} > 0.$$

From these two inequalities it follows that we must have:

$$\sum_{i=1}^{r} \sum_{j=1}^{n} F_{ij}\delta M_{ij} = 0, \tag{95}$$

$$\sum_{i=1}^{r} \sum_{j=1}^{n} \sum_{k=1}^{n} \frac{\partial F_{ij}}{\partial M_{ik}} \delta M_{ij}\delta M_{ik} > 0. \tag{96}$$

Accordingly the system will be in stable equilibrium if the conditions 95 and 96 are satisfied. Equation 95 is the well-known equation from which the conditions of equilibrium of the system are obtained, that is to say the various theorems which constitute the phase rule; the inequality 96 will enable us to establish the theorems which are consequences of the stability of the equilibrium.

If the system admits virtual changes such that

$$\frac{\delta M_{i1}}{M_{i1}} = \frac{\delta M_{i2}}{M_{i2}} = \ldots = \frac{\delta M_{in}}{M_{in}}, \qquad i = 1, 2, \ldots, r, \qquad (97)$$

we shall have for those changes:

$$\sum_{i=1}^{r}\sum_{j=1}^{n}\sum_{k=1}^{n} \frac{\partial F_{ij}}{\partial M_{ik}} \delta M_{ij} \delta M_{ik} = 0.$$

To show this we observe that in this equation the coefficient of δM_{ik} can be written in the following ways:

$$\sum_{j=1}^{n} \frac{\partial F_{ij}}{\partial M_{ik}} \delta M_{ij} = \sum_{j=1}^{n} \frac{\partial^2 \Phi_i}{\partial M_{ij} \partial M_{ik}} \delta M_{ij} = \sum_{j=1}^{n} \frac{\partial F_{ik}}{\partial M_{ij}} \delta M_{ij}.$$

If the equations 97 are satisfied the last of these expressions is proportional to

$$\sum_{j=1}^{n} \frac{\partial F_{ik}}{\partial M_{ij}} M_{ij},$$

and as F_{ik} is a homogeneous function of order zero, this expression is equal to zero.

In the discussion which follows we shall only consider systems whose equilibrium is such that

$$\sum_{i=1}^{r}\sum_{j=1}^{n}\sum_{k=1}^{n} \frac{\partial F_{ij}}{\partial M_{ik}} X_{ij} X_{ik} \overset{=}{>} 0, \qquad (98)$$

according as the equations

$$\frac{X_{i1}}{M_{i1}} = \frac{X_{i2}}{M_{i2}} = \ldots = \frac{X_{in}}{M_{in}}, \qquad i = 1, 2, \ldots, r, \qquad (99)$$

are or are not satisfied. These systems will accordingly be in stable or in indifferent equilibrium.

By a demonstration analogous to the one we have just given we can show that

$$\sum_{i=1}^{r}\sum_{j=1}^{n}\sum_{k=1}^{n} \frac{\partial F_{ij}}{\partial M_{ik}} X_{ij} Y_{ik} = 0, \qquad (100)$$

when

$$\frac{X_{i1}}{M_{i1}} = \frac{X_{i2}}{M_{i2}} = \dots = \frac{X_{in}}{M_{in}}, \qquad i = 1, 2, \dots, r, \qquad (101)$$

or when

$$\frac{Y_{i1}}{M_{i1}} = \frac{Y_{i2}}{M_{i2}} = \dots = \frac{Y_{in}}{M_{in}}, \qquad i = 1, 2, \dots, r. \qquad (102)$$

Let us now return to the consideration of a system in equilibrium, at a temperature T, under a pressure Π and for certain values of the masses M_{ij}. From condition 95 we shall have

$$\sum_{i=1}^{r} \sum_{j=1}^{n} F_{ij} \delta M_{ij} = 0$$

for every virtual change which leaves the temperature, the pressure and the mass of the system unchanged. To express that the system is in equilibrium in a state adjacent to the first state of equilibrium, we must replace T, Π, M_{ij} in the preceding equation by $T + dT$, $\Pi + d\Pi$, $M_{ij} + dM_{ij}$. We thus obtain :

$$d\Pi \sum_{i=1}^{r} \sum_{j=1}^{n} \frac{\partial F_{ij}}{\partial \Pi} \delta M_{ij} + dT \sum_{i=1}^{r} \sum_{j=1}^{n} \frac{\partial F_{ij}}{\partial T} \delta M_{ij}$$

$$+ \sum_{i=1}^{r} \sum_{j=1}^{n} \sum_{k=1}^{n} \frac{\partial F_{ij}}{\partial M_{ik}} dM_{ik} \delta M_{ij} = 0. \qquad (103)$$

Now, when the system is in equilibrium, the volume V and the entropy H of the system are given by the formulas

$$V = \frac{\partial \Phi}{\partial \Pi} = \sum_{i=1}^{r} \sum_{j=1}^{n} \frac{\partial F_{ij}}{\partial \Pi} M_{ij}. \qquad (104)$$

$$-H = \frac{\partial \Phi}{\partial T} = \sum_{i=1}^{r} \sum_{j=1}^{n} \frac{\partial F_{ij}}{\partial T} M_{ij}. \qquad (105)$$

As F_{ij} is a homogeneous function of the masses M_{i1}, M_{i2}, ..., M_{in}, of degree zero, its derivatives with respect to Π and to T are also homogeneous functions of degree zero. It follows then without difficulty, that, for a virtual change which leaves the temperature and the pressure unchanged, the variations of the volume and of the entropy are given by the formulas:

$$\delta V = \sum_{i=1}^{r} \sum_{j=1}^{n} \frac{\partial F_{ij}}{\partial \Pi} \delta M_{ij}, \tag{106}$$

$$-\delta H = \sum_{i=1}^{r} \sum_{j=1}^{n} \frac{\partial F_{ij}}{\partial T} \delta M_{ij}. \tag{107}$$

By means of these formulas we can write equation 103 in the form

$$d\Pi \cdot \delta V - dT \cdot \delta H + \sum_{i=1}^{r} \sum_{j=1}^{n} \sum_{k=1}^{n} \frac{\partial F_{ij}}{\partial M_{ik}} dM_{ik} \delta M_{ij} = 0. \tag{108}$$

From this equation, which is due to Planck,[1] we shall now derive the various theorems relating to the displacement of equilibrium.

Consider first an invariant system. As in this case the temperature and the pressure are fixed we have

$$d\Pi = 0, \qquad dT = 0.$$

The masses of the phases may vary but the concentrations must remain unchanged; accordingly we have

$$\frac{dM_{i1}}{M_{i1}} = \frac{dM_{i2}}{M_{i2}} = \ldots = \frac{dM_{in}}{M_{in}}, \qquad i = 1, 2, \ldots, r.$$

Equations 100 and 101 show us that the last term of equation 108 reduces to zero. In the case of invariant systems each term of equation 108 is thus equal to zero.

Consider now a univariant system. In such a system, at a given temperature, the pressure and the concentrations are determined, but the masses of the phases may vary. We can thus

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[1] Vorlesungen über Thermodynamik, p. 176.

choose a virtual change which will leave the concentrations unchanged; that is to say we may write

$$\frac{\delta M_{i1}}{M_{i1}} = \frac{\delta M_{i2}}{M_{i2}} = \ldots = \frac{\delta M_{in}}{M_{in}}.$$

The third term of equation 108 is then equal to zero and that equation reduces to

$$d\Pi \cdot \delta V - dT \cdot \delta H = 0,$$

or if we write

$$Q = T \cdot \delta H,$$

we get

$$\frac{d\Pi}{dT} = \frac{Q}{T\delta V}. \qquad (109)$$

In this equation Q denotes the quantity of heat absorbed by the system and δV the increase in volume when, at constant temperature and pressure, the system undergoes a change which leaves the concentrations unchanged. The above demonstration of Clapeyron's equation is due to Planck.[1]

Last consider a bivariant or multivariant system. In such a system, if the temperature and the pressure be given, the state of the system is completely determined; it is impossible to choose a virtual change which shall leave the concentrations unchanged. Let us take as a virtual change the real change that takes place when the system passes from one state of equilibrium to the next; that is to say, let us take

$$\delta M_{ij} = dM_{ij}.$$

Inequality 98 shows us that the third term in equation 108 is positive; that equation accordingly takes the form

$$d\Pi \cdot \delta V - dT \cdot \delta H < 0,$$

or, if we write

$$Q = T\delta H,$$

we get

$$d\Pi \cdot \delta V - dT\frac{Q}{T} < 0. \qquad (110)$$

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[1] Vorlesungen über Thermodynamik, p. 176.

In this inequality δV is the change which the volume of the system would undergo and Q the quantity of heat which the system would absorb if the changes which really take place in the concentrations when the system passes from one state of equilibrium to the next, were to take place at constant temperature and pressure.

From the inequality 110 we get the two following results:

$$dT = 0, \qquad d\Pi \cdot \delta V < 0; \qquad (111)$$

$$d\Pi = 0, \qquad dT \cdot Q > 0. \qquad (112)$$

The first of these results gives us Le Châtelier's theorem:[1] If, at a constant temperature, the pressure of a bivariant or multivariant system in equilibrium be increased, there takes place a change in the concentrations which would have for effect a diminution of the volume of the system if the change were to take place at constant temperature and pressure. Similarly a diminution of pressure would cause a change corresponding to an increase of volume.

The second of the preceding results gives us van 't Hoff's theorem:[2] If, under constant pressure the temperature of a bivariant or multivariant system in equilibrium be raised, there takes place a change in the concentrations which would have for effect an absorption of heat if the change were to take place at constant temperature and pressure. Similarly, a lowering of the temperature would cause a change corresponding to the liberation of heat.

In the particular case of a bivariant or multivariant system at an indifferent point, we can vary the masses of the phases without changing the concentrations, that is to say we may take

$$\frac{\delta M_{i1}}{M_{i1}} = \frac{\delta M_{i2}}{M_{i2}} = \cdots = \frac{\delta M_{in}}{M_{in}}, \qquad i = 1, 2, \ldots, r. \qquad (113)$$

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[1] Compt. rend. 99, 786 (1884). Duhem. Annales de la Faculté de Toulouse, 4, N; (1890). Traité élementaire de Mécanique chimique, 1, 145.

[2] Études de Dynamique chimique, 161; Amsterdam, 1884. Duhem. Annales de la Faculté de Toulouse, 4, N; (1890). Traité élementaire de Mécanique chimique, 1, 184.

The third term of equation 108 then reduces to zero and that equation becomes

$$d\Pi \cdot \delta V - dT \cdot \delta H = 0,$$

or if we put

$$Q = T\delta H,$$

we get

$$\frac{d\Pi}{dT} = \frac{Q}{T\delta V}. \qquad (114)$$

In this equation δV is the increase which the volume of the system undergoes and Q the quantity of heat absorbed by the system, supposed to be at an indifferent point, when the masses of the phases are varied without changing the temperature, the pressure or the concentrations. We have already met this extension of Clapeyron's formula.

Consider again a bivariant or a multivariant system. If the system undergoes a reversible isothermal change, we have constantly $dT = 0$. When the system reaches an indifferent point we can choose the variations δM_{ij}, so that equations 113 are satisfied. Equation 108 then becomes

$$d\Pi \cdot \delta V = 0,$$

in which δV is the change which the volume of the system undergoes at the indifferent point when we vary the masses of the phases, but keep the temperature, pressure and concentrations constant. If δV is not equal to zero, we must have

$$d\Pi = 0.$$

We thus obtain the first of Gibbs' theorems:[1] At an indifferent point of a bivariant or multivariant system kept at a constant temperature, the pressure is, in general, a maximum or a minimum.

Similarly, if we consider a reversible change, accomplished under constant pressure, we see that at an indifferent point

$$dT \cdot \delta H = 0,$$

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[1] On the Equilibrium of Heterogeneous Substances, p. 155. Konowalow. Wied. Ann. 14, 48 (1881).

or if we put

$$Q = T\delta H,$$
$$dT \cdot Q = 0.$$

Q denotes the quantity of heat which the system absorbs when, under a constant pressure and at the temperature of the corresponding indifferent point, the system undergoes a change in which the masses of the phases vary while the concentrations remain constant. If we suppose that Q is not equal to zero, we must have

$$dT = 0.$$

We thus obtain the second of Gibbs' theorems:[1] At an indifferent point of a bivariant or multivariant system kept under constant pressure, the temperature is, in general, a maximum or a minimum.

We can obtain an interesting result by comparing equations 109 and 114. For that purpose let us consider a univariant system and the bivariant system which we obtain by removing one of the phases of the univariant system. If, in a Π, T-plane, we draw the curve which represents the temperatures and the equilibrium pressures of the univariant system and also the curve which represents the temperatures and the pressures of the indifferent points of the bivariant system, the comparison of equations 109 and 114 shows us that the two curves are tangent to each other at their point or points of intersection.

Suppose, for example, that the univariant system consists of the three phases: a solid hydrate, a solution of the hydrate in water and a vapor phase, and that the corresponding bivariant system consists of the two phases: solid hydrate and solution. If we notice that in the bivariant system the change in volume which occurs when a portion of the hydrate enters into solution is small in comparison with the quantity of heat absorbed during the same process, we see that the curve of indifferent points is very nearly perpendicular to the axis of temperatures. Accordingly, in the univariant system, when the hydrate and the

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[1] On the Equilibrium of Heterogeneous Substances, p. 155.

solution have the same concentration, the tangent to the equilibrium curve is very nearly perpendicular to the axis of temperatures; it follows that at that point the temperature passes, in general, through a maximum or a minimum. This theorem is due to van der Waals.[1]

We can derive another particular result from the general equation 22. Suppose that the system under consideration is a system of two phases formed by means of two components, and that the concentration of one of the phases is necessarily constant. As examples we may mention the system: salt solution and water vapor and the system: solid salt and solution. Suppose that the variable concentration remains constant, then we shall have

$$\frac{dM_{i1}}{M_{i1}} = \frac{dM_{i2}}{M_{i2}}, \qquad i = 1, 2,$$

and equation 108 will take the form

$$\frac{d\Pi}{dT} = \frac{Q}{T\delta V}.$$

In this formula δV represents the change which the volume of the system undergoes and Q the quantity of heat which the system absorbs during a virtual change accomplished at constant temperature and pressure. This equation has been given by Braun[2] and Natanson.[3]

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[1] Bakhius Roozeboom. Sur les conditions d'équilibre de deux corps dans les trois états, solide, liquide et gazeux, d'après M. v. d. Waals. Recueil des Travaux chimiques des Pays-Bas, 5, 335 (1886). Zeit. phys. Chem. 2, 463 (1888). Duhem. Dissolutions et Mélanges, deuxième Mémoire: les Propriétés physiques des Dissolutions; Travaux et Mémoires des Facultés de Lille, 3, No. 12, 121, (1893). Traité élémentaire de Mécanique chimique, 3, 279.

[2] Wied. Ann. 30, 250 (1887). Duhem. Dissolutions et Mélanges deuxième Mémoire: les Propriétés physiques des Dissolutions; Travaux et Mémoires des Facultés de Lille, 2, No. 12, 29 (1893). Traité élémentaire de Mécanique chimique, 3, 130.

[3] Zeit. phys. Chem. 10, 748 (1892). Duhem. Travaux et Mémoires des Facultés de Lille, 2, No. 12, 72 (1893). Traite élémentaire de Mécanique chimique, 3, 156.

NEW BOOKS

Handbuch der Spectroscopie. *By H. Kayser. Volume I. 17 × 26 cm; pp. xxiv + 781. Leipzig: S. Hirzel, 1900. Price: paper, 40 marks.* — In this huge book of nearly 800 closely-printed large octavo pages, which is but the first of a series of five forthcoming volumes, the author has endeavored to do for spectroscopy something similar to what Wiedemann did for electricity many years ago, when such an attempt was still feasible. The book is, in other words, an exhaustive account of the subject, addressed to the practical physicist, with full and carefully compiled references to the original sources. The subject is presented in five chapters, treating respectively of the history of spectroscopy, of the means now in vogue for producing incandescent vapors, of prisms, of gratings, of the types of spectroscopic apparatus in general, and of the methods of spectroscopic research. It is agreeable to read a book in which the contributions of American physicists are so fundamentally in evidence; though one needs scarcely to be reminded of what Rowland, Langley, Michelson, Draper, Keeler, Wadsworth, Pickering, Crew, and many others have done.

Spectroscopy, like much else in physics, began with Newton, and continued, strangely enough, after the lapse of about 100 years with F. W. Herschell's discovery of the ultra-red, Ritter's discovery of the ultra-violet, and Young's first measurement of wave length in 1802. From Newton (1666) to Wollaston (1802) is a long time to wait for spectrum lines; but even then they were no sooner seen than forgotten. So it was left to the genius of Fraunhofer to virtually reproduce the whole subject, and invent the grating. Fraunhofer already saw both dark and bright lines, as indeed Wollaston and even Young had done before him. The period thence to Kirchhoff and Bunsen was one remarkable for its confused activity, and requires some 70 pages of comment in Kayser's book. Becquerel and Draper had produced their excellent photographs of the solar spectrum. Yet none of the great physicists at work (Young, Brewster, Talbot, Melloni, Draper, Becquerel, Biot, Forbes, Angström, Plücker, and others) reach correct inferences on the equivalence of absorption and emission, except Stewart, whose experiments, as Kirchhoff remarks, are rather a voucher for the possibility of the law than in the nature of a rigorous proof.

It is interesting to contrast with this introductory period the triumphant progress of spectroscopy after Kirchhoff and Bunsen, as detailed in the last 40 pages of the chapter. We need merely refer to the work of Angström and Thalen, the very suggestive work of Lockyer, the labors of Huggins, Vogel, Langley, Crookes, Rowland, Balmer, Schumann, and others of equal note.

In his chapter on incandescent vapors, Kayser begins with an extended discussion of flames in general, followed by descriptions of flame spectrum apparatus. Chemists will be especially interested in Hartley's ingenious oxy-hydrogen flame methods. Arc phenomena, temperatures, and spectra, are described with the same fullness. The chapter reserved for spark spectra contains not only a detailed account of the methods of production, but a critical digest on spark and vacuum tube temperatures, gas density, etc. Figures are given of the different forms of vacuum tubes in use.

The treatment of the theory of prisms is naturally very complete and modern in character. It is not however an original presentation, but follows in the main Czapski's great monograph in Winkelmann's Handbuch der Physik. Prisms, trains, pencils, convergence, are successively discussed in detail. An appreciative account is given of Rayleigh's diffraction method of investigating the distribution of brightness throughout the cross-section of a pencil. The transition of this subject is abrupt, and would be unintelligible to a student not versed in the theory of intensity curves. Having disposed of the effect of a prism on monochromatic light, dispersion is next taken up. Beginning with the conditions determining the linear extent of the spectrum, Kayser discusses dispersive power as depending on the material of the prism, and the geometric variables, in relation to purity of spectrum and resolving power. Rayleigh's famous theorem, that the resolving power is ultimately dependent, for a given kind of glass, on the path difference within the prism of 'the limiting rays of the pencil transversing the prism, is elaborately discussed. An exhibition of the various dispersion formulas, terminating with the Helmholtz-Ketteler equation, finishes the section. The remaining pages of Chapter III. are devoted to the construction and manipulation of prisms. The detailed enumeration of prism forms will be welcomed.

In the chapter on gratings, the introductory account given of Fraunhofer's work is most fascinating. Almost everything that was afterwards done by others in perfecting the grating was foreshadowed and approached with a remarkable degree of perfection by this early observer. Beginning with the well known screw gratings, Fraunhofer investigated the laws of the phenomenon, gradually perfecting his methods till his dividing engine was eventually able to rule 30,000 lines to the inch on glass. He was not, however, able to use this refinement, his best ruling not exceeding 8,000 lines to the inch. The closeness of the lines ruled on glass was far in excess of the resolving power of the microscope of the day, though when Nobert's improved gratings came into the market the microscope also had reached a corresponding degree of perfection. The marked improvement of Rutherford's gratings, and particularly those of Rogers', over Nobert's, was destined to remain without much fruit, inasmuch as Rowland shortly after made his phenomenal step completing the efficiency of the grating. Strange as it may seem, Kayser in this book gives the first description of Rowland's screw and dividing engine.

The treatment given of the theory of the grating is very complete, and follows Rowland, Rayleigh, and Cornu, for plain gratings, and Rowland, Runge, Sirks, Mitchel, and others for concave gratings. Particular attention is given throughout to the equation of errors. The final section devoted to Michelson's echelon spectroscope is evidence of the care with which the author has brought his work up to date.

The first section of the chapter on spectroscopic apparatus is plentifully supplied with figures, and thus in every way a valuable compilation. The next section, on the theory of spectroscopic apparatus in relation to pure spectra, starts with Helmholtz's introductory remarks, seeing that the aim of all cotemporaneous physicists was an ill-directed endeavor to merely increase the width of the spectrum. The whole subject, however, was afterwards remodeled by Lord Rayleigh's rigorous definition of resolving power, both in prisms and in gratings. The modern treatment takes cognizance of the angular dispersion, $d\theta/\lambda$, θ being the deviation, of resolving power, $\lambda/d\lambda$, purity in relation to width of slit as introduced by Schuster, and brightness. Kayser closely follows the papers of Wadsworth in his extensive applications of Lord Rayleigh's theory to practical problems relating to the efficiency of the spectroscope. A special paragraph chronicles the labors of Michelson and of Fabry and Perot on the ultimate resolution of spectrum lines. Succeeding sections treat of the sensitiveness of the eye and of photographic apparatus, with full consideration of the work of Schumann on the ultra-violet, including spectrographic methods based on fluorescence and phosphorescence. The account given of bolometry contains a detailed résumé of the earlier work, such as that of Melloni, de la Provostaye et Dessains, Tyndall, Magnus, and others, even when not directly spectrographic in character. In addition to the thermocouple (both the old and the new forms of Rubens), the radiometer, Weber's electrolytic apparatus, Bell's radiophone, D'Arsonval's and Boys's radiomicrometer, and other apparatus, is considered in turn. The bolometer, however, has remained the chief instrument for thermal spectrometry, in the form reinvented after Svanberg by Langley, and perfected by him to a degree fitting it for the astonishing performances now well known. The book contains a chronological account of Langley's researches, and it is interesting to follow again the steps by which Langley systematically perfected his method. Kayser gives the last of his published results. The bolometer has since become common property; and recent observers, Rubens, Lummer, Kurlbaum, Paschen, Angström, Snow, and others, have increased the scope of the method.

The last chapter of the book is a historical and critical survey of the data of spectrometric research. The sources of absolute data are the independent measurements of Rowland and of Michelson. The table of wave lengths of the former is here fully reproduced in a form convenient for reference.

The author is to be congratulated on the present stage of completion of his great work. One admires throughout the candor of his criticism. That further progress in spectrometry will be stimulated when so trustworthy a book of reference is at hand is obvious.

C. Barus

The Principles of Mechanics. *By Heinrich Hertz. With an Introduction by H. von Helmholtz. Authorized English translation by D. E. Jones and J. T. Walley. 15 × 22 cm; pp. xxviii + 276. New York: Macmillan and Company, 1899. Price: cloth, $3.25.*—This work, which is the English translation of the German original, appeals to us from a double standpoint. It possesses the most extraordinary merit in itself, and it is the last work of one to whom it was given, more than to most of his fellows, to see deeply into the laws of nature, and in whose early death the cause of science has suffered a most serious loss. The genius of Hertz led him to take the most broadly generalized views of nature and to endeavor to reduce large bodies of widely distributed phenomena to expression as the manifestation of a few general laws. Realizing furthermore the fundamental rôle which a truly generalized system of mechanics must play in all physical research, he had set himself the task of developing out of the fundamental concepts of mass, space, time, and a single additional hypothesis, such a system of mechanics as a perfect piece of mathematical logic; and thus containing the expression of this hypothesis in multifarious form, and as applied to the various phenomena of physical nature.

In the introduction to the work three different bases for a system of mechanics are considered and compared in the most comprehensive manner. The first is that upon which rests the usual presentation of the subject at the present time. In the second, energy is made a primary concept, while force appears as its space derivative. In the third method, which is that chosen by Hertz, only three fundamentals are assumed, space, mass and time, while the fourth concept of force or energy is replaced by an hypothesis. This is in effect that we are free to assume the existence of and to conjoin with the visible masses of the universe, other masses obeying the same laws and of such kind that the whole shall thereby become intelligible and conformable to laws developed out of the mutual relations between the three fundamentals, space, time, and mass. The development of the subject proper consists of two parts, kinematics or space-time relations, and mechanics proper or the relations of the three fundamentals, space, time, and mass. For the details of the development, reference must of course be made to the work itself. Its extent however may be summarized by saying that out of this foundation, as treated in the hands of the author, there arises in logical and proper order a complete system of mechanics containing in its entirety what may be known as the Newtonian mechanics, as well as the later additions due to the work of more recent writers.

Referring to the auxiliary hypothesis, it may be noted that in effect it is not new, but is really equivalent to one of the oldest of mechanical starting points, namely the conception that all mechanical processes go on as though the connections between the various parts which act upon each other were fixed. Unfortunately, Hertz has not given examples illustrating the manner in which he has supposed such hypothetical machinery to act. Had the author's life been spared to bring the work to a full conclusion some suggestions of this point might have been given. As it is, however, we may simply consider the hypothesis as one suited to the needs of the problem in hand, and as furnishing through his treatment a logical system of mechanics developed with the greatest ingenuity and in the most perfect mathematical form, and in complete accord with the entire body of the science as accepted at the present time. It must be understood that this work is not in the ordinary sense a textbook of mechanics for the beginner. It does not give the detailed development of the science in the manner required by those first studying the subject, but deals rather with broad generalizations out of which the more elementary treatment may be developed. It is therefore, as noted by the author, only suited to those who already have a general acquaintance with the subject as usually presented in its elementary form.

No review of this work would be complete without a reference to the preface by von Helmholtz, in which he gives a brief sketch of the life of Hertz and of the development of the latter as a student under his direction. This is followed by a luminous discussion of the various modes of viewing mechanical theories, and a most appreciative characterization of the present work as a complete system of mechanics. It should also be noted that to Professor Lenard was left the final revision of a part of the work by the author whose death occurred before its completion in absolutely finished form. This work has been done with the greatest care, having in view the purposes, spirit, and method of the author, and we may feel sure that the work as it is presented to us is very close to the form in which Hertz would have given it, had he been allowed to bring it to a final completion. The translation of the original into English seems to have been done with accuracy and care, and to give in high degree the spirit of the original.

Whatever may be the final form of our theories of mechanics, it is certain that this work of Hertz will take its place as a classic in the literature of the development of the science, and that it will be considered as one of the chief results of his life work which, unfortunately for the cause of science, came to so early a conclusion. *W. F. Durand*

Die Bedeutung der Phasenlehre. *By H. W. Bakhuis Roozeboom. 16 × 24 cm ; pp. 29. Leipzig: Wilhelm Engelmann, 1900. Price: paper, 80pfennigs.* — This is an address delivered at Aachen at the Annual Meeting of the German Physicians and Scientists. After a brief sketch of the phase rule as applied to one-component and two-component systems, the system iron and carbon is discussed. Since the scientific chemistry of the future must be based on the phase rule, it is of great value that the extreme usefulness of the classification should be pointed out whenever possible. *Wilder D. Bancroft*

Lectures on Theoretical and Physical Chemistry. *By J. H. van't Hoff. Translated by R. A. Lehfeldt. Part III. Relation between Properties and Composition. 15 × 23 cm; pp. 143. London: Edward Arnold. Price: bound, 7s. 6d.* — It is a pleasure to call attention to the appearance of the third part of the English translation of van 't Hoff's book. The entire work is now to be had in either German, French or English. *Wilder D. Bancroft*

Organic Chemistry. *By V. v. Richter. Edited by Prof. R. Anschütz. Authorized translation by E. F. Smith. 3rd American from the 8th German Edition. Volume II. Chemistry of the Carbocyclic Series. Philadelphia: P. Blakiston's Son and Co., 1900. Price: cloth, $3.00.* — As in the first volume (4, 138) the detailed description of the members of each group is preceded by a short account of methods of preparation and chemical behavior; where necessary the system of nomenclature is discussed, and reasons for the structural formulæ adopted are advanced. The descriptions themselves are accompanied by historical notes and tables of physical constants; their value is greatly enhanced by copious references to the literature.

It is significant both of the amount and of the direction of recent work in this field, that the "hexacarbocyclic compounds" — benzene, naphthalene, anthracene, etc., and their derivatives — occupy but 400 of the 608 pages of the book; 27 are devoted to the terpenes, 43 to the azoles, 30 to the azines, 18 to the alkaloids, etc., etc.

The compactness and excellent arrangement of the book, the thoroughness with which the material has been collected, and above all the innumerable references to the literature, make Richter by far the best compendium of Organic Chemistry in the English language.

The second volume, like the first, is provided with a table of contents and an index of 63 pages. *W. Lash Miller*

Victor von Richter's Text-Book of Inorganic Chemistry. *Edited by H. Klinger. Authorized translation by Edgar F. Smith. Fifth American from the Tenth German Edition, revised and corrected. 14 × 21 cm; pp. xii + 419. Philadelphia: P. Blakiston's Son and Co., 1900. Price: bound, $1.75.*— Here we have a new edition of what is perhaps the best of the orthodox text-books. The attitude of the author is expressed by the following sentence: "If we seek to give expression to the consitution of the chemical elements and the bodies composed of them, we return, if guided by experience, to the ancient atomic hypothesis which alone is justified by the present condition of chemical and physical investigation." The general arrangement of the book is well-known. The translator has added passages on the theory of dilute solutions, electrolysis of salts, etc., which are valuable. Some of us would have preferred seeing such matters discussed before we were two-thirds of the way through the book; but that would have necessitated an entire rearrangement. The student will have great difficulty (p. 74) in "combining the two laws" of Boyle and of Gay-Lussac, a difficulty which will be increased by the misprint in the second version of Boyle's law. *Wilder D. Bancroft*

The Elements of Physics, *for Use in High Schools. By Henry Crew. 13 × 19 cm; pp. xvi + 353. New York: The Macmillan Company, 1900. Price: bound, $1.10.*—A short time ago we noticed (4, 213) the appearance of the first edition of Prof. Crew's admirable Elements of Physics. A revised edition is now out, in which the following changes have been made:

1. All use of the method of limits, either for defining physical quantities or for other purposes, has been abandoned;
2. All Greek letters, except π, have been replaced by English symbols;
3. All use of trigonometrical functions has been given up;
4. The equations employed have been reduced in number from forty-three to thirty-six;
5. The number of problems has been considerably increased.

The author states that "the purpose of these changes has been to simplify the treatment." Some of them are disappointing; but they doubtless respond to a demand, and are perhaps for the best. The book is a good one; and a long career of usefulness is to be wished for it. *J. E. Trevor*

Die galvanischen und thermoelektrischen Stromquellen. *By. J. Kollert. (Dritter Band, Erste Abteilung, der Handbuch der Elektrotechnik von C. Heinke). 20 × 28 cm; pp. 54. Leipzig: S. Hirzel, 1900. Price: paper, 3 marks).*—This number contains a brief sketch of the various forms of cells most generally in use, together with a discussion of such other matters as the source of energy in the voltaic cell, on the best arrangement of cells in a battery, etc. To many people the most interesting part is the second, which is devoted to thermoelectricity and thermopiles. *Wilder D. Bancroft*

Quantitative Chemical Analysis. *By Frank Clowes and J. Bernard Coleman. Fifth Edition. 12 × 19 cm; pp. xxiv + 592. Philadelphia: P. Blakiston's Son and Co., 1900. Price: bound, $3.50.* — The fact that this manual has gone into a fifth edition bears witness to the appreciation with which it has been welcomed both in England and in this country. The present edition does not materially differ from the preceding one except that an appendix has been added, including supplementary notes on melting-point determinations, and a few special methods of analysis.

The subject-matter of the book covers all the more familiar branches of analytical work, and is divided into sections on: gravimetric methods; volumetric methods; complex quantitative determinations, including the analysis of ores and minerals, organic substances, and water; gas analysis; tables of constants, etc.; and the whole is preceded by an excellent chapter on the methods of accurate work in general.

The book is well illustrated, and forms altogether a most useful handbook for the student of practical chemistry. Now that the methods of teaching chemistry to general students are drifting away from the old routine of qualitative and quantitative analysis, the public to which such books as this appeal become more and more restricted to the technical schools and special students of chemistry in the universities. As the authors say in the preface "the book has been kept within moderate dimensions by omitting unnecessary theoretical matter". It is, in fact, merely a handbook of procedure, not a scientific treatise, and it is only with this distinction clearly in mind, that it is to be recommended.

The omission of the simple and elegant method of calibrating burettes recommended by Ostwald, involving the use of a small pipette attached to the tip, should be made good in a later edition. *A. P. Saunders*

Essentials of Medical and Clinical Chemistry, with Laboratory Exercises. *By Samuel E. Woody. Fourth, revised, edition. pp. viii + 235. Philadelphia: P. Blakiston's Son and Co., 1900.* — This book contains sections on inorganic chemistry (p. 20), analytical tables (p. 3), organic chemistry (p. 47), clinical chemistry (p. 38). References are made repeatedly to many of the applications of chemistry to pharmacy, toxicology, therapeutics, pathology, etc., which are to be met in medical practice. Four hundred laboratory exercises emphazize the *multum in parvo* aspect of the work.

The book will probably be of service in those colleges which pride themselves on the teaching of disconnected facts, and pay little attention to theory. No chemist will admit that it contains the "essentials" of medical or any other chemistry; it would therefore be unwise to predict a great sale for this work in the university medical schools of this country. *H. R. Carveth*

Friedrich Wöhler. *Ein Jugendbildnis in Briefen an Hermann von Meyer. Herausgegeben und mit Anmerkungen versehen von G. W. A. Kahlbaum. 16 × 23 cm; pp. 97. Leipzig: Johann Ambrosius Barth. Price: paper, 2.40 marks; bound, 3.40 marks.* — This little book gathers together something over a dozen letters of the young Wöhler to his friend von Meyer. They were for the most part written in the year 1818 when Wöhler was 18 years of age; Meyer was a year younger; Wöhler, though still a school-boy, was already an enthusiastic chemist; and the pleasure in reading the letters is mainly in his delight over his own experiments.

The world seemed full of new things during those years, in a sense in which one could hardly say it of any time before or after. The isolation of the metals of the alkalies, the discovery of iodine, lithium, selenium, and so many other elements, the establishing of the elementary nature of chlorine,—all these and many other important steps in the science were made either in that year or in those which immediately preceded it, and by all of these Wöhler's imagination was stirred and his eagerness for experimentation kindled.

There is but little of permanent interest in the text of the letters until we come to the last one, written in 1824, from Stockholm; here we have a vivid and delightful picture of Berzelius at work, recalling the familiar description by Wöhler in the Berichte for 1875, but with perhaps an added freshness from being written on the spot.

The editor's notes are too numerous; they burden the page; but here and there they contain information of interest.

On the whole the book is well worth a reading to anyone who cares to picture the science as it then was. *A. P. Saunders*

Contribution a l'étude des déformations permanentes des fils métalliques. *By É. Lenoble. Thèse. Bordeaux, 1900.*—The author observes that a metallic wire, under constant load, stretches with a decreasing velocity that approaches a positive limit. He studies the effect of systematic changes of load w on the changes of length l of wires of platinum, copper, silver, and steel. Under loads far less than the breaking load, cyclical changes of load causes the curve $l = f(w)$ to ascend in a series of loops that are usually counter-clockwise, and that incline upward to the right and terminate in a limiting loop or a double straight line. Many repetitions of the cyclical change slowly displace the limiting loop; and it is displaced by intervening greater changes of load. These results are analogous to those obtained by Marchis for the permanent changes of glass. Under higher loads, the loops tend to become equidistant, and breaking finally results. The author expresses the opinion that the appearance of occasional clockwise loops can be accounted for only on the assumption that the state of the metal is determined, not only by the specific volume and temperature, but in addition by a variable that represents a chemical or allotropic change of the state of the metal, in accordance with Duhem's theory of permanent changes. *J. E. Trevor*

Démonstration du Principe de l'Equivalence. *Troisième Étude sur l'Energetique. By G. Mouret. 13 pp. Lemercier et Alliot.*—The substance of a note submitted to the French academy, but not published in the Comptes Rendus. The author undertakes to demonstrate the constancy of the ratios of mutually transformed heat and work, by comparing any thermodynamic operation with a reversible operation between two sources of heat, the same quantity of work being developed in each process. *J. E. Trevor*

REVIEWS

The object of this department of the Journal is to issue, as promptly as possible, critical digests of all Journal articles that bear upon any phase of Physical Chemistry.

General

The additive properties of the atoms. *S. Meyer. Ber. chem. Ges. Berlin,* **33,** *1918* (*1900*). — If a common property of the elements be a periodic function of their atomic weights, which stands in relation to the atomic volume curve, and if this property be reckoned in a first approximation from the property of the compound, one may expect that this number will only be calculated exactly when the atomic volumes are added to the molecular volume. If one obtain a difference due to expansion or contraction, the position of this property will be displaced on the atomic volume curve in the direction of the maximum or minimum. The magnetization numbers for the halogen compounds and also for some of the oxides are considered. The atomic heat of oxygen cannot be calculated directly, as most oxides are formed with volume contraction.
C. G. L. W.

A comparison of Rowland's mercury thermometers with the Callendar-Griffiths platinum thermometer. *C. W. Waidner and F. Mallory. Phil. Mag.* **48,** *1* (*1899*). — The object of the present work was to explain, if possible, the discrepancy between the mechanical equivalent of heat deduced by the direct method of Joule in Rowland's experiments with the electrical method of Griffiths. Various papers have already been reviewed (2, 504) giving the purport of this work. The present paper is a careful description of a comparison of the mercury thermometers with a platinum thermometer. *H. T. B.*

Heat of combination of metals in the formation of alloys. *A. Galt. Phil. Mag.* [*5*] **49,** *405* (*1900*). — Mixtures and alloys were dissolved in nitric acid and the difference taken as the heat of combination. With zinc and copper, there is a minimum negative heat effect with about 15-20 percent copper, and a maximum positive heat effect with about thirty-eight percent copper. Alloys of silver and copper show little or no heat of combination. *W. D. B.*

Hydrometers of total immersion. *A. W. Warrington. Phil. Mag.* [*5*] **48,** *498* (*1899*). — In order to avoid the error due to the projecting thread, the author slips platinum rings over the neck of a hydrometer until the instrument has practically the same density as the liquid and makes the last adjustment by changing the temperature of the liquid, the hydrometer being totally immersed. Instances are given in which this method has been employed. *W. D. B.*

One-Component Systems

On the assumed isomerism between red and yellow mercuric oxide and on the surface-tension of solids. *W. Ostwald. Zeit. phys. Chem.* 34, *495* (*1900*). — It is shown that the difference in electrical potential detected by Cohen (4, 697) is not due to a real difference between red and yellow mercuric oxide, but to the increased solubility of very fine particles over a coarse-grained substance. It is shown experimentally that the solubility of mercuric oxide varies perceptibly with the fineness of the solid phase, and that this same phenomenon can be observed with other substances, though to a lesser extent. *W. D. B.*

On the physical chemical relations between aragonite and calcite. *H. W. Foote. Zeit. phys. Chem.* 33, *740* (*1900*). — Aragonite can be obtained by quick precipitation from a hot solution; but conductivity measurements and solubility determinations in presence of potassium oxalate show that calcite is the more stable form. While there is no evidence that calcite is ever the less stable form, the solubilities do approach somewhat with rising temperature, so that we are justified in concluding that the change to calcite is accompanied by an evolution of heat. Above 50°, and in the presence of a liquid phase, aragonite apparently starts to change spontaneously into calcite. *W. D. B.*

On the vapor pressures of a series of benzene compounds. *B. Woringer. Zeit. phys. Chem.* 34, *257* (*1900*). — The author has determined the pressure-temperature curves for sixteen substances from a temperature of 0° to a pressure of 800 mm, and has pointed out qualitative relations between pressure differences and constitution. The curve for mesitylene as determined cuts the curves for nine other substances; but, unfortunately, the curve for mesitylene is the one out of the whole, about which the author is least certain. *W. D. B.*

On the thermal properties of normal pentane. *J. Rose-Innes and S. Young. Phil. Mag.* 47, *353* (*1899*). — From a study of the temperatures, pressures, and volumes of isopentane over a wide range of volumes, the relation

$$p = bT - a$$

at constant volume, a and b being constants, was found to hold with considerable accuracy. The present paper is a similar study of normal pentane, but over a smaller range of volumes. The deviations from the empirical relations are small. *H. T. B.*

The Joule-Thomson thermal effect; its connection with the characteristic equation, and some of its thermodynamical consequences. *E. F. J. Love. Phil. Mag.* 48, *106* (*1899*). — From a consideration of the formula assigned to the Joule-Thomson effect, taken as a function of the temperature, and the characteristic gas equation, the author endeavors to show some theoretical basis to the various formulas proposed by different investigators, including those of Kelvin, Boyle-Charles, van der Waals, Rose-Innes and Clausius. Thermodynamic consequences are then discussed and a new method for calculating the ratio of the two specific heats of a gas is given, based on the relation between the intrinsic energy of a gas and its volume. *H. T. B.*

On the thermal conductivity of water. *S. L. Milner and A. P. Chattock.*

Phil. Mag. 48, *46* (*1899*).—By employing an electrical heating device the thermal conductivity of water is determined. It is proposed to use the apparatus again for comparing other liquids to water. *H. T. B.*

On the true density of chemical compounds and their correlation with composition and constitution. *I. Kanonnikoff. Jour. Russ. Soc.* 31, *573* (*1899*).—The true density D is defined to be the ratio, d/v, where d is the density according to the ordinary acceptation of the term, and v is the volume actually occupied by the molecules. The value of v is found by means of measurements of the index of refraction, n, according to the formula $v = \frac{n^2-1}{n^2+1}$, so that $D = \frac{n^2+2}{n^2-1}d$. It was found that the true density varied but little with changes in the state of aggregation of a substance, and that its variation with the temperature could be expressed by means of the equations $D_t = D_0(1 \pm kt)$, the plus sign applying only to water, and the constant K varying with the nature of the substance. A large number of substances were examined, and empiric formulas established for several series of organic compounds.

C. E. L.

On the expansion of porcelain with rise of temperature. *T. G. Bedford. Phil. Mag.* 49, *90* (*1900*).—A determination of the linear expansion of porcelain after the method used by Callendar, and Callendar and Griffiths for glass.

H. T. B.

Two-Component Systems

On the formation and change of mix-crystals of sodium nitrate with potassium nitrate and with silver nitrate. *D. J. Hissink. Zeit. phys. Chem.* 32, *537* (*1900*).—Contrary to the asumption of Carveth (2, 209) potassium and sodium nitrates form two series of mix-crystals. At ordinary temperatures the amount of each that will dissolve in the other is only about one-half of one percent. At the cryohydric point, 218°, the two sets of crystals contain 24 and 85 molecular percents of potassium nitrate respectively. [This makes the abnormal lowering of the freezing-point more, not less, surprising.] Presence of sodium nitrate lowers the inversion temperature of potassium nitrate; but accurate data could not be obtained by the thermometric method.

All mixtures of silver nitrate and sodium nitrate have freezing-points lying between those of the pure components. At 217.5°, there is a quadruple point, two sets of solid solutions being in equilibrium with solution and vapor. The melt always contains more silver nitrate than the crystals in equilibrium with it. The sodium nitrate crystals contain 38 molecular percent of sodium nitrate at 217.5°, and 64.4 percent at 15°. The silver nitrate crystals contain 26 molecular percent of sodium nitrate at 217.5°, 4.5 percent at 138° where the rhombic crystals begin, and 1.6 percent at 15°. The inversion temperature of silver nitrate is lowered from 159.8° tó 138° by the addition of sodium nitrate. At the latter temperature, 138°, there is therefore a quadruple point with three solid solutions in equilibrium and vapor. *W. D. B.*

Iron and steel from the standpoint of the phase rule. *H. W. Bakhuis Roozeboom. Zeit. phys. Chem.* 34, *437* (*1900*). — The author discusses the temperature-concentration diagram for the system carbon and iron. Places in the diagram are found for graphite, martensite, cementite, ferrite, and pearlite, while austenite is discussed. Of course, few, if any, of the points are known with accuracy; but the author's scheme is a very plausible one and will serve as a useful guide to further investigation, even though certain points should prove to need modification. The paper affords another instance of the extreme value of the phase rule, a demonstration which is the more necessary when we notice that phase rule investigations do not appear as physical chemistry in the last *Jahrbuch der Chemie*. *W. D. B.*

Compounds of metals with one another. *N. Kurnakoff. Jour. Russ. Soc.* 31, *927* (*1899*). — The melting-points of a considerable number of sodium and potassium amalgams of varying composition as well as those of some alloys or sodium with either cadmium, lead or bismuth were determined and compared. Nothing especially novel is brought out, and the whole paper is of a preliminary character. *C. E. L.*

The distillation of liquid air and the composition of the gaseous and liquid phases, I. *E. C. E. Baly. Phil. Mag.* [*5*] 49, *517* (*1900*). — The author has determined the boiling-point curve for oxygen and nitrogen at atmospheric pressure, and also the compositions of the coexistent phases. When the logarithms of the ratios of the constituents of the liquid and the vapor phases are plotted as abscissas and ordinates respectively, the resulting curve is a straight line. *W. D. B.*

Properties of liquid mixtures, III. *R. A. Lehfeldt. Phil. Mag.* [*5*] 47, *284* (*1899*). — Addition of large amounts of phenol to water at temperatures above 70° causes little or no change in the vapor-pressure. The vapor-pressure of the dineric system, aniline and water, can be calculated approximately on the assumption that water produces a normal depression in aniline, and aniline a normal depression in water. A concentration-temperature diagram for phenol and water is given, and it is shown that the cryohydric temperature can be calculated approximately by means of the van 't Hoff formula. *W. D. B.*

The compounds of boron and silicon, SiB_3 and SiB_6. *H. Moissan and A. Stock. Ber. chem. Ges. Berlin*, 33, *2125* (*1900*). — The combination of boron and silicon only takes place near the melting-point of silicon. In order to avoid the presence of the oxides of carbon, a special apparatus is described in which the carbon electrodes pass through a long clay tube and are connected by means of a mixture of five parts of crystalline silicon and one part of boron. An alternating current of 45 volts was used. 600 amperes was the amount passed in and the experiment lasted 50 to 60 seconds.

To obtain the triboride, the crystalline mass is boiled with nitric acid which attacks the hexaboride and leaves the triboride comparatively pure after the silicic acid is removed with caustic alkali. Fused caustic alkali attacks the triboride and in this way the hexaboride may be obtained.

The halogens attack these compounds in the reverse order to their atomic weights, although iodine is without action. They are also resistant to the halogen acids. The crystals form an easily fusible alloy with platinum. The specific gravity of SiB_3 is 2.52, that of SiB_6 is 2.47. *C. G. L. W.*

The aqueous fusion of glass, its relation to pressure and temperature. *Carl Barus. Phil. Mag.* 47, *104* (*1899.*) —From a study of the compressibility of water in glass capillaries under high pressure and at a temperature of 185° C, the author finds that the absorption of glass by the water may be expressed in about the proportion of 180 kg. per sq. meter per year.

The absorption increases with temperature and, reasoning on the action of water on silicates in the earth, he concludes "that the action of hot water on rock within the earth constitutes a furnace whose efficiency increases in marked degree with the depth of the seat of reaction below sea-level." *H. T. B.*

The absorption of water in hot glass. *Carl Barus. Phil. Mag.* 47, *461* (*1899*). —Applying pressure to a thread of water in a capillary tube by means of a column of mercury, the temperature being maintained by a vapor bath between 185° and 210°, the water passes through three stages: one of expansion to retain the temperature of the vapor bath, one of great compressibility when the glass is being absorbed by the water which appears white and opaque, and one where, with increased pressure, the compressibility ceases and the water becomes clear again. During the second stage the water does not act as an elastic medium, differing in this respect from the first and third stages. The compressibility in the second stage may reach and exceed 500×10^{-6}. In the third stage, the water glass is a thick viscous fluid, which on cooling solidifies and is not directly distinguishable from igneous glass. From a thermodynamic point of view, two phases of water glass are supposed to exist. *H. T. B.*

The specific gravity, refractive index, and content of solutions of sodium tungstate. *Br. Pawlewski. Ber. chem. Ges. Berlin*, 33, *1223* (*1900*). —A table is given with the above properties of solutions ranging from 2-38 percent. *C. G. L. W.*

On the thermal conductivities of mixtures and their constituents. *C. H. Lees. Phil. Mag.* 49, *286* (*1900*). —In the attempt to express the thermal conductivity of a mixture in terms of the conductivities of its constituents, two formulas have been usually employed, which correspond, using either the masses or volumes of the constituents, to two different kinds of distribution. In one, the constituents are arranged as right prisms with axes perpendicular to two parallel isothermal surfaces through which the heat enters and leaves the medium. In the other, the axes of the prisms are parallel to the isothermal surface. The author in a previous paper discusses a slightly different arrangement, which, when the constituents are equal, is capable of expression in a simple logarithmic formula. The case is that of an equal number of infinitely long right prisms arranged end on, but parallel to the isothermal surface. The observations of Wiedemann, Henneberg, and the author for the thermal conductivity of mixtures, are worked out according to the three formulas and the results are aptly given by the author when he says "that the third formula is the least unsatisfactory." *H. T. B.*

On colloidal solutions of metals. *K. Stöckl and L. Vanino. Zeit. phys. Chem.* 34, *378* (*1900*). —Reply to Zsigmondy (4, 547). *W. D. B.*

Poly-Component Systems

The theory of fractional precipitation of neutral salts and its application in analytical chemistry. *A. Findlay. Zeit. phys. Chem.* 34, *409* (*1900*).—The author points out that where two sparingly soluble salts may be formed, it is not necessarily the least soluble which precipitates first, the relative concentrations being also an important factor. The author then studied the reversible equilibrium

$$\mathrm{PbSO_4} + 2\mathrm{NaIAq} \rightleftarrows \mathrm{PbI_2} + \mathrm{Na_2SO_4}.$$

When lead sulphate and iodide are present as solid phases, the concentration of sulphate as ion should be proportional to the square of the concentration of iodine as ion. This was found to be very nearly true. The equilibrium constant was also determined electrometrically, though not with great accuracy. The author completed his research by adding lead nitrate to the solution.

W. D. B.

On the behavior of ammonia toward salts in aqueous solution. *D. Konowaloff. Jour. Russ. Soc.* 31, *985* (*1899*).—The conclusions arrived at are these:

1. Ammonia in aqueous solutions forms, with salts of silver, copper, zinc, and cadmium, definite compounds corresponding to the general formula, $\mathrm{S}2m\mathrm{NH}_3$, where m is the equivalent of the metal entering into the composition of the salt S.

2. The formation of these compounds arises from substitutions for hydrate water and can serve as most excellent indirect proof of the existence of hydrates of salts in solution.

3. The changes of the pressure of ammonia in solutions of the salts of alkaline and the alkaline-earth metals are subject to an additive law; for an increase in strength of the acid entering into the composition of the salt, the solubility of the ammonia becomes greater, while for an increase in the strength of the base, it becomes smaller.

4. The changes of solubility both of the salts and the ammonia may be explained according to the physico-chemical theory of solutions.

5. The theory of electrolytic dissociation is insufficient to account for the abnormally large values of the osmotic pressure.

6. The values of the osmotic pressure determine the condition of the solvent in the solution, and for the cases of abnormally large values, we find evidence of chemical action between the solvent and the dissolved substance.

7. The physico-chemical theory of solutions agrees with the theory of liquids.

8. The relationship between the values of the maximum molecular electrical conductivity and the electrical conductivity at a given concentration can serve to characterize the degree of hydration; the electrical conductivity depends upon the relative strengths of the acids and the base. *C. E. L.*

On the absorption of nitrogen and hydrogen in aqueous solutions of different substances. *L. Braun. Zeit. phys. Chem.* 33, *721* (*1900*).—Propionic acid appears to have no effect on the solubility of nitrogen or hydrogen in water, at any rate up to normal solutions. The presence of urea does change the absorption coefficient of nitrogen and no experiments were made with hydrogen. The author points with pride to these results as showing that the solubility of a gas is not a function of the concentration in the solution of a non-electrolyte. Sodium chloride and barium chloride both affect the solubility, the change in the absorption coefficient being proportional to the two-thirds power of the concentration. Here again, the author is most impressed by the fact that there is zero disturbance for zero concentration. *W. D. B.*

On the want of uniformity in the action of copper-zinc alloys on nitric acid. *J. H. Gladstone. Phil. Mag.* [*5*] 50, *231* (*1900*). — Experiments are published, showing that the decomposition-products formed when nitric acid acts on a zinc-copper alloy or a corresponding mixture may, and sometimes do, differ very considerably, so that no conclusion as to the heat of formation of the alloys can be deduced from such experiments. *W. D. B.*

The double nitrates of tetravalent cerium and thorium. *R. J. Meyer and R. Jacoby. Ber. chem. Ges. Berlin*, 33, *2135* (*1900*). — The authors have prepared the basic nitrate of cerium in a crystalline condition. Cerium, rubidium, and caesium form double nitrates with ammonium and potassium which have been analyzed. Thorium forms salts corresponding to the types, $ThR'(NO_3)_5.5H_2O$; $ThR'_2(NO_3)_6$; $ThR_{11}(NO_3)_8.8H_2O$. The potassium salt is peculiar. It has the formula $ThK_3H_3(NO_3)_{10}.5H_2O$, and forms spendid plates.

C. G. L. W.

Commercial thorium nitrate. *W. Mulhmann and E. Bauer. Ber. chem. Ges. Berlin*, 33, *2028* (*1900*). — To prepare pure thorium compounds the authors fractionate with potassium chromate. Gadolinium and yttrium are only precipitated after the thorium compound is completely thrown out of solution as the chromate. The thorium nitrate was mixed with the requisite quantity of cerium nitrate and the incandescent value of the mixture determined. The mixture gave a slightly greater value than certain commercial sorts.

The salts of didymium and yttrium are detrimental to the lighting value of thorium nitrate, whereas the impurities found in commercial cerium, viz., neodymium and lanthanum do not appear to affect the qualities of the mantle.

The Auer mixture is viewed as a solid saturated solution of cerium oxide in thorium oxide (0.9 %). When the cerium oxide is above this amount it acts as a foreign substance and as such reduces the value of the mixture.

C. G. L. W.

The action of permanganate solutions on hydrogen peroxide and on Caro's reagent. *A. Baeyer and V. Villiger. Ber. chem. Ges. Berlin*, 33, *2488* (*1900*). — The reduction of permanganate by the action of hydrogen peroxide is not due to the formation of a trioxide of hydrogen. Oxygen gas is set free, and the non-appearance of the gas in former experiments is due to supersaturation of the solution with the gas. In the action of permanganate on sulphomonoperacid (Caro's reagent), hydrogen tetroxide is not formed. In a pure condition these two reagents do not act on one another. Caro's acid decomposes spontaneously into sulphuric acid and hydrogen peroxide. The latter reduces a small quantity of the permanganic acid into manganous sulphate, which acts catalytically on the sulphomonoperacid. A criticism of the previously existing views on the reaction of these reagents is given. The oxidizing action of a mixture of potassium permanganate and Caro's acid is more energetic than any mixture that has been previously employed. Benzene is oxidized at once by this reagent. *C. G. L. W.*

Higher oxids of hydrogen. *A. Bach. Ber. chem. Ges. Berlin,* 33, *1506* (*1900*). — According to the experiments of Bach, one may obtain solutions of hydrogen peroxide which contain more oxygen in an active condition than is necessary for the relation $2KMnO_4 : 5H_2O_2$. This is thought to be due to a higher oxidation of the hydrogen peroxide to compounds of the formula H_2O_3 and H_2O_4 (cf. preceding review). *C. G. L. W.*

The quantitative estimation of ozone. *O. Brunck. Ber. chem. Ges. Berlin.* 33, *1832* (*1900*). — Ozone cannot be estimated with neutral potassium iodide. The results are too low. The potassium iodide must be acid. Either acetic or sulphuric acid may be used. *C. G. L. W.*

Ozone. *A. Ladenburg. Ber. chem Ges. Berlin,* 33, *2282* (*1900*). — A criticism of the work of Brunck (preceding review). Ladenburg claims that the incorrectness of the results of the titration of ozone with neutral potassium iodide has long since been demonstrated by Schönbein and others. *C. G. L. W.*

The supposed change of phosphorus into arsenic. *C. Winkler. Ber. chem. Ges. Berlin,* 33, *1693* (*1900*). — Fittica's assumption, that on treating amorphous phosphorus with ammonium nitrate the following reaction takes place

$$2P + 5NH_4NO_3 = (PN_2O)_2O_3 + 10H_2O + 3N$$

is incorrect. According to Fittica, arsenic is a compound of oxygen and nitrogen with phosphorus. By heating phosphorus with ammonium nitrate it was claimed that phosphorus was partly oxidized yielding the above named compound, which was identical with arsenic. Winkler shows that this unlooked-for result was due to impurities in the phosphorus. Oxidation of phosphorus does not take place under these circumstances, phosphoric acid being formed. *C. G. L. W.*

The preparation of arsenic-free phosphorus. *E. Noelting and W. Feuerstein. Ber. chem. Ges. Berlin,* 33, *2684* (*1900*). — Phosphorus may be prepared free from arsenic by distillation with steam in a current of carbon dioxide. The operation must be performed twice, in order to obtain a perfectly pure product. *C. G. L. W.*

Osmotic Pressure and Diffusion

On the amount by which the mutual action of the ionic charges decreases the osmotic pressure. *V. v. Turin. Zeit. phys. Chem.* 34, *403* (*1900*). — After making certain assumptions, the author deduces a mathematical expression for the decrease in the osmotic pressure due to the static action of the hypothetical charges on the hypothetical ions. *W. D. B.*

The relative rates of effusion of argon, helium, and some other gases. *F. Donnan. Phil. Mag.* [5] 49, *423* (*1900*). — Argon and carbon dioxide effuse faster with reference to oxygen than as calculated by the law of the inverse square root of the density, hydrogen and carbon monoxide at about the calculated rate, while helium apparently effuses more slowly than it should. It is suggested that argon and carbon dioxide fall into line quantitatively if we assume that the expression for an actual gas differs from that for an ideal gas by a term depending on the K of the Joule-Thomson effect. This hypothesis requires that helium should show a negative value for K. *W. D. B.*

On the passage of argon through thin films of india-rubber. *Lord Rayleigh. Phil. Mag.* [*5*] 49, *220* (*1900*). — Argon passes an india-rubber film more readily than nitrogen, but not in such a degree as to render the diffusion process a useful one for the concentration of argon from the atmosphere. *W. D. B.*

Note on the source of energy in diffusive convection. *A. Griffiths. Phil. Mag.* [*5*] 47, *522* (*1899*). — From theoretical considerations and neglecting heat of combination, the heat absorbed, when a solution of density greater than water diffuses upwards through a tube of section A, is independent of the height of the tube and of the velocity of flow and may be expressed thus :

$$H = KgTA.$$

The author refers to the apparatus described in his paper on "Diffusion Convection" and further calculates the rate at which work is done by diffusion in the apparatus. *H. T. B.*

A study of an apparatus for the determination of the rate of diffusion of solids dissolved in liquids. *A. Griffiths. Phil. Mag.* [*5*] 47, *530* (*1899*). — The apparatus consists of a vessel divided into two compartments by a diaphragm, and so arranged that diffusion of an aqueous salt solution can take place, through vertical tubes, from the lower compartment to the upper compartment containing pure water. When in operation, the water and solution are renewed at intervals of about a week, to determine the amount of salt diffused. The apparatus has not so far proved successful on account of many sources of error, which are enumerated by the author, but hopes are entertained of its ultimate success. *H. T. B.*

Velocities

On the transformation of cinchonine. *R. Wegscheider. Zeit. phys. Chem,* 34, *290* (*1900*). — It was found by Skraup that the addition and transformation products, caused by the halogen acids, stand in a constant ratio which is independent of the time. The author shows that this result is incompatible with the hypothesis of the addition-product being an intermediate step. The article is a very interesting one, in that it makes clear the importance to the organic chemist of making quantitative studies. *W. D. B.*

On the disintegration of platinum and palladium wires at high temperatures. *W. Stewart. Phil. Mag.* [*5*] 48, *481* (*1899*). — Reviewed (3, 184) from Wied. Ann. 66, 88 (1898).

On the rate of explosion in gases. *D. L. Chapman. Phil. Mag.* [*5*] 47, *90* (*1899*). — Accepting the suggestion that an explosion is essentially similar to a sound wave, the author develops, by making certain assumptions, a formula showing that the velocity of a permanent explosion is a function of the density of the exploded gas. It is also shown how the specific heat at constant volume may be calculated from the velocity of explosion. The pressure of explosion is also obtained by the aid of two formulas, and for an explosion of equal volumes of cyanogen and oxygen it is found to be 57 atmospheres. *H. T. B.*

Electromotive Forces

On the controversy concerning Volta's contact force. *O. Lodge. Phil. Mag.* [*5*] 49, *351 454* (*1900*). — The first part of the paper is devoted to an argument that the Peltier effect is a measure of the potential difference between two metals. This is followed by an approving statement of the osmotic pressure theory of the cell, and then comes a discussion of the electron theory. It is much to be regretted that Professor Lodge and Lord Kelvin do not come together and decide on the points on which they disagree and the reasons for such disagreement. This firing away at long range is profitless, especially while each assumes that the other is ignorant of the elementary principles of physics. *W. D. B.*

Contact electricity. *F. S. Spiers. Phil. Mag.* [*5*] 49, *70* (*1900*). — The object of the work is to determine the cause of the Volta effect. The difficulties to be overcome are treated at some length and as a result an apparatus is devised, which combines the Ayrton and Perry method with the Kelvin compensation method. The measurements were made of the contact E. M. F. with the metals in vacuum and air, and when hot or cold. It was found that air was retained by the metals in vacuum to such an extent as to render it necessary to devise some special means to obviate it. A method of burning the oxygen in hydrogen and at the same time heating the metals was adopted, but even this was found insufficient, and at a high vacuum of pure dry hydrogen there was still sufficient oxygen left to oxidize the surface of an aluminum plate.

The paper concludes by stating "that it is utterly futile to draw any positive conclusions whatever concerning the seat of the E. M. F. in Volta's phenomenon based on experiments made in what usually passes for vacuum."

H. T. B.

Cadmium standard cells. *J. Henderson. Phil. Mag.* [*5*] 48, *152* (*1899*). — A brief description of tests made on a type of cadmium cell, where the cadmium sulphate solution was replaced by cadmium sulphate crystals. The temperature coefficient was found to vary between 0.009 percent and 0.002 percent, which is to be expected in spite of the utmost care in construction and purification of materials. The author's conclusions that "the cadmium cell is distinctly superior to any modification of the Clark cell" is not indicated by his own results.

H. T. B.

The reversibility of voltaic cells. *T. S. Moore. Phil. Mag.* [*5*] 49, *491* (*1900*). — The author has studied zinc-copper and cadmium-copper cells, using the corresponding sulphate and chloride solutions; also the Clark cell. The internal resistances were determined from two observations on the potential difference between the electrodes, and also from an observation on closed circuit

with a reverse current passing through the cell. The two values agree very well, showing the reversibility of the cells. [This is a very surprising result for copper in cupric chloride solutions, since the electrode is not reversible.]
W. D. B.

On the theory of the electrolytic solution-pressure. *R. A. Lehfeldt. Phil. Mag.* [*5*] 48, *430* (*1899*); *Zeit. phys. Chem.* 32, *360* (*1900*). — Starting from the assumption of an electrical double layer at the contact between metal and solution, the author "arrives at the conclusion that, in order to produce the solution-pressure attributed to zinc, 1.27 grams of the metal would have to pass into the ionic form per square centimeter immersed, which is obviously not the case."
W. D. B.

Note on the theory of solution-pressure. *S. R. Milner. Phil. Mag.* [*5*] 49, *417* (*1900*). — The author gives a new deduction of the Nernst formula for the difference of potential between a metal and solution. His proof as to the effect of other substances in the solution is sound only so long as we make the assumption that the solution-pressure is not unchanged by such addition. Lehfeldt's difficulty in regard to the solution-pressure (preceding review) is dismissed with the explanation of "variation from the gas laws." *W. D. B.*

Electromotive behavior of substances with several oxidation stages, I. *R. Luther and D. R. Wilson. Zeit. phys. Chem.* 34, *491* (*1900*). — The author shows that it is possible to deduce the potential difference $Cu \mid CuSO_4$ from measurements of $Cu \mid CuCl$ in KCl and $Pt \mid CuCl$ in $CuSO_4 + KCl$. The calculated value was practically identical with that found experimentally. It was also shown that the concentration of copper as ion in a copper sulphate solution is not changed by the addition of potassium chloride or bromide. *W. D. B.*

Novel thermo-electric phenomena. *W. F. Barrett. Phil. Mag.* 49, *309* (*1900*). — The large electrical resistance of a sample of nickel steel with 5 percent of manganese, led the author to determine its thermo-electric properties. When coupled with a wire of pure iron, the thermo-electric force rose with the temperature to about 300°, when it became almost exactly steady up to 1000°. Experiments with the alloy were made coupled with other metals. Other iron alloys were tried and, in general, it was found that the indications of the temperature were not always the same, but depended on whether the couple was being heated or cooled.
H. T. B.

On some effects of twist on the thermo-electric qualities of iron. *K. Tsuruta. Phil. Mag.* [*5*] 50, *223* (*1900*). — The author draws the following conclusions:

That in soft iron of certain kinds there exists the phenomenon of thermo-electric hysteresis with respect to twist (at least when combined with longitudinal tension);

That other things being equal, the hysteresis is reversed at a certain twist;

That mechanical agitation has its own effects, which are reversed as the hysteresis is reversed.
W. D. B.

The passive state in metals. *W. Hittorf. Zeit. phys. Chem.* 34, *385* (*1900*). — Passive iron gradually becomes active and the same is true of nickel and cobalt. This leads the author to the assumption that passivity is a sort of electrical hysteresis, the element being brought into the passive state by electrical stress in presence of certain anions. The author rejects the hypothesis of a film of oxide and brings the phenomenon in line with the behavior of lead and silver in certain solutions in which they form peroxides. The article contains a number of most interesting observations on the conditions governing the passivity of iron, nickel, and chromium. *W. D. B.*

The magnetic properties of the alloys of iron and aluminium. *S. W. Richardson. Phil. Mag.* 49, *121* (*1900*). — The author investigates the alloys of aluminium and iron in a way similar to the well known experiments of Hopkinson on alloys of iron and nickel. The alloys behave magnetically as though they consisted of two distinct media superposed. A number of B and H curves are given as well as B and T curves, and B and μ curves. The experiments were carried over a range of temperature extending from about − 83° to 900°. *H. T. B.*

Electrolysis and Electrolytic Dissociation

Electrolysis of the alkali salts of organic acids. *J. Petersen. Zeit. phys. Chem.* 33, *99, 295, 698* (*1900*). — The author has electrolyzed solutions of the potassium salts of formic, acetic, propionic, butyric, isobutyric, isovalerianic, valerianic, trimethyl acetic, capronic, oxalic, malonic, succinic, methyl malonic, pyrotartaric, ethyl malonic, and sebacic acids. The author worked with large quantities of material, passing a current of about one-half ampere, in one case, for nearly seven hundred hours. The gases and liquids formed were all identified and determined quantitatively as far as possible. The conclusions drawn by the author are hardly commensurate with the labor expended. *W. D. B.*

The electrolytic preparation of benzidine. *W. Löb. Ber. chem. Ges. Berlin*, 33, *2329* (*1900*). — In the reduction of nitrobenzene either in alkaline or in acid solution, the number of intermediate products, under ordinary circumstances, is great and the reduction cannot be stopped at the wished-for product. The most favorable conditions for the formation of benzidine are the primary formation of azobenzene in acid solution, or of azoxybenzene in alkaline solution, and the subsequent reduction of the compounds to benzidine in an acid electrolyte. The reductions took place in a porous cup, the bottom of which, filled with mercury, served as the cathode. Vigorous stirring was found to be of service. In the reduction of azobenzene to benzidine, perfect absorption of hydrogen takes place. Eighty percent of benzidine was obtained. The yield of diphenyline was at the highest 7 percent. In the direct reduction of nitrobenzene in an alcoholic solution of sodium acetate or sodium hydroxide, and the subsequent reduction of the same mixture in acid solution, a yield of 76-80 percent of benzidine was obtained. In aqueous solution the reduction of nitrobenzene to azoxybenzene, and the reduction of this compound to benzidine was accomplished. The latter takes place in alcoholic solution of sulphuric acid. *C. G. L. W.*

The reduction of succinimide to pyrrolidon. *J. Tafel and M. Stern. Ber. chem. Ges. Berlin*, 33, *2224* (*1900*). — The reduction of succinimide takes place with great readiness in sulphuric acid solution. The electrical efficiency at the start was 85 percent. The introduction of 0.2 mg. of platinum in the form of the chloride completely inhibits the reduction. A number of preparations with pyrrolidon is described. *C. G. L. W.*

The affinity constants for some cyclic organic acids with seven carbon atoms in the ring. *W. A. Roth. Ber. chem. Ges. Berlin*, 33, *2032* (*1900*). — The molecular conductivity of α isophenylacetic acid $= 0.00367$. Rothmund obtained the constant 0.00379 for this acid. For the β acid the value is 0.00401. For the Δ_1 cycloheptencarboxylic acid, $C_7H_{11}.COOH$, he obtained the numbers 0.000992 and 0.000928. The constant for Δ_2 cyclohexencarboxylic acid varied from 0.002715 to 0.002606. *C. G. L. W.*

The constitution of uranyl salts. *H. Ley. Ber. chem. Ges. Berlin*, 33, *2658* (*1900*). — The uranyl salts of the stronger acids are but slightly hydrolyzed at ordinary temperatures. The salts dissociate normally, the radical (UrO_2) acting as a metallic ion. *C. G. L. W.*

Notes on platinum thermometry. *H. L. Callendar. Phil. Mag.* [*5*] 47, *191* (*1899*). — The author reviews and explains a large amount of data on platinum thermometers which has been accumulating since the date of his previous paper on the same subject (1892). The general arrangement of the paper is made with a view of showing the superiority of the platinum resistance thermometer over other temperature measuring instruments, as well as to point out the ease and facility with which "platinum" temperatures may be obtained and reduced to the air scale. The generally accepted notation and nomenclature is explained and the proposal made that it be generally adopted as a standard. The paper is one of value to those using the electrical resistance thermometer. *H. T. B.*

On a practical thermometric standard. *H. L. Callendar. Phil. Mag.* [*5*] 48, *519* (*1899*). — The necessity for some accurate and trustworthy thermometric standard led the author to submit a proposal to the Electrical Standard Committee of the British Association for the adoption of the platinum-resistance-thermometer as a practical standard of reference for scientific research. The draft of proposals is given in the present paper and, in addition, obvious reasons why such a scale might be adopted. *H. T. B.*

On the variation of the resistance of certain amalgams with temperature. *R. S. Willows. Phil. Mag.* [*5*] 48, *433* (*1899*). — The author finds that the resistance of a zinc or cadmium amalgam at a given temperature is a function of the previous history of the amalgam, while this is not the case with amalgams of tin or magnesium. These hysteresis phenomena are attributed to dissociation of unspecified compounds. *W. D. B.*

On the influence of proximity of mass upon electric conduction-resistance. *G. Gore. Phil. Mag.* [*5*] 49, *558* (*1900*). — The author having previously shown the influence of the presence of a mass of heavy substance near one of the poles of a voltaic cell, experiments are tried on the possibility of influence on the electric conduction-resistance of metal wires. The result shows that there is no influence whatever. *H. T. B.*

On the theory of the conduction of electricity through gases by charged ions. *J. J. Thomson. Phil. Mag.* [5] 47, *253* (*1899*). — The author gives a very complete discussion of the theory of the conduction of electricity by charged ions and develops certain equations in relation to the electric intensity in a gas, which are obtained from considerations of the production of ions in gases, their recombination and movements. *H. T. B.*

On the masses of the ions in gases at low pressures. *J. J. Thomson. Phil. Mag.* [5] 48, *547* (*1899*). — It has been conclusively shown that the charge on an ion produced in a gas by the action of cathode rays is the same as the charge carried by the hydrogen ion in electrolysis. It is shown in the present paper that the ratio of the mass of the ion to the charge, $\frac{m}{e}$, for negative electrification, in the case of the action of ultra-violet light on a rarefied gas, or the electrification produced by an incandescent carbon filament is the same as the ratio for cathode rays. This ratio is of the order of 6.8×10^{-6}, while the same ratio for electrolysis is of the order 10^{-4}. It follows that the charge, e, being the same, that the mass, m, of the negative ion in a gas must be about the one-thousandth part of a hydrogen atom. The positive ion is, on the contrary, of the same relative size as the atom, as is shown by the ratio of $\frac{m}{e}$ being the same as in ordinary electrolysis.

The author considers from the general results that the negative ion must be of fundamental importance in any theory of electrical action, and considers that it may be the fundamental quantity in terms of which all electrical quantities may be expressed. He considers that the gaseous atom may consist of a large number of corpuscles which are equal to each other and that the mass of one of these corpuscles is the same as the negative ion in a gas at low pressures, or about 3×10^{-26} of a gramme. When electrified, one corpuscle splits off from the aggregation to form the negative ion and leaves the positive ion of greater mass. Electrification would then depend on the splitting up of the atom itself.
H. T. B.

The discharge of electricity through argon and helium. *R. J. Strutt. Phil. Mag.* [5] 49, *293* (*1900*). — The author measures the cathode fall of potential in the case of helium and argon, experiencing much difficulty with the latter on account of the curling of the positive discharge column around the test electrode on to the back of the cathode. This was finally overcome by introducing a test electrode in the shape of a platinum plate nearly filling the tube. The cathode fall for helium was found to be 226 volts, or very nearly the value found by Warburg for nitrogen. That of argon was found to be 167 volts. With an aluminum electrode this was reduced to 100 volts. The author further studies the conductivity of helium under the influence of Röntgen rays, and compares, by that means, the rate of production of ions with that for air. The rate of production of the ions in helium was found to be about one-half that in air.
H. T. B.

On Mr. Morris-Airey's paper on electrolytic conduction in gases. *J. J. Thomson. Phil. Mag.* [5] 49, *404* (*1900*). — A letter pointing out that Mr. Morris-

Airey's conclusions that when the electrical discharge passes through a mixture of hydrogen and chlorine there is no appreciable transport of the chlorine through the hydrogen, are not indicated by experiment. *H. T. B.*

On the variation in the electric intensity and conductivity along the electric discharge in rarefied gases. *H. A. Wilson. Phil. Mag.* [*5*] 49, *505* (*1900*).—The author extends the work of Graham by obtaining curves of the variation of electric intensity along continuous discharges for air and hydrogen besides nitrogen. The sudden positive drop at the anode is discussed, and the effect noticed by Skinner of a negative electrification near the anode is confirmed, but the author considers that it may due to some influence of the exploring wires. As such a condition of negative electric intensity must necessitate a source of E. M. F., it is suggested that the source is provided by positive ions shot off from the anode under the very large drop in potential and sufficient to carry them against a negative intensity for a short distance. The electric conductivity of the gases is also studied and the variation in conductivity in the striated positive column is shown. *H. T. B*

Uranium radiation and the electrical conductivity produced by it. *E. Rutherford. Phil. Mag.* [*5*] 47, *109* (*1899*).—An exposition and careful study of uranium radiation from the point of view of the ionization theory of gases. An electrical method was employed and the rate of leak between two zinc plates, kept at a difference of potential of 50 volts, when metallic uranium or a compound of uranium was spread between them, was determined. This was done by connecting one plate to a battery and the other to an electrometer, one pole of the battery and one pair of quadrants of the electrometer being also connected to earth. The experiments showed that the radiation emitted by the uranium is complex, consisting of two distinct types which the author terms the α and β radiation. The first type was found to be very easily absorbed by a few layers of aluminum foil and to depend chiefly on the surface of the uranium, while the second is capable of very great penetration and depends also on the thickness of the layer. It was found that the transparency of aluminum for the β radiation is over 100 times as great as for the α radiation, and that the opacity of the metals Al, Cu, Ag and Pt, for the β radiation follows the same order as their atomic weights. The β radiation was found to have the same penetrating power as the radiation from an X-ray bulb. The author suggests that possibly the α radiation is a secondary radiation set up at the surface of the uranium by the β radiation. The absorption of the radiation in gases is studied and found to be least in hydrogen and greatest in CO_2 and apparently follows the same order as the density of the gases. Many other points are treated of in the paper, including the effect of pressure on the absorption, the total amount of ionization in different gases, the rate of recombination of the ions and a comparison of the velocities of the ions in Röntgen and uranium conduction in which the identity of the ions produced by the two types of radiation is indicated. *H. T. B.*

On the velocity and mass of the ions in the electric wind in air. *A. P. Chattock. Phil. Mag.* [*5*] 48, *401* (*1899*).—Considering the dissociation of a gas into positive and negative ions from a point discharge on to a metal plate, the author shows by two methods the identity of the ions to those studied by Rutherford and Zeleny. *H. T. B.*

Dielectricity and Optics

The spectra of hydrogen and the spectrum of aqueous vapor. *J. Trowbridge. Phil. Mag.* [*5*] 50, *338* (*1900*). — The following conclusions are drawn :

"When a condenser discharge is sent through a rarefied gas which is confined in a glass vessel, the gas can no longer be considered in the dry state ; for aqueous vapor is liberated from the glass. When a sufficiently powerful condenser-discharge is employed, dry hydrogen, dry nitrogen, and rarefied air give substantially the same characteristic spectrum. When a very powerful steady battery-current is used to excite the tubes filled with these gases, various compounds of nitrogen and oxygen, nitrogen and hydrogen, are formed if aluminum electrodes are employed.

"The four-line spectrum of hydrogen in the solar atmosphere is an evidence of aqueous vapor, and therefore of oxygen, in the sun.

"Conclusions in regard to the temperature of the stars, exhibiting hydrogen spectra, are misleading if based upon conditions of temperature and pressure in glass vessels ; for conditions of electrical dissociation, of aqueous vapor, for instance, in the presence of an excess or lack of supply of oxygen, are the controlling ones rather than conditions of the mere pressure of the gas.

"X-ray phenomena, produced by a steady battery-current, strongly suggest an electrical theory of the origin of the sun's corona." *W. D. B.*

Radio-active barium and polonium. *F. Giesel. Ber. chem. Ges. Berlin,* 33, *1665* (*1900*). — To obtain a strongly radio-active substance from uranium nitrate, the concentrated solution of this salt acidified with sulphuric acid is treated with enough barium chloride to avoid precipitation of the sulphate in the concentrated solution. On dilution with water the barium salt is precipitated, strongly contaminated with a radio-active substance. According to Debierne, the active substance in the precipitate is actinium, and not radium. *C. G. L. W.*

A radio-active substance emitted from thorium compounds. *E. Rutherford. Phil. Mag.* [*5*] 49, *1* (*1900*). — In the present paper the author shows that, in addition to the ordinary type of radiation emitted by thorium compounds, there are radio-active particles given off which maintain their radio-active properties for several minutes. The term "emanation" is given to these particles. They have the power of ionizing gases and of passing through thin layers of metal and with ease through a considerable thickness of paper. A thin or thick layer of thorium oxide, which is used to study the "emanation", exhibits markedly different properties. The thin layer produces little of the "emanation" as compared to the ordinary form of radiation, while the thick layer shows the reverse. The velocity of these particles is exceedingly slow, the slightest current of air in the room being sufficient to blow them about. The author briefly considers the origin and nature of this emanation, which he treats more in detail in the next paper. *H. T. B.*

Radio-activity produced in substances by the action of thorium compounds. *E. Rutherford. Phil. Mag.* [5] 49, *161* (*1900*). — The power of setting up radio-activity in bodies, which is shown by the radiation from thorium compounds, the author considers connected with the "emanation" previously described from the same compounds. This secondary radiation can be induced in all bodies, can be concentrated by an electric field and exist for hours after the exciting rays have been removed. The rate of decay of the radio-activity was found to be according to a logarithmic curve. The increase was found also to follow a definite relation. The effect of E. M. F., of pressure and of gases was carefully studied, and various mechanical and chemical tests were applied, in addition, to throw some light on the nature of this induced radiation. A fine platinum wire, upon which the thorium rays had been concentrated was carefully weighed and subjected to microscopical tests, but although it gave out strong radiation, nothing of the nature of fine dust particles could be detected. The radiation could be reduced very considerably by wiping the surface with a cloth or fine sandpaper, but in order to remove it completely, it was found necessary to remove the surface layer by long rubbing.

The radio-activity of platinum was not much affected by washing in water, caustic soda, or nitric acid. On the other hand, sulphuric or hydrochloric acid had the power of destroying the intensity of the radiation in a short time. In one test the author shows that the cause of the radiation must be due to small particles, for on removing the radiation from a piece of platinum with dilute sulphuric acid and evaporating the acid to dryness, the residue was found to be radio-active. *H. T. B.*

Thorium radiation. *R. B. Owens. Phil. Mag.* [5] 48, *360* (*1899*). — The author finds that the radiation emitted by thorium and its compounds is not divisible into two such distinct types as was found by Rutherford for uranium.

The method of experiment was essentially the same as that used by Rutherford. Determining the absorption of the radiation by different thicknesses of aluminum foil, it was found that the radiation consists of a readily absorbable kind forming the largest proportion and of apparently a simple nature following the absorption law, and a penetrating type of a complex nature, consisting of a number of component parts and thus unlike the β radiation found for uranium. When screens of paper were used instead of aluminum, a different effect was noticed, the first layer cutting down the conduction current 50 per cent.

The effect of pressure on the conduction current is very carefully studied and the results are found to agree with the ionization theory. *H. T. B.*

Thermal radiation in absolute measure. *J. T. Bottomley and J. C. Beattie. Phil. Mag.* [5] 49, *543* (*1900*). — The experiments described in the present paper form a continuation of Bottomley's previous work. Radiation surfaces of platinum wires are compared in vacuum by electrical heating and the energy loss per unit of area per second determined, as well as the temperature of the wire, from its electrical resistance. Wires of bright polished surface are compared with wires over which a thin layer of soot has been deposited. Wires of different diameters are also compared. *H. T. B*

CONTENTS

[*Continued from second page of cover*]

CONTENTS

ON THE LIQUEFACTION OF A MIXTURE OF TWO GASES. COMPOSITION OF THE LIQUID AND OF THE VAPOR[1]

BY P. DUHEM

Consider[2] a mixture, formed by taking masses $\mathfrak{M}_1$ and $\mathfrak{M}_2 = X\mathfrak{M}_1$, of two liquefiable gases 1 and 2, and suppose that, at the constant temperature T, this mixture is subjected to pressure. If the temperature T is inferior to a certain temperature, which depends upon the concentration X of the mixture and which we shall denote by $\tau(X)$, we can state the following proposition:

There exist two limiting pressures, which depend upon the temperature T, $\Pi_0(T)$ and $\Pi_1(T)$, the second being, in general, greater than the first, such that, under pressures less than $\Pi_0(T)$ or greater than $\Pi_1(T)$, the mixture is homogeneous, while under pressures intermediate between $\Pi_0(T)$ and $\Pi_1(T)$, the mixture of mean concentration X is in part liquid and in part vapor.

The two pressures $\Pi_0(T)$, $\Pi_1(T)$ are equal only in an exceptional case, namely, when the point $[T, \Pi_0(T)]$ of the plane TOΠ lies on the *Gibbs-Konowalow line.*

At temperatures above $\tau(X)$, the mixture of concentration X remains homogeneous whatever the pressure.

If, in the plane TOΠ, we draw the two curves C_0, C_1, which represent the equations

$$\Pi = \Pi_0(T), \quad \Pi = \Pi_1(T),$$

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[1] Translated from the author's manuscript by Paul Saurel.

[2] The principles used in this paper are explained in our "Traité élémentaire de Mécanique chimique fondée sur la Thermodynamique," 4, 109. These principles follow from the investigations of van der Waals, of Kuenen, and from our own.

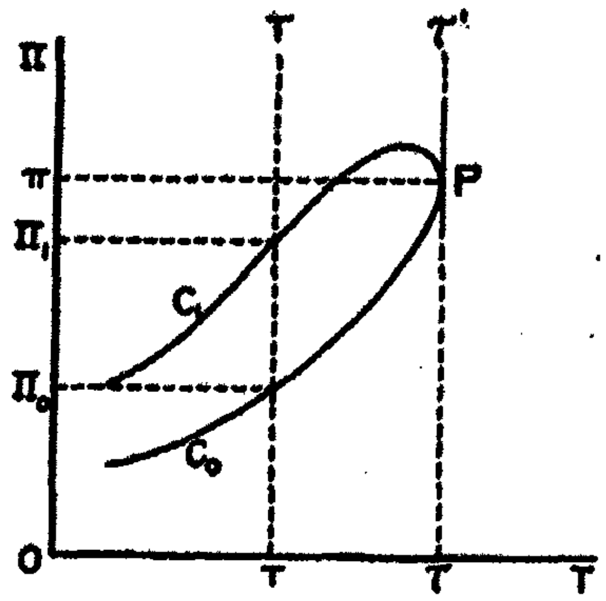

Fig. 1

these curves (Fig. 1) will lie on the left-hand side of the line $\tau\tau'$ which represents the equation

$$T = \tau(X).$$

In reality, these two lines form but a single analytic line which is called the *limiting line of the mixture of mean concentration* X.

Except in a very special case, which we shall not discuss here, the limiting line is tangent to the line $T = \tau(X)$ at a point P, of coordinates $\tau(X)$ and π (X), which van der Waals calls *point of critical contact* of the mixture of mean concentration X.

The two branches which the limiting line of a mixture of concentration X possesses at temperatures lower than $\tau(X)$, never cut each other. If the limiting line passes through a point of the Gibbs-Konowalow line, the two branches are tangent to each other at that point, but do not cross.

When the mixture of mean concentration X passes from the heterogeneous to the homogeneous state, one of the two phases, liquid and vapor, into which it was divided, disappears. If the vanishing phase is the liquid phase, the point of passage is a *dew point;* if the vanishing phase is the vapor phase, the point of passage is a *boiling point.*

The limiting line can accordingly be divided into two branches called respectively *dew line* and *boiling line.*

The point C, of coordinates $\mathfrak{T}(X)$, $\mathfrak{P}(X)$, which divides the limiting line of the mixture of concentration X into a dew line and a boiling line is the *critical point* of that mixture.

When X varies, the point $\mathfrak{T}(X)$, $\mathfrak{P}(X)$ describes a line which is the *critical line* of the two gases under consideration.

When X varies, the limiting line of the mixture of concentration X also varies. This line accordingly admits of an envelope, and this envelope is the critical line. The critical point of the mixture of concentration X is accordingly the point where the limiting line of that mixture touches its envelope.

At temperatures lower than the critical temperature $\mathfrak{T}(X)$, the boiling line of the mixture of concentration X lies, in general, above the dew line of the same mixture. We must except, however, the case where the limiting line passes through a point of the Gibbs-Konowalow line; at such a point the dew line and the boiling line are tangent. If the limiting line of the mixture of concentration X passes through a Gibbs-Konowalow point, this point always corresponds to a temperature lower than the critical temperature $\mathfrak{T}(X)$ of the same mixture.

The line $T = \mathfrak{T}(X)$ meets the limiting line in two points of which one is the critical point. There are thus two cases to be distinguished, according as the critical point is the lower or the higher of the two points of intersection.

First Case. Case of Retrograde Condensation.

The line $T = \mathfrak{T}(X)$ *meets the limiting line in two points; the critical point* C *is the higher of these two points.*

In this case (Fig. 2), the part of the limiting line which corresponds to temperatures higher than $\mathfrak{T}(X)$ belongs to the dew line.

If, at a constant temperature higher than $\mathfrak{T}(X)$, we compress a mixture of mean concentration X, there appears, when we reach a certain pressure, a drop of liquid. The liquid mass at first increases with the pressure, then, as the pressure is increased, the liquid mass passes through a maximum, diminishes and disappears. This phenomenon is called *retrograde condensation.*

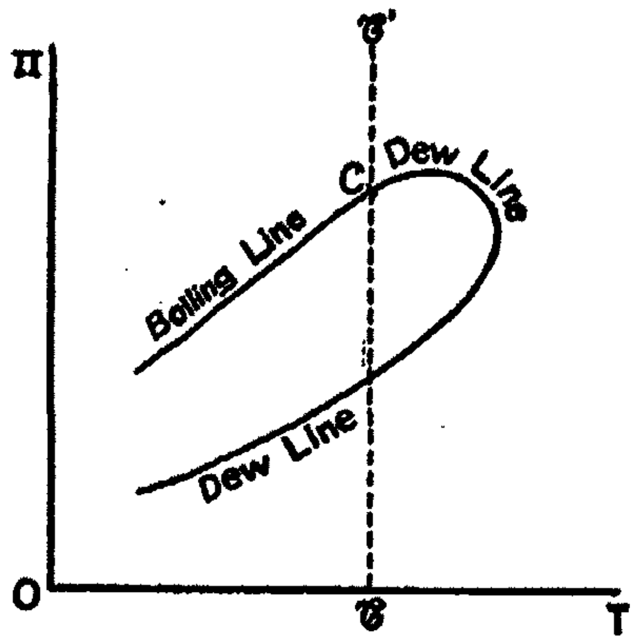

Fig. 2

Second Case. Case of Retrograde Vaporization.

The line $T = \mathfrak{T}(X)$ *meets the limiting line in two points; the critical point* C *is the lower of these two points.*

In this case (Fig. 3), the part of the limiting line which corresponds to temperatures higher than $\mathfrak{T}(X)$ belongs to the boiling line.

If, at a constant temperature higher than $\mathfrak{T}(X)$, we compress a mixture of mean concentration X, the mixture is at first homogeneous and liquid. When we reach a certain pressure a bubble of vapor appears and the mass of vapor at first increases with the pressure. Then as the pressure is still further increased, the mass of vapor passes through a maximum, diminishes and finally disappears. This phenomenon is called *retrograde vaporization.*

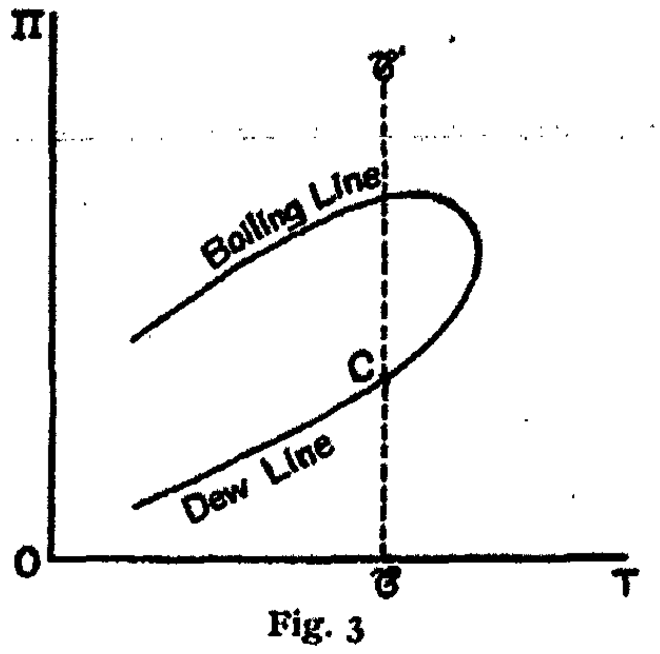

Fig. 3

When we compress, at a constant temperature T, a mixture of mean concentration X, it may happen that the parallel to the pressure axis on which the representative point is moving passes through a Gibbs-Konowalow point of the mixture. In this case the mixture behaves like a single fluid. When the pressure becomes equal to the pressure of the Gibbs-Konowalow point, the state of equilibrium of the system, which up to that moment consisted of a homogeneous vapor phase, becomes indifferent. As soon as the pressure becomes greater than the pressure of the Gibbs-Konowalow point, the system consists of a homogeneous liquid phase. During the liquefaction the liquid and the vapor have the same concentration, namely, the mean concentration of the mixture.

These phenomena occur only in the exceptional case where the temperature corresponds to a Gibbs-Konowalow point; in every other case, while the pressure varies between the two values that we have denoted by $\Pi_0(T)$ and $\Pi_1(T)$, the system consists of two phases, liquid and vapor. These two phases have different concentrations, the one greater than, the other less than the mean concentration of the mixture. When the pressure varies, each of these concentrations varies. It is these variations which we wish to study.

Under the pressure Π, at the temperature T, the mixture of mean concentration X is divided into two phases, a liquid phase of concentration S and a vapor phase of concentration s. As the system, which is formed by means of two independent components, is divided into two phases, it is bivariant. Accordingly, the equilibrium concentrations of the two phases depend only upon the pressure Π and the temperature T; they depend neither upon the mean concentration of the mixture, nor upon the masses of the two phases.

In such a mixture, the liquid phase contains a mass M_1 of the fluid 1 and a mass $M_2 = SM_1$ of the fluid 2. The vapor phase contains a mass m_1 of the fluid 1 and a mass $m_2 = sm_1$ of the fluid 2. The total mass of the fluid 1 is $\mathfrak{M}_1$ and the total mass of the fluid 2 is $\mathfrak{M}_2 = X\mathfrak{M}_1$. We have accordingly the relations

$$m_1 + M_1 = \mathfrak{M}_1,$$
$$sm_1 + SM_1 = X\mathfrak{M}_1.$$

The mass of the vapor is

$$p = m_1 + m_2 = (1 + s)m_1.$$

The mass of the liquid is

$$P = M_1 + M_2 = (1 + S)M_1.$$

The total mass of the system is

$$\mathfrak{T} = \mathfrak{M}_1 + \mathfrak{M}_2 = (1 + X)\mathfrak{M}_1.$$

If the pressure Π and the temperature T are not the coordinates of a Gibbs-Konowalow point, S is not equal to s and we can get from the preceding equations the formulas

$$p = \frac{S - X}{S - s} \, \frac{1 + s}{1 + X} \, \mathfrak{T},$$

$$P = \frac{s - X}{s - S} \, \frac{1 + S}{1 + X} \, \mathfrak{T}.$$

These formulas give us the mass of the vapor and the mass of the liquid, under the pressure Π and at the temperature T, in a mixture of total mass $\mathfrak{P}$ and of mean concentration X.

These formulas lead at once to an important proposition.

Let the mean concentration X vary in such manner as to approach *s*; the mass P of the liquid will approach zero. In like manner, let the mean concentration X approach S; the mass *p* of the vapor will approach zero.

Thus *if* s *and* S *are the concentration of the vapor and the concentration of the liquid which remain in equilibrium with each other under the pressure* Π, *at the temperature* T, *the dew line of the mixture of mean concentration* s *and the boiling line of the mixture of mean concentration* S *pass through the point* (T, Π).

Thus, if a point (T, Π) lies within the limiting line of a mixture of mean concentration X, there pass through that point at least one dew line and one boiling line.

If, through that point, there pass a *single* dew line and a *single* boiling line, and if *s* is the concentration of the mixture to which the dew line belongs, and S the concentration of the mixture to which the boiling line belongs, then, under the pressure Π and at the temperature T, the mixture of mean concentration X will consist of a liquid phase of concentration S and a vapor phase of concentration *s*.

Accordingly, if we have drawn a fine network of limiting lines corresponding to mean concentrations which are known and which differ but little one from another, we can determine without difficulty how the concentration of the liquid phase and the concentration of the vapor phase vary in a mixture of mean concentration X which is compressed, at the temperature T, from the pressure $\Pi_0(T)$ to the pressure $\Pi_1(T)$.

Can it happen that two distinct dew lines or two distinct boiling lines pass through the same point (T, Π)?

Let us suppose, for example, that the point (T, Π) belongs both to the boiling line of the mixture of mean concentration S and to the boiling line of the mixture of mean concentration S′.

Thus, at the temperature T, a liquid mixture of concentration S and a liquid mixture of concentration S′ have the same vapor-pressure Π. According if, at the constant temperature T, we vary the concentration of the liquid mixture from S to S′, the vapor pressure will not vary constantly in the same direction. At least one of its values, the value π, will be a maximum or a minimum. The point (T, π), therefore, belong to a Gibbs line.

From which the following proposition:

In order that two distinct boiling lines should pass through the same point, the system under consideration must possess a Gibbs-Konowalow line.

The same condition is necessary in order that two distinct dew lines should pass through the same point.

Accordingly, if the mixture does not possess a Gibbs-Konowalow line, the simple conditions which we have admitted as hypotheses are certainly realized.

On the other hand, if the mixture possesses one or several Gibbs-Konowalow lines, there may pass through a point (T, Π), within the limiting line of a mixture of concentration X, several dew lines and several boiling lines. A discussion will be necessary to decide which dew line and which boiling line give the composition of the vapor and the composition of the liquid in the mixture of mean concentration X, at the temperature T and under the pressure Π.

These two lines will be, *for the mixture of mean concentration* X, *the useful dew line* and the *useful boiling line* which pass through the point (T, Π).

Thus, *through every point* (T, Π) *which lies within the limiting line of the mixture of concentration* X, *there pass one and only one useful dew line, and one and only one useful boiling line.*

A dew line or a boiling line, useful for the mixture of mean concentration X, *can not end in a critical point.*

For, let us suppose that a boiling line, belonging to a mixture of concentration S, is a useful line for the mixture of concentration X and that, in its useful part, there lies the critical point of the mixture of concentration S. What useful dew line must be associated with it at the critical point? The liquid phase of concentration S has become the critical phase of concentration S. As this phase can be in equilibrium with itself alone, we must associate with the boiling line under consideration, the dew line having the same concentration S. In other words, when the representative point (T, Π) reaches the point under consideration, the mixture of mean concentration X will be in a homogeneous critical state of concentration S. Unless S = X, this is impossible.

A dew line or a boiling line, useful for a mixture of mean concentration X, *can cease being useful only by crossing the limiting line of the mixture of mean concentration* X.

For, let us imagine that a boiling line L, corresponding to the concentration S, is a useful line for the mixture of mean concentration X on one side of a point M, lying within the limiting line of that mixture, and that, on the other side of the point M, it is a useless line for the same mixture. Let us take on the line L and beyond the point M an adjacent point M′. At the point M′, the useful boiling line is no longer the line L, but the line L′, of concentration S′.

When the temperature and the pressure vary continuously, the concentration of the liquid phase of the mixture of mean concentration X also varies continuously. If then the point M′ is made to approach M, the concentration S′ should approach the concentration S. In other words, the point M would be the intersection of two boiling lines L and L′ corresponding to two concentrations S and S′ infinitely near to each other, that is to say, it would be the critical point of the mixture of concentration S. By the preceding proposition, we know that this is impossible.

When the temperature and the pressure of a mixture of mean concentration X vary continuously, the concentration of the liquid phase and the concentration of the vapor phase also vary continuously. From which the following proposition:

In a mixture of mean concentration X, *the useful dew lines* *follow each other continuously, beginning with the dew line of the mixture of concentration* X, *the useful boiling lines follow each other continuously, beginning with the boiling line of the mixture of concentration* X.

Can a boiling line, which is useful for a mixture of mean concentration X, cut the boiling line of that mixture? If this were possible, it would cut the useful boiling lines which are infinitely near to the boiling line of concentration X. Then, for certain points lying within the limiting line of the mixture of concentration X, we should have two useful boiling lines, which is impossible. From which the following proposition :

A boiling line which is useful for the mixture of mean concentration X *can cut the limiting line of that mixture only in a point of the dew line part.*

Similarly, *a dew line which is useful for the mixture of mean concentration* X *can cut the limiting line of that mixture only in a point of the boiling line part.*

Can a straight line, parallel to the pressure axis, cut in more than one point a boiling line which is useful for the mixture of mean concentration X?

Let us suppose that the line TT′, parallel to the axis OΠ (Fig. 4), meets a boiling line APB in two points A and B, and that, in the neighborhood of these two points, the boiling line is useful for the mixture of concentration X. The critical point of the line under consideration can not lie on the arc APB, for if it did, the line APB would be a boiling line in one of the two points A, B, and a dew line in the other. Moreover, neither A nor B can be the critical point, for a boiling line can not reach its critical point in its useful part. The critical point of the line APB will thus lie outside of the arc APB and at a finite distance from its extremities.

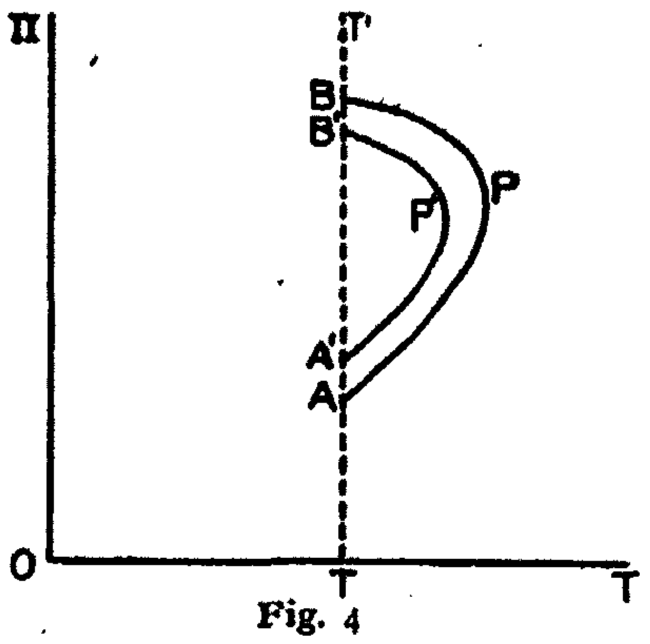

Fig. 4

The critical point of the limiting line to which APB belongs is the point of intersection of this line with a limiting line infinitely close to it. Accordingly, if we take on the segment AB a point A′ near A, we can take it so near that the limiting line through A′, A′P′B′, will cut the limiting line APB in a point outside the arc APB and at a finite distance from the extremities of that arc.

The points A and B lie within the limiting line of the mixture of concentration X; the same is therefore true of the points A′, B′. Accordingly, through each of these two points there passes a boiling line which is useful for the mixture under consideration. When the points A′ and B′ approach A and B respectively, these useful boiling lines must approach the parts of the line APB which pass through A and B. Accordingly, these two boiling lines must belong to the line A′P′B′; the arc A′P′B′ is thus, throughout its whole extent, a boiling line.

We are thus led to the following proposition:

If a line TT′ *parallel to the pressure axis, cuts a boiling line which is useful for the mixture of concentration* X, *in two points* A, B, *we can always find another boiling line, which is useful for the same mixture and which cuts the line* TT′ *in two points* A′, B′, *such that the segment* A′B′ *lies within the segment* AB *and the two lengths* AA′ *and* BB′ *are finite.*

From this we conclude without difficulty that, *if the line* TT′ *cuts a boiling line which is useful for a mixture of concentration* X, *in two points* A, B, *it is tangent between* A *and* B *to another boiling line which is also useful for the same mixture.*

In like manner, it can be shown that, *if a line* TT′, *parallel to the pressure axis, cuts a dew line which is useful for a mixture of concentration* X, *in two points* A, B, *it is tangent between* A *and* B *to another dew line which is also useful for the same mixture.*

On the limiting line of the mixture of mean concentration X there is always one and only one point, the point P, in which the curve is tangent to a line parallel to OΠ. This point is on the dew line if the mixture is one for which retrograde condensation occurs, and on the boiling line if the mixture is one for which retrograde vaporization occurs. To fix our ideas, let us consider a system of the first kind.

The dew lines which are useful for the mixture of concentration X follow each other continuously, beginning with the dew line of the mixture of concentration X. If we take those sufficiently near to the dew line of concentration X, we shall find on each of them a point P′ (Fig. 5), near P, at which the tangent will be parallel to OΠ.

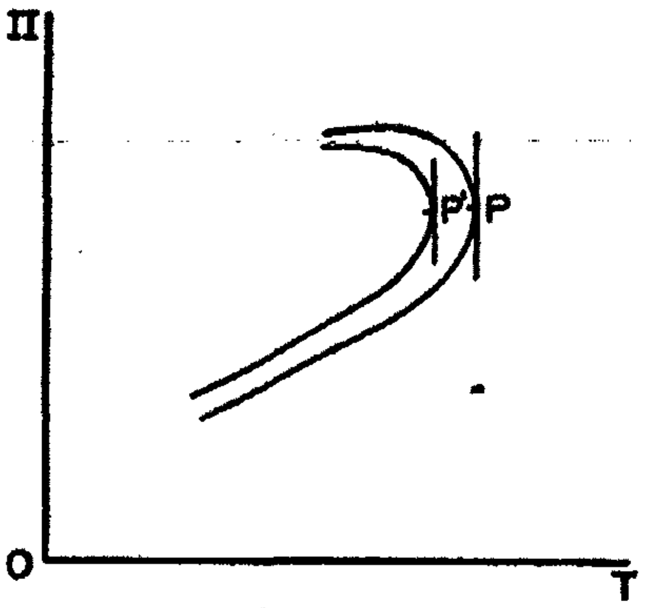

Fig. 5

Thus, *if the mixture of concentration* X *is one for which retrograde condensation occurs, the dew lines which are useful for this mixture and which are sufficiently near the limiting dew line have each a point at which the tangent is parallel to the pressure axis.*

Can it happen that for certain dew lines, which are useful for the mixture of concentration X, there is no tangent parallel to OΠ?

Such a dew line belongs to a certain limiting line which possesses a tangent parallel to OΠ. But the point of tangency may be on a part of the dew line in which it is no longer useful for the mixture under consideration, or again it may be on the boiling line.

Suppose we follow the useful dew line, going towards that point of the corresponding limiting line for which the abscissa is a maximum. In the first case, before we reach that point, the dew line will have ceased to be useful; the dew line must therefore have crossed the limiting line of the mixture of concentration X. In the second case, before we can reach the point under consideration, we shall have passed the critical point, and as a useful line can not reach its critical point, the dew line has again crossed the limiting line of the mixture of concentration X.

The useful dew lines of the mixture of concentration X may thus be divided into two groups. Those of the first group have a point, on their useful part, and, consequently, within the limiting line of the mixture of concentration X, where the tangent is parallel to OΠ. Those of the second group rise constantly from left to right and reach the boiling line of the mixture of concentration X.

As the useful dew lines follow each other continuously, the passage from one group to the other must take place at a dew line for which the point of tangency of the tangent parallel to OΠ is the point in which this dew line crosses the boiling line of the mixture of concentration X.

This result, with those that we have already obtained, gives us the following proposition:

IF THE MIXTURE OF MEAN CONCENTRATION X IS ONE FOR WHICH RETROGRADE CONDENSATION OCCURS, *the locus of the point at which the useful dew lines have a tangent parallel to* OΠ *includes a branch which begins at the point* P *at which the dew line of the mixture under consideration has such a tangent and which ends at a point* Q *of the boiling line of the same mixture.* (Fig. 6).

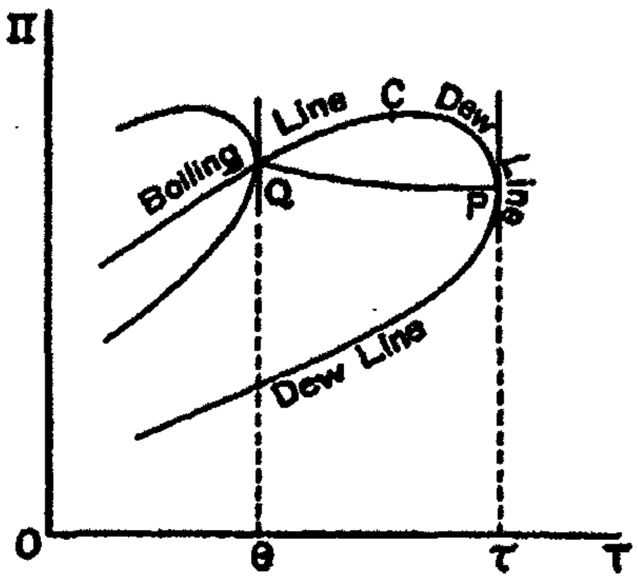

Fig. 6

WE SHALL ADMIT THAT THE LOCUS DOES NOT POSSESS ANY OTHER BRANCH AND THAT NO BOILING LINE WHICH IS USEFUL FOR THE MIXTURE OF MEAN CONCENTRATION X HAS A TANGENT PARALLEL TO OΠ.

Analogous reasoning leads to the following:

IF THE MIXTURE OF MEAN CONCENTRATION X IS ONE FOR WHICH RETROGRADE VAPORIZATION OCCURS, *the locus of the points at which the useful boiling lines have a tangent parallel to* OΠ *includes a branch which begins at the point* P (Fig. 7), *at which the boiling line of the* *mixture under consideration has such a tangent and which ends at a point Q of the dew line of the same mixture.*

WE SHALL ADMIT THAT THE LOCUS DOES NOT POSSESS ANY OTHER BRANCH AND THAT NO DEW LINE WHICH IS USEFUL FOR THE MIXTURE OF MEAN CONCENTRATION X HAS A TANGENT PARALLEL TO OΠ.

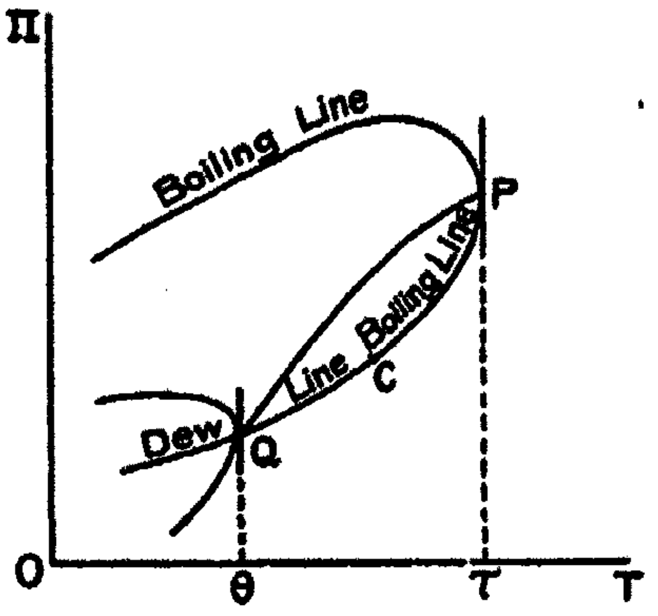

Fig. 7

Accordingly, whether the mixture of mean concentration X be one for which retrograde condensation occurs or one for which retrograde vaporization occurs, the temperatures to be studied can be divided into three categories:

The *first category* includes the temperatures which are lower than θ, the temperature of the point which we have denoted by Q.

The *second category* includes the temperatures which lie between θ and the temperature $\mathcal{T}$ of the critical point.

The *third category* includes the temperatures which lie between $\mathcal{T}$ and the greatest abscissa of the limiting line of the mixture under consideration.

If we take a temperature of the first category as the constant abscissa of a line parallel to OΠ, this line will touch neither a useful dew line nor a useful boiling line. It follows then, from what precedes, that it cannot cut twice either a useful dew line or a useful boiling line. This gives us the following proposition:

Let T *be a temperature lower than the temperature* θ *of the point* Q *and let us increase the pressure from the value* $\Pi_0(T)$ *to the value* $\Pi_1(T)$*; the concentration of the liquid varies always in the same direction, and the same is true of the concentration of the liquid.*

When the pressure has the value $\Pi_0(T)$, the representative point is a dew point of the mixture of mean concentration X which is being studied; the vapor has then the concentration X. When the pressure has the value $\Pi_1(T)$, the representative point is a boiling point of the same mixture; the liquid has then the concentration X.

When the pressure has the value Π, intermediate between $\Pi_0(T)$ and $\Pi_1(T)$, the mixture of mean concentration X consists of two phases, a liquid phase of concentration S and a vapor phase of concentration s. As X must lie between S and s, we may write the inequalities

$$(s - S)(s - X) > 0,$$
$$(s - S)(X - S) > 0.$$

$(s - X)$ is the total variation which the concentration of the vapor undergoes when the pressure increases from $\Pi_0(T)$ to Π; $(X - S)$ is the total variation which the concentration of the liquid undergoes when the pressure increases from Π to $\Pi_1(T)$.

If we notice that the concentration of each of the two phases varies always in the same direction, we see that the concentration of the vapor and the concentration of the liquid are both increasing functions of the pressure or both decreasing functions according as $(s - S)$ is positive or negative.

From which the two following propositions:

When, at constant temperature, the pressure is increased, the concentration of the liquid and the concentration of the vapor both vary in the same direction.

An increase in pressure increases, as well in the liquid as in the vapor, the proportion of that one of the two fluids 1 *and* 2 *which is present in the vapor in greater proportion than in the liquid.*

$(s - S)$ is equal to zero if the temperature chosen corresponds to a Gibbs-Konowalow point of the mixture of mean concentration X. According as we take a temperature lower than or higher than this temperature, $(s - S)$ will have different signs. From which the following proposition:

During an isothermal compression at a temperature T *lower than θ, the concentration of the liquid and the concentration of the vapor both vary in the same direction. This direction is different according as the temperature is higher or lower than that which determines, for the mixture under consideration, a Gibbs-Konowalow point.*

Let us now suppose that the isothermal compression takes place at a temperature higher than θ. There are two cases to be considered according as the mixture is one for which retrograde condensation occurs, or one for which retrograde vaporization occurs.

FIRST CASE

Mixture for which retrograde condensation occurs

A parallel to $O\Pi$ does not touch any boiling line which is useful for the mixture, and, consequently, does not cut any such line in two points. From which the following proposition:

When the pressure increases from $\Pi_0(T)$ *to* $\Pi_1(T)$, *the concentration of the liquid phase varies always in the same direction.*

Let T and T' be two neighboring temperatures. The useful boiling line, of concentration S_1, has a point whose abscissa is T (Π_1 is its ordinate) and a point whose abscissa is T' (Π_1' is its ordinate); the useful boiling line of concentration S_2, nearly equal to S_1, has also a point whose abscissa is T, its ordinate being Π_2, and a point whose abscissa is T', its ordinate being Π_2'.

If the mixture under consideration has no Gibbs-Konowalow point between the temperatures T and T', we can take these temperatures so near to each other that the boiling line of concentration S_1 does not cut the limiting line of the mixture under consideration between the points (T, Π_1) and $(T' \Pi_1')$, and that the same is true of the boiling line of concentration S_2 between the points (T, Π_2) and (T', Π_2').

As these, boiling lines both rise from left to right, and, moreover, as two useful boiling lines can not cut each other within the limiting line of the mixture under consideration, the two differences $(\Pi_2 - \Pi_1)$ and $(\Pi_2' - \Pi_1')$ will have the same sign. From which the following proposition:

At temperatures higher than that of the last Gibbs-Konowalow point of the mixture under consideration, an isothermal compression produces in the liquid phase a change of concentration whose direction is independent of the temperature.

We can, as before, write the inequality

$$(s-S)(X-S)>0.$$

Moreover, if the temperature is lower than the critical temperature $\mathfrak{T}$ of the mixture under consideration, X is the concentration of the liquid phase under the pressure $\Pi_r(T)$ which corresponds to a boiling-point. We can therefore state the following theorem:

At any temperature lower than the critical temperature of the mixture under consideration, an isothermal compression increases, in the liquid phase, the proportion of that one of the two fluids 1 *and* 2 *which is present in greater proportion in the vapor than in the liquid.*

Let us consider a temperature T lying between the temperature θ of the point Q and the critical temperature $\mathfrak{T}$, and let us draw (Fig. 8) that parallel to OΠ, which has T for an abscissa. This line meets the curve PQ in a point M, and, consequently, it is tangent at M to a certain useful dew line. Let Σ be the concentration which corresponds to that dew line.

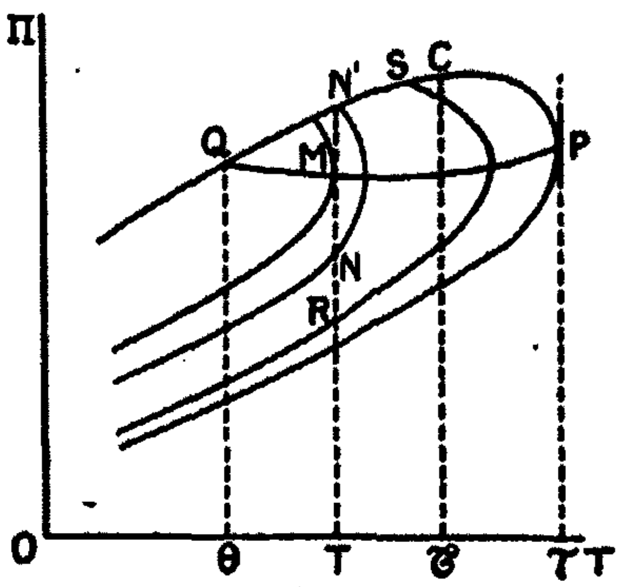

Fig. 8

To the concentrations between X and Σ and sufficiently near to Σ, correspond useful dew lines which meet the line TM in two points, one below and the other above M.

On the other hand, if we consider a concentration lying between X and Σ and infinitely near to X, the useful dew line, corresponding to that concentration, at first lies within the dew line of the mixture, infinitely near to it, and finally crosses the boiling line of the mixture at a point infinitely near to the critical point C. This useful dew line accordingly meets the line TM in a single point whose ordinate exceeds $\Pi_0(T)$ by an infinitely small quantity.

Similarly, to concentrations lying between X and Σ and sufficiently near to X correspond useful dew lines which meet the line TM in a single point. These lines cut the boiling line of the mixture of concentration X in points which lie between the critical point of the mixture and the point N′ in which the line TM cuts the boiling line.

There is one useful dew line which passes through the point N′ after having met the line TM in a point N situated below M. This line corresponds to a concentration S lying between X and Σ. This line separates the useful dew lines which meet, in one point, the line TM from the useful dew lines which meet the same line in two points. These various results carry with them the following proposition:

Let T *be a temperature lying between the temperature* θ *of the point* Q *and the critical temperature* $\mathfrak{T}$ *of the mixture of mean concentration* X. *Let us increase the pressure above the pressure* $\Pi_0(T)$. *The concentration* s *of the vapor, at first equal to* X, *varies in a certain direction until the pressure* $\pi(T)$ *is reached; the concentration of the vapor is then equal to* Σ. *Then as the pressure increases from* $\pi(T)$ *to* $\Pi_1(T)$, *the concentration of the vapor varies in the opposite direction from* Σ *to a value* S *lying between* X *and* Σ.

Let S and s be the concentration of the liquid and of the vapor phase which coexist at the temperature T under the pressure Π. We can, as before, write the inequality

$$(s-S)(s-X)>0.$$

$(s-X)$ has, therefore, the same sign as $(s-S)$.

Let us suppose that the pressure Π is greater than $\Pi_0(T)$, but less than $\pi(T)$. The concentration of the vapor then varies in but one direction. If we notice that X is the value of this concentration when $\Pi=\Pi_0(T)$, we see that a small increase given to an initial pressure lying between $\Pi_0(T)$ and $\pi(T)$ produces in the concentration of the vapor a change whose sign is the same as that of $(s - X)$ or of $(s - S)$. Therefore:

When the pressure increases from $\Pi_0(T)$ *to* $\pi(T)$, *the concentration of the vapor varies in the same direction as the concentration of the liquid; the vapor becomes richer in the fluid which is present in greater proportion in the vapor than in the liquid. When the pressure increases from* $\pi(T)$ *to* $\Pi_1(T)$, *the concentrations of the vapor and the liquid vary in opposite directions; the vapor becomes poorer in the fluid which is present in greater proportion in the vapor than in the liquid.*

Finally, let us consider a temperature T, higher than the critical temperature 𝔗 of the mixture under consideration, but lower than the temperature τ, and let us compress the mixture at that temperature T.

The representative line meets PQ in M (Fig. 9). It therefore touches at M a certain useful dew line which corresponds to the concentration Σ; $\pi(T)$ is the ordinate of the point M.

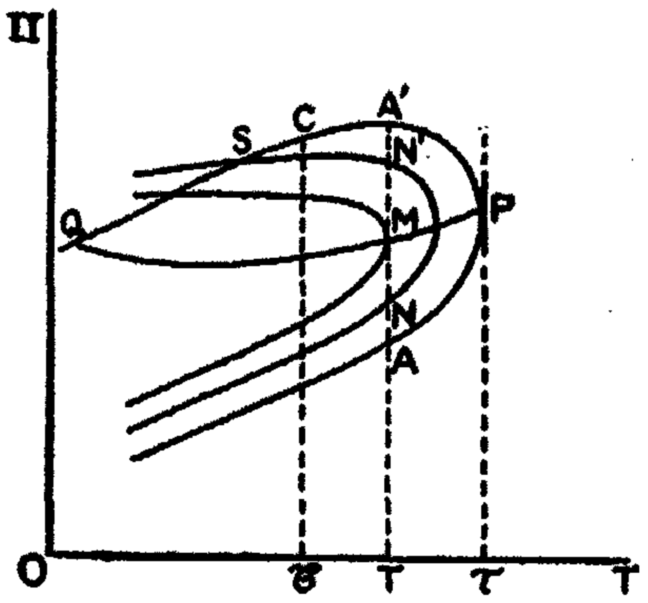

Fig. 9

Let us take a point N on the line TM between the point A whose ordinate is $\Pi_0(T)$ and the point M whose ordinate is $\pi(T)$. Through this point there passes one useful dew line whose concentration lies between X and Σ. This dew line meets the line TM a second time at point N′, between M and the point A′ whose ordinate is $\Pi_1(T)$. We have, accordingly, the following proposition:

Let T *be a temperature in the region of retrograde condensation. When the pressure increases from* $\Pi_0(T)$ *to* $\pi(T)$, *the concentration of the vapor varies from* X *to* Σ *and always in the same direction. When the pressure increases from* $\pi(T)$ *to* $\Pi_1(T)$, *the concentration varies constantly in the opposite direction from* Σ *to* X.

We might repeat here, as in the preceding case, considerations which would lead to the following conclusions:

When the pressure increases from $\Pi_0(T)$ *to* $\pi(T)$, *the concentration of the vapor varies in the same direction as the concentration of the liquid. The vapor becomes richer in the fluid which is present in greater proportion in the vapor than in the liquid. When the pressure increases from* $\pi(T)$ *to* $\Pi_1(T)$, *the concentration of the vapor and the concentration of the liquid vary in opposite directions. The vapor becomes poorer in the fluid which is present in greater proportion in the vapor than in the liquid.*

These various results can be represented graphically.

Let us suppose that the temperature is higher than the temperature of the last Gibbs-Konowalow point of the mixture of mean concentration X. The sign of $(s - S)$ will not change. Let us suppose that the index 1 denotes the *more volatile* of the two fluids, that is to say, the one which is present in greater proportion in the vapor than in the liquid. $(s - S)$ will then be negative and the preceding results will be represented by the three accompanying diagrams (Fig. 10). The line L_0L_1 represents the concentration of the liquid; the line V_0V_1 represents the concentration of the vapor.

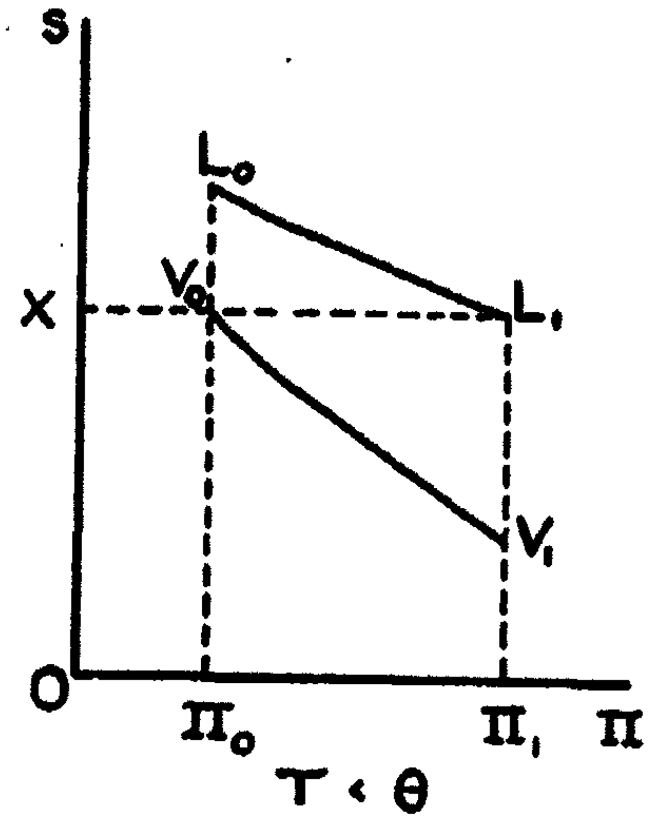

Fig. 10*a*

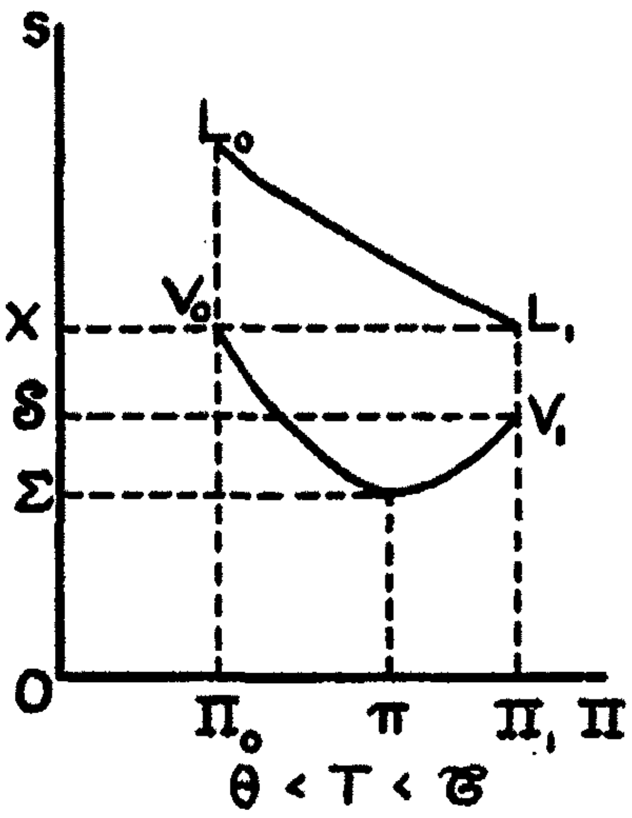

Fig. 10*b*

SECOND CASE

Mixture for which retrograde vaporization occurs

This case can be treated in the same way as the first. We shall not repeat the demonstrations, but shall content ourselves with stating the results.

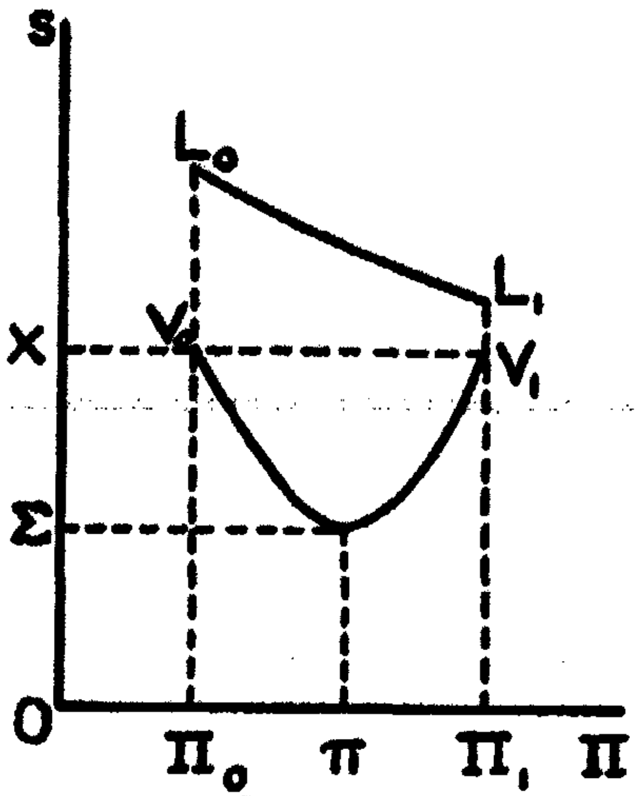

Fig. 10c

When, at a temperature T, *higher than the temperature θ of the point* Q, *the pressure increases from* $\Pi_0(T)$ *to* $\Pi_1(T)$, *the concentration of the vapor varies always in the same direction.*

The direction of the variation does not depend upon the temperature.

At any temperature lower than the critical temperature of the mixture under consideration, an isothermal compression produces in the vapor-phase an increase in the proportion of that one of the fluids 1 *and* 2 *which is present in greater proportion in the vapor than in the liquid.*

Let T *be a temperature lying between the temperature θ of the point* Q *and the critical temperature of the mixture of concentration* X. *Let us increase the pressure above* $\Pi_0(T)$. *The concentration of the liquid, starting with the value* S, *will at first vary in a certain direction until the pressure reaches the value* $\pi(T)$. *The concentration of the liquid will then have the value* Σ, *such that* S *lies between* X *and* Σ. *Then, as the pressure continues to increase from* $\pi(T)$ *to* $\Pi_1(T)$ *the concentration of the liquid varies in the opposite direction until it reaches the value* X.

When the pressure increases from $\Pi_0(T)$ *to* $\pi(T)$ *the concentration of the liquid and the concentration of the vapor vary in* *opposite directions. The liquid becomes poorer in that one of the fluids* 1 *and* 2 *which is present in the liquid in smaller proportion than in the vapor. When the pressure increases from* $\pi(T)$ *to* $\Pi_1(T)$, *the concentration of the liquid and the concentration of the vapor vary in the same direction. The liquid becomes richer in the fluid which is present in the liquid in smaller proportion than in the vapor.*

Let T *be a temperature higher than the critical temperature. When the pressure increases from* $\Pi_0(T)$ *to* $\pi(T)$, *the concentration of the liquid varies, always in the same direction, from the value* X *to a certain value* Σ. *When the pressure increases from* $\pi(T)$ *to* $\Pi_1(T)$, *the concentration of the liquid varies in the opposite direction from* Σ *to* X.

When the pressure increases from $\Pi_0(T)$ *to* $\pi(T)$, *the concentration of the liquid and the concentration of the vapor vary in opposite directions. The liquid becomes poorer in the fluid which is present in the liquid in smaller proportion than in the vapor. When the pressure increases from* $\pi(T)$ *to* $\Pi_1(T)$, *the concentration of the liquid varies in the same direction as the concentration of the vapor. The liquid becomes richer in the*

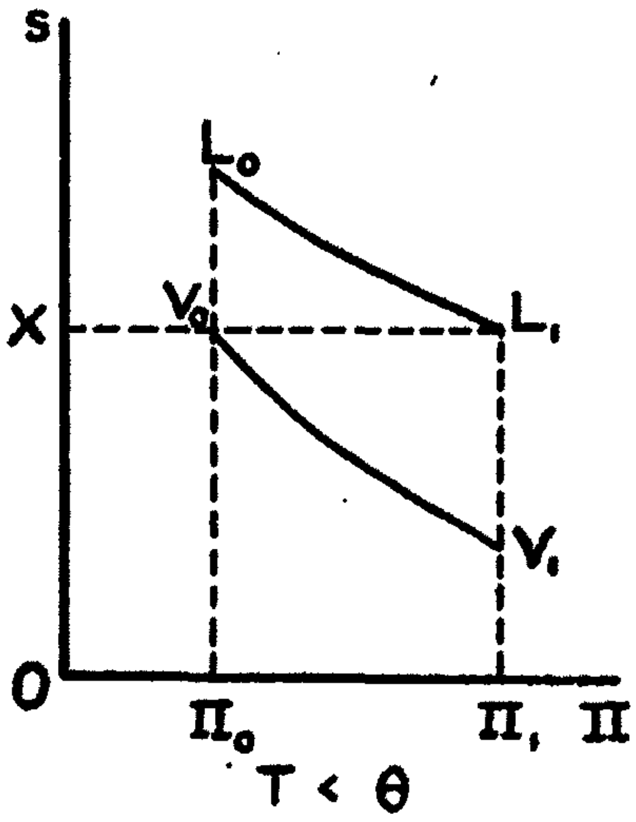

Fig. 11*a*

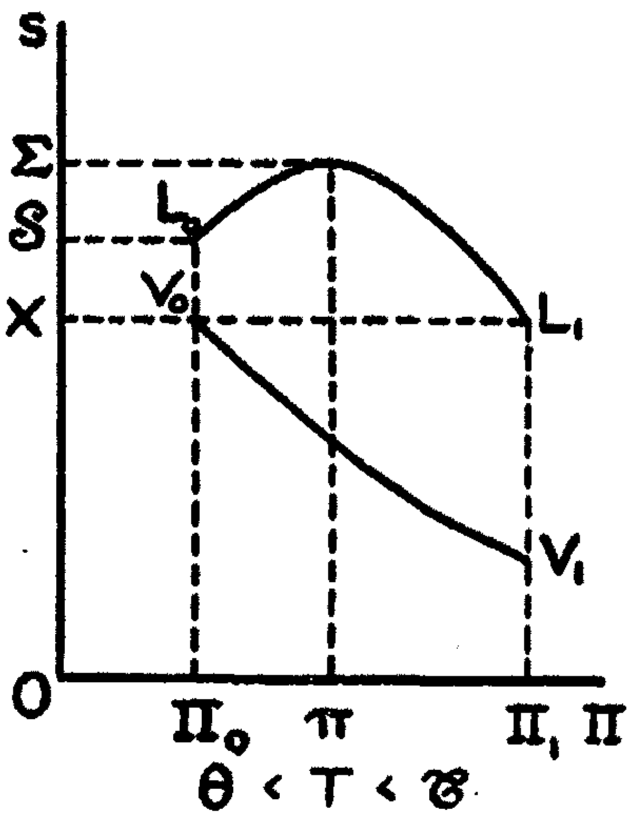

Fig. 11*b*

fluid which is present in the liquid in smaller proportion than in the vapor.

If, in this second case, we make the assumptions which, in the first case, enabled us to draw Fig. 10, we can represent the preceding results by the three accompanying diagrams (Fig. 11).

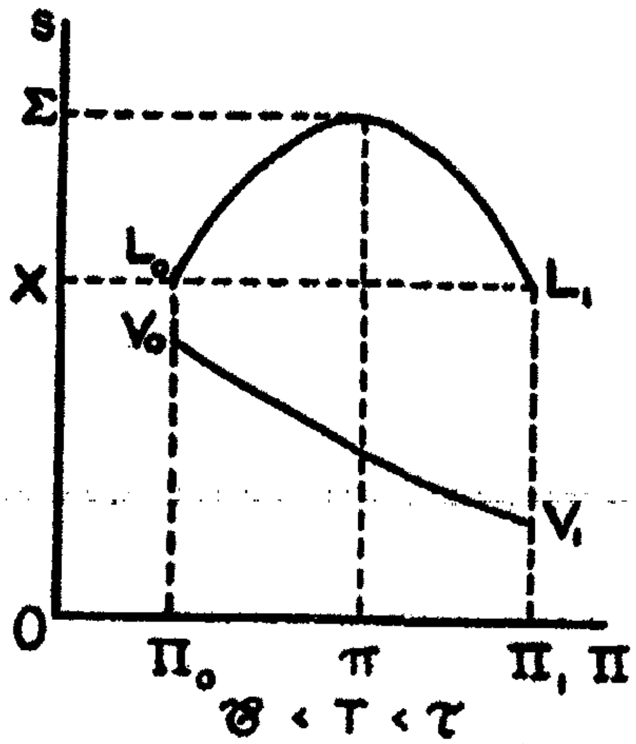

Fig. 11c

The propositions that we have established show that it is possible to study during an isothermal compression, the changes of composition of the liquid and of the vapor when we have drawn a sufficiently fine network of limiting lines.

Caubet[1] has drawn such a network for the mixtures: carbon dioxide and methyl chloride, carbon dioxide and sulphur dioxide, sulphur dioxide and methyl chloride; and he has been able,[2] in accordance with the previous propositions, to follow the composition of the liquid phase and of the vapor phase.

Bordeaux, August 3, 1900.

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[1] G. Caubet. Compt. rend., 130, 167, 828; 131, 108 (1900).

[2] G. Caubet. Société des Sciences physiques et naturelles de Bordeaux, meetings of June 14 and July 19, 1900.

TOXIC ACTION OF ELECTROLYTES UPON FISHES

BY LOUIS KAHLENBERG AND HUGO F. MEHL

Several investigations on the toxic action of various aqueous solutions upon plants have been made in this laboratory. It was thought desirable to carry out similar researches with animals; and, after a few preliminary experiments, fishes were found to be subjects upon which experiments of the kind contemplated could readily be performed.

The chief aim of this investigation is to compare various dilute aqueous solutions that conduct electricity by observing how long fishes can live in them. The following is an outline of the method of experimentation. A fish of small size — see definite data in the tables below — was placed in 500 cc of the solution to be tested, which was contained in a porcelain casserole of about 1 liter capacity, and the time required to produce death was carefully noted. Control experiments were conducted in each case, using distilled water, for of course a fish will die in so small an amount of water when the limited amount of dissolved oxygen that it contains has been largely consumed. In noting the time necessary for the fish to succumb, it was at first thought best to pronounce the animal dead when all motion had ceased. This was found to be impracticable, however, for owing to slight muscular contraction that in some cases continued for an appreciable time, the time at which death occurred would not be sufficiently sharply defined. When a fish is placed in a toxic solution, the phenomena observed vary somewhat with the nature of the solution; generally, however, the fish moves about in a lively manner, which movements may in some cases culminate in attempts to jump out of the dish.[1] After a time the

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[1] To prevent the fish from getting out of the dish, a glass plate was placed over the casserole in such cases. This plate did not fit the dish closely, however, and so did not entirely prevent the circulation of air beneath it.

movements of the fish become less pronounced; it finally loses control of its motions, and turns over on its back. The latter phenomena occurs suddenly, and though the fish generally continues to move somewhat after its ventral side has turned up, it never again regains control of its motions and the latter soon cease entirely. Because the time at which the fish turns over on its back is so well defined, it was taken in each case as the time at which death occurred. In the tables given below, then, the figures in the column headed "time required to produce death" really indicate the time that elapsed from the instant that the fish was placed in the solution to the moment when its ventral side turned upwards. The post-mortem appearances of the specimens killed in various solutions are of interest and will consequently be given below in each case. After death had occurred, the length and also the weight of each fish was ascertained, the former to about 1 mm and the latter to within 0.01 gram. These data are included in the tables that follow. The experiments were conducted at room temperature, between 18° and 20° C.

Three different species of fish were used in the experiments, viz.: —rock-bass (*amblo-plites rupestris*), the common shiner, also called dace or redfin (*n.megalop refinesque*), and brook-trout (*salvelinus fontinalis*). A few tests were also made with the ordinary yellow perch (*perca flavescens*). All the specimens except the brook-trout were caught in Lake Mendota[1] near the shore. The investigations were made during the months of October and November, and when in the latter month cold weather came and the fishes sought deeper water, it seemed at first that no further tests could be made at that time. However, through the kindness of Mr. James Nevin, to whom we feel especially indebted, some very fine specimens of brook-trout were obtained from the Wisconsin State Fish Hatcheries, located near Madison. The fishes were of as nearly the same weight and length as could very well be obtained in any quantity, the extreme variations (leaving the perch out of consideration) being 0.5 to

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[1] At Madison, Wisconsin.

5 grams, and 25 to 102 mm. They were all of the spring's hatch and were from four to six months old. During the night they were kept in a large perforated pail suspended in the lake, and during the day when they were wanted for experimentation, they were kept near at hand in an aquarium through which coursed a continuous stream of fresh lake water. The vitality of the fishes was thus impaired as little as possible during the time they were held in captivity. Moreover, the experiments were conducted as soon as possible after the fish were caught, usually on the same day. As the fishes are all of well known species, a detailed description of them may here be omitted.

The experimental results are given in Tables I. to IV., which are self-explanatory. The strengths of the solutions are indicated in each case in terms of equivalent normal solutions.

Dilute solutions of hydrochloric, nitric, and sulphuric acids, were tested with rock-bass. The results obtained are presented in Table I.

TABLE I

Rock-bass (*amblo-plites rupestris*)

Length	Weight	Solutions	Time required to produce death
32 mm	0.55 gram	*n*/100 HCl	6 min
51 "	3.00 "	" "	7 " 30 sec
25 "	0.85 "	" "	6 "
Aver. 36 "	1.46 "		6 30 "
32 "	1.30 "	*n*/100 HNO_3	6 " 30 "
45 "	2.30 "	" "	7 "
51 "	2.30 "	" "	7 "
Aver. 43 "	1.96 "		6 " 50 "
32 "	0.55 "	*n*/100 H_2SO_4	7 "
32 "	0.52 "	" "	6 "
45 "	1.94 "	" "	9 "
Aver. 36 "	1.00 "		7 " 20 "

Length	Weight	Solutions	Time required to produce death
Aver. 32 mm	1.47 gram	$n/250$ HCl	9 min
32 "	1.32 "	" "	8 " 30 sec
32 "	1.24 "	" "	9 "
Aver. 32 "	1.34 "		8 " 50 "
32 "	1.64 "	$n/250$ HNO_3	9 " 30 "
32 "	1.60 "	" "	9 "
32 "	1.34 "	" "	8 " 30 "
Aver. 32 "	1.53 "		9 "
32 "	1.14 "	$n/250$ H_2SO_4	9 " 30 "
32 "	1.24 "	" "	9 " 30 "
32 "	1.40 "	" "	10 " 30 "
Aver. 32 "	1.26 "		9 " 50 "
38 "	1.17 "	$n/500$ HCl	12 "
38 "	1.55 "	" "	11 "
38 "	1.20 "	" "	11 "
Aver. 38 "	1.27 "		11 " 20 "
32 "	1.15 "	$n/500$ HNO_3	12 "
38 "	1.45 "	" "	12 "
32 "	1.25 "	" "	13 "
Aver. 34 "	1.28 "		12 " 20 "
38 "	1.32 "	$n/500$ H_2SO_4	14 " 30 "
38 "	1.27 "	" "	13 "
38 "	0.85 "	" "	14 "
Aver. 38 "	1.14 "		13 " 50 "
32 "	1.45 "	$n/1000$ HCl	18 " 30 "
45 "	2.10 "	" "	20 "
32 "	1.55 "	" "	21 "
Aver. 36 "	1.70 "		19 " 50 "

Length	Weight	Solutions	Time required to produce death
38 mm	1.87 gram	$n/1000$ HNO_3	23 min 30 sec
45 "	1.50 "	" "	20 "
38 "	1.85 "	" "	21 "
Aver. 40 "	1.77 "		21 " 30 "
38 "	1.70 "	$n/1000$ H_2SO_4	22 " 30 "
51 "	2.65 "	" "	25 "
51 "	2.30 "	" "	27 "
Aver. 47 "	2.22 "		24 " 50 "
38 "	2.20 "	$n/1500$ HCl	47 " 30 "
38 "	2.15 "	" HNO_3	47 "
38 "	2.30 "	" H_2SO_4	49 "
38 "	1.87 "	distilled water	6 hrs 40 min

It will be observed that $n/100$ is the strongest solution of the mineral acids given in the table. In a normal solution of any of these acids or of caustic potash a fish does not survive longer than five to ten seconds, while even in a $n/10$ solution, death occurs in less than a minute, so that these relatively strong solutions could not be used to obtain accurate measurements. Hydrochloric, nitric, and sulphuric acid solutions stronger than $n/500$ cause blood to ooze from the gills of the fish. The more concentrated the solution, the more pronounced the hemorrhage. The acid evidently destroys the delicate protective tissues and lays the blood vessels bare. It is interesting to notice that solutions that cause no hemorrhage also have but a very faint sour taste, the limit at which the sense of taste can still experience sourness being at about $n/800$. The gills change from their beautiful maroon to a dark brown, and finally to a dirty gray color, owing to coagulation of blood. There can be little doubt that death occurs because of the destruction of the breathing apparatus of the animal. The general appearance of the fish after death is changed but little. Some of the mucus has been removed from the scales; the mouth is open; the color remains about the same.

An inspection of the results shows that a slight difference in the weight of a fish makes but little difference in the time that it is able to survive in the solution; this is also shown by the results of the other tables given below. It is, of course, not to be expected that two fishes of the same species will have exactly the same vitality or resisting power simply because they happen to be of the same length and weight; individuality does come in as a factor in nearly all biological specimens to a certain extent.

The results in Table I. indicate that HCl and HNO_3 have nearly the same destructive effect, the toxic action apparently being a little stronger in the case of the former acid. Sulphuric acid is a little less virulent in its action than the other two acids. This appears even in the *n*/1500 solution, the weakest one tested. It is well to bear in mind that the toxic action of these acids upon rock-bass is in about the same order as it is upon bacteria and higher plants. The nature of the action of these three acids was, furthermore, alike as far as was ascertained from the behavior of the fishes in the solutions and from the post-mortem examinations. The action of the acids must therefore be ascribed to that which they have in common, namely their replaceable hydrogen. As far as the results in Table I. are concerned, it may of course be held with propriety that they harmonize with the theory of electrolytic dissociation, namely, that it is the hydrogen ions that kill the fish. The character of these particular results would hardly warrant an attempt to make a sharp quantitative comparison between the toxic effect of these acids and their degree of hydrogen dissociation. Unfortunately, a number of solutions of acid sodium salts have not yet been tested with fishes, as they have with plants[1] and by means of the sense of taste.[2] It is contemplated to make such tests when it is again possible to obtain the fishes necessary for the work. It is extremely likely that such tests will show (as they have done in the case of plants and taste) that the assumption that the observed toxic effect is caused by so-called hydrogen ions is not tenable.

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[1] Kahlenberg and Austin. Jour. Phys. Chem. 4, 553 (1900).

[2] Kahlenberg. Ibid. 4, 33, 533 (1900).

Table II. gives the results obtained with shiners. It will be observed that hydrochloric, nitric and sulphuric acids were tested with this species, and that in addition, caustic potash, common salt, and the nitrate and sulphate of silver were used.

TABLE II

Shiner (*n.megalop rafinesque*)

Length	Weight	Solution	Time required to produce death
51 mm	1.52 gram	*n*/100 HCl	20 sec
38 "	1.10 "	*n*/100 HNO_3	15 "
32 "	0.50 "	*n*/100 H_2SO_4	20 "
51 "	1.95 "	*n*/250 HCl	45 "
51 "	1.95 "	" "	45 "
64 "	2.35 "	" "	1 min 15 sec
Aver. 55 "	2.08 "		55 "
38 "	1.55 "	*n*/250 HNO_3	1 " 30 "
51 "	1.55 "	" "	1 " 20 "
45 "	1.15 "	" "	1 " 20 "
Aver. 33 "	1.38 "		1 " 23 "
38 "	0.85 "	*n*/250 H_2SO_4	2 "
38 "	1.00 "	" "	2 " 15
51 "	0.95 "	" "	2 " 10 "
Aver. 42 "	0.93 "		2 " 8 "
38 "	0.75 "	*n*/500 HCl	3 "
38 "	0.70 "	" "	2 "
38 "	0.70 "	" "	2 "
Aver. 38 "	0.72 "		2 " 20 "
38 "	0.75 "	*n*/500 HNO_3	2 "
38 "	0.85 "	" "	2 " 15 "
38 "	1.05 "	" "	3 " 5 "
Aver. 38 "	0.88 "		2 " 26 "

Length	Weight	Solution	Time required to produce death
45 mm	0.65 gram	*n*/500 H_2SO_4	3 min
38 "	0.95 "	" "	4 " 30 sec
38 "	1.15 "	" "	4 " 45 "
Aver. 40 "	0.92 "		4 " 5 "
38 "	0.95 "	*n*/1000 HCl	5 "
38 "	0.95 "	" "	4 "
64 "	2.65 "	" "	4 "
Aver. 47 "	1.30 "		4 " 40 "
51 "	1.45 "	*n*/1000 HNO_3	5 "
51 "	1.25 "	" "	4 "
51 "	1.35 "	" "	4 "
Aver. 51 "	1.35 "		4 " 20 "
38 "	0.90 "	*n*/1000 H_2SO_4	6 "
38 "	1.05 "	" "	6 "
45 "	1.15 "	" "	6 " 30 "
Aver. 40 "	1.03 "		6 " 10 "
76 "	3.25 "	*n*/2000 HNO_3	27 "
38 "	1.05 "	distilled water	6 hrs 10 min
38 "	1.75 "	*n*/10 KOH	25 sec
51 "	2.10 "	" "	35 "
51 "	2.05 "	" "	30 "
Aver. 47 "	1.96 "		30 "
51 "	2.15 "	*n*/100 KOH	1 min 10 sec
76 "	2.95 "	" "	1 " 25 "
38 "	1.75 "	" "	1 " 16 "
Aver. 55 "	2.28 "		1 " 16 "
38 "	1.65 "	*n*/500 KOH	1 " 40 "
51 "	2.15 "	" "	1 " 45 "
76 "	3.25 "	" "	1 " 42 "
Aver. 55 "	2.31 "		1 " 42 "

Length	Weight	Solution	Time required to produce death
51 mm	2.05 gram	*n*/1000 KOH	2 min 10 sec
64 "	2.55 "	" "	2 " 30 "
51 "	1.95 "	" "	2 " 15 "
Aver. 55 "	2.18 "		2 " 18 "
38 "	1.45 "	*n*/2000 KOH	4 " 30 "
51 "	1.85 "	*n*/1 NaCl	1 " 10 "
38 "	1.35 "	" "	1 " 25 "
38 "	1.45 "	" "	1 " 25 "
Aver. 42 "	1.55 "		1 " 20 "
38 "	1.65 "	*n*/2 NaCl	3 " 40 "
51 "	2.10 "	" "	4 "
38 "	1.55 "	" "	3 " 45 "
Aver. 42 "	1.76 "		3 " 50 "
76 "	3.05 "	*n*/4 NaCl	40 "
64 "	2.45 "	" "	35 "
Aver. 70 "	2.75 "		37 " 30 "
25 "	0.60 "	*n*/10000 $AgNO_3$	2 " 50 "
38 "	1.45 "	" "	2 " 45 "
25 "	0.70 "	" "	2 " 50 "
Aver. 29 "	0.92 "		2 " 47 "
64 "	2.55 "	*n*/10000 Ag_2SO_4	2 " 55 "
32 "	1.25 "	" "	2 " 45 "
32 "	1.15 "	" "	2 " 50 "
Aver. 53 "	1.65 "		2 " 50 "
76 "	2.95 "	*n*/20000 $AgNO_3$	4 " 50 "
38 "	1.45 "	" "	4 " 25 "
38 "	1.75 "	" "	4 " 50 "
Aver. 51 "	2.05 "		4 41

Length	Weight	Solution	Time required to produce death
38 mm	1.55 gram	*n*/20000 Ag_2SO_4	4 min 50 sec
38 "	1.60 "	" "	4 " 25 "
38 "	1.45 "	" "	5 " 25 "
Aver. 38 "	1.53 "		4 " 53 "
38 "	1.70 "	*n*/50000 $AgNO_3$	5 " 20 "
38 "	1.75 "	" "	5 " 20 "
38 "	1.65 "	" "	6 " 30 "
Aver. 38 "	1.70 "		5 " 43 "
32 "	1.15 "	*n*/50000 Ag_2SO_4	5 " 15 "
51 "	2.10 "	" "	5 " 45 "
51 "	2.20 "	" "	5 " 45 "
Aver. 44 "	1.81 "		5 " 35 "
38 "	1.65 "	*n*/100000 $AgNO_3$	8 " 30 "
51 "	2.05 "	" "	9 " 20 "
51 "	2.10 "	" "	9 " 5 "
Aver. 47 "	1.93 "		8 " 58 "
51 "	1.95 "	*n*/100000 Ag_2SO_4	9 " 25 "
38 "	1.55 "	" "	8 " 45 "
64 "	2.85 "	" "	9 " 25 "
Aver. 51 "	2.11 "		9 " 11 "

A comparison of the results of Table II. with the corresponding ones of Table I. shows that shiners succumb much more readily to the action of acid solutions than do rock-bass. It is well to note in this connection that both species live about the same length of time in distilled water — see Tables I. and II. — as do also brook-trout and perch — see Tables II. and IV. The shiner is a much softer fish than the bass. The membranes of the former are much more delicate and more readily attacked by acids, which is evident from the more profuse hemorrhage from the gills in corresponding solutions.

Table II. shows that in *n*/100 solutions, death occurred five seconds sooner in HNO_3 than in HCl and H_2SO_4, the time being twenty seconds for each of the latter acids. It will be observed, however, that the specimen placed in HNO_3 was only one-third as heavy as that introduced into HCl. More tests with *n*/100 acids were not made because the number of fishes at hand was limited, and because death occurred so quickly as to make errors in estimating the time relatively great. The results in the case of the solutions weaker than *n*/100 are much more reliable. It will be noted that in *n*/250 solution of HNO_3, shiner survives for 83 seconds, while in *n*/250 HCl death occurs after 55 seconds, and this in spite of the fact that the specimens in HNO_3 were not so large as those placed in the HCl. Again, in *n*/250 H_2SO_4 shiner survives for 128 seconds; to be sure the specimens used in this acid were somewhat lighter and consequently probably somewhat less resistant than those used in HCl and HNO_3. In *n*/500 solutions HCl and HNO_3 show about the same toxic power, the time being 140 and 146 seconds respectively; *n*/500 H_2SO_4, however, permits the fish to live for 245 seconds. In the *n*/1000 solutions HCl and HNO_3 again show the same toxic action, while H_2SO_4 still lags behind, the time for the latter being 370 seconds, while for the former two acids it is 280 and 260 seconds, respectively. Here again, then, as in the case of rock-bass, HCl and HNO_3 exert approximately the same toxic effect; but H_2SO_4 is relatively much weaker in its action than in the previous case. Indeed the action of H_2SO_4 is so weak as compared with that of HCl and HNO_3, that the assumption that the effect is due to hydrogen ions cannot be held here, for in dilute solutions like *n*/1000 HCl and HNO_3 are practically completely dissociated (if the theory of electrolytic dissociation be assumed) and the same is almost true of H_2SO_4—compare the results of Kohlrausch's conductivity measurements.[1]

It will be observed that a *n*/100 KOH solution is less destructive than a *n*/100 of the strong mineral acids, but a *n*/500 KOH solution is much more toxic than *n*/500 acid, the fish sur-

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[1] See Ostwald. Lehrbuch d. Allgem. Chemie, II,, 2te Auflage.

viving only 76 seconds in the former, but 140 seconds in the latter. In the *n*/1000 KOH again, the specimens survived but 138 seconds, while in the equivalent solution of HCl they live double that length of time. On the basis of the dissociation theory the action of KOH must be ascribed to the OH ions. The effect that the K ions would have at these dilutions is exceedingly slight, as any one may easily assure himself by placing a fish in a KCl solution of equivalent strength. Again, KOH solutions must be assumed to be fully as highly dissociated as HCl solutions of equivalent strength. It is, therefore, difficult to explain, on the basis of the dissociation theory, why KOH solutions change their toxicity so slightly on dilution as compared with equivalent HCl solutions. Death is no doubt caused by the caustic action of the potash on the membranes of the fish, especially on the membranes of the gills. Hemorrhages occurred in the *n*/10 and *n*/100 solutions, the blood being rapidly coagulated in thick clots. The fish acquired a glossy appearance, simulating in some cases a metallic luster. A fluid of the consistency of glycerine dropped from the dead fish when lifted from the solution. The eyes seemed not affected. The mouth was partly open; the gill chambers were relaxed; and the gills were strongly attacked. Bleeding occurred in *n*/500 and *n*/1000 solutions; it was slight, however, and the blood was soon coagulated.

In a *n*/10 NaCl solution, a shiner survives for several hours. It will be seen from the the table that *n*/1, *n*/2, and *n*/4 solutions were used. A *n*/1 solution of NaCl kills the shiner in about the same time that a *n*/250 solution of HNO_3 does. A *n*/2 solution of NaCl is, however, considerably less toxic than a *n*/500 HNO_3 solution, while *n*/4 NaCl is less harmful than *n*/2000 HNO_3. Shiners killed in NaCl solutions remain normal in appearance. Hemorrhages do not occur; the gills retain their normal appearance; the mouth is closed, but not tightly.

The tremendous toxic power of the solutions of the nitrate and sulphate of silver as compared with the other solutions tested is at once evident from the table. It further appears that the sulphate and nitrate of silver have about the same toxic action;

that is, of course, readily ascribed to that which they have in common, namely, their silver content. In terms of the dissociation theory it is the Ag ion that here exerts the toxic effect, since these salts are both practically completely dissociated at these high dilutions (see table) and since the anions are practically harmless at such high dilutions. Fishes killed in these silver solutions assumed a pinkish hue. The mouth was closed. Bleeding did not occur. The gill chambers were tightly closed and the gills were corroded, being of a dirty gray appearance. In solutions stronger than *n*/1000 the specimens were killed very quickly, so that no very accurate measurements of the time that they survive could be made.

Table III. now follows, giving the results obtained with brook-trout. It will be observed that a larger variety of solutions was tested with this species.

TABLE III

Brook-trout (*salvelinus fontinalis*)

Length	Weight	Solution	Time required to produce death
51 mm	2.35 gram	*n*/100 HCl	55 sec
76 "	2.30 "	*n*/1000 HCl	8 min
64 "	2.85 "	distilled water	7 hrs 20 min
89 "	4.10 "	*n*/50 $CH_3.CO.OH$	3 min 25 sec
38 "	1.90 "	" "	3 " 25 "
Aver. 64 "	3.00 "		3 " 25 "
38 "	1.85 "	*n*/100 $CH_3.CO.OH$	12 " 35 "
38 "	1.75 "	" "	11 " 46 "
Aver. 38 "	1.80 "		12 " 10 "
51 "	2.30 "	*n*/1000 $CH_3.CO.OH$	36 "
64 "	2.75 "	*n*/10 HF	40 "
76 "	3.12 "	" "	40 "
Aver. 70 "	2.93 "		40 "

Length	Weight	Solution	Time required to produce death
76 mm	3.26 gram	*n*/100 HF	4 min 15 se
64 "	2.84 "	" "	3 " 50 "
Aver. 70 "	3.05 "		4 " 2 "
76 "	3.35 "	*n*/500 HF	15 "
89 "	3.86 "	" "	13 " 30 "
Aver. 83 "	3.60 "		14 " 15 "
76 "	3.36 "	*n*/10 Na_2CO_3	7 "
64 "	2.78 "	*n*/100 Na_2CO_3	4 " 15 "
38 "	1.86 "	" "	4 " 10 "
Aver. 51 "	2.32 "		4 " 12 "
89 "	4.35 "	*n*/10 $Na_2B_4O_7$	6 "
76 "	3.11 "	" "	5 "
Aver. 83 "	3.73 "		5 " 30 "
89 "	4.42 "	*n*/1 NaCl	60 "
64 "	2.86 "	" "	55 "
Aver. 71 "	3.64 "		57 "
76 "	3.24 "	*n*/2 NaCl	2 " 50 "
64 "	2.90 "	" "	2 " 45 "
Aver. 70 "	3.07 "		2 " 47 "
102 "	5.24 "	*n*/1 KCl	55 "
64 "	3.00 "	" "	50 "
Aver. 83 "	4.12 "		52 "
64 "	2.94 "	*n*/2 KCl	2 " 10 "
76 "	3.25 "	" "	2 " 5 "
Aver. 70 "	3.09 "		2 " 7 "

Length	Weight	Solution	Time required to produce death
76 mm	3.32 gram	*n*/4 KCl	31 min
64 "	3.25 "	" "	30 "
—	—		—
Aver. 70 "	3.28 "		30 "
89 "	4.25 "	*n*/10 $KClO_3$	27 "
76 "	3.65 "	" "	25 "
—	—		—
Aver. 83 "	3.95 "		26 "
76 "	3.50 "	*n*/100 KCN	1 " 10 sec
64 "	2.80 "	" "	1 " 5 "
—	—		— —
Aver. 70 "	3.10 "		1 7
102 "	5.20 "	*n*/1000 KCN	1 " 45 "
38 "	1.90 "	" "	1 " 25 "
—	—		— —
Aver. 70 "	3.55 "		1 " 32 "
102 "	5.10 "	*n*/10000 KCN	2 " 20 "
76 "	3.45 "	" "	2 " 10 "
—	—		— —
Aver. 89 "	4.27 "		2 " 15 "
89 "	3.85 "	*n*/50000 KCN	4 " 20 "
89 "	3.76 "	" "	4 "
—	—		— —
Aver. 89 "	3.80 "		4 10
89 "	4.30 "	*n*/10 $CaCl_2$	4 " 45 "
64 "	2.85 "	" "	4 " 30 "
—	—		— —
Aver. 76 "	3.57 "		4 " 37 "
64 "	2.94 "	*n*/100 $CaCl_2$	2 hrs 40 min
64 "	2.95 "	*n*/1 $MgSO_4$	23 min
64 "	2.65 "	" "	24 " 30 sec
—	—		— —
Aver. 64 "	2.80 "		23 " 45 "
64 "	2.95 "	*n*/100 $ZnSO_4$	1 hr 20 min

Length	Weight	Solution	Time required to produce death
64 mm	2.88 gram	*n*/100 $CdSO_4$	45 min
76 "	3.50 "	*n*/100 $NiSO_4$	65 "
89 "	4.12 "	" "	75 "
Aver. 87 "	3.81 "		70 "
76 "	3.20 "	*n*/100 $CuSO_4$	27 "
51 "	2.45 "	" "	25 "
Aver. 63 "	2.82 "		26 "
64 "	2.75 "	*n*/500 $CuSO_4$	40 "
76 "	3.30 "	*n*/100 $HgCl_2$	1 " 25 sec
76 "	3.45 "	" "	1 " 40 "
Aver. 76 "	3.37 "		1 " 32 "
102 "	5.50 "	*n*/1000 $HgCl_2$	2 " 50 "
64 "	3.10 "	" "	2 " 45 "
Aver. 83 "	4.30 "		2 " 47 "
64 "	2.95 "	*n*/10000 $HgCl_2$	11 " 15 "
64 "	2.90 "	" "	10 " 30 "
Aver. 64 "	2.92 "		10 " 52 "
89 "	5.20 "	*n*/100000 $HgCl_2$	1 hr 15 min
89 "	4.75 "	*n*/1000 $AgNO_3$	1 min 30 sec
76 "	4.00 "	" "	1 " 35 "
Aver. 83 "	4.37 "		1 " 32 "
76 "	3.65 "	*n*/10000 $AgNO_3$	4 " 30 "
76 "	3.45 "	" "	4 " 30 "
Aver. 76 "	3.55 "		4 " 30 "
76 "	3.30 "	*n*/100000 $AgNO_3$	17 "
115 "	5.50 "	(0.1 g Atropine per l)	7 " 10 "
64 "	3.20 "	(0.1 g Strychnine " l)	7 " 40 "

The results in Table III. show that brook-trout survives longer in *n*/100 and *n*/1000 HCl solutions than does shiner, but not as long as rock-bass. The results obtained with acetic acid are interesting. They show that *n*/50 acetic acid solution is much more toxic in character than *n*/1000 HCl. Inasmuch as the electrical conductivity of solutions of acetic acid shows that *n*/50 acetic acid is electrolytically dissociated to the extent of about 2.9 percent, such a solution contains 1 gram H ions in 1724 liters. Now if toxicity depended solely upon the H ions in the case of this acid, *n*/50 acetic acid should have the same effect as a *n*/1724 HCl solution; as a matter of fact, it has a much greater toxic effect than *n*/1000 HCl, as already stated. The general appearance of fishes killed with acetic acid is about the same as that of those destroyed with mineral acids. No hemorrhage was observed. The gills were dark brown, having a dirty gray fringe.

Fishes killed in HF solutions also had about the same appearance as those that were acted upon by the other acids mentioned. Bleeding did not occur. The results in Table III. show that HF solutions are not nearly as toxic in their action as are solutions of HCl. It was further observed that a fish 64 mm long lived over an hour in *n*/1000 HF solution, which clearly shows the relatively weak poisonous character of this acid. It is of interest to note in this connection that Paul and Krönig[1] found that in stronger solutions HF is a much more powerful disinfectant than the other mineral acids.

Sodium carbonate solutions have about the same destructive power as HF solutions of equivalent strength, which is evident from a comparison of the figures in the last column of Table III. for *n*/100 solutions of these substances. A fish killed in Na_2CO_3 solutions retains in general its normal appearance. The mouth and gill chambers are closed, though not tightly, and the gills have a maroon color. Just before the fish succumbs to the action of the solution the gill chambers and mouth open wider, the gills separate somewhat, and all finally becomes rigid.

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[1] Zeit. phys. Chem. 21, 414 (1896).

The same general behavior was also noted in the case of solutions of $ZnSO_4$, $CdSO_4$, $NiSO_4$, and $CuSO_4$.

From Table III. it appears that a *n*/10 borax solution is somewhat less toxic than *n*/100 Na_2CO_3. The fishes destroyed by the borax solution have about the same appearance as those acted upon by dilute solutions of sodium carbonate.

The data obtained with common salt solutions show that brook-trout are more strongly affected by brine than are shiners. Further, the table shows that KCl solutions are slightly more destructive than are NaCl solutions of equivalent strength. Brook-trout killed in KCl or NaCl solutions retain their normal appearance. The gills are blood red, the mouth and gill chambers are closed; and no hemorrhage occurs.

A *n*/10 $KClO_3$ solution exercises a slightly greater destructive effect than a *n*/4 KCl solution. The post-mortem appearances of the specimens are about the same as those in the case of KCl solutions.

The extremely toxic action of KCN solutions is evident from the table. Here as in the case of the action of KOH on shiners (Table II.), the length of time that the fish survives increases relatively slightly with the dilution of the solution. Table III. shows that *n*/50000 KCN is more destructive than *n*/10000 $AgNO_3$. In the case of *Lupinus albus* it was found that $AgNO_3$ is much more poisonous than KCN. Brook-trout killed in KCN solutions have a normal appearance, except that they acquire a somewhat darker luster.

Calcium chloride solutions are more harmful than potassium chloride solutions, as is evident from Table III. The general post-mortem appearances of the specimens are the same as those of the KCl solutions, except that the gills have slightly gray edges. In *n*/1 $CaCl_2$ solutions, brook-trout die in from 15 to 45 seconds.

According to Table III., it takes over 23 minutes for a brook-trout to succumb in a *n*/1 $MgSO_4$ solution, from which fact the relatively slight destructive action of this salt is evident. The post-mortem appearances are nearly the same as in the case of NaCl.

Zinc sulphate solutions are not very toxic, as is evident from the fact that a trout lived for over an hour in a a *n*/100 solution. The mouth of the dead fish was wide open; the gill chambers were relaxed; the body was rather limp and had more of a metallic luster; the gills were of a grayish color. The table further indicates that $CdSO_4$ is more poisonous than $NiSO_4$, and that $CuSO_4$ is more powerful in its destructive effects than either of these. A trout killed in $CdSO_4$ solution had purplish gill chambers; its mouth was wide open; its gills were grayish; its body was flexible and had a somewhat metallic luster. Trout that succumbed in $NiSO_4$ solution had maroon gills, partly opened mouths, relaxed gill chambers. Their bodies became darker after a time. Specimens killed by $CuSO_4$ solutions had wide open mouths and gills with a slightly bluish tinge. Their bodies also became darker after a time as in the case of the victims of the $NiSO_4$ solutions.

Solutions of $AgNO_3$ are more toxic than equivalent solutions of $HgCl_2$. The same was found to be true in the case of *Lupinus albus.* While $HgCl_2$ is less active than $AgNO_3$, it nevertheless is extremely destructive as the results show. Trout killed in $HgCl_2$ solutions acquired a grayish metallic luster and were surrounded by a translucent coating. The mouths and gill chambers were wide open. As in the case of the silver salts, $HgCl_2$ destroys the protective tissues of the gills. Hemorrhage does not result.

To enable those that may desire to do so to make a comparison of the toxic action of the various solutions with the effect of solutions of the alkaloids, two tests were made, one with atropine and the other with strychnine. The strength of the solutions was 0.01 percent in each case. It will be observed that their toxicity is not very different. The trout swam about violently in the solutions, especially in the strychnine solution. After death, the bodies of the fish became rigid and the mouths and gill chambers were wide open. The gills were blood-red. No hemorrhage was observed.

The results of the few experiments that were performed with perch are given in Table IV.

TABLE IV

Perch (*perca flavescens*)

Length	Weight	Solution	Time required to produce death
127 mm	26 grams	*n*/1000 HCl	55 min
" "	27.5 "	*n*/1000 HNO_3	50 "
" "	26 "	*n*/1000 H_2SO_4	1 hr 40 min
" "	32.5 "	*n*/2000 HNO_3	6 " 40 "
" "	32.5 "	distilled water	7 " 40 "

It will be noticed that the perch were much heavier than the specimens previously used and that they survived much longer in the *n*/1000 solutions of the strong mineral acids than did the fish in the other cases. Here, too, HNO_3 and HCl have approximately the same toxic power, while H_2SO_4 is apparently only one-half as effective. According to the explanation that the theory of electrolytic dissociation gives of the poisonous properties of these acids, namely that their effect is due to H ions, H_2SO_4 in *n*/1000 solutions ought to have nearly the same effect as the equivalent solutions of HCl and HNO_3.

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LABORATORY APPARATUS FOR DECOMPOSITION VOLTAGES

BY WILDER D. BANCROFT

Although the importance of decomposition voltages in electrolytic separations is now recognized, there are relatively few laboratories where the matter is taken up experimentally. One reason for this seems to be that the methods hitherto in use involve pieces of apparatus which are often not to be found in analytical laboratories. Such things as tuning-forks, galvanometers, Lippman electrometers and even Clark cells are usually conspicuous by their absence. Another reason is that the fall of potential between the electrodes for a given current density varies with the apparatus used, and measurements of potential differences are comparable only so long as the general dimensions remain unchanged. I have therefore modified Le Blanc's original method slightly, making it somewhat more convenient for student use. The current is read on a mil-ammeter and the potential difference between the electrodes measured with a high resistance voltmeter. The general arrangement is shown in Fig 1. The ammeter is at A, the voltmeter at V, the electrolytic cell at C. There is a contact key in the voltmeter circuit and a switch close to the ammeter. The external current is obtained by tapping in at different points on a large resistance frame connected either with storage cells or with a dy-

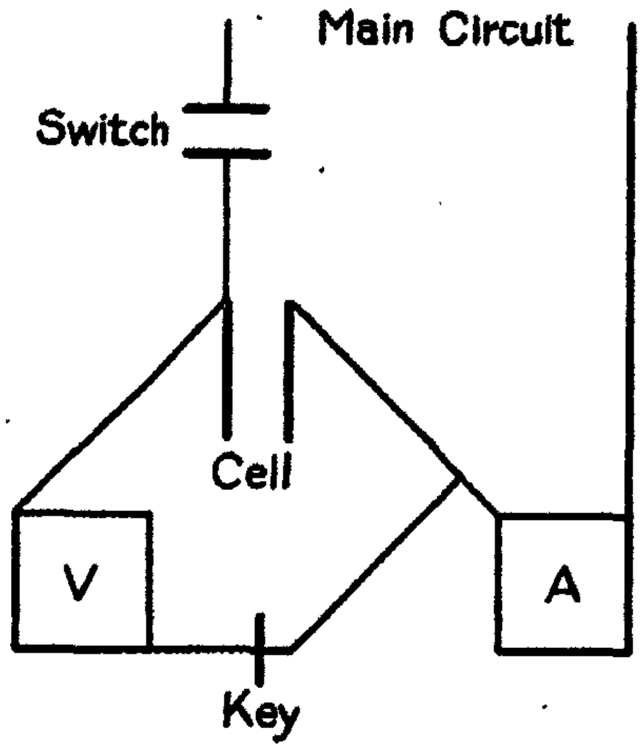

Fig. 1

namo circuit. The ammeter was a Weston instrument with ten scale divisions to a mil-ampere. The voltmeter was also a Weston instrument reading 1.5 volts with one hundred and fifty scale divisions. It had an internal resistance of four thousand ohms and was placed in series with a ten thousand ohm resistance. Under these circumstances, the resistance of the solution can be neglected. The electrodes used have been platinum wires, one millimeter in diameter and just over three centimeters long, making a total surface for each of very closely one square centimeter. In some experiments, the glass tubes holding the wires were passed through the two holes of a rubber stopper and the wires then dipped into a beaker containing the solution to be examined. In other experiments, the solution was placed in a U-tube and the electrodes introduced into the two arms. The use of platinum points instead of wires does not seem to be of any real advantage. The general course of an experiment is shown in Table I., where the data are given in the order in which they were obtained.

TABLE I

M/1 $ZnSO_4$		M/100 $ZnSO_4$		M/1 H_2SO_4	
Volts	Mil-amp.	Volts	Mil-amp.	Volts	Mil-amp.
0.60	0.02	2.22	0.07	0.66	——
1.01	0.02	2.32	0.07	0.97	——
1.50	0.04	2.41	0.07	1.17	0.05
2.07	0.06	2.45	0.07	1.40	0.08
2.16	0.06	2.48	0.07	1.61	0.12
2.24	0.07	2.51	0.15	1.68	0.13
2.49	0.25	2.56	0.26	1.82	0.37
2.22	0.07	2.76	0.80	1.75	0.20
2.29	0.07	Decomposition-point about 2.48–9 V.		1.85	0.50
2.36	0.07			1.89	0.60
2.45	0.17			Decomposition-point about 1.68–170 V.	
2.50	0.37				
2.22	0.06				
2.34	0.07				
2.31	0.06 after 8′				
2.41	0.06 " 8′				
2.59	0.67 " 2′				
Decomposition-point about 2.43 V.					

On increasing the potential difference, the current rises slowly up to a certain point, when it suddenly increases rapidly. These results are more instructive than those of Le Blanc in that they show the 'residual' current as a normal and regular phenomenon below the decomposition-point. On the other hand, the values obtained are potential differences and not electromotive forces of polarization. If the curve after passing the decomposition-point were really a straight line, we could say that the electromotive force of polarization was constant and that the pitch of the curve was a measure of the resistance of the solution. This is not strictly true, though the line is approximately straight. We can get the value of the decomposition voltage by extrapolation to the point of zero current. This comes out about 2.43 volts for M/1 $ZnSO_4$ and about 1.68-1.70 volts for M/1 H_2SO_4, results which agree well with the 2.415 and 1.68 found by Le Blanc. The method is not really satisfactory as a means of determining decomposition voltages accurately for the error is too large. The readings in Table I. are those after the current reading has become approximately constant. This occurs very quickly below the decomposition-point, not so quickly above it. For all practical purposes, one may call the current constant when it varies less than two-hundredths of a mil-ampere in a minute. This leaves room, however, for a certain amount of personal error which may become quite important in extrapolation. For this reason I should say that an accuracy of a couple of hundredths of a volt was as much as could be hoped for. The experiments with M/100 $ZnSO_4$ show a rise in decomposition voltage with dilution; but that is as much as one is justified in saying. When it comes to a second bend in the potential-current curve, due to a second decomposition-point, the electromotive force of polarization is, of course, not at all the same as the measured potential difference.

In actual electrolytic work, however, we do not care about the decomposition voltage because this refers, strictly speaking, to zero current and zero resistance between the electrodes, whereas we actually use finite apparatus and finite currents.

With the apparatus just described, one can take the actual platinum dish and the actual solution which is to be used, determine the curve in a relatively short time and note the actual potential difference under which the second ion discharges, and then one has the data necessary for intelligent work.

It should be noticed that it is not necessary to have either an accurate voltmeter or an accurate ammeter so long as all the measurements are made with the same instruments, and are not intended for publication. If one finds that the second ion discharges under a potential difference of two volts as shown by the voltmeter, one can run up to 1.8 volts by the same instrument during electrolysis, quite regardless of the fact that the absolute voltmeter readings may be entirely wrong.

With this apparatus, it is perfectly easy for the student to work out for himself in a relatively short time the conditions under which two metals can be separated, the effect of adding acid, the existence or non-existence of a complex ion, the conditions for a crystalline deposit, etc., etc. I am convinced that some such drill as this is essential if the student is to have a really intelligent understanding of his work.

One experiment that we have tried is so admirably suited for a lecture experiment that I venture to describe it, even though it may be familiar to many. If five percent of concentrated nitric acid be added to a zinc sulphate solution, hydrogen is evolved at the cathode on electrolysis between platinum electrodes. On increasing the current density sufficiently, zinc precipitates. According to the dissociation theory, this takes place because the concentration of acid in the immediate neighborhood of the cathode has been reduced so much that the decomposition-point for zinc has been reached. If this hypothesis is true, stirring the solution should cause the zinc to dissolve if already precipitated, or should prevent precipitation. Both these phenomena are easily realized. Breaking the circuit also causes almost instantaneous disappearance of the zinc.

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ON A THEOREM OF VAN DER WAALS

BY PAUL SAUREL

Let us consider a chemical system of r phases formed by means of n independent components. Gibbs has shown[1] that when the system is in equilibrium there exists for each phase a relation of the form

$$v_i d\Pi = \eta_i d\mathrm{T} + m_{i1} d\mu_{i1} + m_{i2} d\mu_{i2} + \dots + m_{in} d\mu_{in},$$
$$i = 1, 2, \dots, r, \qquad (1)$$

in which Π and T denote the pressure and the temperature, v_i and η_i denote the volume and the entropy of the unit of mass of the i-th phase, m_{ij} denotes the mass of the j-th component which is contained in the unit of mass of the i-th phase, and μ_{ij} denotes the chemical potential of the j-th component in the i-th phase.

Moreover, when the system is in equilibrium we have the relations

$$\mu_{1j} = \mu_{2j} = \dots = \mu_{rj}, \qquad j = 1, 2, \dots n, \qquad (2)$$

so that in a reversible change we have

$$d\mu_{1j} = d\mu_{2j} = \dots = d\mu_{rj}, \qquad j = 1, 2, \dots n. \qquad (3)$$

Consider now a univariant system, that is to say a system for which $r = n + 1$. We can, in this case, eliminate from the $n + 1$ equations 1, the n $d\mu$'s. The result of the elimination is[2]

$$\begin{vmatrix} v_1, & m_{11}, & m_{12}, & \dots, & m_{1n} \\ v_2, & m_{21}, & m_{22}, & \dots, & m_{2n} \\ \vdots & \vdots & \vdots & & \vdots \\ v_{n+1}, & m_{n+1,1}, & m_{n+1,2}, & \dots, & m_{n+1,n} \end{vmatrix} d\Pi$$

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[1] On the Equilibrium of Heterogeneous Substances, p. 154.

[2] On the Equilibrium of Heterogeneous Substances, p. 154.

$$= \begin{vmatrix} \eta_1, & m_{11}, & m_{12}, & \ldots, & m_{1n} \\ \eta_2, & m_{21}, & m_{22}, & \ldots, & m_{2n} \\ \vdots & \vdots & \vdots & & \vdots \\ \eta_{n+1}, & m_{n+1,1}, & m_{n+1,2}, & \ldots, & m_{n+1,n} \end{vmatrix} d\mathrm{T}. \qquad (4)$$

This equation of Gibbs' will enable us to establish van der Waals' theorem. Let us consider first a two component univariant system; equation 4 then becomes

$$\frac{d\Pi}{d\mathrm{T}} \begin{vmatrix} v_1, & m_{11}, & m_{12} \\ v_2, & m_{21}, & m_{22} \\ v_3, & m_{31}, & m_{32} \end{vmatrix} = \begin{vmatrix} \eta_1, & m_{11}, & m_{12} \\ \eta_2, & m_{21}, & m_{22} \\ \eta_3, & m_{31}, & m_{32} \end{vmatrix}. \qquad (5)$$

If the concentrations of two of the phases, for example the phases 1 and 2, become equal, this equation may be written in the form:

$$\frac{d\Pi}{d\mathrm{T}} \begin{vmatrix} v_1 - v_2, & 0, & 0 \\ v_2, & m_{21}, & m_{22} \\ v_3, & m_{31}, & m_{32} \end{vmatrix} = \begin{vmatrix} \eta_1 - \eta_2, & 0, & 0 \\ \eta_2, & m_{21}, & m_{22} \\ \eta_3, & m_{31}, & m_{32} \end{vmatrix},$$

or, better,

$$(v_1 - v_2)\frac{d\Pi}{d\mathrm{T}} \begin{vmatrix} m_{21}, & m_{22} \\ m_{31}, & m_{32} \end{vmatrix} = (\eta_1 - \eta_2) \begin{vmatrix} m_{21}, & m_{22} \\ m_{31}, & m_{32} \end{vmatrix}. \qquad (6)$$

If the concentrations of the third phase are not equal to those of the first two, the determinant which appears in this equation is not equal to zero and we may write the equation in the form:

$$\frac{d\Pi}{d\mathrm{T}} = \frac{\eta_2 - \eta_1}{v_2 - v_1}. \qquad (7)$$

If the difference $v_2 - v_1$ is very small in comparison with $\eta_2 - \eta_1$, $\frac{d\Pi}{d\mathrm{T}}$ will be very large. In other words, the curve which represents the temperatures and the equilibrium pressures of the univariant system will have a tangent very nearly perpendicular to the axis of temperatures. Thus the temperature passes, in general, through a maximum or a minimum.

This theorem, which is due to van der Waals,[1] has been verified experimentally by Roozeboom.[2] A demonstration of the theorem has been given also by Duhem.[3]

We can go somewhat further. In a univariant system the variable concentrations are functions of the temperature or of the pressure. We may therefore write

$$\frac{dm_{ij}}{d\mathrm{T}} = \frac{dm_{ij}}{d\Pi} \cdot \frac{d\Pi}{d\mathrm{T}} \,. \tag{8}$$

When the concentrations of the phases 1 and 2 become equal, $\frac{d\Pi}{d\mathrm{T}}$ becomes very large; consequently, if

$$\frac{dm_{ij}}{d\Pi} \neq 0, \tag{9}$$

$\frac{dm_{ij}}{d\mathrm{T}}$ will be very large. Thus, when the concentrations of the two phases become equal, the curve which represents the relation between the temperature and a variable concentration m_{ij} will have a tangent almost perpendicular to the axis of temperatures. This theorem which is also due to van der Waals has been experimentally verified by Roozeboom.

The two theorems which we have just established can be extended without difficulty to a univariant system formed by means of more than two components. For, if the concentrations of the phases 1 and 2 become equal, equation 4 can be written in the form

$$(v_1 - v_2)\frac{d\Pi}{d\mathrm{T}} \begin{vmatrix} m_{21}, & m_{22}, & \ldots, & m_{2n} \\ m_{31}, & m_{32}, & \ldots, & m_{3n} \\ \vdots & \vdots & & \vdots \\ m_{n+1,1}, & m_{n+1,2}, & \ldots, & m_{n+1,n} \end{vmatrix}$$

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[1] Roozeboom. Sur les conditions d'équilibre de deux corps dans les trois états, solide, liquide et gazeux, d'après M. v. d. Waals. Recueil des Travaux chimiques des Pays-Bas, 5, 335 (1886). Roozeboom. Zeit. phys. Chem. 2, 463 (1888).

[2] Recueil des Travaux chimiques des Pays-Bas, 4, 356 (1886). Zeit. phys. Chem. 2, 454 (1888).

[3] Dissolutions et Mélanges, deuxième Mémoire: les Propriétés physiques des Dissolutions; Travaux et Mémoires des Facultés de Lille, 3, No. 12, 121, (1893). Traité élémentaire de Mécanique chimique, 3, 279.

$$= (\eta_1 - \eta_2) \begin{vmatrix} m_{21}, & m_{22}, & \dots, & m_{2n} \\ m_{31}, & m_{32}, & \dots, & m_{3n} \\ \vdots & \vdots & & \vdots \\ m_{n+1,1}, & m_{n+1,2}, & \dots, & m_{n+1,n} \end{vmatrix}.$$

If the determinant which appears in this equation is not equal to zero, that is to say if the bivariant system which we obtain by suppressing the phase 1 is not at an indifferent point, the last equation can be put into the form :

$$\frac{d\Pi}{dT} = \frac{\eta_2 - \eta_1}{v_2 - v_1},$$

and we need only repeat the preceding demonstrations to establish van der Waals' theorems in the general case.

NEW BOOKS

Die Continuität des gasförmigen und flüssigen Zustandes. *By J. D. van der Waals. Zweiter Theil: Binäre Gemische. 15 × 22 cm; pp. 192. Leipzig: Johann Ambrosius Barth, 1900. Price: paper, 5; bound, 6 marks.* — In 1899 van der Waals published, in German, a revised edition of his famous treatise on the continuity of the aeriform and liquid states of a single fluid. This is now followed, a year later, by a second volume, on the continuity of the fluid states of two-component systems.

The first fifty pages of this second volume contain a reprint of van der Waals's paper of 1890, "The Molecular Theory of a Body which is Composed of Two Different Substances," which furnished the starting-point for the vigorous researches that have been prosecuted in Holland during the past ten years. The remainder of the book is devoted to a systematic detailed discussion of the theory as it stands at the present moment. This part is stated to be essentially a reproduction of the corresponding portion of van der Waals's lectures on thermodynamics.

The book is a very weighty contribution to the current literature of physical chemistry. For, the investigation of the critical phenomena, and of the thermodynamic properties in general, of two-component fluids; and especially the search for the form of the characteristic equation

$$f(p, v, \theta, x) = 0$$

of these systems; is one of the most important of the problems of physical chemistry that are now being systematically studied. And in this work van der Waals is at the present time unquestionably the leader. His book is hard reading; but no one who undertakes to acquire an acquaintance with the present state of inquiry in this field can dispense with its study.

The volume is dedicated to its author's able coadjutor, Professor Kamerlingh Onnes of Leiden. The translation from the Dutch has been made by J. J. van Laar.

J. E. Trevor

Chemisches Praktikum. *Experimentelle Einführung in preparative und analytische Arbeiten, auf physikalisch-chemischer Grundlage. By R. Abegg and W. Herz. 13 × 20 cm; pp. 114. Göttingen: Vanderhoeck und Ruprecht, 1900. Price: bound, 3.60 marks.* — The experience of the authors — teachers in the Breslau Laboratory — has shown them that the introduction of modern theory into an elementary chemical course is both essential and satisfactory. This book illustrates their methods. The student is first required to study a number of typical reactions, such as the preparation of hydrogen, chlorine, ammonia, etc. Then follow sections on electrolytic dissociation, electro-affinity, conductivity, ion reactions, law of mass action, solubility, hydrolysis, complex ions, and anomalous reactions. The methods of recognition of the various cations and anions are then detailed, and summarized in complete analytical tables.

The paragraphs on hydrolysis, complex ions and anomalous reactions, and the detailed directions for anion detection, are especially to be commended. Among essential points which seem to have been overlooked are discussions of oxidation and reduction reactions, the quantitative relations involved in a study of chemical equations, and the application of the mass-law to cases where the separating phases are gaseous or liquid.

The authors have certainly presented their subject very well; even if the presentation rests mainly on the application of the ion theory. Theirs is one point of view: but qualitative analysis does not allow one to deal solely with dilute solutions under conditions as subject to variation and control as those under which the theory of electrolytic dissociation applies. The book is good; it will grow, and improve in its growth. *H. R. Carveth*

Lehrbuch der Differential- und Integralrechnung, *und der Anfangsgründe der analytischen Geometrie. Mit besonderer Berücksichtigung der Bedürfnisse der Studierenden der Naturwissenschaften. Bearbeitet von H. A. Lorentz. Unter Mitwirkung des Verfassers übersetzt von G. C. Schmidt. 15 × 23 cm; pp. 476. Leipzig: Johann Ambrosius Barth, 1900. Price: paper, 10; bound, 11 marks.*—This interesting book is another of the many recent attempts to provide students of physics, chemistry, or engineering with a short-cut to the mathematical knowledge that is requisite for their work. That there is a real demand for texts of this kind is evidenced by the appearance of such books as the well-known ones of Fuhrmann, Nernst and Schoenflies, Young and Linebarger, Perry, and Appel. It is indeed widely felt that the needs of many students would be best met by a textbook that aims to develop only the mathematical topics that they require to use, and that illustrates these topics by applications drawn from their own special subjects, and not exclusively from geometry and algebra. Lorentz, in common with other teachers of applied mathematics, seems to have had experience with students who have not digested their preliminary mathematical training. In the preface to the original Dutch edition of his book, he complains that the existing textbooks on the calculus are too "mathematical" to be well adapted to the needs of [many] students of the physical sciences. He points out that these students, who are interested primarily in the simpler applications of the subject, can employ their time more profitably than in much of the customary study of the properties of curves and surfaces. So, in the absence of a suitable text, Lorentz undertook to write one.

His book begins with a chapter on algebraic and exponential functions, and logarithms; and then gives an outline treatment of plane trigonometry, analytical geometry, differential and integral calculus, Fourier's series, and differential equations. Everything is made simple and clear, and is enforced by suitable examples. The chapter on Fourier's series is especially lucid. The book is extremely well written, and Professor Schmidt has put it into very readable German. One would be glad to see it appear in English.

A possible objection to a book of this sort, however, no matter how well it may be done, is that interest is lost by divorcing the study of the mathematical methods from that of the subjects in which they are to be used. If the mathematics is to be learned as a tool, let it be learned as it is wanted. This could be well done by means of an outline treatise on mathematical physics, in which the different mathematical topics are introduced as they are required. Two birds would then be killed by the same stone, the interest in the mathematical tool would be sustained, and a valuable association would be formed with each mathematical operation introduced. A large book would not be necessary; for the essential framework of every topic of mathematical physics is a relatively simple matter. Indeed, if desired, the whole thing might perhaps be done in connection with a treatment of mechanics alone, or of mechanics and thermodynamics together. Such a book, if well written, would be far more interesting and instructive than any of the existing makeshifts, even than so good a one as this book by Lorentz.

J. E. Trevor

Scientific Memoirs. *No. 8. The Effects of a Magnetic Field on Radiation. Edited by E. P. Lewis. xvii + 102 pp. No. 9. The Laws of Gravitation. Edited by A. Stanley Mackenzie. viii + 160 pp. No. 10. The Wave Theory of Light. Edited by Henry Crew. xiv + 162 pp. New York: The American Book Company. 13 × 20 cm. Cloth. Price: $0.75, $1.00, and $1.00, respectively.*—Three new volumes of the series of Scientific Memoirs have reached us. The first of them, No. 8 of the series, contains two papers by each of the investigators Faraday, Kerr, and Zeeman, on magneto-optic phenomena, together with biographical sketches of these three men. The papers range in date from 1845 to 1897. A clear and interesting outline of the history of the subject, with regard both to experiment and to theory, is given in the preface by the editor, Professor E. P. Lewis, of the University of California. The volume is completed by an extensive bibliography.

No. 9 of the series, on the Laws of Gravitation, is edited by Professor Mackenzie, of Bryn Mawr College. It contains a history of the subject before the appearance of Newton's Principia; extracts from Newton; Bouguer's *The Figure of the Earth*; the Bertier controversy; the experiments of Maskelyne and of Cavendish; an account of experiments made since Cavendish; a table of results of experiments; biographical sketches of Newton, Bouguer, and Cavendish; and an extensive and carefully compiled bibliography.

The next number, on the Wave Theory of Light, is edited by Professor Crew, of Northwestern University. After a fascinating introductory account of the development of the subject, the volume contains the original texts of work by Huyghens, Thomas Young, Fresnel, and Arago and Fresnel. A compact bibliography is appended.

Each volume is provided with an index.

J. E. Trevor

Ostwald's Klassiker der exakten Wissenschaften.

No. 110. Die Gesetze des chemischen Gleichgewichtes für den verdünnten, gasförmigen oder gelösten Zustand. Von J. H. van 't Hoff. Herausgegeben von Georg Bredig. 106 pp. Price: 1.60 marks.

No. 114. Briefe ueber thierische Elektricität. Von Alessandro Volta. Herausgegeben von A. J. von Oettingen. 162 pp. Price: 2.50 marks.

No. 115. Versuch über die Hygrometrie. I. Heft. Von H. B. de Saussure. Herausgegeben von A. J. Oettingen. 168 pp. Price: 2.60 marks.

No. 118. Untersuchungen unter den Galvanismus. Von Alessandro Volta. Herausgegeben von A. J. von Oettingen. 99 pp. Price: 1.60 marks.

Leipzig: Wilhelm Engelmann, 1900.

These recent issues of Ostwald's *Klassiker* maintain the interest and value of this notable series. The one on the theory of dilute solutions contains the three papers published together by van 't Hoff in the Transactions of the Swedish Academy in 1886. The two on galvanism contain Volta's publications between 1792 and 1800. The remaining number is a first part of Saussure's Experiments on Hygrometry. The volumes contain, as usual, biographical sketches of the authors, and careful annotations of the texts. *J. E. Trevor*

An Elementary Treatise on Dynamics, containing Applications to Thermodynamics. *Third edition, revised and enlarged. By Benjamin Williamson and Francis A. Tarleton. 13 × 19 cm; pp. xvi + 560. New York: Longmans, Green and Co., 1900.* — In this new edition of a well-known treatise on dynamics, the entire work has been revised. Portions of the subject have been expanded, especially that on generalized coordinates in connection with the methods of Lagrange and of Hamilton; and the article on the motion of a rigid body under the action of no forces has been to a great extent rewritten.

But the work is of interest to the readers of this Journal chiefly on account of its neat and compact exposition of the theory of thermodynamics. This treatment has the distinguishing qualities of Williamson's style: clearness, terseness, and a development in short sections that follow one another according to a good arrangement. No very important omissions are noticeable. Many interesting details are presented in the form of carefully annotated problems; and many problems are added for practice. A careful reading of the whole would give a student an excellent start toward gaining a grasp of this important and most interesting subject. *J. E. Trevor*

The Principles of Mechanics. *An Elementary Exposition for Students of Physics. By Frederick Slate. Part I. 13 × 19 cm; pp. x + 299. New York: The Macmillan Company, 1900. Price: cloth, $1.90.* — This work is an introductory treatise on mechanics, for college students. The author seeks to aid students in getting at the heart of this subject, by developing it as a branch of physics, and not as a branch of applied mathematics, and by giving a painstaking study of the elements before proceeding to the more comprehensive generalizations. His guiding idea appears to be that of Kirchhoff, that mechanics is a description in simple form of the motions of bodies. The notation of the calculus is freely used.

The present volume treats uniplanar motion only; the unconstrained motion of a rigid body, and the generalized principles of mechanics, being reserved for a second volume. One-half of the present book is devoted continuously to building up a knowledge of the necessary conceptions, and unfolding their content. The remainder is concerned with auxiliary discussions of center of mass, moment of inertia, and dimensions; and to the usual range of applications. The book is carefully written, and will repay careful study.

J. E. Trevor

An Introduction to Modern Scientific Chemistry. *By Dr. Lassar-Cohn. Translated from the second German edition by M. M. Pattison Muir. 12 × 17 cm; pp. viii + 348. New York: D. Van Nostrand Company, 1901. Price: bound, $2.00.* — This volume is an English version of Lassar-Cohn's *Einführung in die Chemie*, which was noticed in this Journal, 4, 622. It is a clearly written embodiment of a course of university extension lectures. The treatment begins with water and hydrogen; passes through the halogens to the laws of combination and the atomic and molecular hypotheses; continues with a systematic treatment of the non-metals; and concludes with a half-dozen metals and the periodic law. The book is an attractive one, and has been well translated. The very poor illustrations of the original have been retained.

J. E. Trevor

Annuaire pour l'An 1901. *Publié par le Bureau des Longitudes. 10 × 15 cm. Paris: Gauthier-Villars. Price: paper, 1.50 francs.* — The familiar *Annuaire*, with its extensive collection of tabulated astronomical, physical, chemical, etc., data, appears promptly, as usual, for the current year. The special articles are on electric transportation of force, by Cornu; the revision of the Peruvian meridian arc, by Poincaré; and several reports of conferences, addresses, etc. The numbering of the hours of the day from 0 to 24 is retained.

J. E. Trevor

Ueber die Entwickelung der exakten Naturwissenschaften im 19 Jahrhundert, *und die Betheiligung der deutschen Gelehrten an dieser Entwickelung. By J. H. van 't Hoff. 15 × 23 cm; pp. 18. Hamburg: Leopold Voss, 1900. Price: paper, 80 pf.* — An address made before the *Naturforscherversammlung*, at Aachen. It is an entertaining brief review of the progress made in the study of mathematics, physics, and chemistry, during the nineteenth century.

J. E. Trevor

REVIEWS

The object of this department of the Journal is to issue, as promptly as possible, critical digests of all Journal articles that bear upon any phase of Physical Chemistry.

General

The atomic weight of nitrogen. *J. Dean. Jour. Chem. Soc.* 77, *117* (*1900*).—The ratio of silver to cyanogen in silver cyanide is found to be 107.93 : 26.032. Taking 12.001 for carbon, this would give 14.031 for nitrogen. The author titrated excess of silver with standard bromide solution instead of taking the mean of the end-points reached from the two opposite sides.

W. D. B.

On a new radio-active element, actinium. *A. Debierne. Comptes rendus,* 130, *906* (*1900*).—The recognizable base is thorium, but the author hopes to be able to show that thorium is really not radio-active, and that it is contaminated by the new element, actinium. *W. D. B.*

On the heat of combustion of some very volatile liquids. *M. Berthelot and Delépine. Comptes rendus,* 130, *1045* (*1900*).—Thermochemical data.

The heats of combustion and of formation of compounds containing iodine. *M. Berthelot. Comptes rendus,* 130, *1094* (*1900*).—Thermochemical data.

Action of hydrogen peroxide on barium hydroxide. *de Forcrand. Comptes rendus,* 130, *716*, *778*, *834* (*1900*).—Thermochemical data.

Heat of formation of anhydrous and hydrated strontium peroxide. *de Forcrand. Comptes rendus,* 130, *1017* (*1900*).—Thermochemical data.

Heat of neutralization of hydrogen peroxide by lime. *de Forcrand. Comptes rendus,* 130, *1250*, *1308* (*1900*).—Thermochemical data.

A quartz thermometer for high temperatures. *A. Dufour. Comptes rendus,* 130, *775* (*1900*).—The author has made a quartz thermometer with tin as registering liquid. *W. D. B.*

A thermocalorimeter. *G. Massol. Comptes rendus,* 130, *1126* (*1900*).—The author has modified the Regnault instrument, substituting sulphuric acid for alcohol, and introducing a reservoir at the top similar to that in the Walferdin and Beckmann thermometers. *W. D. B.*

One-Component Systems

The maximum pressure of naphthalene vapor. *R. W. Allen. Jour. Chem.*

Soc. 77, *400* (*1900*). — The vapor-pressure curve for naphthalene has been determined by observing the loss of weight when measured, volumes of air were passed over solid naphthalene, and these results were afterwards checked by direct barometric measurements. *W. D. B.*

The maximum pressure of camphor vapor. *R. W. Allen. Jour. Chem. Soc.* 77, *413* (*1900*). — Vapor-pressure determinations for camphor by evaporation and by barometric measurements (Cf. preceding review). *W. D. B.*

On the law of Cailletet and Mathias and the critical density. *S. Young. Phil. Mag.* [*5*] 50, *291* (*1900*). — From an examination of the data for thirty substances, the author finds that the law of Cailletet and Mathias appears to be true when the ratio of the actual to the theoretical density at the critical point has the value 3.77. The density is expressed as the mean of the densities of liquid and saturated vapor.

The curvature of the "diameter" for stable substances is generally so slight that the critical density may be calculated from the mean densities of liquid and saturated vapor at temperatures from about the boiling-point to within a few degrees of the critical point by the expression

$$D_t = D_0 + at.$$

H. T. B.

On the minimum volume of liquids. *D. Berthelot. Comptes rendus*, 130, *713* (*1900*). — The author points out that the safest way of obtaining the covolume is by an extrapolation based on Cailletet and Mathias's law of the rectilinear diameter. The values thus obtained for twenty substances are given in tabular form. *W. D. B.*

Specific gravities of the halogens at their boiling-points, and of oxygen and nitrogen. *J. Dingman and W. Ramsay. Jour. Chem. Soc.* 77, *1228* (*1900*). — The specific gravity of iodine is 3.706 at 184.35°; of chlorine 1.56 at a temperature below its boiling-point; while the density of fluorine is estimated indirectly as 1.108 at its boiling-point. The value for nitrogen appears to be 0.7914 at 195.5°. This gives an atomic volume of 19.52, corresponding to the value 17.4 for pentavalent nitrogen in combination. *W. D. B.*

The preparation and properties of solid ammonium cyanate. *J. Walker and J. K. Wood. Jour. Chem. Soc.* 77, *21* (*1900*). — Solid ammonium cyanate can be prepared by leading ammonia and cyanic acid into ether cooled to −14°, or by mixing the cold gases in a current of hydrogen. The instable melting-point is somewhere about 80°, the mass then solidifying to urea and melting at 130°. The heat of reaction is 49 K for the solids and about 75 K for the change in aqueous solution. *W. D. B.*

Vapor-pressures, specific volumes, and critical constants of di-isopropyl and di-isobutyl. *S. Young and E. C. Forley. Jour. Chem. Soc.* 77, *1126* (*1900*). — The boiling-point of di-isopropyl is 58.08°; the specific gravity is 0.67948 at 0°-4°; the critical temperature is 227.4°. The corresponding values for di-isobutyl are 109.2°, 0.71021, 276.8°. *W. D. B.*

Vapor-pressures, specific volumes, and critical constants of normal octane. *S. Young. Jour. Chem. Soc.* 77, *1145* (*1900*). — The boiling-point is 125.8° and the specific gravity is 0.71848 at 0°–4°. The critical temperature is 296.2°, pressure 18730 mm, and density 0.2327. *W. D. B.*

Vapor-density of dried mercurous chloride. *H. B. Baker. Jour. Chem. Soc.* 77, *646* (*1900*). — Carefully dried mercurous chloride gives a vapor-density corresponding to the formula Hg_2Cl_2 and the vapor does not amalgamate gold. *W. D. B.*

Theory of the constant-volume gas-thermometer. *J. Rose-Innes. Phil. Mag.* [*5*] 50, *251* (*1900*). — The author points out that the weak point of the method adopted by Lord Kelvin in the integration of the fundamental equation for the constant-volume gas-thermometer to infinite values of v and t along the isopiestic is that it is necessary to assume that an empirical relation, which represents the Joule-Thomson effect for a small range, necessarily holds at any temperature. The author shows that it is possible to obviate this extrapolation by transforming the differential equation before integration. Applying the formula so obtained to calculate the absolute value of the freezing-point of water, the result was found to be in close agreement with the value obtained by Lord Kelvin by the constant-pressure gas-thermometer. The characteristic equation of a nearly perfect gas is treated by making further transformations from the author's differential equation. The paper concludes by discussing Mayer's hypothesis and the difference in the methods adopted by Joule and Lord Kelvin for testing it. *H. T. B.*

Notes on gas-thermometry. *P. Chappuis. Phil. Mag.* [*5*] 50, *433* (*1900*). — Owing to the necessity of using nitrogen for high temperature work, the author gives the result of careful measurements on the coefficient of dilatation of nitrogen. The maximum divergence from the normal hydrogen scale between 0° and 100° is 0.01° and 40° C. The coefficient reaches a minimum value at 80° C and then increases.

A determination of the sulphur boiling-point by the constant-volume nitrogen thermometer shows it to be 445.2° C instead of the value obtained by Callendar and Griffiths, i. e., 444.53° C. This the author attributes to various causes enumerated in the paper at some length. The consequences of so radical a change in the sulphur point if found to be correct would considerably influence the values of air-temperature as measured with platinum electrical thermometers.

The value of δ in the different formulas, equal to 1.50 for a standard sample of wire, calibrated according to the Callendar-Griffiths method, would require to be changed to 1.538 on the assumption of the author's value of the S. B. P. *H. T. B.*

Preparation of pure hydrobromic acid. *A. Scott. Jour. Chem. Soc.* 77, *648* (*1900*). — Since phosphorus almost invariably contains arsenic, the author advocates the sulphur dioxide method. *W. D. B.*

Two-Component Systems

The allotropic changes of alloys of iron and nickel. *L. Dumas. Comptes rendus,* 130, *1311* (*1900*). — Up to 25.84 percent of nickel, the points of irreversible transformation are above 0° ; starting from 27.12 percent of nickel, the transformation point for cooling lies below 0°, the value for 29.94 percent nickel lying below —78°. At 25.84 percent nickel, there occur points both of reversible and of irreversible transformation, the temperature at which the reversible change takes place rising with increasing percentage of nickel. *W. D. B.*

Solubility of benzophenone. *E. Derrien. Comptes rendus*, 130, *721* (*1900*). — Isolated solubility determinations in about twenty solvents. *W. D. B.*

On the liquefaction of mixtures of carbon dioxide and sulphur dioxide. *F. Caubet. Comptes rendus*, 130, *828* (*1900*). — The author has determined the boiling-point and dew-point curves for a number of mixtures of carbon dioxide and sulphur dioxide. All mixtures show retrograde condensation.

W. D. B.

Poly-Component Systems

Action of hydrogen on antimony sulphide. *H. Pélabon. Comptes rendus*, 130, *911* (*1900*). — The author has studied the reaction $Sb_2S_3 + 3H_2 \rightleftarrows 2Sb + 3H_2S$. At 440° both the antimony and the sulphide are solid and the ratio of the two gases is found to be independent of the absolute amount of the two solid phases. At 610° the sulphide of antimony is liquid and dissolves the metallic antimony. The ratio of the gases varies with the amount of antimony until so much is added that antimony separates as solid phase. *W. D. B.*

Solubility of a mixture of salts having a common ion. *C. Touren. Comptes rendus*, 130, *908*, *1252* (*1900*). — The author has determined isotherms for potassium nitrate and chloride, for potassium nitrate and bromide, and for potassium chloride and bromide in aqueous solutions. Equivalent quantities of potassium chloride and of potassium bromide have exactly the same effect on the solubility of the potassium nitrate. Potassium bromide and chloride give one continuous curve instead of two intersecting curves. The author is perfectly clear as to the theoretical significance of this. *W. D. B.*

Note on partially miscible aqueous inorganic solutions. *J. S. Newth. Jour. Chem. Soc.* 77, *775* (*1900.*) — Saturated potassium carbonate and strong aqueous ammonia form two liquid layers, and the temperatures at which these phases become identical vary with the amount of water present. *W. D. B.*

Chemical reactions produced in a solution ; vapor-pressure of the solvent. *A. Ponsot. Comptes rendus*, 130, *782* (*1900*). — A cyclical proof to show that, at constant pressure and temperature, a reversible reaction always increases the vapor-pressure of the solvent, provided the solvent takes no part in the reaction. This is interesting, of course, but one cannot help wondering whether it would hold true for the change of paraldehyde into acetaldehyde, for instance, or for the reaction between alcohol and acetic acid in benzene solution. It is very easy to overlook things even in the simplest thermodynamic proof. *W. D. B.*

Limited chemical reactions in homogeneous systems. *A. Ponsot. Comptes rendus*, 130, *829* (*1900*). — The author shows that the equilibrium in a homogeneous gaseous mixture is independent of the nature and concentration of substances not entering into the reaction. He also claims that, at equilibrium, the volume is a minimum for constant pressure and temperature, which is certainly not true. The author further deduces Valson's law of the moduli, ostensibly without use of the electrolytic dissociation hypothesis, though, as a matter of fact, he postulates the acid and basic radicals as independent constituents.

W. D. B.

The combination of sulphur dioxide and oxygen. *E. J. Russell and N. Smith. Jour. Chem. Soc. 77, 340 (1900).*—The following conclusions were drawn:

1. When a mixture of sulphur dioxide and oxygen is allowed to stand over certain metallic oxides at the ordinary temperature, combination takes place to a certain extent between the two gases, owing to the "surface action" exerted by the metallic oxide.

2. With the same oxide, the amount of the sulphur trioxide formed depends on the extent of the surface of the oxide.

3. With the same oxide, this amount depends also on the state of the surface. It appears to be least with freshly precipitated oxides which are not yet dried, and to increase if the oxide has been moderately heated or kept for a long time so as to become dry.

4. The amount appears to be absolutely dependent on a simultaneous combination of the oxide with the sulphur dioxide, and in fact seems to proceed concurrently with this. ...

5. The most striking instance of this surface action is afforded by manganese peroxide, some twenty percent of the sulphur dioxide being converted into sulphur trioxide. If the materials are carefully dried by means of phosphorus pentoxide, no combination takes place as, even after standing several days, no change in volume can be detected. By drying the mixture, combination of manganese dioxide and sulfur dioxide is thus prevented, as is also the surface action of the oxide which brings about the union of sulphur dioxide and oxygen.

6. When sulphur dioxide and oxygen are passed over heated platinized pumice, combination diminishes as the materials are more completely dried, and can be made very small. *W. D. B.*

Influence of the nascent state on the combination of dry carbon monoxide and oxygen. *E. J. Russell. Jour. Chem. Soc. 77, 361 (1900).*—Pure carbonyl sulphide will not explode if sparked with oxygen. With a small amount of impurity, some carbonyl sulphide is decomposed into carbon monoxide and sulphur, without these substances reacting with the excess of oxygen. The same thing is true of mixtures of carbonyl sulphide and nitrous oxide. The state of affairs following on a violent reaction—such as explosion of carbon disulphide or chlorine monoxide—has a considerable influence in bringing about a combination of carbon monoxide and oxygen, but there is no satisfactory proof that nascent carbon monoxide differs appreciably from the ordinary gas.

W. D. B.

The decomposition of chlorates. *W. H. Sodeau. Jour. Chem. Soc. 77, 137, 717 (1900).*—The author's experiments are explained by him on the assumption of two independent reactions, the evolution of oxygen, and the evolution chlorine and oxygen. With potassium chlorate there are only traces of

chlorine set free; in the slow decomposition of barium chlorate, the amount of free chlorine is less than one-thousandth of the chlorine in the salt. With lead chlorate the decomposition-products are lead chloride, lead peroxide, oxygen and chlorine; about eighty-seven percent of the chlorine is set free.
W. D. B.

The persulphuric acids. *T. M. Lowry and J. H. West. Jour. Chem. Soc.* 77, *950* (*1900*). — The authors have determined the amount of persulphuric acid formed when hydrogen peroxide is added to sulphuric acids of varying concentrations. If we assume that the mass law applies, without corrections for electrolytic dissociation, the results point to the existence of pertetrasulphuric acid, $H_2S_4O_{14}$. *W. D. B.*

The reducing action of calcium carbide. *Geelmuyden. Comptes rendus,* 130, *1026* (*1900*). — At the temperature of the electric furnace, calcium carbide reduces iron pyrites, galena, magnesium sulphide, and antimony sulphide to the metal; aluminium sulphide is not reduced; boric anhydride is converted into calcium boride. *W. D. B.*

Preparation of the phosphides of iron, nickel, cobalt, and chromium. *J. Maronneau. Comptes rendus,* 130, *657* (*1900*). — The phosphides of iron, nickel, cobalt, and chromium have been prepared by heating the metal in question in the electric furnace together with the phosphide of copper.
W. D. B.

The separation of the rare earths. *R. Chavastelon. Comptes rendus,* 130, *781* (*1900*). — The author precipitates everything except thorium by means of an alkaline sulphite, or else he gets the thorium and cerium alone in solution by the action of bicarbonates on the mixed oxides. *W. D. B.*

A new method of fractioning some of the rare earths. *E. Demarçay. Comptes rendus,* 130, *1019* (*1900*). — The method consists in the fractional crystallization of the double magnesium nitrates in nitric acid. *W. D. B.*

Velocities

On the velocity of solidification and viscosity of supercooled liquids. *H. A. Wilson. Phil. Mag.* [*5*] 50, *238* (*1900*). — Considering the expression which the author previously obtained to represent the velocity of solidification (3, 423), if F, the latent heat of fusion of one gram of the solid, *a*, the thickness of the surface of separation of liquid and solid, and A, the force required to give unit velocity to one gram of the liquid diffusing through itself, be all regarded as constant, then

$$v = C\frac{S}{V},$$

where C is a constant, S is the actual supercooling, and V is the viscosity of the liquid.

The present paper contains experimental data taken to test this formula. The substances chosen were salol, benzoic anhydride, benzophenone, and azobenzene. The results show that the velocity of solidification of a pure substance varies directly as the actual supercooling at which solidification occurs, and inversely as the viscosity of the liquid. *H. T. B.*

Electromotive Forces

On the thermo-electric properties of several alloys. *A. Cornu. Comptes rendus*, 130, *1300* (*1900*). — The author has made measurements with ten nickel steels, three aluminum bronzes, five bronzes, five brasses, four German silvers.
W. D. B.

Negative electrification of the secondary rays produced by the Röntgen rays. *P. Curie and G. Sagnac. Comptes rendus*, 130, *1013* (*1900*). — While the Röntgen rays themselves have no perceptible negative charge, the secondary rays show this phenomenon, the effect being especially marked with platinum and lead.
W. D. B.

The electric charge on the deflectable radium rays. *P. and S. Curie. Comptes rendus*, 130, *647* (*1900*). — The rays from radium which can be deflected by a magnetic field are charged with negative electricity. *W. D. B.*

Electrolysis and Electrolytic Dissociation

Electrolysis of the nitrogen hydrides and of hydroxylamine. *E. C. Szarvasy. Jour. Chem. Soc.* 77, *603* (*1900*). — If a current density exceeding 1.5 amp/cm² be employed, the nitrogen evolved at the anode will be very closely one-third the volume of the hydrogen evolved at the cathode, whether the electrolyte be ammonia, or ammonia and sodium chloride. With hydrazine hydrate, chloride, or sulphate, the ratio is one to two at all the current densities tried. With azo-imide or the sodium salt, the ratio was three to one.
W. D. B.

Electrolytic determination of the lead in lead sulphate and lead chromate. *C. Marie. Comptes rendus*, 130, *1032* (*1900*). — Lead sulphate is dissolved by nitric acid and ammonium nitrate; so is lead chromate. The resulting solutions are electrolyzed.
W. D. B.

Electrolytic preparation of induline dyes. *E. C. Szarvasy. Jour. Chem. Soc.* 77, *207* (*1900*). — Reviewed (4, 699) from Zeit. Elektrochemie, 6, 403 (1900).

On the electrolytic preparation of potassium chlorate. *A. Brochet. Comptes rendus*, 130, *718* (*1900*). — The author endorses Oettel's views on the subject.
W. D. B.

A comparison of platinum thermometers of different degrees of purity. *H. M. Tory. Phil. Mag.* [*5*] 50, *421* (*1900*). — In all, five wires were compared between 400° and 1000° with the result that, although the temperature coefficient varied as much as 40 percent, the platinum temperatures agreed to 9° at 1000°. The same order of accuracy was shown on the air temperatures obtained by the usual difference formula, and was to be attributed to the wide difference in the degrees of purity of the wires. It was found that a simple linear formula could be obtained showing the relation between the platinum temperatures, which gives a ready and accurate method of comparing different samples of wire with different constants. A standard wire could thus be selected having a definite sulphur boiling-point and a definite silver melting-point. The formula reads

$$pt = pt_1 + apt_1 + b,$$

where *a* and *b* are constants. The effects of annealing and wire drawing are carefully studied. *H. T. B.*

Notes on the measurements of some standard resistances. *R. T. Glazebrook. Phil. Mag.* [*5*] 50, *410* (*1900*). — The paper includes a description of four methods which may be used to compare multiples of a unit resistance, and at the same time includes some observations showing the order of accuracy attained. *H. T. B.*

The genesis of the ions in the discharge of electricity through gases. *J. J. Thomson. Phil. Mag.* [*5*] 50, *278* (*1900*). — In the case of the discharge of electricity through a gas, the ionization produced results from the motion through the gas of ions or corpuscles already present. Under the influence of the electric field, velocity and kinetic energy is imparted to the ions which when reaching a certain, or as the author calls critical value, produces fresh ions by the collision of the ions with surrounding molecules. This dissociation goes on increasing, giving rise to an increasing number of fresh ions until the conductivity of the gas rises to such a value as to reduce the strength of the electric field to the critical value, or the point where each ion produces but one successor. This beautifully explains the fact that it requires a field of definite strength to send a discharge through a gas, for it shows that the electric field must be over the critical value in order to produce ions over and above the small number initially present. An explanation is also given of the fact that the current between two electrodes increases with their distance apart within certain limits. For with a distance comparable with the mean free path of an ion the chances of collision and the production of fresh ions will be reduced; hence with increasing distance the number of collisions increases. The phenomenon of striated discharge through rarefied gas is also one immediately explained in the light of the views set forth so clearly in the present paper. *H. T. B.*

Considerations regarding the theory of electrons. *W. M. Orr. Phil. Mag.* [*5*] 50, *269* (*1900*). — Considering the theory of electrons as developed by Larmor, the author attempts to explain by an illustrative model the machinery bringing about the mobility of the electrons, the question of "free mobility" as given being considered by Larmor as one of the fundamental postulates. A short mathematical analysis, modified by Larmor, is given bearing on the theory, showing that the assumptions made do not account for attractions or repulsions between electrons without including "free mobility". *H. T. B.*

The dissociation constants of very weak acids. *J. Walker and W. Cormack. Jour. Chem. Soc.* 77, *5* (*1900*). — An apparatus was devised in which solutions of gaseous acids could be diluted to definite strengths without being in communication with air. The following dissociation constants (multiplied by 10^{10}) are given: acetic acid, 180000; carbonic acid, 3040; hydrogen sulphide, 570; boric acid, 17; hydrocyanic acid, 13; phenol, 1.3. These correspond to the following percentage dissociations in decinormal solution: acetic acid, 1.3; carbonic acid, 0.174; hydrogen sulphide, 0.075; boric acid, 0.013; hydrocyanic acid, 0.011; phenol, 0.0037. The conductivity of the water 0.7×10^{-6} mercury units was allowed for on the assumption that it was due to carbonic acid as impurity. *W. D. B.*

The dissociation constant of hydrazoic acid. *C. A. West. Jour. Chem. Soc. 77, 705 (1900).* — The value of *k* from the conductivity measurements is 0.0000198 in decinormal solutions and 0.0000186 for the inversion of cane-sugar. Hydrazoic acid is therefore a trifle more dissociated than acetic acid at this dilution. *W. D. B.*

Relations between electrolytic conductivity and internal friction in salt solutions. *P. Massoulier. Comptes rendus, 130, 773 (1900).* — When glycerine is added to M/15 $CuSO_4$ at 15°, the change in electrical resistance is very closely proportional to the change in viscosity; but this is no longer the case when glycerine is added to M/40 $CuSO_4$ at 0°. *W. D. B.*

On the toxicity of the compounds of the alkaline earths with reference to the higher vegetables. *H. Coupin. Comptes rendus, 130, 791 (1900).* — Barium salts are apt to be poisonous both to animals and plants. Strontium and calcium salts are relatively non-toxic to animals, but are, as a rule, poisonous to plants. *W. D. B.*

Dielectricity and Optics

The dielectric constant and dispersion of ice for electromagnetic radiations. *C. Gutton. Comptes rendus, 130, 1119 (1900).* — On varying the length of the waves from 14 cm to 2088 cm, the index of refraction *n* changes from 1.76 to 1.50, and the dielectric constant n^2 from 3.10 to 2.25. *W. D. B.*

The refractive and magnetic rotatory powers of some benzenoid hydrocarbons. *W. H. Perkin. Jour. Chem. Soc. 77, 267 (1900).* — The magnetic rotations and refractive powers of the following hydrocarbons have been determined: benzene, toluene, ethyl benzene, propyl benzene, isopropyl benzene, isobutyl benzene, cymene, *o*-xylene, *m*-xylene, *p*-xylene, pseudocymene, mesitylene, tetraethyl-benzene. The preparations were unusually pure. Experiments on the magnetic rotation of mixtures showed that a marked falling-off from the calculated value occurs only in the aliphatic series, and not universally even there. The author has improved the usual method of reading the scale and vernier of a spectrometer by introducing a long narrow telescope, so arranged that its eye-piece is situated just below that of the observing telescope. *W. D. B.*

Note on the refraction and magnetic rotation of hexamethylene chlorohexamethylene and dichlorohexamethylene. *S. Young and E. C. Fortey. Jour. Chem. Soc. 77, 372 (1900).* — New determinations with a pure specimen of hexamethylene, the magnetic rotation being now 5.664 at 15° and the molecular refraction 45.824 for H_α. *W. D. B.*

The absorption spectra of ammonia, methylamine, hydroxylamine, aldoxime, and acetoxime. *W. N. Hartley and J. J. Dobbie. Jour. Chem. Soc. 77, 318 (1900).* — The absorption band in purified commercial ammonia is shown to be due to traces of pyridine. The spectra of methylamine, hydroxylamine, aldoxime and acetoxime were also studied. *W. D. B.*

Spectrographic studies in tautomerism. *W. N. Hartley and J. J. Dobbie. Jour. Chem. Soc. 77, 498 (1900).* — The authors have determined and measured

the spectra of alcoholic solutions of the ethyl esters of dibenzoyl succinic acid. The results are in harmony with the theoretical views of Knorr. It was possible to follow the gradual change of the enol form into the keto esters.
W. D. B.

The curves of the molecular vibrations of benzantialdoxime and benzsynaldoxime. *W. N. Hartley and J. J. Dobbie. Jour. Chem. Soc. 77, 509 (1900).* —The two forms of benzaldoxime give identical spectra. *W. D. B.*

A study of the absorption spectra of *o*-oxycarbanil and its alkyl derivatives in relation to tautomerism. *W. N. Hartley, J. J. Dobbie, and P. G. Paliatreas. Jour. Chem. Soc. 77, 839 (1900).* — It appears that *o*-oxycarbanil is chiefly the lactam form in solution. *W. D. B.*

Ultra-violet absorption spectra of some closed chain carbon compounds, II. *W. N. Hartley and J. J. Dobbie. Jour. Chem. Soc. 77, 846 (1900).* — The substances studied were dimethylpyrazine, hexamethylene, and tetrahydrobenzene. The band of dimethylpyrazine is both wider and more persistent than that of pyridine. The spectrum of the other two substances confirm the view that "the banded spectrum is shown only by substances which possess the true benzenoid structure." *W. D. B.*

The transparency of aluminum for the radium radiation. *H. Becquerel. Comptes rendus, 130, 1154 (1900).* — The author has arranged things so that rays, passing through aluminum and impinging on an opaque object, cast a shadow which can be deflected by a magnet, while the source of the light is evidently the radium and not the aluminum. *W. D. B.*

The transmission of radium radiation through substances. *H. Becquerel. Comptes rendus, 130, 979 (1900).* — Experiments are described to show that, when a fluorescent screen is held very near a radio-active substance, some of the rays actually pass through the screen. *W. D. B.*

On the reflection and refraction of cathode rays and of the deflectable radium rays. *P. Villard. Comptes rendus, 130, 1010 (1900).* — Experiments to show that most of the rays passing through or reflected from other substances are due to a secondary emission. *W. D. B.*

On the property of certain substances in losing their phosphorescence on heating and regaining it on cooling. *G. Le Bon. Comptes rendus, 130, 891 (1900).* — Three samples of barium bromide containing radio-active matter were found to lose their power of emitting light when heated to 200° and to regain it on cooling. The author then experimented with other substances and found that quinine sulphate does the same thing. In this particular case, the phenomenon is apparently connected with the hydration and dehydration of the salt.
W. D. B.

Fluorescence of certain metallic compounds under the influence of Röntgen and Becquerel rays. *P Bary. Comptes rendus, 130, 776 (1900).* — The author has determined which salts of the alkaline metals and of the alkaline earths become fluorescent when exposed to the Röntgen and Becquerel rays. Without exception, the chlorides are fluorescent. *W. D. B.*

Crystallography, Capillarity and Viscosity

Investigations into capillarity. *Lord Rayleigh. Phil. Mag.* [*5*] 48, *321* (*1899*). — The first part of the paper is a study of the weight of drops in their relation to the size of the tube from which they are forming, and it was found by the author that the weight of a drop of any liquid, of which the density and surface-tension are known, can be calculated by the expression

$$Mg = 3.8\,T a,$$

a being the radius of the tube and T the capillary tension.

Considering the views of Gernez, that the activity of a glass or metal rod to liberate bubbles of gas from supersaturated gaseous solutions is due to a thin film of air, it is found that when the activity is destroyed by heating, and the rod enclosed in a hermetically sealed tube for seven years in contact with air, that the activity is not restored. Whereas when exposed to the air of the laboratory for a few days, activity is restored. The position maintained by Tomlinson that the activity is due to a thin film of grease appears to be substantially correct.

In regard to colliding jets the author discusses the causes influencing the condition for rebound or amalgamation of the drops, and studies the behavior in atmospheres of different gases. Air, oxygen and coal gas, were without effect, while carbonic acid, nitrous oxide, sulphurous anhydride, and steam at once caused union. Hydrogen was found to act in a peculiar manner, sometimes causing union and sometimes without effect. From experiments on the tension of contaminated water-surfaces and a consideration of molecular magnitudes, it is found that the tension of a thin film of oil on water must be the same as that of pure water. A change in tension must ensue for the oil film spreading out over water and corresponds to the point where repulsive forces resisting contraction cease to act, or to the formation of a complete layer one molecule thick.

The diameter of a molecule of oil is found to be about 10^{-6} mm.

H. T. B.

Viscosity of solutions. *R. Hosking. Phil. Mag.* [*5*] 49, *274* (*1900*). — By the method of Thorpe and Rodger (1894) for the determination of the viscosity of liquids, the author proposes to extend the work to embrace some typical solutions. As a preliminary result, to find out the limit of accuracy of his apparatus, the viscosity for water for three different temperatures was determined and compared with the results of Poiseuille, Sprung, Slotte, and Thorpe and Rodger. Only two solutions are given in this paper: sodium chloride and sugar.

H. T. B.

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CONTENTS

ON THE DIELECTRIC CONSTANTS OF NITRILES

BY HERMAN SCHLUNDT

INTRODUCTION

Recent investigations on the dissociative power of solvents and the electrical conductivity of non-aqueous solutions by Dutoit and Friderich,[1] Kahlenberg and Lincoln,[2] and Lincoln,[3] show that salts dissolved in acetonitrile, propionitrile and benzonitrile yield solutions that conduct well. For example, Dutoit and Friderich[4] found the molecular conductivity at 25° C of silver nitrate dissolved in acetonitrile to be 54.5 at a dilution of 1 g-mol in 8 liters, and 118.3 at a dilution of 1 g-mol in 128 liters. The molecular conductivity of aqueous solutions of silver nitrate at 18° C, according to Kohlrausch,[5] is 88.6 at a dilution of 1 g-mol in 10 liters, and 103.3 at a dilution of 1 g-mol in 166.7 liters. It appears then that dilute solutions of silver nitrate in acetonitrile have a greater molecular conductivity than the corresponding aqueous solutions. The molecular conductivity of silver nitrate dissolved in benzonitrile, although lower than the conductivity of aqueous solutions, is still of considerable magnitude. For example, Lincoln[6] found the molecular conductivity of silver nitrate dissolved in benzonitrile, at 25° C, to be 5.18 and 16.38 at the respective dilutions of 1 g-mol in 9.43 and 151.96 liters.

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[1] Bull. Soc. Chim. (Paris) (3) 19, 321 (1898).

[2] Jour. Phys. Chem. 3, 12 (1899).

[3] Trans. Wis. Acad. Sciences, Arts and Letters, 12, 395. Also Jour. Phys. Chem. 3, 457 (1899).

[4] l. c.

[5] Wied. Ann. 26, 161 (1885).

[6] l. c.

Assuming the dissociation theory, the conclusion to be drawn from these results is, that acetonitrile and benzonitrile possess dissociating power in a high degree. On the basis of Nernst's[3] and Thomson's[4] argument that the greater the dielectric constant of solvents the greater is their dissociative power, the nitriles should have high values for their dielectric constants.

The dielectric constant of benzonitrile was measured by Drude[5] and found to be 26.0 at 21° C. Drude measured the dielectric constant of another nitrile, namely, benzyl cyanide, but his extensive investigation does not include any of the nitriles of the aliphatic series. In view of the great dissociating power of acetonitrile, it seemed of special interest to determine its dielectric constant and that of some of its homologues, and at the suggestion of Prof. Kahlenberg the investigation was undertaken.

Lincoln's[1] measurements of the electrical conductivity of salts dissolved in pyridine show that it must be added to the list of solvents that possess marked dissociating power. Its dielectric constant was therefore also measured, and the value will be found appended to the results found for the nitriles investigated. The homologues of pyridine, the substituted ammonias, together with other compounds, are now being investigated.

During the progress of his researches on non-aqueous solutions, Prof. Kahlenberg has collected a choice lot of preparations, which he kindly placed at my disposal. This greatly facilitated the experimental part of my work, and I desire to express to him my thanks for this favor.

Method and Apparatus

In measuring the dielectric constants the method devised and elaborated by Drude[1] was used. It is unnecessary for me

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[1] Zeit. phys. Chem. 13, 531 (1893).

[2] Phil. Mag. 36, 320 (1893).

[3] Zeit. phys. Chem. 23, 267 (1897).

[4] l. c.

[5] l. c. See also Wied. Ann. 55, 633 (1895); 58, 1; 59, 17 (1896); 60, 28, 500 (1897).

to give a complete description of this method and of the details of the apparatus employed, since Drude has already done this. The reader is therefore simply referred to Drude's original article after reading which the additional remarks on the method that are contained in the paragraphs that now follow will be much better understood.

The apparatus used for these measurements was a trifle larger than the one described by Drude. The wave-length of the electrical waves in the two parallel wires in air was about 84 cm, as compared with 74 cm of the apparatus employed by Drude. A vacuum tube containing hydrogen was used to determine the settings for maximum resonance. It served very well indeed for this purpose.

Of the two methods described by Drude, the first is the more accurate, but it necessitates the use of comparatively large quantities of substance, at least 200 cc, which, in most cases, were not available. Moreover, the poisonous nature of the nitriles made it desirable to work with small quantities which could be kept in a closed cell while under investigation. Drude's "second" method, although less accurate, was therefore chosen. This method enables one to operate with less than a cubic centimeter of solvent and gives results accurate to within 2 percent. In this method the substance to be measured is introduced into a small condenser, which is placed in the secondary circuit. The length of the secondary circuit is then adjusted for maximum resonance. The dielectric constant corresponding to the length noted is found from a calibration curve representing the results obtained in calibrating the apparatus for the particular condenser.

Three cells similar in form, but of different capacities, served as condensers. The apparatus was calibrated for each cell with the liquids recommended by Drude, namely, benzene, acetone, water, mixtures of benzene and acetone, and mixtures of acetone and water. Seventeen liquids whose dielectric constants range from 2.26 to 80.9 at 19° C were prepared. The benzene used for these calibrating solutions was Kahlbaum's thiophene-free preparation, purified by crystallization. Its boiling-point was 79.2° C under 744.6 mm. pressure. The acetone was Kahlbaum's preparation; it was prepared from the bisulphite compound. It boiled at 55.7° under 746 mm of pressure. The water used had a specific conductivity of 3.6×10^{-6}.

In calibrating, the "zero" of the apparatus, obtained by placing a straight piece of copper wire in place of the cell, was frequently redetermined, as a change in the position of certain parts of the apparatus may produce a change of the "zero" point. This precaution was also taken whenever solvents of unknown dielectric constant were under examination. As a check on any change in the capacity of the cells, the calibrating liquids whose dielectric constants were nearest in value to that found for the solvent under examination were introduced into the cell and the settings for maximum resonance determined. In this way any change in the position of the condenser plates could be readily detected. This procedure also gives all the necessary data for calculating the dielectric constant according to the formula developed by Drude,[1]

$$D = D_1 + (D_2 - D_1)\frac{\cot\frac{2\pi l}{\lambda} - \cot\frac{2\pi l_1}{\lambda}}{\cot\frac{2\pi l_2}{\lambda} - \cot\frac{2\pi l_1}{\lambda}},$$

in which λ is the wave-length of the electric waves in air, D is the dielectric constant sought, l is the setting for maximum resonance when the cell contains the solvent whose dielectric constant is sought; D_1, l_1, and D_2, l_2, are the dielectric constants and settings of the calibrating solutions. In working with pyridine the dielectric constant was calculated by this formula, using 84 cm for λ. The value found was the same as the value obtained with the aid of the calibration curve.

From 10 to 30 settings for maximum resonance were made for each solvent examined, and the average of these was the value used for obtaining the dielectric constant.

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[1] l. c., p. 290.

The methods of dehydrating and rectifying the various solvents will be found under the head of each particular solvent in the statement of results given below.

A series of trial experiments was at first made with the apparatus in order to test it thoroughly. The dielectric constants of ethyl ether, chloroform, ethyl benzoate, salicylic aldehyde, benzonitrile, and nitrobenzene were measured; and the results obtained agreed very well with those given by Drude. It is therefore, entirely superfluous to again report the numerical results obtained for these substances.

Experimental Results

The dielectric constants of the following aliphatic nitriles were measured: hydrocyanic acid, acetonitrile, propionitrile, butyronitrile, isopropyl cyanide, valeronitrile, isobutyl cyanide, and capronitrile. In the aromatic series benzonitrile, benzyl cyanide, and orthotoluonitrile were measured.

Hydrocyanic Acid

The sample of hydrocyanic acid used was prepared in the usual way by slowly adding a strong aqueous solution of potassium cyanide to sulphuric acid of sp. gr. 1.25 in a retort connected with a reflux condenser kept at 30° C. The gas was then dried at 30° C by passing it through a series of three large U-tubes, kept at 30° C, and containing fused calcium chloride. The gas was condensed in a tube provided with glass stop-cocks suspended in a bath at 0°. A colorless liquid was thus obtained, which left no residue upon evaporation. Some of the liquid was introduced into the cell adapted for the measurement of liquids having a high dielectric constant. The cell was securely stoppered and the measurements were made at 21° C. No appreciable absorption was observed, the position for maximum resonance being about as well defined as in the case of acetone. The dielectric constant found is higher than the dielectric constant of water. This necessitated an extrapolation of the calibration curve in order to get an approximate value. The dielectric constant found in this way is 95.0 ± 3.5.

After this exceedingly high result had been obtained a second sample of hydrocyanic acid was prepared by redistilling the first sample from a water-bath kept at 30° C. The gas was again passed through the drying tubes and condensed as before. Measurements with this sample gave the same readings for maximum resonance as in the first case. The temperature coefficient is negative; but it was not accurately determined.

The specific conductivity of the sample of hydrocyanic acid was not determined; but an investigation of the conductivity and other properties of salts dissolved in hydrocyanic acid is now in progress in this laboratory. Perhaps the specific conductivity will be low enough to permit the use of Nernst's apparatus for determining the dielectric constant. The improved form of Nernst's apparatus as described by Turner[1] will soon be at hand, when an attempt to measure the dielectric constant of hydrocyanic acid by means of it will be made.

Acetonitrile

The sample of acetonitrile first measured was obtained by distilling a sample of Kahlbaum's make. Its boiling-point was very constant, being 80.9° C under a pressure of 745 mm. The average of four determinations gave the value 36.5 for the dielectric constant at 21° C.

A second sample, prepared bv Prof. Kahlenberg from the Kahlbaum preparation by dehydrating it with phosphorus pentoxide and redistilling twice was measured. Its boiling-point was 80.7° under 749 mm pressure. The measurements were made at 22° and gave the same result as was obtained with the first sample.

A third sample, also furnished by Prof. Kahlenberg, was finally measured. This sample was twice dehydrated with larger quantities of phosphorus pentoxide than were used in the previous case, and was distilled from phosphorus pentoxide. It had a boiling-point of 80.2° C under a pressure of 736 mm. The dielectric constant was calculated by the formula given above and found to be 36.1 at 21°.

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[1] Zeit. phys. Chem. 35, 385 (1900).

Propionitrile

This sample was Schuchardt's preparation. Its boiling-point was 94.6°. The average of four determinations at different times gave the value 26.5 for the dielectric constant at 22° C. The absorption was slight.

Butyronitrile

The sample tested was Schuchardt's preparation. It was redistilled from calcium chloride. Its boiling-point was 116.5° to 118° C under 742 mm of pressure. The average of three different determinations was 20.3 at 21° C.

Isopropyl Cyanide

The sample was Schuchardt's preparation. It was dehydrated with calcium chloride and redistilled. Its boiling-point was 106°–107° C under 744 mm pressure. The average of three determinations gave the value 20.4 for its dielectric constant at 24° C.

Valeronitrile (normal)

The sample was obtained from Schuchardt. It was redistilled from calcium chloride, and the portion which distilled between 137°–139° C, under 743 mm of pressure, was taken for the measurements. Its dielectric constant was found to be 17.4 at 21° C.

Isobutyl Cyanide

The sample was Schuchardt's preparation; it was redistilled from calcium chloride, and the portion distilling between 129°–130.5° C under a pressure of 742 mm was taken for the measurements. Its dielectric constant was found to be 17.95 at 22° C.

Capronitrile

The sample used was obtained from Schuchardt. It was redistilled from calcium chloride, and the portion distilling between 153°–154° C, under 743 mm pressure, was taken for the measurements. Its dielectric constant was found to be 15.5 at

22° C. The higher members of the series show a slight amount of absorption; but the maximum resonance is still well enough defined without increasing the intensity of the oscillations in the secondary circuit.

Toluonitrile (ortho)

Schuchardt's preparation was redistilled from calcium chloride. A straw-colored distillate, boiling at 200°–201° C, under a pressure of 733 mm, was thus obtained. Its dielectric constant was found to be 18.5 at 23° C. It showed slight absorption.

Pyridine

The first sample was Schuchardt's preparation. It was redistilled and found to boil from 115.5° to 117° under 745 mm pressure. With this several measurements were made, the average of the results for the dielectric constant being 12.35 at 21° C.

A second sample was furnished by Prof. Kahlenberg. Kahlbaum's best preparation was carefully purified by him according to the method given by Ladenburg.[1] The portion boiling at 114° C under 744.6 mm of pressure, was used for the measurements. The dielectric constant was found to be 12.55 at 20° C, a result which agrees well with the foregoing. The settings for maximum resonance were well defined.

Quinoline

Two samples of quinoline were measured. The first was obtained by redistilling Schuchardt's preparation marked, "Quinoline from Coal Tar." The portion which distilled at 232° C under 746 mm of pressure, was measured. Its dielectric constant was found to be 8.7 at 22° C.

The second sample was a synthetic preparation, made by Messrs. Maxon and Thomas in this laboratory according to the method of Skraup. The boiling-point of the sample measured was 232° C under 746 mm of pressure. Its dielectric constant

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[1] Liebig's Annalen, 247, 1 (1888).

was found to be 8.9 at 20.5° C. The agreement is close enough to fall within the limit of error. The absorption is slight. These values of the dielectric constant agree well with the result, 8.9, obtained by Turner,[1] who worked with Nernst's apparatus.

The foregoing results are summarized in the following table, the third column giving the temperatures at which the dielectric constants were determined.

TABLE I

Solvent	Formula	$t°$	Dielectric constant (Air = 1)
Hydrocyanic acid	HCN	21	95
Acetonitrile	CH_3CN	21	36.4
Propionitrile	C_2H_5CN	22	26.5
Butyronitrile	C_3H_7CN	21	20.3
Isopropyl cyanide	$(CH_3)_2CHCN$	24	20.4
Valeronitrile(*n*)	C_4H_9CN	21	17.4
Isobutyl cyanide	$(CH_3)_2CHCH_2CN$	22	17.95
Capronitrile	$(CH_3)_2CHCH_2CH_2CN$	22	15.5
Benzonitrile[2]	C_6H_5CN	21	26.0
Benzyl cyanide[3]	$C_6H_5CH_2CN$	21	14.9
Toluonitrile (ortho)	$C_6H_4<\begin{smallmatrix}CH_3\\CN\end{smallmatrix}$	23	18.4
Pyridine	C_5H_5N	21	12.4
Quinoline[4]	C_9H_7N	21	8.8

The results obtained with the aliphatic nitriles are also presented graphically in Curve I. in the accompanying figure. The dielectric constants are plotted as ordinates, and the members of the homologous series are noted as abscissæ, a definite distance being chosen for each addition of CH_2.

Curve II. represents Drude's[5] values for the dielectric constants of the alcohols, while Curve II(*a*). presents approximately

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[1] Zeit. phys. Chem. 35, 385 (1900).

[2] Measured by Drude, who found 26.0 at 21° C.

[3] Drude found 15.0 at 19° C.

[4] Turner found 8.9 with Nernst's apparatus.

[5] l. c.

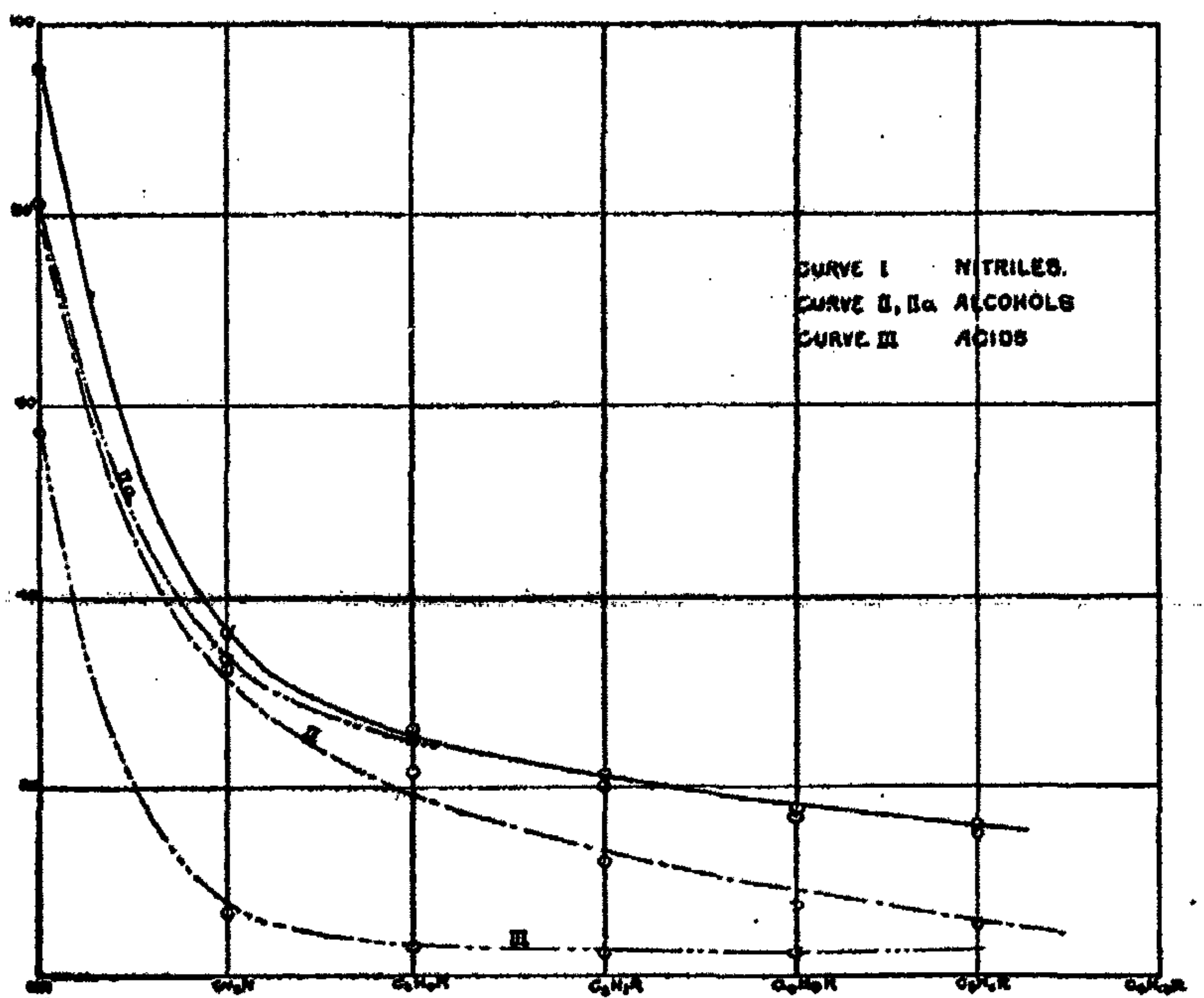

FIGURE I.

the values obtained by Thwing,[1] Nernst,[2] and Tereschin[3] for the dielectric constants of the alcohols. Curve III. represents the values obtained by Drude for the dielectric constants of the fatty acids. Hence in Curve I., R represents the cyanogen group (CN), in Curves II. and II(*a*), R represents the hydroxyl group (OH), while in Curve III. it represents the carboxyl group (COOH).

Discussion of Results

The high dielectric constant found for hydrocyanic acid is of special interest from a theoretical point of view, since by the Nernst-Thomson rule, that the greater the dielectric constant of a solvent, the greater is its dissociating power, hydrocyanic acid should show extraordinary dissociating power. The

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[1] Zeit. phys. Chem. 14, 286 (1894).

[2] Ibid., 14, 622 (1894).

[3] Wied. Ann. 36, 792 (1889).

publication of the electrical conductivity measurements of salts dissolved in hydrocyanic acid, which are in progress in this laboratory, will therefore be awaited with interest.

The marked differences in the physical properties between the first two members of any homologous series are well exemplified here by the great differences in the dielectric constants between hydrocyanic acid and acetonitrile, water and methyl alcohol, formic acid and acetic acid. The curves show that an increase in the size of the molecule by the addition of carbon and hydrogen lowers the dielectric constant. This also holds for the aromatic nitriles and for pyridine and quinoline.

The isomeric nitriles examined have nearly the same dielectric constant, the iso-compounds showing a slightly higher value.

A comparison of the values of the dielectric constants of the alcohols and nitriles by means of Curves I. and II. shows that for high frequency oscillations the nitriles have higher values for their dielectric constants throughout than the corresponding alcohols. For oscillations of low frequency the values for the dielectric constants of the higher members of the alcohol series are nearly the same as the values found for the corresponding nitriles with high frequency oscillations. Compare Curves II(*a*) and I. Since the nitriles show but slight absorption, the dielectric constants when determined with Nernst's apparatus will probably agree closely with the values found with Drude's apparatus.

The researches of Dutoit and Friderich[1] on the electrical conductivity of salts dissolved in acetonitrile, propionitrile, and butyronitrile show that the dissociating power decreases in the order in which the solvents are named. Their dielectric constants also decrease in the order named, thus supporting the Nernst-Thomson rule. This relation between the dielectric constant and the electrical conductivity is illustrated by the following table. The molecular conductivity measurements are taken from the work of Dutoit and Friderich. In the table μ stands

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[1] l. c.

for the molecular conductivity at 25° C, and v the number of liters in which one gram-molecule of silver nitrate is contained.

TABLE II

Solvent	v	μ_v	Dielectric constant at 21° C.
Acetonitrile	64.0	103.7	36.4
Propionitrile	63.7	46.0	26.5
Butyronitrile	75.6	25.4	20.3

Propionitrile and benzonitrile have about the same dielectric constant; but the molecular conductivities of silver nitrate dissolved in these nitriles are quite different, as a comparison of the results in the following table shows. The molecular conductivities for silver nitrate in benzonitrile are taken from Lincoln's[1] work. The molecular conductivities for silver nitrate are taken from the work of Dutoit and Friderich.[2]

TABLE III

Benzonitrile		Propionitrile	
v	μ_v at 25° C.	v	μ_v at 25° C.
24.06	7.66	32.0	34.9
58.98	11.19	63.7	46.0
83.92	13.41		

The molecular conductivities of silver nitrate dissolved in pyridine and in butyronitrile furnish another interesting comparison.

TABLE IV

Solvent	v	μ_v at 25°	Dielectric constant
Butyronitrile[3]	75.6	25.4	20.3
	150.4	32.1	
Pyridine[4]	60.9	30.17	12.4
	140.7	36.21	

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[1] l. c., p. 422.

[2] l. c., p. 330.

[3] Dutoit and Friderich. l. c., p. 331.

[4] Lincoln. l. c., p. 423.

While Table II. shows that the Nernst-Thomson rule holds for the three members of the same homologous series, Table III. demonstrates that chemically analogous substances having about the same dielectric constants may nevertheless yield solutions (containing the same solute) with very different electrical conductivities. Table IV. shows conclusively that a pyridine solution of silver nitrate conducts better than a corresponding one in butyronitrile, notwithstanding the fact that the dielectric constant of pyridine is only 61 percent of that of butyronitrile. We have here then a striking case in which the Nernst-Thomson rule does not hold. It is well in this connection to bear in mind the fact that Goodwin and Thompson[1] have found that liquid ammonia is also a striking exception to the Nernst-Thomson rule.

It is evident from the above results that the Nernst-Thomson rule holds at best only for the members of the same homologous series. It is also clear that the dielectric constant of a solvent is not the sole factor determining whether solutions in that solvent will conduct electricity or not.

I am indebted to Prof. Kahlenberg for his suggestions and assistance, and I take this means of acknowledging the same.

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Jan. 30, 1901.

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[1] Phys. Review, 8, 43 (1899).

THE FUNDAMENTAL EQUATION OF A MULTIPLE POINT

BY PAUL SAUREL

At the triple point formed by the intersection of the three curves which represent in the pressure-temperature plane the equilibrium of three one-component univariant systems, there exists a well known relation between the slopes of the three curves. The object of the present note is to show that at any multiple point an analogous relation exists between the slopes of the intersecting curves.

Consider the multiple point which represents in the pressure-temperature plane an invariant system of $n + 2$ phases formed by means of n independent components. If one of the phases of the invariant system be removed there remains a univariant system. To each of the $n + 2$ univariant systems which can be formed in this way, there corresponds a curve in the pressure-temperature plane. Let us consider the univariant system which has been obtained by removing the first phase of the invariant system and let us denote the slope of the corresponding curve by $\frac{d\Pi_1}{dT_1}$. The slope is given by an equation which is due to Gibbs,[1] and which can be written in either of the forms:

$$\frac{d\Pi_1}{dT_1} \begin{vmatrix} v_2, & m_{21}, & \dots, & m_{2n} \\ v_3, & m_{31}, & \dots, & m_{3n} \\ \vdots & \vdots & & \vdots \\ v_{n+2}, & m_{n+2,1}, & \dots, & m_{n+2,n} \end{vmatrix}$$

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[1] On the Equilibrium of Heterogeneous Substances, p. 154. Cf. Jour. Phys. Chem. 5, 50 (1901).

$$= \begin{vmatrix} \eta_2, & m_{21}, & \ldots, & m_{2n} \\ \eta_3, & m_{31}, & \ldots, & m_{3n} \\ \vdots & \vdots & & \vdots \\ \eta_{n+2}, & m_{n+2,1}, & \ldots, & m_{n+2,n} \end{vmatrix},$$

$$\frac{dT_1}{d\Pi_1} \begin{vmatrix} \eta_2, & m_{21}, & \ldots, & m_{2n} \\ \eta_3, & m_{31}, & \ldots, & m_{3n} \\ \vdots & \vdots & & \vdots \\ \eta_{n+2}, & m_{n+2,1}, & \ldots, & m_{n+2,n} \end{vmatrix}$$

$$= \begin{vmatrix} v_2, & m_{21}, & \ldots, & m_{2n} \\ v_3, & m_{31}, & \ldots, & m_{3n} \\ \vdots & \vdots & & \vdots \\ v_{n+2}, & m_{n+2,1}, & \ldots, & m_{n+2,n} \end{vmatrix}.$$

In these equations v_i and η_i denote the volume and the entropy of the unit of mass of the i-th phase, and m_{ij} denotes the mass of the j-th component, which is present in the unit of mass of the i-th phase.

If to the above equations we add the equations which correspond to the other univariant systems (the signs of the equations with even indices having previously been changed), we obtain :

$$\begin{vmatrix} \dfrac{d\Pi_1}{dT_1}, & v_1, & m_{11}, & \ldots, & m_{1n} \\ \dfrac{d\Pi_2}{dT_2}, & v_2, & m_{21}, & \ldots, & m_{2n} \\ \vdots & \vdots & \vdots & & \vdots \\ \dfrac{d\Pi_{n+2}}{dT_{n+2}}, & v_{n+2}, & m_{n+2,1}, & \ldots, & m_{n+2,n} \end{vmatrix}$$

$$= \begin{vmatrix} 1, & \eta_1, & m_{11}, & \ldots, & m_{1n} \\ 1, & \eta_2, & m_{21}, & \ldots, & m_{2n} \\ \vdots & \vdots & \vdots & & \vdots \\ 1, & \eta_{n+2}, & m_{n+2,1}, & \ldots, & m_{n+2,n} \end{vmatrix},$$

$$\begin{vmatrix} \frac{dT_1}{d\Pi_1}, & \eta_1, & m_{11}, & \ldots, & m_{1n} \\ \frac{dT_2}{d\Pi_2}, & \eta_2, & m_{21}, & \ldots, & m_{2n} \\ \vdots & \vdots & \vdots & & \vdots \\ \frac{dT_{n+2}}{d\Pi_{n+2}}, & \eta_{n+2}, & m_{n+2,1}, & \ldots, & m_{n+2,n} \end{vmatrix} = \begin{vmatrix} 1, & v_1, & m_{11}, & \ldots, & m_{1n} \\ 1, & v_2, & m_{21}, & \ldots, & m_{2n} \\ \vdots & \vdots & \vdots & & \vdots \\ 1, & v_{n+2}, & m_{n+2,1}, & \ldots, & m_{n+2,n} \end{vmatrix}.$$

In these equations $\frac{d\Pi_i}{dT_i}$ denotes the slope at the multiple point of the curve which corresponds to the univariant system obtained from the invariant system by removing the i-th phase. Moreover, the values of v_i, η_i, m_{ij} are the equilibrium values which correspond to the pressure and the temperature of the multiple point.

If we recollect that from the definition of the concentrations m_{ij} we have

$$\sum_{j=1}^{n} m_{ij} = 1, \qquad i = 1, 2, \ldots, n+2,$$

it follows without difficulty that the determinants which form the right-hand members of the last pair of equations are identically equal to zero. We thus obtain the following equations, which are due to Riecke:[1]

$$\begin{vmatrix} \frac{d\Pi_1}{dT_1}, & v_1, & m_{11}, & \ldots, & m_{1n} \\ \frac{d\Pi_2}{dT_2}, & v_2, & m_{21}, & \ldots, & m_{2n} \\ \vdots & \vdots & \vdots & & \vdots \\ \frac{d\Pi_{n+2}}{dT_{n+2}}, & v_{n+2}, & m_{n+2,1}, & \ldots, & m_{n+2,n} \end{vmatrix} = 0, \qquad (1)$$

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[1] Göttinger Nachrichten, p. 223 (1890). Zeit. phys. Chem. 6, 268 (1890).

$$\begin{vmatrix} \frac{dT_1}{d\Pi_1}, & \eta_1, & m_{11}, & \ldots, & m_{1n} \\ \frac{dT_2}{d\Pi_2}, & \eta_2, & m_{21}, & \ldots, & m_{2n} \\ \vdots & \vdots & \vdots & & \vdots \\ \frac{dT_{n+2}}{d\Pi_{n+2}}, & \eta_{n+2}, & m_{n+2,1}, & \ldots, & m_{n+2,n} \end{vmatrix} = 0. \qquad (2)$$

If the invariant system is formed by means of a single component, we have

$$m_{11} = m_{21} = m_{31} = 1,$$

and equations 1 and 2 become

$$\begin{vmatrix} \frac{d\Pi_1}{dT_1}, & v_1, & 1 \\ \frac{d\Pi_2}{dT_2}, & v_2, & 1 \\ \frac{d\Pi_3}{dT_3}, & v_3, & 1 \end{vmatrix} = 0, \qquad \begin{vmatrix} \frac{dT_1}{d\Pi_1}, & \eta_1, & 1 \\ \frac{dT_2}{d\Pi_2}, & \eta_2, & 1 \\ \frac{dT_3}{d\Pi_3}, & \eta_3, & 1 \end{vmatrix} = 0.$$

Developing the determinants, we obtain:

$$(v_2 - v_3)\frac{d\Pi_1}{dT_1} + (v_3 - v_1)\frac{d\Pi_2}{dT_2} + (v_1 - v_2)\frac{d\Pi_3}{dT_3} = 0, \qquad (3)$$

$$(\eta_2 - \eta_3)\frac{dT_1}{d\Pi_1} + (\eta_3 - \eta_1)\frac{dT_2}{d\Pi_2} + (\eta_1 - \eta_2)\frac{dT_3}{d\Pi_3} = 0. \qquad (4)$$

Equation 3, which has been called the fundamental equation of the triple point, was established almost simultaneously by Riecke[1], Natanson[2] and Duhem.[3] From it can be derived equations which had previously been used by Kirchhoff,[4] by Planck,[5] and by Robert von Helmholtz.[6]

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[1] Zeit. phys. Chem. 6, 413 (1890).

[2] Wied. Ann. 42, 178 (1891).

[3] Zeit. phys. Chem. 8, 367 (1891). Traité élémentaire de Mécanique chimique, 2, 105.

[4] Pogg. Ann. 103, 206 (1858).

[5] Wied. Ann. 15, 446 (1882).

[6] Wied. Ann. 30, 401 (1887).

We may put equations 1 and 2 into more suggestive forms, but before doing this a few preliminaries are necessary. Consider again the univariant system formed by removing the phase 1 from the invariant system, and suppose that at the temperature and under the pressure of the multiple point the system undergoes a reversible change in which the mass of the i-th phase is increased by δM_i. Some of these increments will of course be negative. The condition that, during the change under consideration, the total mass of each component remains the same, is expressed by the equations:

$$\sum_{i=2}^{n+2} m_{ij}\delta M_i = 0, \qquad j = 1,\ 2,\ \ldots,\ n.$$

From these n homogeneous equations we can obtain at once the ratios of the $n+1$ increments. These ratios are given by the equations:

$$\frac{\delta M_2}{\begin{vmatrix} m_{31}, & m_{32}, & \ldots, & m_{3n} \\ m_{41}, & m_{42}, & \ldots, & m_{4n} \\ \vdots & \vdots & & \vdots \\ m_{n+2,1}, & m_{n+2,2}, & \ldots, & m_{n+2,n} \end{vmatrix}} = \frac{\delta M_3}{-\begin{vmatrix} m_{21}, & m_{22}, & \ldots, & m_{2n} \\ m_{41}, & m_{42}, & \ldots, & m_{4n} \\ \vdots & \vdots & & \vdots \\ m_{n+2,1}, & m_{n+2,2}, & \ldots, & m_{n+2,n} \end{vmatrix}} = \ldots$$

$$= \frac{\delta M_{n+2}}{(-1)^n\begin{vmatrix} m_{21}, & m_{22}, & \ldots, & m_{2n} \\ m_{31}, & m_{32}, & \ldots, & m_{3n} \\ \vdots & \vdots & & \vdots \\ m_{n+1,1}, & m_{n+1,2}, & \ldots, & m_{n+1,n} \end{vmatrix}} . \qquad (5)$$

Consider now the coefficient of $\frac{d\Pi_1}{dT_1}$ in equation 1. The equations just written show that this coefficient is proportional to

$$v_2\delta M_2 + v_3\delta M_3 + \cdots + v_{n+2}\delta M_{n+2}. \tag{6}$$

If the δM's be so chosen that each of the fractions in equation 5 is equal to unity, the coefficient under consideration becomes equal to the expression 6. But this last expression is the increase which the volume of the system undergoes during the reversible change that we have been considering. We shall denote this change in volume by δV_1.

In the same way it may be shown that, for a suitable choice of the increments δM, the coefficient of $\frac{d\Pi_i}{dT_i}$ is equal to the change in the volume of the i-th univariant system during the corresponding reversible change at the multiple point. Denoting this change in volume by δV_i, we may write equation 1 in the form

$$\delta V_1 \frac{d\Pi_1}{dT_1} + \delta V_2 \frac{d\Pi_2}{dT_2} + \cdots + \delta V_{n+2} \frac{d\Pi_{n+2}}{dT_{n+2}} = 0. \tag{7}$$

Similarly, it can be shown that equation 2 may be written in the form

$$\delta H_1 \frac{dT_1}{d\Pi_1} + \delta H_2 \frac{dT_2}{d\Pi_2} + \cdots + \delta H_{n+2} \frac{dT_{n+2}}{d\Pi_{n+2}} = 0. \tag{8}$$

In these equations, δV_i and δH_i are the changes in the volume and the entropy of the i-th univariant system during a reversible change at the multiple point. This reversible change is such that the change in the mass of the phase k is equal to that minor of the determinant 1, which corresponds to the product $\frac{d\Pi_i}{dT_i} \cdot v_k$, or, what is the same thing, to that minor of the determinant 2 which corresponds to the product $\frac{dT_i}{d\Pi_i} v_k$.

Since the changes under consideration are reversible, we may write:

$$\delta H_i = \frac{Q_i}{T},$$

in which T denotes the temperature of the multiple point and Q_i denotes the heat absorbed by the i-th univariant system during the corresponding change at the multiple point. Equation 8 may thus be written in the second form :

$$Q_1\frac{dT_1}{d\Pi_1}+Q_2\frac{dT_2}{d\Pi_2}+\cdots+Q_{n+2}\frac{dT_{n+2}}{d\Pi_{n+2}}=0, \qquad (9)$$

Equations 7, 8 and 9 are the generalizations of equations 3 and 4; any one of them might be called the fundamental equation of the multiple point.

The demonstration that we have just given follows directly from Riecke's equations. The following demonstration, while essentially the same as the preceding, may perhaps seem simpler.

For each of the univariant systems that we have considered there holds an equation of the form

$$\frac{d\Pi_i}{dT_i}=\frac{\delta H_i}{\delta V_i},$$

in which δH_i and δV_i are the simultaneous changes of entropy and volume during a reversible change at constant temperature and under constant pressure. The changes in the masses are here subject only to the conditions 5 for the system 1 and to the analogous conditions for the other systems.

The above relation enables us to write, for the multiple point,

$$\sum_{i=1}^{n+2}\delta V_i\frac{d\Pi_i}{dT_i}=\sum_{i=1}^{n+2}\delta H_i,$$

$$\sum_{i=1}^{n+2}\delta H_i\frac{dT_i}{d\Pi_i}=\sum_{i=1}^{n+2}\delta V_i.$$

Let us suppose that each of the fractions in equations 5 is equal to λ_1, and that each of the fractions in the equations for the i-th univariant system is equal to λ_i. Then it can be seen without much difficulty that

$$\sum_{i=1}^{n+2} \delta H_i = \lambda_1 \begin{vmatrix} \eta_2, & m_{21}, & \dots, & m_{2n} \\ \eta_3, & m_{31}, & \dots, & m_{3n} \\ \vdots & \vdots & & \vdots \\ \eta_{n+2}, & m_{n+2,1}, & \dots, & m_{n+2,n} \end{vmatrix}$$

$$- \lambda_2 \begin{vmatrix} \eta_1, & m_{11}, & \dots, & m_{1n} \\ \eta_3, & m_{31}, & \dots, & m_{3n} \\ \vdots & \vdots & & \vdots \\ \eta_{n+2}, & m_{n+2,1}, & \dots, & m_{n+2,n} \end{vmatrix} + \dots$$

$$(-1)^{n+1} \lambda_{n+2} \begin{vmatrix} \eta_1, & m_{11}, & \dots, & m_{1n} \\ \eta_2, & m_{21}, & \dots, & m_{2n} \\ \vdots & \vdots & & \vdots \\ \eta_{n+1}, & m_{n+1,1}, & \dots, & m_{n+1,n} \end{vmatrix}$$

$$= \begin{vmatrix} \lambda_1, & \eta_1, & m_{11}, & \dots, & m_{1n} \\ \lambda_2, & \eta_2, & m_{21}, & \dots, & m_{2n} \\ \vdots & \vdots & \vdots & & \vdots \\ \lambda_{n+2}, & \eta_{n+2}, & m_{n+2,1}, & \dots, & m_{n+2,n} \end{vmatrix}.$$

Similarly, it may be shown that

$$\sum_{i=1}^{n+2} \delta V_i = \begin{vmatrix} \lambda_1, & v_1, & m_{11}, & \dots, & m_{1n} \\ \lambda_2, & v_2, & m_{21}, & \dots, & m_{2n} \\ \vdots & \vdots & & & \vdots \\ \lambda_{n+2}, & v_{n+2}, & m_{n+2,1}, & \dots, & m_{n+2,n} \end{vmatrix}.$$

If now we take

$$\lambda_1 = \lambda_2 = \dots = \lambda_{n+2} = \lambda,$$

and if we recollect that

$$\sum_{j=1}^{n} m_{ij} = 1, \qquad i = 1, 2, \dots, n+2,$$

it follows that the determinants in the preceding equations are identically equal to zero. We thus obtain as before,

$$\sum_{i=1}^{n+2} \delta V_i \frac{d\Pi_i}{dT_i} = 0,$$

$$\sum_{i=1}^{n+2} \delta H_i \frac{dT_i}{d\Pi_i} = 0.$$

In our first demonstration, λ has the value unity.

New York, January 26, 1901.

ON A PROPERTY OF THE PRESSURE-VOLUME DIAGRAM

BY PAUL SAUREL

In a recent article,[1] Duhem has shown that, if a network of limiting lines of the binary system formed by means of two liquefiable gases be traced in the pressure-temperature plane, such a network will enable us to determine without difficulty the concentrations of the two phases which can coexist at a given temperature and under a given pressure. I wish to call attention to the use which can be made of the corresponding network of limiting lines in the volume-pressure plane.

To a mixture of two liquefiable gases of mean concentration $S = \frac{\mathfrak{M}_2}{\mathfrak{M}_1}$, $\mathfrak{M}_1$ and $\mathfrak{M}_2$ being the masses of the two components, there corresponds, in the volume-pressure plane, a certain limiting line.[2] This limiting line is divided into two parts, called respectively dew line and boiling line, the point of division being the point whose coordinates are the critical specific volume and the critical pressure of the mixture of mean concentration S.

Through each point of the volume-pressure plane there passes an isotherm of the mixture of mean concentration S. Thus, to each point of the v-Π plane, there correspond, not only its coordinates v and Π, but also a mean concentration S, which can be chosen at pleasure, and a temperature T, which is determined by the choice of S.

From this it follows that the abscissa of a point P on a dew line of the mixture of mean concentration S is equal to the specific volume of a vapor phase of concentration S, when that

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[1] Jour. Phys. Chem. 5, 91 (1901).

[2] Cf. Duhem. Traité élémentaire de Mécanique chimique, 4, 144.

phase is under a pressure Π, equal to the ordinate of P, and at a temperature T, equal to the temperature of the isotherm, of the mixture S, which passes through P.

Similarly, the abscissa of a point Q on the boiling line of the mixture of mean concentration S is equal to the specific volume of a liquid phase of concentration S, when that phase is under a pressure Π, equal to the ordinate of Q, and at a temperature T, equal to the temperature of the isotherm, of the mixture S, which passes through Q.

Let us suppose that there has been drawn in the volume-pressure plane a network of limiting lines corresponding to binary systems of different mean concentrations, and let us consider two phases in equilibrium at the temperature T and under the pressure Π. As Duhem has shown, the network of limiting lines in the T-Π plane will enable us to determine the concentrations S_1 and S_2 of the two phases, vapor and liquid.

Turn now to the volume-pressure diagram. The point on the dew line of the mixture S_1 whose ordinate is Π will have an abscissa which we shall denote by v_1. v_1 will be the specific volume of the vapor phase in our two-phase system. The temperature T of the system is the same as the temperature of the isotherm of the mixture S_1, which passes through the point (v_1, Π).

Similarly, let us denote by v_2 the abscissa of the point of the boiling line of the mixture S_2, whose ordinate is Π. v_2 will be the specific volume of the liquid phase in our two-phase system. The temperature T of the system is the same as the temperature of the isotherm of the mixture S_2 which passes through the point (v_2, Π).

If we denote the masses of the phases by M_1 and M_2, and the mean specific volume by v, we have the equation

$$v = \frac{M_1 v_1 + M_2 v_2}{M_1 + M_2}. \qquad (1)$$

We may now restate our results in the following manner: Given a two-phase system in equilibrium at the temperature T and under the pressure Π. From the network of limiting lines in the temperature-pressure plane, we determine S_1 and S_2, the concentrations of the two phases, vapor and liquid. Through the point (v, Π), which is supposed to be known, draw a line parallel to the axis of volumes. This line intersects the dew line of the mixture S_1 at a point (v_1, Π) and the boiling line of the mixture S_2 at a point (v_2, Π). v_1 and v_2 are the specific volumes of the two phases, vapor and liquid. Finally, equation 1 shows that the point (v, Π) divides the line (v_2, Π), (v_1, Π) in the ratio of the masses of the phases: $M_1 : M_2$.

New York, February 3, 1901.

DISSOCIATION STUDIES, II

BY WILDER D. BANCROFT

Rather over a year ago, H. W. Bakhuis Roozeboom[1] discussed the general case of systems in which two liquid modifications occur, taking into account the effects due to passive resistances and so-called false equilibria. The existence, possible or actual, of three temperature zones is recognized. We have first the zone in which there is no change of one modification into the other. This we will call the zone of passive resistance. Next we have the zone in which a partial conversion may occur, but in which the final equilibrium is not independent of the initial concentration. This we will call the zone of the false[2] or bilateral equilibrium. Lastly, we have the zone in which the final equilibrium is independent of the initial concentration. This we will call the zone of reversible equilibrium. If the fusion temperatures for mixtures of the two modifications fall within the first or second zone, it ought to be possible to reach the zone of reversible equilibrium by raising the temperature.

Although attempts have been made in this laboratory during the last two years to realize experimentally the phenomena predicted by Roozeboom, we have not yet found a system which will give satisfactory results. Charring, explosions, or secondary reactions are apt to be disturbing factors before the temperatures of reversible equilibrium are reached. We can eliminate many of these difficulties, if we can displace the temperature limits of the

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[1] Zeit. phys. Chem. 28, 659 (1899).

[2] I have kept the phrase 'false equilibrium' because it is the one used by Duhem; but it seems to me that it would be much better if it were used to describe systems in which no change takes place, so that we could speak of the zone of false equilibrium, of bilateral equilibrium, and of reversible equilibrium.

zones. This can be done in some cases, possibly in all, by the use of catalytic agents. By the addition of a trace of a suitable catalytic agent, the zone of reversible equilibrium can practically be superimposed upon the zone of passive resistance, and the characteristics of the two zones can be studied within the same range of temperatures. Though it is not universally admitted that there is a zone of passive equilibrium in which no changes take place, this need make no difference in our interpretation of the experimental data. There is no question but that there are systems in which no measurable reaction takes place within certain time limits. If therefore, we confine our experimental studies to times falling well within these time limits, the system is then experimentally one for which there is a zone of passive resistance. Whether the catalytic agent accelerates a reaction which is already progressing with immeasurable slowness, or whether it causes a reaction to take place which would otherwise not occur, is a point which is not vital in the present discussion.

In this paper I shall consider the different modifications of ethylaldehyde, namely acetaldehyde, paraldehyde, and metaldehyde. We shall see that our theory accounts for all the experimental facts that have been observed and enables us to predict phenomena which were either not obtained or not recorded by previous investigators. We will begin by a consideration of the equilibrium relations between acetaldehyde and paraldehyde. When no catalytic agent is present, we should get the phenomena common to two-component systems. When a catalytic agent is present, we should get the phenomena characteristic of a one-component system on working slowly, and those characteristic of a two-component system on working rapidly. It will be assumed throughout, when considering equilibrium phenomena, that the catalytic agent is present in such small quantities that we do not need to treat it as another component.

Acetaldehyde is not known as a solid; the boiling-point of the liquid is about +21° under 760 mm. Its vapor-density corresponds to the formula CH_3CHO. Paraldehyde is a solid, melting at + 12° according to Lieben,[1] and at + 10.5° according to Kekulé, and Zincke.[2] It boils at about 124° under 760 mm, and its vapor-density[3] corresponds to the formula $(CH_3CHO)_3$. Acetaldehyde is miscible in all proportions with water, while paraldehyde is not, one hundred volumes of water dissolving twelve volumes of paraldehyde at 13° and only about half as much at 100°. The general consensus of opinion among those who have worked with these substances is that pure paraldehyde does not change into acetaldehyde nor acetaldehyde into paraldehyde. I quote from Kekulé and Zincke.

"We are able to confirm the statement of Geuther and Carthmell that carefully purified aldehyde undergoes no change either after long heating, or long cooling, or long standing. A polymeric change is always connected with the presence of certain substances which appear to have a ferment-like action. In most cases, both aldehyde modifications are formed simultaneously; metaldehyde being formed especially at low temperatures, paraldehyde at ordinary or higher temperatures. If, as has often happened to us, a polymeric change takes place in a supposedly pure aldehyde to which no foreign substance has been added consciously, our experience causes us to believe that one must assume that in some way a foreign substance has become present."

On the other hand, many substances act as catalytic agents and produce reversible equilibrium. Among these may be mentioned carbonyl chloride, hydrochloric acid, sulphur dioxide, zinc chloride, acetyl chloride, acetyl bromide, sulphuric acid, cyanogen, and ethyl iodide. Mercuric bromide[4] is said to act at 90°, but not at 16°. The change of aldehyde into paraldehyde is accompanied by a marked evolution of heat.

When no catalytic agent is present, Duhem's theory leads

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[1] Liebig's Annalen, 162, 142 (1872). Cf. However, Tröger. Ber. chem. Ges. Berlin, 25, 3316 (1892).

[2] Liebig's Annalen. Suppl. Band. 1, 115 (1861).

[3] Ibid. 162, 144 (1872). Cryoscopic measurements in phenol lead to the same formula.

[4] Franchimont. Recueil trav. Pays. Bas. 1, 239 (1892).

us to expect that paraldehyde and aldehyde will behave, when taken singly, like one-component systems, while mixtures will show the properties of two-component systems. Acetaldehyde can be distilled without decomposition and so can paraldehyde. The freezing-point of paraldehyde is lowered and also its boiling-point by addition of acetaldehyde. Mixtures of the two can be separated by fractional distillation, and nothing abnormal is to be detected during the process.[1]

In the presence af a catalytic agent, all this is changed. At ordinary temperatures the liquid obtained is the same whether we start from paraldehyde or acetaldehyde. It consists chiefly of paraldehyde. Kekulé and Zincke[2] found 0.998 for the density of pure paraldehyde at 15°, and 0.805 for pure aldehyde. When equilibrium was established, the density was about 0.986. If we assume that there is no metaldehyde in this solution and that there is neither expansion nor contraction on mixing, we could say definitely that there was only about six percent acetaldehyde present. While there may be an error of one or two percent either way, this may be taken as a probable value.

Since the change of acetaldehyde into paraldehyde is accompanied by an evolution of heat, there must be more acetaldehyde in the solution at higher temperatures than at 15°. Owing to the greater volatility of acetaldehyde, the relative concentration of this substance in the vapor might be expected to be much higher than in the liquid.[3] With slow fractional distillation, we should therefore get pure acetaldehyde in the distillate provided the catalytic agent were not volatile. Since the equilibrium concentration would continually be restored in the distilling flask, we should thus convert paraldehyde quantitatively into acetaldehyde. As a matter of fact, paraldehyde is converted into acetaldehyde by distilling with sulphuric acid. Under these circumstances, the boiling-point should remain con-

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[1] Kekulé and Zincke. Liebig's Annalen, 162, 137 (1872).

[2] l. c. 136.

[3] This is not necessarily the case; hydrochloric acid and water furnish an exception.

stant during the distillation. Kekulé and Zincke found that the thermometer in the boiling liquid remained practically constant at 44°–45°, while the condensing vapor showed the temperature of 21°–22°, the boiling-point of acetaldehyde. When the catalytic agent is volatile, less constant temperatures are obtained. Kekulé and Zincke[1] explain this as follows:

"The volatile ferments pass over during the distillation; the concentration of paraldehyde therefore increases in the distilling flask and the boiling-point necessarily rises. On the other hand, the volatile ferments bring about, even in the condenser, a partial change of acetaldehyde into paraldehyde, and the vapors therefore have a boiling-point higher than that of acetaldehyde."

Owing to the amount of heat evolved during the change of acetaldehyde into paraldehyde, it may happen, when any considerable quantity of a volatile catalytic agent is present, that the distillate will be raised to its boiling-point in spite of artificial cooling.[2]

If we distil rapidly, we should expect to find the distillate containing both modifications, even when the catalytic agent is not volatile. Under these circumstances, the temperature in the distilling flask should rise. These phenomena have been observed.

If we heat acetaldehyde together with a catalytic agent in a flask with a reverse cooler, the boiling-point should rise until the equilibrium concentration was reached, and should then remain constant. Conversely, the boiling-point would fall if we started from paraldehyde. This seems not to have been observed directly, but the experiments of Kekule and Zincke show that it must be the case. It is to be observed that temperature fluctuations would probably occur, since the condensed vapor would be chiefly acetaldehyde and would evolve heat as it passed back into paraldehyde. As a matter of fact, Kekulé and Zincke

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[1] Kekulé and Zincke. l. c. 139.

[2] Kekulé and Zincke. l. c. 138.

observed fluctuations of four degrees in the distillation temperature.

If we pass from a consideration of boiling-points to freezing-points, we should expect to find that the entire solution would solidify to paraldehyde at temperatures below that of the triple point. This has actually been observed;[1] but no one has yet determined the upper limit at which this can occur. It is obvious, however, that the stable triple point cannot coincide with the melting-point of pure paraldehyde.

While the equilibrium relations for acetaldehyde and paraldehyde have been worked out in a satisfactory manner experimentally, the same cannot be said of the equilibrium relations for acetaldehyde and metaldehyde. Metaldehyde is solid at ordinary temperatures, and sublimes at 112°-115°, the condensed vapors consisting chiefly of acetaldehyde, together with some unchanged metaldehyde. From the percentage composition and the vapor-density, Hanriot and Oeconomides[2] calculate that the formula for metaldehyde should be written $(CH_3CHO)_3$, so that the substance is isomeric with paraldehyde. This conclusion is confirmed by the cryoscopic measurements of Tröger[3] with phenol as solvent. At 20° the vapor-pressure is about one millimeter.

The behavior of metaldehyde on heating shows that this substance can be converted into acetaldehyde, at any rate above 100°, even when no catalytic agent is present. The reverse change appears not to take place spontaneously,[4] though such a phenomenon seems to occur when a little acetaldehyde is left in a large flask. Kekulé and Zincke[5] consider this anomalous result as possibly due to the catalytic action of ozone formed during the slow oxidation of the acetaldehyde.

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[1] Kekulé and Zincke. l. c. 138.

[2] Ann. chim. phys. (5) 25, 226 (1882). Cf. Orndorff and White. Amer. Chem. Jour. 16, 51 (1894).

[3] Ber. chem. Ges. Berlin, 25, 3316 (1892). Cf. Orndorff and White. Amer. Chem. Jour. 16, 57 (1894).

[4] Hanriot and Oeconomides. l. c. 228.

[5] l. c. 147.

According to Kekulé and Zincke[1] metaldehyde can be obtained from acetaldehyde by adding a catalytic agent and cooling to zero or lower. "If one adds to pure acetaldehyde small quantities of hydrochloric acid gas, carbonyl chloride, sulphur dioxide, or dilute sulphuric acid and cools at once, preferably in a freezing mixture, metaldehyde separates in fine long needles, which sometimes form a fine network throughout the entire mass of the liquid. Only a small portion of the acetaldehyde is converted into metaldehyde and the amount of the latter does not increase on long standing; but rather decreases and the metaldehyde may disappear completely, especially if an energetically acting ferment is present in considerable amount and if the temperature is not kept sufficiently low. Together with metaldehyde, paraldehyde always appears in greater or less amount."

The disappearance of the metaldehyde after it has been once formed becomes intelligible if we assume that paraldehyde is the stable modification. Through the action of the catalytic agent, metaldehyde is formed in the liquid as an intermediate or contemporary stage in the formation of paraldehyde. We get, therefore, metaldehyde or a mixture of metaldehyde and paraldehyde crystallizing; but the metaldehyde is continually being converted into paraldehyde and must decrease in amount so soon as the rate of change of acetaldehyde into metaldehyde becomes less than the rate of change of metaldehyde into paraldehyde. Increasing the concentration of the catalytic agent and raising the temperature both increase the rate of formation of paraldehyde, and are unfavorable, experimentally, to the formation of metaldehyde.

It is now evident that there should be two ways of getting large quantities of metaldehyde. If we start with a relatively low concentration of the catalytic agent, we shall get pure metaldehyde crystallizing at first. If we decant off the liquid just before it becomes saturated with respect to paraldehyde and distil, we can convert the decanted liquid into acetaldehyde. This can be cooled once more, and the cycle repeated. In this

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[1] l. c. 146.

way, it would be possible theoretically to convert nearly all the acetaldehyde into metaldehyde. Practically there is always some loss in distillation, owing to charring or oxidation. This method was actually worked out by Kekulé and Zincke. A more convenient method would be to find a catalytic agent which should bring about a relatively rapid change of acetaldehyde into metaldehyde and a relatively slow change of the latter into paraldehyde. This is feasible. Hanriot and Oeconomides[1] report that they had at one time five hundred grams of metaldehyde "which separated from commercial acetaldehyde during the severe winter of 1879–1880." Although it was not expressly so stated, one would conclude from these words that this was a case of plain crystallization without intermediate distillations. Fehling found that calcium chloride will cause metaldehyde to separate at ordinary temperatures. Kekulé and Zincke[2] confirm this, adding that the conversion is slow and continuous, the metaldehyde once formed undergoing no further change.

We have already seen that metaldehyde sublimes at 112°–115° with partial conversion into acetaldehyde. Kekulé and Zincke[3] state that when heated in sealed tubes for a couple of hours at 112°–115°, metaldehyde goes over completely into acetaldehyde. On the other hand, Hanriot and Oeconomides[4] say that not more than half of the metaldehyde is changed into acetaldehyde when heated for forty hours at 200°. From the theory we know that metaldehyde must have a melting-point, the temperature of which we can find more or less approximately by heating very rapidly. On the other hand, if we can avoid the formation of paraldehyde, there must be a stable triple point above which metaldehyde will liquefy completely if given time and below which acetaldehyde will solidify completely to metaldehyde. Nothing is known definitely about either of these points, and, in fact, there has been no careful study of the

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[1] l. c. 226.

[2] l. c. 147.

[3] l. c. 149.

[4] l. c. 227.

equilibrium relations. The only other matter of interest is that on passing hydrochloric acid gas into metaldehyde, a mixture of paraldehyde and acetaldehyde is formed,—which was to have been expected.

When it comes to the equilibrium relations between metaldehyde and paraldehyde, there are practically no facts beyond the one already cited that metaldehyde is instable with respect to paraldehyde in presence of a powerful catalytic agent. Tröger has recorded an observation that a specimen of supposedly pure metaldehyde changed after standing several years into paraldehyde. This is interesting and in line with our general theory. It would be unsafe, however, to lay much stress on this, because Tröger also states that during the same period of time a supposedly pure specimen of paraldehyde changed over very largely to acetaldehyde. Since there can be but little doubt that this latter observation is erroneous, one necessarily loses confidence in the first. This matter is further complicated by the change of metaldehyde into a tetraldehyde, as observed by Orndorff and White. This form apparently exists as solid, liquid and vapor. It is instable, but nothing else is really known about it.

If we leave this tetraldehyde out of account, we can predict that there must be an instable eutectic point with metaldehyde and paraldehyde as solid phases; with certain catalytic agents it might also be possible to realize a stable triple point. These are matters which call for investigation before we can be said to have a complete or satisfactory knowledge of the aldehyde modifications. I have held this paper back for a year, hoping that I might find time to investigate these matters experimentally, but circumstances have prevented this.

So far we have considered the modifications two by two. There are no data which will warrant the construction at this time of a triangular diagram. All that we know is that the stable triple point lies in the field in which paraldehyde is solid phase.

We can predict, however, that there must be an instable eutectic point with metaldehyde and paraldehyde as solid phases; with certain catalytic agents it might also be possible to realize a stable triple point. These are matters which call for investigation before we can be said to have a complete or satisfactory knowledge of the three aldehyde modifications. In a system containing two modifications only, the change of concentration is represented graphically by a straight line from the initial concentration to the equilibrium concentration. This is not necessarily the case in a system where three modifications are possible and where reversible equilibrium is the result of a catalytic agent. Under these circumstances, the change of concentrations as the system approaches equilibrium will be represented by a curved line, presumably varying with each catalytic agent. As we know practically nothing about specific reaction velocities, and even less about catalytic agents, it is impossible to make definite predictions in the present state of our knowledge. It is certain, however, that the effect of two catalytic agents should be studied with more thoroughness than has yet been the case. The action of calcium chloride in converting acetaldehyde into metaldehyde apparently without formation of paraldehyde is very curious. Still more remarkable is the behavior of mercuric bromide, which is said by Franchimont[1] to have no effect on paraldehyde after two days' action at 16°, while it works explosively at 90°. No one knows what happens between these two temperatures.

Although we have been considering throughout this paper the specific case of ethyl aldehyde, the discussion has been general in all save form and the principles laid down apply to all cases coming under this head. The reversible change of chloral into metachloral in presence of sulfuric acid is analogous to the reversible change of acetaldehyde into paraldehyde. The equilibrium between formaldehyde and oxymethylene is of the same nature, though this latter reaction differs from the others in that it is apparently reversible even when no catalytic agent is present. It is certain that one could find two melting-points

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[1] Recueil Trav. Pays-Bas. 1, 239 (1892).

for metachloral and for oxymethylene, a higher one reached by rapid heating and a lower one obtained by slow heating.

The main points of this paper are:—

1. The displacement of equilibrium zones by catalytic agents.

2. The general discussion of systems in which three modifications occur.

3. The application of Duhem's theory to the case of ethyl aldehyde.

4. The different relative accelerating effects of different catalytic agents as shown experimentally.

Cornell University,
March, 1900.

NEW BOOKS

Comparative Physiology of the Brain and Comparative Psychology. *By Jacques Loeb. 15 X 21 cm; pp. x + 303. New York: G. P. Putnam's Sons, 1900. Price: bound: $1.75.*— As stated by the author, the purpose of this book is to serve as a short introduction to the comparative physiology of the central nervous system. After a chapter devoted to fundamental facts and conceptions, eight chapters give details of experiments performed on medusae, ascidians, actinians, echinoderms, worms, arthropods, mollusks, and vertebrates. Of the remaining eleven chapters, two present experiments on the cerebellum and the cerebral hemispheres; seven treat respectively of forced movements, orientation and function of elements of segmental ganglia, animal instincts, central nervous system and heredity, associative memory in animals, anatomical and psychic localization, and disturbances of associative memory; while a final chapter presents some starting points for a future analysis of the mechanics of associative memory. A list of the principal original papers used is given at the end of each chapter.

Throughout the book it is evident that the author has earnestly endeavored to base his conclusions upon experimental facts. He has aimed to substitute *real* physiological processes for current metaphysical conceptions.

A few of the striking conclusions reached may be briefly stated as follows: In reflexes, nerves act simply as better conductors than undifferentiated protoplasm, no special reflex mechanisms being located in the central nervous system and ganglia; a center of coordination for various functions, as for instance the heart-beat, is unnecessary; the importance of segmental ganglia as illustrated in arthropods is also evident in vertebrates; animal instincts are to be explained by tropisms, heliotropism, stereotropism, etc., as are the habits of plants; the cerebral hemispheres are the seat of associative memory, a term used instead of the usual word consciousness; the brain acts as a whole and not as a series of parts each devoted to a special purpose. The general trend of the book goes to show that the central nervous system has really fewer functions to perform than has commonly been supposed.

The author emphasizes the importance of physical chemistry as an aid in solving physiological problems, and especially those of the nervous system. "The true problem with which the physiology of the reflexes is concerned is the mechanics of protoplasmic conductivity. This problem is no longer a biological problem, but a problem of physical chemistry." "If we are anxious to develop a dynamics of the various life phenomena, we must remember that the colloidal substances are the machines which produce the life phenomena."

The author has in reality not been able to use any of the results of physicochemical research. It is true that in a few instances he speaks of the effects of

Na, K, Ca, etc., ions, but he might just as well have spoken of the effects of sodium, potassium, calcium, etc., salts. The theory of electrolytic dissociation promises but little for advance in physiology. But if the author has not been able to make much use of physical chemistry, it is because physical chemistry, in spite of its rapid growth, offers but little as yet that can be used by the physiologist toward solving just those problems that are perhaps the greatest ones before the scientist. How meager is our knowledge of the properties of colloidal substances, for example; and yet the behavior of colloids, especially in presence of small amounts of various salts, is of the utmost importance for physiology. No doubt we shall, ere many years, be able to explain protoplasmic conductivity and the dynamics of colloidal matter; now that chemists have ceased to concern themselves solely with the discovery and analysis of new compounds, the biologists are beginning to recognize that morphology and histology alone can never unravel the mysteries of physiological activity, and are seeking for that which physics, chemistry, and especially physical chemistry have to offer to aid them in their work. It is undoubtedly true that the life problem is preeminently one of physical chemistry.

It is really interesting and inspiring to read Professor Loeb's book. There can hardly be any doubt that it will meet with opposition. The spirit in which the volume is written, however, is such as to appeal to every real lover of truth. The book will undoubtedly stimulate many to renewed activity, and for this reason, if for no other, its advent is to be hailed with joy.

Louis Kahlenberg

Practical Electro-Chemistry. *By Bertram Blount. 14 × 21 cm; pp. xi + 374. New York: The Macmillan Company, 1900. Price: bound, $3.25.* — The headings of the chapters are: introduction; winning and refining of metals by electrolytic means in aqueous solution; winning and refining of metals in igneous solution; carbides, borides and silicides; electro-deposition of metals; alkali, chlorine, and their products; electrolytic manufacture of organic compounds; power. Everything considered, this is a very satisfactory book. In the metallurgical part, more attention is paid to fact and less to untested improvements than is the case in the corresponding book by Borchers. The chapter on the electrolysis of the alkali chlorides is welcome though by no means so full or so accurate as it should be. The last chapter on the relative values of different forms of power is also useful. While the potential difference under which a reaction takes place is of great importance, the calculation of efficiency with reference to voltage as well as to current is not very satisfactory because the potential difference varies with the distance between the electrodes. It is not correct to take the value calculated from the heat effect as necessarily giving the minimum decomposition voltage. In spite of a few blemishes, the book is the most satisfactory work of its kind to appear in any language.

Wilder D. Bancroft

Laboratory Instructions in General Chemistry. *By Ernest A. Congdon. 14 × 21 cm; pp. vii + 110 Philadelphia: P. Blakiston's Son and Co., 1901. Price: $1.00.* — This manual is designed to be used in conjunction with any of the standard textbooks of elementary chemistry. It gives, therefore, detailed directions for the performance of the experiments which are essential to such a course, — the preparation of elements and compounds, and the investigation and comparison of their properties and reactions. The selection of the experiments has been well made, attention having apparently been directed to the amplification of apparatus and method. A number of advanced problems are suggested, which are to be performed only after consultation with the instructor. The students are frequently directed how to avoid certain dangers; in the case of arsine (exp. 209) this is neglected.

A very satisfactory feature of the manual is that from the start the student makes use of his most important instruments,—the balance, thermometer, and manometer. Since the teacher must draw attention to the fact that the instruments are not by any means perfect, does it not seem preferable to tell a student how closely a weighing should be made in place of stating "Accurately weigh" (p. 92 and other places)?

That solubility determinations of gases, liquids, and solids are made and that the plotted results (p. 33) are understood by the students is assuredly a sign of promise and progress; such can not be said of an attempt to teach chemical reactions (experiment 29) before a single quantitative experiment, or even the preparation of an element has been attempted, and also of the almost complete omission of oxidation reactions.

The most interesting feature is the appendix where there are gathered the directions for the experimental modification of the laws of chemistry, the presentation of which most chemical teachers are, as a rule, too lazy, too overworked, or too ignorant to attempt. The objects of these experiments are: the verification of the laws of conservation, combining proportions, behavior of gases; the determination of molecular weights by vapor-density and lowering of the freezing-point; of equivalent and atomic weights; and methods of analysis.

To every teacher of chemistry, this book is necessary, since its methods merit trial, comparison, and criticism; in the hands of a competent instructor it will be one of the best of our elementary manuals. *H. R. Carveth*

Evolution of the Thermometer. *By Henry Carrington Bolton. 12 X 16 cm; pp. 98. Easton: The Chemical Publishing Company, 1900. Price: $1.00.* — This is a short monograph covering the years from 1592 to 1743. From it we learn that the credit for the first thermometer is due to Galileo, who made use of an air thermometer with water or alcohol seal. The measurement of heat changes by means of the expansion of a liquid in a sealed tube was put in practice about 1644 by Ferdinand II, of Tuscany. [On page 32, the date 1654 appears to be a misprint.] Boyle introduced the idea of a fixed point, using the freezing-point of anise-seed oil because he believed that the melting-point of ice varied with the latitude. About the same time in 1664, Hooke made thermometers with the freezing-point of water as a fixed point. Five years later, in 1669, Honoré Fabri suggest the use of two fixed points with an arbitrary number of degrees between them. His choice of a higher point, the highest heat in summer, was not destined to be adopted, and it was not until 1694 that Renaldini advocated the selection of the freezing-points and boiling-points of water as the standards.

It is not clear who first used mercury as an expanding liquid, but this is not important since Fahrenheit's instruments were so much better than anything previously known that the thermometer in general and the mercury thermometer in particular may be considered as his invention. Not only did he take great pains in the matter of workmanship, but he recognized some of the sources of error due to the nature of the glass containing-vessel. His selection of a scale was unfortunate and seems not to have been based on anything. In spite of this, his scale, or a modification of it, is still in use in all English-speaking countries. The way this came about was very natural. For years, Fahrenheit's thermometers were the best in the world and a merely theoretical criticism would not be likely to count for much with people who still use pounds, ounces, pennyweights, and other abominations.

On the scale suggested by Celsius in 1742, the boiling-point of water was taken as zero and the melting-point of water as one hundred. The inversion of this scale is due to Christin of Lyons, who worked it out in 1743 independently of Celsius, though his scale is always known by the latter's name.

Mr. Bolton has written a very interesting little book, but he has been misguided enough to have it bound in a way that is not to be forgiven.

Wilder D. Bancroft

Analyse des Gaz. *Par M. E. Pozzi-Escot. (Encyclopédie Scientifique des Aide-Mémoire). 11 × 19 cm; pp. 200. Paris: Gauthier-Villars.* — The headings of the chapters are: sampling; apparatus; reagents; analytical characteristics of the more important gases; qualitative study of gases; analysis of gaseous mixtures; analytical apparatus; heating power of gases.

Wilder D. Bancroft

Les Diastases et leurs Applications. *By M. E. Pozzi-Escot. (Encyclopédie Scientifique des Aide-Mémoire. 12 × 19 cm; pp. 216. Paris: Gauthier-Villars. Price: paper, 2 50; boards, 3 francs.* — At first sight it might seem that the diastases lay outside the realm of the physical chemist. A perusal of this little volume will convince one of the contrary. The study of the laws according to which the ferments work is physical chemistry pure and simple. The analogy between these organic ferments and the so-called inorganic ferments of Bredig is very striking and interesting. This volume is not quite as one-sided as many French books are; but it can certainly lay more claim to being interesting than to being complete. *Wilder D. Bancroft*

Engineering Chemistry. *A manual of quantitative chemical analysis for the use of students, chemists and engineers. By Thomas B. Stillman. 15 × 22 cm; pp. xxii + 503. Easton: The Chemical Publishing Co., 1900. Price: $4.50.* — The secondary title of this book shows that it is a manual of quantitative analysis for the use of engineers and others. It is an interesting commentary on the chemistry of to-day that such a manual can be sold, and legitimately, under the title of Engineering Chemistry. Since engineering chemistry is, for the present, analytical chemistry pure and simple, comment on what it might be is superfluous.

There is an immense amount of ground covered in the book, special stress being laid on "gas analysis and valuation, blast-furnace practice, the heating value of fuels, the purification of water for technical purposes, lubrication, car illumination, and the examination of Portland cement"

Wilder D. Bancroft

Handbook of Practical Hygiene. *By D. H. Bergey. 14 × 19 cm; pp. 164. Easton: The Chemical Publishing Co., 1899. Price: $1.50.*—The subdivisions of the book are: atmospheric air; water; soil; sanitary analysis of foods; ventilation and heating. Of these, the first is the most interesting because, in addition to the analysis of the air, there are paragraphs devoted to humidity, hygrometers, evaporation of moisture from the earth's surface, measurement of solar radiation, and measurement of terrestrial radiation. The section on the sanitary analysis of foods takes up milk, butter, meat and meat products, flour, vinegar, coffee and tea, and the detection of preservatives. Five pages are devoted to the question of ventilation and heating. There is a good index. *Wilder D. Bancroft*

The Chemists' Pocket Manual. *A practical handbook containing tables, formulas, calculations, physical and analytical methods for the use of chemists, assayers, metallurgists, manufacturers, and students. By Richard K. Meade. 10 × 15 cm; pp. 204. Easton: The Chemical Publishing Co., 1900. Price: bound in red morocco, with flap and elastic, for pocket use, $2.00.*—This seems to be an excellent little book and it contains a great deal of information in a small compass. The reviewer would prefer to see the Joule defined as a volt-coulomb, and he would suggest adding two other pages in the second edition, and giving the boiling-point and freezing-point constants for most of the solvents studied. This would be of advantage to the hygienic chemist as well as to the physical chemist. The composition of manganine should also be given.

Wilder D. Bancroft

Commercial Organic Analysis. *By Alfred H. Allen. Third Edition, illustrated, with Revisions and Addenda by the Author and Henry Leffmann. Vol. II., Part I.; 16 × 23 cm; pp. x + 387. Philadelphia: P. Blakiston's Son and Co., 1899. Price: cloth, $3.50.*—Owing to the fact that the hasty revision of this book was rendered necessary by the danger of an unauthorized reprint, the present volume has been practically rewritten and revised by Dr. Leffmann. It was impossible to submit manuscript or proof-sheets to Mr. Allen, although the American editor had his cooperation through correspondence and large amount of manuscript notes, clippings, and references which he utilized. It is, of course, unfortunate that Dr. Leffmann was unable to have Mr. Allen's advice, for his large practical experience and wide familiarity with the subject would have been of great value, and would have added greatly to the value of the book. Notwithstanding all these disadvantages, the present volume is a distinct improvement on the second edition. Some idea of the book may be gained from the following brief review of its contents. The fixed oils and fats are first considered, their general characters are discussed, the method of extraction and purification are given and their physical and chemical properties outlined. A special chapter is devoted to the constitution and chemical properties of the fats, oils, and waxes, another to their classification, and then the examination of the fixed oils for foreign matters is taken up. Finally, the identification of the fixed oils and the special characters and modes of examining fatty oils is considered. After this come chapters devoted to the higher fatty acids, soaps, glycerol and cholesterol. The most important additions to the present volume are the following: the bromine thermal method, methods for the determination of glycerol, the acetyl number, various tests for oxidation of oils, the composition of dynamites and smokeless powders, and the official methods for their examination.

For the analytical chemist, the book is simply indispensible, and as a reference book it should be in the library of every chemist. *W. R. Orndorff*

REVIEWS

The object of this department of the Journal is to issue, as promptly as possible, critical digests of all Journal articles that bear upon any phase of Physical Chemistry.

General

The atomic weight of radio-active barium. *S. Curie. Comptes rendus*, 131, *382* (*1900*). — The atomic weight of barium from barium chloride came out 138, while a specimen of the same salt containing a large amount of radium gave 174 as against 146 previously obtained (4, 400). *W. D. B.*

The true atomic weights of ten elements deduced from recent publications. *G. Hinrichs. Comptes rendus*, 131, *34* (*1900*). — The following atomic weights are adopted : H 1, C 12, O 16, Cl 35.5, Br 80, S 32, Na 23, Ag 108, Ba 137, Bo 11. The author maintains that the difference between the 'atomic ratio' and the 'analytical ratio' falls within the limit of experimental error in the recent determinations of the atomic weight of boron, and that, therefore, the value of 11.00 is the correct one. *W. D. B.*

Thermochemistry of the ethylene diamines. *M. Berthelot. Ann. Chim. Phys.* (*7*) 20, *163* (*1900*). — Reviewed (4, 415) from Comptes rendus, 129, 687, 694, 743 (1899).

On the mercury alkyls. *M. Berthelot. Ann. Chim. Phys.* (*7*) 20, *158* (*1900*). — Reviewed (4, 401) from Comptes rendus, 129, 918 (1900).

Investigations in the uric series. *M. Berthelot. Ann. Chim. Phys.* (*7*) 20, *189* (*1900*). — Reviewed (4, 401) from Comptes rendus, 130, 360 (1900).

Studies on the isomerism of the sulphocyanates. *M. Berthelot. Ann. Chim. Phys.* (*7*) 20, *197* (*1900*). — Reviewed (4, 401) from Comptes rendus, 130, 441 (1900).

Investigations on the metallic derivatives of acetylene. *M. Berthelot and M. Delépine. Ann. Chim. Phys.* (*7*) 19, *5* (*1900*). — Reviewed (4, 401) from Comptes rendus, 129, 361 (1899).

Thermochemistry of lactic acid. *M. Berthelot and M. Delépine. Ann. Chim. Phys.* (*7*) 20, *149* (*1900*). — Reviewed (4, 401) from Comptes rendus, 129, 920 (1899).

Thermochemical studies on the chief alkaloids of opium. *E. Leroy. Ann. Chim. Phys.* (*7*) 21, *87* (*1900*). — Reviewed (4, 219, 401) from Comptes rendus, 128, 1107 ; 129, 220 (1899).

Heat of neutralization of hydrocarbonyl ferrocyanic acid compared with that of hydroferrocyanic acid. *J. A. Müller. Ann. Chim. Phys.* (7) 20, *377* (*1900*). — Reviewed (4, 416) from Comptes rendus, 129, 962 (1899), but ascribed by a misprint to J. A. Miller.

Model to illustrate the movement of ions. *F. Kohlrausch. Zeit. phys. Chem.* 34, *559* (*1900*). — A mechanical model for lecture demonstration. The relative movements of the ions are illustrated by means of small metal cylinders hung on strings which pass over concentric pulleys at different diameters. *A. P. S.*

Model to illustrate the movement of ions. *W. L. Miller and F. B. Kenrick. Zeit. phys. Chem.* 35, *440* (*1900*). — The mechanical principle on which this model is constructed is the same as that employed by Kohlrausch (see preceding review), but this appears to be, on the whole, a more serviceable piece of apparatus for lecture demonstration than the other. *A. P. S.*

One-Component Systems

Note on the melting-point of lithium. *G. W. A. Kahlbaum. Zeit. anorg. Chem.* 23, *220* (*1900*). — A sample prepared by A. Guntz of Nancy, melted at 186°. The value given by Bunsen and Mathiessen was 180°. *W. D. B.*

The boiling-points of zinc and cadmium. *D. Berthelot. Comptes rendus*, 131, *380* (*1900*). — By means of electric heating, the error due to radiation is reduced to a minimum. The mean of five measurements gives 920° as the boiling-point of zinc. The corresponding value for cadmium is 778°. *W. D. B.*

Studies on the vapors given off by the two forms of mercuric iodide. *D. Gernez. Ann. Chim. Phys.* (7) 20, *384* (*1900*). — Reviewed (4, 220) from Comptes rendus, 128, 1516 (1899).

Note on the article of B. Woringer entitled: On the vapor-pressure of a series of benzene compounds. *A. Winkelmann. Zeit. phys. Chem.* 35, *480* (*1900*). — Contains a correction of certain statements in the article (3, 73) regarding previous work by Winkelmann. *A. P. S.*

On two loci relative to the densities of liquid carbonic acid and its saturated vapor. *E. H. Amagat. Comptes rendus*, 131, *91* (*1900*). — It is pointed out that what M. Mathias has proved is that the diameter of the curve for the densities of liquid and vapor, and the diameter for points at which liquid and vapor have the same volume, cannot both be straight lines. It is possible, however, that either may be curved and the other straight, or that both may be slightly curved. *W. D. B*

The law of corresponding states. *D. Berthelot. Comptes rendus*, 131, *175* (*1900*). — A statement of the belief that the law of corresponding states is absolutely accurate if we displace the zeros of volume and temperature by amounts varying with each substance [See 4, 546]. *W. D. B.*

Some points on isomerism in the aromatic series. *Oechsner de Coninck. Ann. Phys. Chim.* (7) 20, *136* (*1900*). — "Aromatic isomers fall into pairs whether one studies the qualitative reactions, solubilities, melting- and boiling-points, densities, heats of solution, heats of formation, or whether one considers their tendency to react or not to react." *W. D. B.*

Two-Component Systems

On the alloys of antimony and tin. *W. Reinders. Zeit. anorg. Chem.* 25, *113* (*1900*). — The freezing-point curve rises steadily from the melting-point of pure tin, 232°, to that of pure antimony, 622°. There are three quadruple points, at about 243°, 310°, and 430°. The first and last solid phases are mix-crystals of antimony in tin and of tin in antimony respectively. The two intermediate phases are not known definitely, but the author inclines to SbSn and Sb_4Sn_3 or Sb_5Sn_4. To the reviewer $SbSn_2$ seems quite as probable from the evidence as SbSn. From 10-40 percent Sb we have cubical crystals which by forty percent are beginning to change. At fifty percent there are no cubes left, the mass being chiefly flat plates, the edges not forming right angles. This seems inconsistent with the views of the cubes being SbSn. The author is non-committal as to the cubes and plates being identical or not. If they are not identical, the cubes cannot have the formula SbSn. If they are identical, then there is nothing in the paper to show the crystalline form of the second set of compounds. *W. D. B.*

Contributions to our knowledge of amalgams, II. *W. Kerp and W. Böttger. Zeit. anorg. Chem.* 25, *1* (*1900*). — The authors have determined the freezing-point curves from 0° to 100° for a number of amalgams and have analyzed the coexistent solid and liquid phases. With sodium amalgam, $NaHg_6$ is apparently solid phase up to about 40.5°; from there to about 150° we have $NaHg_5$. $LiHg_5$ is solid phase over the whole range, 0° to 100°. Below 0° KHg_{14} is stable; from about 0° to 71°, we have KHg_{12}; from 71° to 75°, KHg10; and above 75° a solid solution. Below 0° $RbHg_{12}$ separates; but it is not certain whether the solid phase above this temperature is a solid solution or not. Below 30° we have $SrHg_{12}$; above 30° a solid solution. Below 30° the solid phase is $BaHg_{13}$; from 30° to 100° it is $BaHg_{12}$. Cadmium amalgam crystallizes as Cd_2Hg_7 from 0° to about 44°; at higher temperatures, a solid solution is formed. No definite results could be obtained for zinc amalgam because the composition of the solid phase appeared to vary with the time. This would seem to indicate the formation of an instable precipitate which reached equilibrium very slowly.

In the case of the solid sodium amalgams, a little less sodium is found than is called for by the formulas. This is very probably due to the presence of mother-liquid. On the other hand, pressing the crystals changes the composition. The authors attribute this to a lowering of the inversion point. While this is possible, a change of 40° under moderate pressure is surprising and seems less probable than a change of composition of a solid solution. The matter could easily be settled definitely by holding the amalgam at 0° under constant pressure until equilibrium is reached and seeing whether the final composition was or was not $NaHg_6$ [Cf. following review]. *W. D. B.*

The amalgams of sodium and potassium. *A. Guntz and Ferée. Comptes* *rendus*, 131, *182* (*1900*). — The authors deny the statement of Kerp, that different crystals of sodium amalgam are obtained under moderate pressure. They believe in the existence of $NaHg_8$ at temperatures below zero, of $NaHg_6$ at ordinary temperatures; of $NaHg_5$ at temperatures above 100°. Under pressures of 200–1200 kg/cm², both $NaHg_6$ and $NaHg_5$ pass into $NaHg_4$. At 19° a potassium amalgam KHg_{18} is obtained. At ordinary pressures, KHg_{12} is the stable form passing under pressure into what is thought to be KHg_{10}. The authors are distinctly handicapped in their work by their ignorance of the phase rule.

W. D. B.

Cryoscopic and ebullioscopic studies. *A. Battelli and A. Stefanini. Nuovo Cimento*, (*4*) 9, *5* (*1899*); *Ann. Chim. Phys.* (*7*) 20, *64* (*1900*). — After a long discussion of the sources of error in freezing-point determinations, the authors describe their own experiments with dilute sugar solutions. Their apparatus was protected on all sides, including the top; they used boiled-out water; the stirring was mechanical; corrections were applied for convergence temperature, etc. At different times they used a Beckmann thermometer, a resistance thermometer, and a thermopile. For solutions containing from 0.7 to 14 g of sugar per liter they find a molecular depression rising from 1.84 to 1.88. As a more dilute solution (0.34 g) gave 2.02, they conclude that the value is constant at 1.87. Boiling-point measurements with potassium antimony tartrate were made at dilutions of eight, sixteen, and thirty-two liters. The molecular weights were 287, 304, 329, which they call practically constant at 322, though one does not quite see why there should not be electrolytic dissociation. The accuracy of the results seems to stand in no obvious relation to the precautions which they took.

W. D. B.

Note on the solubility of mercury halides and especially mercuric iodide in organic solvents. *O. Sulc. Zeit. anorg. Chem.* 25, *399* (*1900*). — A few experiments were made to determine the solubility of the chloride, bromide, iodide, and cyanide of mercury in chloroform, carbon tetrachloride, bromoform, ethyl bromide, ethyl iodide, and ethylene dibromide. Mercuric iodide was then determined in nineteen solvents. The author states that these last measurements were made at the boiling-points of the solvents; but this could only be strictly true in case mercuric iodide were absolutely insoluble, because the solutions were heated on a water-bath. Since the solid phase was sometimes yellow crystals and sometimes yellow and red crystals mixed, it seems fair to assume that these so-called solubility determinations are fortuitous data referred to fictitious temperatures.

W. D. B.

Solubility of cupric chloride in organic solvents. *Oechsner de Coninck. Comptes rendus*, 131, *58* (*1900*). — Qualitative experiments. *W. D. B.*

Liquefaction of methyl chloride and sulphur dioxide. *F. Caubet. Comptes rendus*, 131, *108* (*1900*). — A diagram showing the boiling curves and dew curves for seven mixtures of methyl chloride and sulphur dioxide. Two of the curves show loops, there being a temperature and pressure at which liquid and vapor of the same composition are in equilibrium. Others of the curves show transitions from this type to the normal. Owing to the very slight difference between the boiling pressures and the dew pressures, the phenomena of retrograde condensation could not be observed experimentally. *W. D. B.*

The extraction of oxygen by solution at low temperature. *G. Claude. Comptes rendus*, 131, *447* (*1900*). — Attempts have been made to find a solvent which should dissolve oxygen much more readily than nitrogen at low temperatures; but all efforts have proved fruitless. *W. D. B.*

Preparation and properties of two borides of silicon: SiB_3 and SiB_6. *H. Moissan and A. Stock. Comptes rendus*, 131, *139* (*1900*). — The authors have prepared the borides SiB_3 and SiB_6 by heating boron in electrically fused silicon. These compounds scratch the ruby, but do not scratch the polished face of a diamond. The density of SiB_3 is 2.52 and that of SiB_6 is 2.47. Both substances conduct electricity. *W. D. B.*

On the composition by volume of hydrofluoric acid. *H. Moissan. Ann. Chim. Phys.* (7) 19, *531* (*1900*). — Reviewed (4, 409) from Comptes rendus, 130, 544 (1900).

Poly-Component Systems

Action of hydrogen on the sulphide of arsenic. *H. Pélebon. Comptes rendus*, 131, *416* (*1900*). — Above 300°, hydrogen and the sulphide of arsenic reacts, and the reaction is reversible. At 610° the percentage of hydrogen in the gas is about 93 percent of the total, provided hydrogen is in excess and there is still liquid sulphide of arsenic in the tube. If arsenic in excess be added, the ratio falls to 78.7. With an excess of arsenic and no liquid sulphide, the ratio is 64.9. *W. D. B.*

The equilibrium between lead, zinc, and their fused chlorides. *W. Reinders. Zeit. anorg. Chem.* 25, *126* (*1900*). — On electrolyzing fused mixtures of zinc and lead chlorides, the resulting alloy does not have the equilibrium concentration. The actual concentrations at equilibrium were therefore determined by direct experiment. When the fused mixture contains over 0.1 percent lead chloride, the metal in equilibrium is practically pure lead. The author has also measured the electromotive force of cells of the type $Zn + Pb \mid ZnCl_2 + PbCl_2 \mid PbCl_2 \mid Pb$. *W. D. B.*

Solubility of a mixture of salts having a common ion. *C. Touren. Comptes rendus*, 131, *259* (*1900*). — Assuming complete dissociation for potassium carbonate, the curve for the solubility of potassium nitrate in potassium carbonate solutions coincides for part of its course with those for potassium nitrate in solutions of potassium chloride and potassium bromide. The solubility of potassium nitrate is increased by carbonic acid, so the solubility isotherm for the salt in presence of potassium bicarbonate is not comparable with the others. *W. D. B.*

On the solubility of the carbonates of the alkaline earths in water containing carbon dioxide. *G. Bodländer. Zeit. phys. Chem.* 35, *23* (*1900*). — A discussion of the experimental results of Schloesing [Comptes rendus, 74, 1552 (1872); 75, 70 (1872)] on the solubility of carbonates of calcium and barium, and of

Engel [Comptes rendus, 100, 144 (1885)] on magnesium carbonate. Van 't Hoff's formula (Vorlesungen, 1, 149) applied only for infinite dilution; the author deduces a formula which applies for finite dilutions. In the case of calcium carbonate it takes the form:

$$HCO_3' = 12.69 \sqrt[3]{K_1CO_2}.$$

The first dissociation of the bicarbonate into $Ca^{\cdot\cdot}$ and $2HCO_3'$ is found to be about 20,000 times greater than the second into $H^{\cdot}$ and CO_3'', so that the concentration HCO_3' is practically a measure of the total concentration. CO_2 in the formula represents the pressure of carbon dioxide in atmospheres. The formula holds for all those carbonates of the group which are very sparingly soluble; only the value K_1 is different for different individuals. *A. P. S.*

Absorption, V. *J. M. van Bemmelen. Zeit. anorg. Chem.* 23, *111* (*1900*). — Colloidal metastannic acid absorbs hydrochloric acid in a marked fashion. The distribution ratio is not constant. At 15° and in presence of saturated water vapor, the colloid contains 2.2 reacting weights of H_2O to one of SnO_2. If we consider the whole of this water as solvent, the concentration of potassium chloride in the colloid is less than in the solution. It is not certain, however, that the colloid contains so much water in concentrated solutions, or that the whole of it should be considered as water. If half of it is part of the stannic acid, the concentration of potassium chloride in the colloid is greater than in the solution. However one calculates it, the distribution ratio for potassium chloride is approximately constant and thus differs markedly from the corresponding ratio for hydrochloric acid. *W. D. B.*

Absorption, VI. *J. M. van Bemmelen. Zeit. anorg. Chem.* 23, *321* (*1900*). — A general discussion of the phenomena attending the absorption of solutes by colloids. This includes a study of the qualitative distribution of a solute between an absorbing substance and a solution. The case of colloids in colloids is treated first; then the absorption of crystalline substances. In the latter case, it is shown that the absorption depends on the nature and state of the colloid, on the nature of the liquid solvent, on the nature and concentration of the solute, and on the temperature. A special section is devoted to the absorption of two substances with resulting chemical reactions, and yet another to the case of absorption with hydrolysis. The last three pages treat of the change in absorption when the gel changes, either by passing into another modification or into the crystalline state. *W. D. B.*

The effect of neutral salts on the partial pressure of ammonia in aqueous solutions. *W. Gaus. Zeit. anorg. Chem.* 25, *236* (*1900*). — The author has determined the change in the partial pressure of ammonia when neutral salts are added to aqueous ammonia. The change was measured by passing electrolytic gas through the solution into hydrochloric acid and determining the conductivity of the acid. With the salts of the alkalies, an increase of pressure is observed: with other salts a decrease, the decrease being largest with the silver and copper salts. *W. D. B.*

Equilibrium phenomena in the distribution of an acid between ammonia and sparingly soluble metal hydroxides. *W. Herz. Zeit. anorg. Chem.* 23, *222*;

24, *123* (*1900*). — When zinc sulphate, nitrate or chloride reacts with ammonia, the resulting equilibria cannot be represented by the theoretical formula Zn $1.5/NH_4 =$ *const.* On the other hand, the empirical formula $Zn/NH_4 =$ *const* represents the facts very well so long as ammonia is not present in excess.

Beryllium hydroxide is so insoluble that ammonia precipitates it quantitatively from solutions of beryllium salts. Cadmium salts behave like the corresponding zinc salts. *W. D. B.*

Aqueous tin chloride solutions. *W. von Kowalewsky. Zeit. anorg. Chem.* 23, *1* (*1900*). — The reaction between tin tetrachloride and water is a reversible one, less acid being formed the higher the temperature. The auther concludes that the colloidal stannic hydroxide reduces the conductivity of hydrochloric acid about twenty-five percent. *W. D. B.*

On the behavior of some halide compounds of the carbon group analogous to stannic chloride. *W. von Kowalewsky. Zeit. anorg. Chem.* 25, *189* (*1900*). — The reaction between titanium tetrachloride and water is a reversible one; but if the solution be heated, titanic acid precipitates and does not react on cooling. With silicon tetrachloride and water, the reaction runs practically to an end. *W. D. B.*

On the determination of sulphuric acid in presence of iron; a note on solid solutions and on the hydrolysis of chromium and iron. *T. W. Richards. Zeit. anorg. Chem.* 23, *383* (*1900*). — Attention is called to the fact that Küster and Thiel in their papers (3, 251; 4, 150, 411) have overlooked important papers by Richards, by Schneider, and by Gladding. It is further pointed out that the distribution ratio, if any, must refer to the undissociated salt, a view which is confirmed by the influence of hydrochloric acid on the occlusion of barium chloride by barium sulphate. While Küster and Thiel assume that $Ba[Fe(SO_4)_2]_2$ is occluded, the author inclines to the view that it is really a basic salt because acidifying the solution decreases the occlusion, while increased hydrolysis due to dilution increases the occlusion. *W. D. B.*

The determination of sulphuric acid in presence of iron, IV. *F. W. Küster and A. Thiel. Zeit. anorg Chem.* 25, *319* (*1900*). — The authors state that they did not overlook the paper by Jannasch and Richards, and that they do not accept the hypothesis of Richards (preceding review). *W. D. B.*

Some complex silver salts. *K. Hellwig. Zeit. anorg. Chem.* 25, *157* (*1900*). — Silver iodide, cyanide, chloride, sulphocyanate, and bromide are soluble in silver nitrate solutions in the order named, the iodide being the most soluble. Silver cyanide, sulphocyanate, iodide, and bromide are soluble, in the order named, in solutions of the potassium salts of the corresponding acids, the cyanide being the most soluble. In all these cases, complex salts exist to a greater or lesser extent in solution, as shown by boiling-point determinations. The following double salts were prepared: $Ag_3I(NO_3)_2$, $Ag_2I(NO_3)$, $Ag_2Br(NO_3)$, $Ag_3CN(NO_3)_2$, $Ag_3SCN(NO_3)_2$, K_2AgI_3, $KAgI_2$, $KAg(SCN)_2$. In the case of the silver nitrate complex salts, the nitrate is anion and we have a complex cation.
W. D. B.

The oxidation of cobalt and cerium salts in alkaline solution. *A. Job. Ann. Chim. Phys.* (*7*) 20, *205* (*1900*). — Ferric salts dissolve in sodium pyrophosphate solution and are then colorless. In such a solution, it is easy to titrate ferrous iron with permanganate. Cobalt salts dissolve in concentrated solution of potassium bicarbonate with a pink color. On adding chlorine or hydrogen peroxide, the color changes to a green, very like that of concentrated solutions of nickel salts. This is due to the formation of a cobaltic salt. In acid solutions, the cobaltic salt is reduced by hydrogen peroxide.

Cerous salts, dissolved in aqueous potassium carbonate, oxidize in the presence of air to perceric salts, which latter react with the former, making ceric salts. In acid solutions, hydrogen peroxide changes ceric salts into stable perceric salts. From potassium carbonate solutions of perceric salts, a stable perceric double carbonate crystallizes, which decomposes only at 200°. We thus have salts corresponding to cerous oxide, Ce_2O_3, ceric oxide, CeO_2, perceric oxide CeO_3. In addition, the behavior of perceric solutions in the presence of hydrogen peroxide indicates the existence of a salt corresponding to the oxide CeO_4. This is a most interesting and valuable paper, and the work has been done in a very creditable manner. *W. D. B.*

Hydrogenization of acetylene and ethylene by finely divided platinum. *P. Sabatier and J. B. Senderens. Comptes rendus*, 131, *40* (*1900*). — Cold platinum black acts on a current of mixed acetylene and hydrogen, forming chiefly ethane when hydrogen is in excess, and chiefly ethylene when acetylene is in excess. At higher temperatures, the reaction takes place more readily and condensation products are also formed. Platinum black reduces hydrogen and ethylene at first to ethylene, but owing to slight carburation, soon ceases to be active unless heated. *W. D. B.*

The action of reduced nickel on acetylene. *P. Sabatier and J. B. Senderens. Comptes rendus*, 131, *187* (*1900*). — When no hydrogen is present, nickel only reacts to any extent with acetylene when the temperature is raised above 180°. A number of substances are formed, including liquids as well as gases. When hydrogen is present, its reaction with acetylene makes the nickel incandescent and a series of complex reactions takes place. *W. D. B.*

Action of finely divided platinum, cobalt, and iron on acetylene and ethylene. *P. Sabatier and J. B. Senderens. Comptes rendus*, 131, *267* (*1900*). — The action of finely divided platinum, cobalt, and iron on acetylene and on ethylene is very similar to that of nickel except that the nickel puffs up much more than the other metals. *W. D. B.*

Correction to the systematic detection of anions. *R. Abegg and W. Herz. Zeit. anorg. Chem.* 25, *405* (*1900*). — A few modifications of the original scheme (4, 636) have been introduced in order to obviate some difficulties brought up by Fresenius. *W. D. B.*

Action of hydrofluoric acid and of fluorine on glass. *H. Moissan. Ann. Chim. Phys.* (*7*) 19, *516* (*1900*). — Reviewed (4, 412) from Comptes rendus, 129, 799 (1900).

On the simultaneous phenomena of oxidation and hydration in organic compounds under the influence of oxygen and light. *M. Berthelot. Ann. Chim. Phys.* (*7*) 20, *42* (*1900*). — Reviewed (4, 412) from Comptes rendus, 129, 627 (1899).

Velocities

Periodic phenomena in the solution of chromium in acids, I. *W. Ostwald. Zeit. phys. Chem.* 35, *33* (*1900*). — Hittorf has shown that chromium exists in three different modifications; in one of them the metal appears as a readily oxidizable substance standing between zinc and cadmium in the electrochemical series and dissolving readily in acids with formation of chromous compounds and hydrogen; in the second it is about like mercury in its position in the electro-chemical series, is not attacked by acids, but when made the anode in a current of sufficient pressure, it dissolves forming chromic acid; while in the third form it yields chromic compounds.

Ostwald, in repeating some of Hittorf's experiments with the first of these varieties, noticed that the velocity of reaction with acids varied periodically. In the ordinary case of the solution of a metal in an acid, if the velocity of reaction be measured by the rate of evolution of hydrogen, it will be found that this is at first slow, then more or less rapidly increases to a maximum, after which it gradually falls, reaching in the end zero, where either the acid or the metal is all used up. In the case of chromium the reaction begins in the usual way, the maximum is reached, and the velocity of evolution then diminishes; but instead of dropping continuously to zero, it turns at a certain point and begins to rise again, and this process, repeating itself an indefinite number of times, gives rise to a series of maxima and minima.

The acids used by Ostwald were mainly hydrochloric and sulphuric. The ingenious arrangement made use of by him to render the reaction self-registering cannot be described here.

The results lead to the conclusion that the seat of the phenomenon is in the metal and not in the acid used. Two pieces of metal in the same solution give a curve representing the sum of their velocities of reaction; and since the periods at which the maxima recur are not the same for the two pieces, the curve resulting evidently has the form of two curves superposed on one another. If the two pieces of metal be brought into contact, the curve at once becomes simple and takes on the period which is the smaller of the two. A piece of "active" chromium brought into contact with a piece which is "inactive," transforms it into the active variety. The length of period characteristic of a given piece of the metal depends partly on the treatment to which it has previously been subjected; but it does not follow that pieces which have received the same treatment will show the same behavior. On the contrary, when three pieces were treated as nearly as possible alike and then put into acid, they gave curves showing the widest differences. Since previous treatment has no constant effect, the peculiarity must lie in the substance of the metal and not on its surface.

At this stage of the investigation, some new and purer material was taken up, and the whole phenomenon at once ceased to make its appearance; the metal dissolved like any other, and all attempts to cause it to take on the peculiarities previously observed were in vain. It was therefore necessary to return to the older material in order to continue the work. The method by which this peculiar form of chromium may be produced will be made the subject of a special article by Ostwald and Goldschmidt later on.

Some pieces gradually lose the property of "vibrating" in the process of solution, and, while they may be made active again by being taken out of the liquid and brought into contact with an active piece, the property is gradually lost when they are further dissolved. The influence of the concentration of the acid is in the direction that the periods are longer the more dilute the acid employed. A rise in temperature shortens the length of the period, and this change is, in some cases, in quantitative agreement with the general rule that a rise of 10 degrees causes approximately a doubling of any reaction velocity; this rule, however, is not invariable here.

The chapter on the influence of added substances is a complex and surprising one. Even the mixing of the two acids, sulphuric and hydrochloric, gives rise to a considerable increase in complexity of the curves, and in every case to a dying out of the vibration after the lapse of a certain time. Addition of potassium chromate, colloidal platinum, or copper chloride had little effect. On the other hand, the addition of potassium iodide caused a marked retardation of the periods and beyond a certain concentration causes the disappearance of the vibrations altogether. Potassium sulphocyanate and cyanides show much the same effect; but formaldehyde is the most powerful of all these "retarders," and its effects are noticeable even at very great dilution. Other substances on the contrary cause a decrease in the length of the periods, i. e., they hasten the recurrence of the maxima. Such are nitric acid and the nitrates, chlorates, bromates, etc. These are all oxidizing agents, while the retarders are all reducing agents; it is of interest to note that hydrogen peroxide falls into the latter class according to its action here.

The vibrations may also be observed when a galvanometer is put in circuit with the dissolving chromium and a platinum electrode placed in the vessel. The maxima and minima correspond to a potential difference in the metal of about 0.1 V. *A. P. S.*

Periodic phenomena in the solution of chromium in acids, II. *W. Ostwald. Zeit. phys. Chem.* 35, *204* (*1900*). — Pursuing the investigation, the author finds that a piece of chromium in the first stage of solution apparently gives up to the acid its power of calling forth the phenomenon of vibration; for if the same piece of metal be washed and transferred to fresh acid, it vibrates for a time and then becomes dormant, but if it be allowed to carry with it a small quantity of the original acid, the vibrations continue for a considerably longer period. If after it has become dormant it is again transferred to the original acid, the vibrations begin anew; and the acid which has already been in contact with a vibrating piece, acts the same as the original acid. This "active" acid retains its property for weeks, but can be weakened by dilution with fresh acid. The property is shown not to be due to chromium or hydrogen in solution. It is not regained by a dormant piece when allowed to remain in the air. These results which seemed to involve the whole problem in a further degree of complexity, were at last found to be due to the influence of the little bags in which the pieces of chromium were hung, for when these were suspended in glass they were no longer active; this refers however only to one preparation of the metal, made by fusion with gypsum, for the original stock showed the phenomenon of vibration, no matter how suspended. It was found then that the material of the bags contained starch, and this as well as dextrine was shown to have a very marked influence in bringing about the phenomenon of vibration. The influence of dextrine is noticeable even at a dilution of 0.00001 per cent. Inorganic colloids have no effect, but analogous organic substances, such as gum arabic, gum tragacanth, etc., show a marked action; the experiments on these substances lead in the end to the conclusion that the "dextrine" action is a property of all carbohydrates, and is the more developed the higher the molecular weight. The action of these bodies was not the same on the original first sample of chromium, with which their action brought forth great irregularities.

The rest of the article is given up to a more exact study of the described curves, and the conditions favorable or unfavorable to their uniformity.

A. P. S.

Action of bromine on phenyl-sulphon-acetic acid in phenyl-sulphon-propionic acid in aqueous solution; a contribution to chemical kinetics. *L. Ramberg. Zeit. phys. Chem.* 34, *561* (*1900*). — The reaction, which results in the formation of dibrom-methyl-phenyl-sulphone, carbon dioxide, and hydrobromic acid, probably occurs in one of two ways:

(*a*) $C_6H_5SO_2CH_2COOH + 2Br_2 = C_6H_5SO_2CHBr_2 + CO_2 + 2HBr.$

In this case it is truly a trimolecular reaction, and should give a constant when the ordinary formula is applied.

(*b*) It may go on in stages, as:

(1) $C_6H_5SO_2CH_2COOH + Br_2 = C_6H_5SO_2CHBrCOOH + HBr.$
(2) $C_6H_5SO_2CHBrCOOH + Br_2 = C_6H_5SO_2CBr_2COOH + HBr.$
(3) $C_6H_5SO_2CBr_2COOH = C_6H_5SO_2CHBr_2 + CO_2.$

In this case, if (1) goes on with measurable velocity and (2) instantaneously, the reaction will be purely bimolecular; if the velocities of (1) and (2) are alike, the reaction velocity follows a more complex formula which contains two constants. Since the concentration of unchanged bromine is the value used to determine the course of the change, reaction (3) does not come into consideration at all. The reaction of bromine on α-phenyl-sulphon-propionic acid, which results in the formation of the substance $CH_3(C_6H_5SO_2)CBrCO_2H$ is also studied, and the author is led to the following conclusions: The first of the two reactions goes on in several stages, while the second is a case of simple substitution. For very dilute solutions the reaction velocity is in both cases approximately proportional to the product of the concentration of the substances; but in concentrated solution to the product of the concentration of the acid and the square root of the concentration of the bromine. The relative velocity of the reaction increases with increasing dilution. *A. P. S.*

On the velocity of solution of solid bodies. *L. Bruner and S. Tolloczko.*

Zeit. phys. Chem. 35, *283* (*1900*). — The authors have determined the rate of solution of a number of substances and are led to give their support to the theory of Noyes and Whitney, that the whole question is one of diffusion; that the dissolving substance is always surrounded by a thin layer of saturated solution, and hence that the problem of a direct action between solid and unsaturated solution is beyond our reach. The formula employed contains a factor representing the area exposed at the beginning, and gives a very satisfactory constant; yet the surfaces show erosion at the end, hence the actual area suffers considerable change during the process; this lends support to the assumption that the action is really between a film of saturated solution and the surrounding medium, and not between this and the surface of the solid itself.

A. P. S.

The effect of hydrobromic acid on the rate of reaction of bromine on trimethylene. *G. Gustavson.* *Comptes rendus*, 131, *273* (*1900*). — The addition of traces of HBr_5H_2O causes bromine at first to react very readily with trimethylene. The author attributes the final decrease in the reaction velocity to the breaking up of the combinations of bromine with hydrobromic acid, an explanation which is so vague as not to deserve the name of an explanation at all.

W. D. B.

The combustion of gases. *S. Tanatar.* *Zeit. phys. Chem.* 35, *340* (*1900*). — It is well known that a mixture of gases which explode — say hydrogen and oxygen — in combining proportions will do so in the presence of a foreign gas, or of an excess of one of these gases themselves, only when the quantity of the inactive gas is below a certain percentage, generally a moderately high one. The author finds that as little as 11-12 percent of propylene prevents the explosion of hydrogen and oxygen, and gives as an explanation that the oxygen goes to the combustion of the propylene and not of the free hydrogen, the products being carbon monoxide and water.

A. P. S.

On the velocity of the explosion wave in acetylene. *M. Berthelot and H. Le Chatelier.* *Ann. Chim. Phys.* (*7*) 20, *15* (*1900*). — Reviewed (4, 413) from Comptes rendus, 129, 427 (1899).

On the explosion of potassium chlorate. *M. Berthelot.* *Ann. Chim. Phys.* (*7*) 20, *11* (*1900*). — Reviewed (4, 413) from Comptes rendus, 129, 926 (1899).

Electromotive Forces

On the electrocapillary functions of aqueous solutions. *Gouy.* *Comptes rendus*, 131, *255* (*1900*). — The author has studied the form of the pressure-potential curve for different electrolytes in capillary tubes. The variation in the height of the column from the value for sulphuric acid is as much as ten percent in some cases. The curves are not symmetrical, the positive side and the maximum varying with the nature of the anion, while the nature of the cathode determines the form of the negative side.

W. D. B.

The potential of silver in solutions of its mixed salts. *F. W. Küster and A. Thiel.* *Zeit. anorg. Chem* 23, *25* (*1900*). — The potential of difference between silver and a solution obtained by precipitating silver nitrate with varying relative amounts of potassium chloride and bromide varies continuously with the amount of bromide. [Cf. 4, 635]. *W. D. B.*

On the potential of the iodine electrode. *F. W. Küster and F. Crotogino. Zeit. anorg. Chem.* 23, *87* (*1900*). — A preliminary notice. The complete paper was reviewed (4, 697) from Zeit. anorg. Chem. 24, 225 (1900).

The decomposition voltage of fused and solid electrolytes. *C. C. Garrard. Zeit. Elektrochemie*, 6, *214* (*1899*); *Zeit. anorg. Chem.* 25, *273* (*1900*). — The author has determined the decomposition points for fused lead chloride, lead bromide, lead iodide, cadmium chloride, cadmium bromide, cadmium iodide, silver chloride, silver bromide, silver iodide, sodium iodide, potassium iodide, zinc chloride, zinc bromide, cuprous chloride; for solid lead bromide and silver iodide; for saturated solutions of lead chloride, cadmium chloride, and oxalic acid.

Some of the salts showed two decomposition points. With lead bromide and with oxalic acid a marked increase of internal resistance was obtained as soon as the decomposition point was passed. *W. D. B.*

The thermo-electricity of steels. *G. Belloc. Comptes rendus*, 131, *336* (*1900*). — The change of the electromotive force with the temperature shows two minima and one maximum for soft iron containing only a trace of carbon, soft steel containing three-tenths percent carbon, and hard steel containing 1.25 percent carbon. *W. D. B.*

Electrolysis and Electrolytic Dissociation

Study of the electrolysis of alkali chloride solutions, with a diaphragm. *F. Foerster and F. Jorre. Zeit. anorg. Chem.* 23, *158* (*1900*). — An exhaustive discussion of the losses due to the evolution of oxygen, formation of hypochlorites, and diffusion of caustic potash into the anode chamber. This last is the most serious difficulty and one that seems unavoidable unless one invents a diaphragm impermeable to hydroxyl as ion, discovers a non-aqueous solution corresponding to pyridine for lithium chloride, or uses a mercury cathode. Experiments are also given illustrating the theoretical views. With platinum iridium anodes, the yield in alkali drops rapidly from about ninety to about fifty-five percent, while the yield of chlorine is somewhat lower. Carbon anodes, if of good quality, do not alter the conditions appreciably, though there is of course some evolution of carbon dioxide, also some disintegration. The diaphragm used was Pukall's material and probably gave better results than would any of the substances used in technical work. *W. D. B.*

The electrolysis of fused salts. *R. Lorenz. Zeit. anorg. Chem.* 23, *97* (*1900*). — Attention is called to the sources of error in the electrolysis of fused salts. Owing to diffusion and distillation the yield may drop to zero and the determinations of decomposition values may be worthless. For more extensive experimental data, see the paper by Helfenstein (4, 636). *W. D. B.*

Electrolysis of concentrated hypochlorite solutions. *A. Brochet. Comptes rendus*, 131, *340* (*1900*). — When a concentrated sodium hypochlorite solution is electrolyzed, the reduction is at first greater than the oxidation. This ceased to be the case as soon as the hypochlorite concentration fell below seven per-cent. *W. D. B.*

Electrolytic precipitation of bismuth. *D. Balachewsky. Comptes rendus,* 131, *179* (*1900*). — The important points in getting a good adherent deposit of bismuth are: slightly acid solution; absence of large amounts of Cl, Br, and I; maximum current density 0.00060 amp/cm^2; matt electrodes. *W. D. B.*

Electrolytic determination of cadmium. *D. Balachewsky. Comptes rendus,* 131, *384* (*1900*). — Cadmium can be precipitated quantitatively on a copper cathode from a cadmium sulphate solution acidified with nitric acid, the current density changing from 0.004 amp/cm^2 at the beginning to c.006 amp/cm^2 at the end of the operation. A method similar to that for bismuth (preceding review) can also be used. *W. D. B.*

On the dissociating powers of some inorganic solvents. *P. Walden. Zeit. anorg. Chem.* 25, *209* (*1900*). — The author has investigated the solvents BCl_3, PCl_3, PBr_3, $SbCl_5$, $SiCl_4$, $SnCl_4$, SO_2, Br_2, $POCl_3$, $AsCl_3$, $SbCl_3$, S_2Cl_2, $SOCl_2$, SO_2Cl_2, the first eight of which show no dissociating tendency, while the remaining six dissociate binary salts to a greater or lesser extent.

The following empirical conclusions are formulated:

Binary salts are the most easily dissociated electrolytically.

Acids, ternary salts, and quarternary salts are often practically undissociated in solvents in which binary salts conduct well.

The dissociating power of a solvent is a function of its nature, and of the type and nature of the solute.

If we arrange the inorganic solvents according to the periodic system, we find that the elements N, P, As, and Sb of the fifth group, and O and S of the sixth group, in combination with one another, with hydrogen, or with the halides, are the ones which furnish the dissociating solvents. *W. D. B.*

The effect of non-electrolytes on the conductivity of electrolytes. *A. Hantzsch. Zeit. anorg. Chem.* 25, *332* (*1900*). — Addition of small amounts of urea, alcohol, acetone, ether, urethane or pyridine to solutions of sodium chloride, potassium chloride, sodium hydroxide or hydrochloric acid causes changes of conductivity of less than ten percent. Pyridine and thiourea decrease the conductivity of silver nitrate thirty percent or more, while ammonia has a very slight effect. From this, the author concludes that all three substances form compounds in solution with silver nitrate. Something more than "logic's priceless gift" is to be discerned here. *W. D. B.*

Salt formation in alcoholic solution. *S. Tanatar and B. Klimenko. Zeit. phys. Chem.* 35, *94* (*1900*). — The authors bring forward some further material in support of certain observations recorded in an earlier paper (3, 431). The data here recorded are the heats of neutralization of potash and ammonia with five organic acids. *A. P. S.*

Dielectricity and Optics

On uranium radiation. *H. Becquerel. Comptes rendus,* 131, *137* (*1900*). —

The author mixes uranium chloride with barium chloride and then precipitates the barium as sulphate (method of Debierne). The barium sulphate carries down with it a radio-active substance. After eighteen such operations, the uranium salt in solution is found to be only one-sixth as active as at first. It is therefore uncertain whether the activity of uranium salts is or is not due to uranium. *W. D. B.*

An artificial radio-active barium. *A. Debierne. Comptes rendus,* 131, *333* (*1900*). — If barium chloride be allowed to stand in a solution containing a very active salt of actinium, it becomes itself active and this activity may be intensified by recrystallization. The spectrum of this barium chloride does not show the lines of radium and the salt loses its activity in time. *W. D. B.*

The spectrum of radium. *E. Demarçay. Comptes rendus,* 131, *258* (*1900*). — A sample of fairly pure chloride of radium showed a weak barium spectrum while the radium lines, especially 3814.7, 4340.8 and 4683.2, were very distinct. No new radium lines were detected. *W. D. B.*

Gadolinium. *E. Demarçay. Comptes rendus,* 131, *344* (*1900*). — The author has prepared a considerable quantity of the double nitrate of magnesium and gadolinium, and gives in tabular form the spectral lines of gadolinium and their relative intensities. The most persistent are 3549.3 and 3545.7. *W. D. B.*

On some new spectra of the rare earths. *E. Demarçay. Comptes rendus,* 131, *386* (*1900*). — The wave-lengths are given for eight lines belonging presumably to turbium. There is also a discussion of several groups of rays which cannot be assigned definitely to any element. *W. D. B.*

On organic solutions of ferric chloride. *Oechsner de Coninck. Comptes rendus,* 131, *275* (*1900*). — In solutions containing no water and no methyl alcohol, dissolved ferric chloride gives off chlorine only after long exposure to sunlight. *W. D. B.*

New investigations on argon and its compounds. *M. Berthelot. Ann. Chim. Phys.* (*7*) 19, *66* (*1900*). — Reviewed (4, 419) from Comptes rendus, 129, 71 (1899).

On the combination of carbon bisulphide with hydrogen and with nitrogen. *M. Berthelot. Ann. Chim. Phys.* (*7*) 19, *145* (*1900*). — Reviewed (4, 419) from Comptes rendus, 129, 133 (1899).

Note on the combination of nitrogen with oxygen. *M. Berthelot. Ann. Chim. Phys.* (*7*) 19, *154* (*1900*). — Reviewed (4, 419) from Comptes rendus' 129, 137 (1899).

Action of argon and of nitrogen on mercury alkyls. *M. Berthelot. Ann. Chim. Phys.* (*7*) 19, *89* (*1900*). — Reviewed (4, 419) from Comptes rendus, 129, 378 (1899).

Crystallography, Capillarity and Viscosity

On the composition of the surface layers of aqueous solutions. *J. v. Zawidski. Zeit. phys. Chem.* 35, 77 (*1900*). — Saponine was added to solutions of hydrochloric and acetic acids in water, and air bubbles were then blown through. The foam was collected and analyzed. It was found to be more concentrated than the original solutions, though the difference is small.

A. P. S.

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ON A THEOREM OF LE CHATELIER

BY PAUL SAUREL

By considering an elementary cycle, Le Chatelier has recently established[1] a very simple relation between the slopes of the concentration curves of two bivariant binary systems under constant pressure, at their point of intersection. It may be of interest to note that the relation in question follows immediately from well-known formulas.

Consider a bivariant binary system consisting of two phases of variable concentration. The equations which govern the displacement of equilibrium in such a system have been put into the following simple form by van der Waals:[2]

$$v_{2.1}dp = \frac{w_{2.1}dT}{T} + (x_2 - x_1)\left(\frac{\partial^2\zeta}{\partial x_1^2}\right)_{p,T} dx_1,$$

$$v_{1.2}dp = \frac{w_{1.2}dT}{T} + (x_1 - x_2)\left(\frac{\partial^2\zeta}{\partial x_2^2}\right)_{p,T} dx_2.$$

Using the notation which we have employed in a previous paper,[3] it can be shown that these equations are equivalent to the following:

$$\frac{\delta V_{21}}{\delta M_1} d\Pi - \frac{\delta H_{21}}{\delta M_1} dT + M_1 \begin{vmatrix} m_{11}, & m_{12} \\ m_{21}, & m_{22} \end{vmatrix} \frac{\partial F_{12}}{\partial M_{11}} \frac{dm_{11}}{m_{11}m_{12}} = 0, \quad (I)$$

$$\frac{\delta V_{12}}{\delta M_2} d\Pi - \frac{\delta H_{12}}{\delta M_2} dT + M_2 \begin{vmatrix} m_{11}, & m_{12} \\ m_{21}, & m_{22} \end{vmatrix} \frac{\partial F_{21}}{\partial M_{22}} \frac{dm_{22}}{m_{21}m_{22}} = 0. \quad (II)$$

In these equations T and Π denote the temperature and the pressure, M_i denotes the mass of the i-th phase, M_{ij} the mass of j-th component which appears in the i-th phase, m_{ij} the mass of the j-th component which appears in the unit of mass of the i-th

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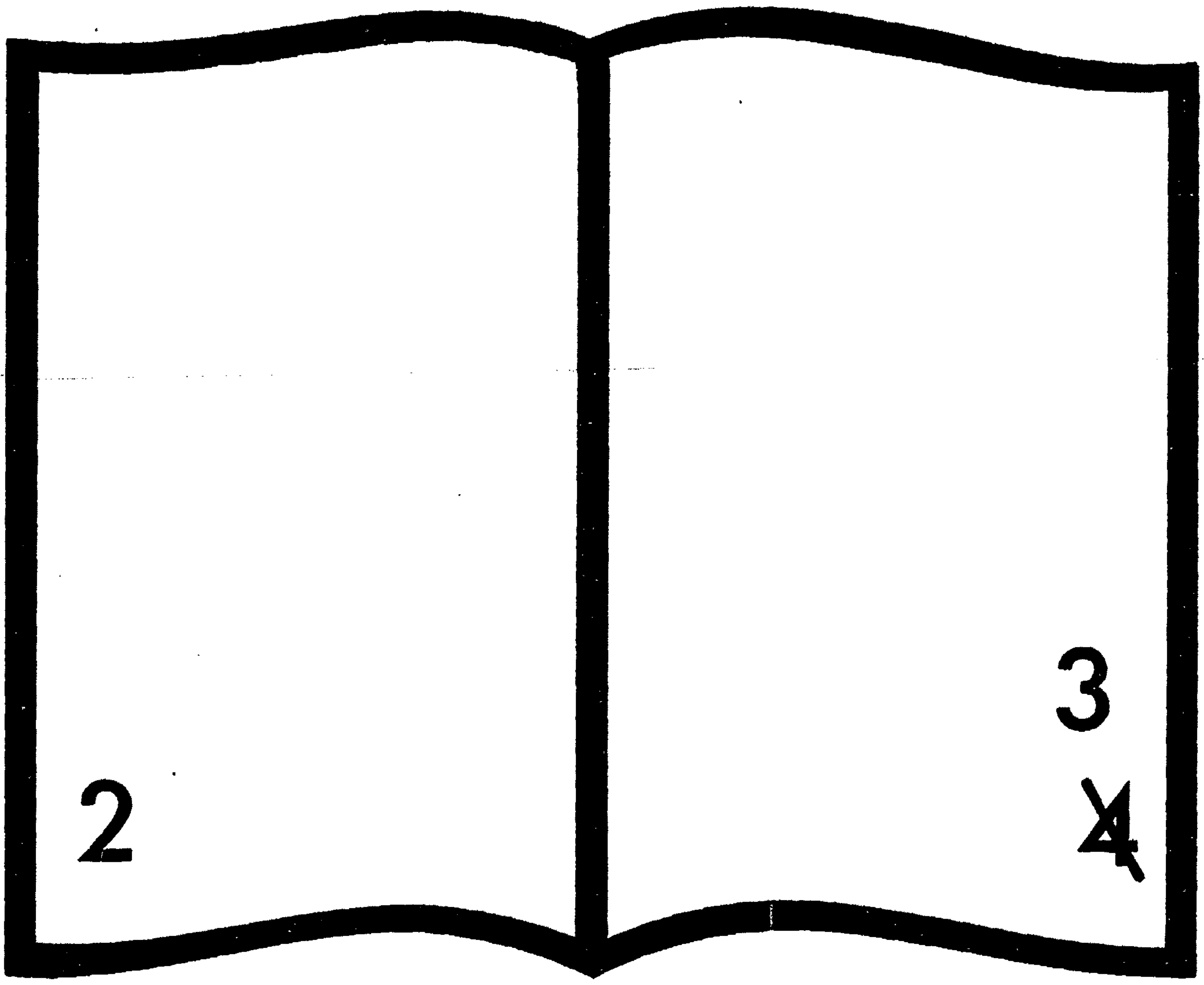
[1] Comptes rendus, 130, 1606 (1900).

[2] Die Continuität des gasförmigen und flüssigen Zustandes, 2, 112, 179 (1900).

[3] Jour. Phys. Chem. 5, 21 (1901).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phase, and F_{ij} is what may be called the chemical potential of the j-th component in the i-th phase. δV_{21} and δH_{21} are the changes in the volume and the entropy of the system due to a virtual change at constant temperature and under constant pressure, such that the mass of the first phase is increased by a small mass δM_1 which has been taken from the second phase without changing the concentrations of that phase. Similarly, δV_{12} and δH_{12} denote the changes in the volume and the entropy of the system due to a virtual change at constant temperature and under constant pressure, such that the mass of the second phase is increased by a small mass δM_2, which has been taken from the first phase without changing the concentrations of that phase.

If one of the phases of the bivariant system, say the second, have a fixed composition, then it can be shown that equations I and II are to be replaced by a single equation of the form I.

Consider now at the temperature T and under the pressure Π a univariant binary system consisting of the phases 1, 2, 3. Consider also the bivariant system formed by the phases 1, 2 and the bivariant system formed by the phases, 1, 3.

Under the constant pressure Π, the slope of the concentration curve of the phase 1 in the system of phases 1, 2 is given by the equation:

$$\frac{\delta H_{21}}{\delta M_1} dT = M_1 \begin{vmatrix} m_{11}, & m_{12} \\ m_{21}, & m_{22} \end{vmatrix} \frac{\partial F_{12}}{\partial M_{11}} \frac{dm_{11}}{m_{11} m_{12}}.$$

δM_1 in this equation denotes the increase in the mass of the first phase caused by the addition of a small portion of the second phase; if then we denote the accompanying increase in the mass of the second phase by δM_2, we shall have

$$\delta M_1 + \delta M_2 = 0.$$

This enables us to write the preceding equation in the form

$$-\frac{\delta H_{21}}{\delta M_2} dT = M_1 \begin{vmatrix} m_{11}, & m_{12} \\ m_{21}, & m_{22} \end{vmatrix} \frac{\partial F_{12}}{\partial M_{11}} \frac{dm_{11}}{m_{11} m_{12}}. \qquad (1)$$

Similarly, under the constant pressure Π, the slope of the concentration curve of the phase 1 in the system of phases 1, 3 is given by

$$-\frac{\delta H_{31}}{\delta M_3}\,dT = M_1 \begin{vmatrix} m_{11}, & m_{12} \\ m_{31}, & m_{32} \end{vmatrix} \frac{\partial F_{12}}{\partial M_{11}}\,\frac{dm_{11}}{m_{11}m_{12}}. \qquad (2)$$

From equations 1 and 2 we find at once for the ratio of the slopes of the two concentration curves at their point of intersection:

$$\frac{\left(\frac{dm_{11}}{dT}\right)_{12}}{\left(\frac{dm_{11}}{dT}\right)_{13}} = \frac{\delta H_{21}}{\delta H_{31}} \cdot \frac{\delta M_3 \begin{vmatrix} m_{11}, & m_{12} \\ m_{31}, & m_{32} \end{vmatrix}}{\delta M_2 \begin{vmatrix} m_{11}, & m_{12} \\ m_{21}, & m_{22} \end{vmatrix}}. \qquad (3)$$

This equation may be put into a more suggestive form. For this purpose consider a reversible change, at the temperature T and under the pressure Π, which consists in increasing the mass of the phase 1 at the expense of the phases 2 and 3. If the masses of the phases be increased by δM_1, δM_2, δM_3, we have the following relations:

$$\delta M_1 + \delta M_2 + \delta M_3 = 0,$$
$$m_{11}\delta M_1 + m_{21}\delta M_2 + m_{31}\delta M_3 = 0,$$
$$m_{12}\delta M_1 + m_{22}\delta M_2 + m_{32}\delta M_3 = 0.$$

From the last two equations we get

$$\frac{\delta M_1}{\begin{vmatrix} m_{21}, & m_{22} \\ m_{31}, & m_{32} \end{vmatrix}} = \frac{\delta M_2}{\begin{vmatrix} m_{31}, & m_{32} \\ m_{11}, & m_{12} \end{vmatrix}} = \frac{\delta M_3}{\begin{vmatrix} m_{11}, & m_{12} \\ m_{21}, & m_{22} \end{vmatrix}}.$$

If then we take δM_2 and δM_3 equal to the determinants which appear beneath them in these fractions, equation 3 takes the simple form

$$\frac{\left(\frac{dm_{11}}{dT}\right)_{12}}{\left(\frac{dm_{11}}{dm}\right)_{13}} = -\frac{\delta H_{21}}{\delta H_{31}}. \qquad \text{(III)}$$

If we denote by Q_{21} and Q_{31} the quantities of heat absorbed during the virtual changes to which δH_{21} and δH_{31} refer, we have

$$Q_{21} = T\delta H_{21},$$
$$Q_{31} = T\delta H_{31},$$

and equation 3 takes the form

$$\frac{\left(\frac{dm_{11}}{dT}\right)_{12}}{\left(\frac{dm_{11}}{dT}\right)_{13}} = -\frac{Q_{21}}{Q_{31}}. \qquad \text{(IV)}$$

We thus obtain the following theorem, which is due to Le Chatelier:[1] Consider at the temperature T and under the pressure Π, a univariant binary system consisting of the phases 1, 2, 3. Consider also, under the pressure Π, the two bivariant binary systems formed by the phases 1, 2 and 1, 3. If the phase 1 is a phase of variable concentration, to each of these systems there will correspond a curve giving the relation between the temperature and the concentration of the phase 1. These two curves intersect at a point which corresponds to the univariant system. The ratio of the slopes of the concentration curves at that point is equal to the negative of the ratio of the quantities of heat absorbed during two virtual changes which separately leave the concentrations of the phases 2 and 3 unchanged, and which taken together constitute a reversible change for the univariant system.

It will be observed that the demonstration assumes that the phase 1 is a phase of variable concentration, but that no assumption is made concerning the phases 2 and 3.

In conclusion, it may be observed that a demonstration entirely analogous to that used above, yields the following relation between the slopes of two intersecting concentration curves, which correspond to a given temperature:

$$\frac{\left(\frac{dm_{11}}{d\Pi}\right)_{12}}{\left(\frac{dm_{11}}{d\Pi}\right)_{13}} = -\frac{\delta V_{21}}{\delta V_{31}}. \qquad \text{(V)}$$

New York, March 24, 1901.

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[1] Comptes rendus, 130, 1608 (1900).

ON A THEOREM OF ROOZEBOOM

BY PAUL SAUREL

Bakhuis Roozeboom has given a very simple demonstration of the following theorem:[1] Consider a bivariant binary system consisting of the two phases: a liquid solution and a solid solution, and suppose that the addition of a small quantity of one of the components to the liquid phase lowers the temperature of solidification. Then the concentration of that component is greater in the liquid phase than in the solid phase. The object of the present note is to call attention to the fact that this theorem is an immediate consequence of a well-known equation of van der Waals.

The equations which govern the displacement of equilibrium in a bivariant binary system in which the composition of each phase is variable, have been put into a very simple form by van der Waals.[2] Using the notation explained in a previous note,[3] these equations take the form:

$$\frac{\delta V_{21}}{\delta M_1} d\Pi - \frac{\delta H_{21}}{\delta M_1} d\Gamma + M_1 \begin{vmatrix} m_{11}, & m_{12} \\ m_{21}, & m_{22} \end{vmatrix} \frac{\partial F_{12}}{\partial M_{11}} \frac{dm_{11}}{m_{11}m_{12}} = 0, \quad (I)$$

$$\frac{\delta V_{12}}{\delta M_2} d\Gamma - \frac{\delta H_{12}}{\delta M_2} d\Gamma + M_2 \begin{vmatrix} m_{11}, & m_{12} \\ m_{21}, & m_{22} \end{vmatrix} \frac{\partial F_{21}}{\partial M_{22}} \frac{dm_{22}}{m_{21}m_{22}} = 0. \quad (II)$$

Duhem has shown,[4] moreover, that when the system is in stable equilibrium, the following inequalities hold

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[1] Zeit. phys. Chem. 30, 389 (1899). Archives néerlandaises (2) 3, 419 (1899).

[2] Die Continuität des gasförmigen und flüssigen Zustandes, 2, 112, 179 (1900).

[3] Jour. Phys. Chem. 5, 277 (1901).

[4] Le Potential thermodynamique, p. 35 (1886). Dissolutions et Mélanges. Premier Mémoire. Travaux et Mémoires des Facultés de Lille, 3, No. 11, 85 (1893). Traité élémentaire de Mécanique chimiqne, 3, 10 (1898).

$$\frac{\partial F_{12}}{\partial M_{11}} < 0, \qquad \frac{\partial F_{21}}{\partial M_{22}} < 0. \tag{1}$$

Equations I and II give immediately the following equations for the slopes of the concentration curves which correspond to a given pressure:

$$\frac{\delta H_{21}}{\delta M_1}\, dT = M_1 \begin{vmatrix} m_{11}, & m_{12} \\ m_{21}, & m_{22} \end{vmatrix} \frac{\partial F_{12}}{\partial M_{11}} \frac{dm_{11}}{m_{11}m_{12}}, \tag{2}$$

$$\frac{\delta H_{12}}{\delta M_2}\, dT = M_2 \begin{vmatrix} m_{11}, & m_{12} \\ m_{21}, & m_{22} \end{vmatrix} \frac{\partial F_{21}}{\partial M_{22}} \frac{dm_{22}}{m_{21}m_{22}}. \tag{3}$$

If we suppose that the phase 1 is the liquid phase and the phase 2 the solid phase, then it may be assumed that the virtual change which consists in the addition of a small portion of the phase 2 to the phase 1 is accompanied by an increase in entropy, while the virtual change which consists in the addition of a small portion of the phase 1 to the phase 2 is accompanied by a decrease in entropy. We may accordingly assume the two inequalities

$$\frac{\delta H_{21}}{\delta M_1} > 0, \qquad \frac{\delta H_{12}}{\delta M_2} < 0. \tag{4}$$

If now the addition of a small mass of the component 1 to the phase 1 lowers the temperature of solidification, we must have

$$\frac{dm_{11}}{dT} < 0. \tag{5}$$

Equation 2 and inequalities 1, 4 and 5 then yield at once

$$\begin{vmatrix} m_{11}, & m_{12} \\ m_{21}, & m_{22} \end{vmatrix} > 0,$$

or

$$\begin{vmatrix} m_{11}, & 1 \\ m_{21}, & 1 \end{vmatrix} > 0,$$

or, finally,

$$m_{11} - m_{21} > 0. \tag{6}$$

The concentration of the first component is accordingly greater in the liquid than in the solid phase, and Roozeboom's theorem is thus established.

Incidentally, it may be observed that from equation 3 and inequalities 1, 4 and 6, it follows that

$$\frac{dm_{22}}{dT} > 0,$$

or, replacing dm_{22} by its equal $-dm_{21}$, that

$$\frac{dm_{21}}{dT} < 0. \tag{7}$$

Accordingly, the slopes of the concentration curves, at corresponding points, have the same sign. We may then state Roozeboom's theorem in the second form: If the addition of a small mass of one of the components to the solid phase lowers the melting-point of that phase, the concentration of that component is greater in the liquid than in the solid phase.

New York, March 24, 1901.

THE LATENT HEATS OF EVAPORATION OF A NUMBER OF ORGANIC NITROGEN-BEARING COMPOUNDS

BY LOUIS KAHLENBERG

The latent heats of evaporation of the following substances were determined: amyl amine, dipropyl amine, diisobutyl amine, valeronitrile, and *α*-picoline. The amyl amine was of Kahlbaum's manufacture and the other compounds were Schuchardt's preparations. The amyl amine was dried with fused caustic potash and then redistilled. A considerable fraction passed over at 95° under a barometric pressure of 723 mm. This was used in the experiments. The dipropyl amine was dried with fused caustic potash and then redistilled. It passed over between 108° and 108.5° at a barometric pressure of 745 mm. The diisobutyl amine was also dried with fused caustic potash and redistilled. Its boiling-point was quite constant at 134.5° under a barometric pressure of 735 mm. The valeronitrile was dried for a long time with fused calcium chloride, after which it was redistilled. The product passed over between 128° and 130° at 741 mm barometric pressure. The *α*-picoline had stood over fused caustic potash for weeks before being redistilled. Upon distilling it, it was found that a large fraction passed over at 129° under a pressure of 745 mm. This sample was used in making the determinations.

The specific heats of these compounds — which must be known in order to make the calculation of their latent heats of vaporization at the boiling-points possible — were determined by means of Berthelot's[1] method. The results obtained are presented in Table I.:

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[1] Berthelot. Mécanique chimique, 1, 275, 278.

TABLE I

Substance	Range of temperature	Specific heat
Amyl amine	90°–21°	0.6105
"	91°–22°	0.6166
		Average 0.6136
Dipropyl amine	100°–21°	0.5980
"	101°–22°	0.5963
		Average 0.5972
Diisobutyl amine	130°–22°	0.5701
"	130°–22°	0.5711
		Average 0.5706
Valeronitrile	121°–23°	0.5184
"	121°–23°	0.5203
		Average 0.5199
α-Picoline	123°–22°	0.4353
"	124°–22°	0.4330
		Average 0.4342

The determinations of the latent heats of evaporation were made by means of the apparatus previously described.[1] The results obtained are given in Table II., the headings of which are self-explanatory. It was thought best to indicate in each case the actual amount evaporated and also the change of temperature sustained by the calorimeter.

The last column of Table II. gives the constants of Trouton's rule for the substances investigated. Inasmuch as water gives the constant 25.9 and the alcohols yield constants of about the same order,[2] and since according to the determinations of Ramsay and Shields[3] the molecules of these substances when in

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[1] Kahlenberg. Jour. Phys. Chem. 5, 215 (1901).

[2] Compare Louguinine. Ann. Chim. Phys. (7) 13, 349 (1898).

[3] Jour. Chem. Soc. 53, 1089 (1893).

TABLE II

Substance	Barometer	Boiling-point	Amount evaporated	Rise in tem. of calorm'r.	Specific heat	Latent heat of evaporation of 1 gram	$\frac{MH}{T}$
Amyl amine	723	95°	27.588 g	3.337°	0.6136	98.9	
"	723	95°	25.804	3.119	0.6136	98.6	
						Average 98.75	23.3
Dipropyl amine	745	108°–108.5°	30.149	3.237	0.5972	75.77	
"	745	108°–108.5°	29.090	3.123	0.5972	75.60	
						Average 75.69	20.0
Diisobutyl amine	735	134.5°	25.205	2.789	0.5701	66.0	
"	735	134.5°	29.181	3.209	0.5701	65.7	
						Average 65.85	20.8
Valeronitrile	741	128°–130°	27.178	3.478	0.5199	95.96	
"	741	128°–230°	28.149	3.596	0.5199	95.95	
						Average 95.95	19.8
α-Picoline	745	129°	35.530	4.083	0.4342	90.52	
"	745	129°	35.676	4.117	0.4342	90.89	
						Average 90.75	21.0

the liquid state are associated, a high constant has been taken as indicative of association of liquid molecules.[1] The underlying thought seems to be that, (1) the Trouton constant is proportional to the latent heat of vaporization, and (2) the latter, in the case of an associated liquid, represents not simply the work of changing the liquid molecules from the liquid to the gaseous state — as in the case of non-associated liquids — but it includes also the work of separating the polymerized molecules into simple ones. On this basis the molecules of amyl amine would be somewhat polymerized in the liquid state; whereas, on the other hand, dipropyl amine, diisobutyl amine, valeronitrile and α-picoline when in the liquid state would have simple molecules. The latent heat of evaporation of diethyl amine has been determined by Nadejdine,[2] who found 91.0 at the boiling-point 58°. This gives 20.0 as the Trouton constant of this substance, and hence, when liquid, its molecules like those of dipropyl- and diisobutyl amine, are also not polymerized.

The latent heats of evaporation of acetonitrile, benzonitrile and pyridine previously[3] determined yield 20.1, 19.5, and 20.7 respectively, as the values of the Trouton constant, which would show that these substances also have simple molecules when in the liquid state. This agrees with the determinations of Louguinine,[4] who has further concluded that the liquid molecules of propionitrile, butyronitrile and capronitrile are simple. Valeronitrile then simply exhibits a behavior common to nitriles, and α-picoline behaves like pyridine, which might have been expected. The latter substance is rather difficult to obtain in a perfectly pure condition. It may indeed be readily freed from water by drying with fused caustic potash, but it is difficult to rid it of picoline, with which it is apt to be contaminated. Picoline, however — because of its low latent heat of evaporation

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[1] Compare Louguinine. l. c. 289.

[2] Jour. Russ. Chem. Soc. 16, 222 (1884). See also Landolt and Börnstein's tables.

[3] Kahlenberg. l. c.

[4] Arch. des Sciences naturelles de Genève, 9, 5–26 (1899).

90.75, as compared with that of pyridine 104.0[1] — would by its presence clearly reduce the latent heat of evaporation of pyridine, to which fact attention has been directed before.

From the data in Table II., the molecular rise of the boiling-point, or the so-called boiling-point constant K, may be calculated according to the Arrhenius-Beckmann formula

$$K = \frac{0.02\ T^2}{H}.$$

The calculation yields the following values of K: for amyl amine 27.42; for diethyl amine[2] 24.07; for dipropyl amine 38.35; for diisobutyl amine 50.43; for valeronitrile 33.69; and for α-picoline 35.61.

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Madison, Wis.,
March 1901.

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[1] Kahlenberg. l. c.

[2] From Nadejdine's determination. l. c.

ON THE TOXIC VALUE OF MERCURIC CHLORIDE AND ITS DOUBLE SALTS

BY JUDSON F. CLARK

The toxic properties of mercuric chloride have been known since time immemorial. Its special value as a germicide has been recognized by the biological and medical professions ever since the publication of Koch's[1] classic work in 1881. Quite a large amount of work has been done on it from time to time since that date, the general results of which have confirmed the conclusion arrived at by Koch that mercuric chloride is one of the most powerful poisons known for all forms of animal and vegetable life. It has also been shown that while the lower forms of life, such as putrefying and pathogenic bacteria, are particularly susceptible to it, its value as a disinfectant is in many cases of practical sanitation greatly impaired, and may even be entirely destroyed by the presence of an excess of albuminous matters in the material to be disinfected, and its affinity for such substances, whether dead or living. In the chemical reaction which results the mercuric chloride as well as the proteid is precipitated in the form of an extremely insoluble and consequently harmless mercury albuminate.

In an endeavor to overcome this difficulty in practical use, investigators have studied the effect of adding various substances to the pure $HgCl_2$ solution. The substances most frequently added have been the chlorides of the alkalies and other metals, iodides, bromides, and other salts, such as potassium cyanide, and sulphocyanide, sodium nitrate, etc.; also various acids, particularly hydrochloric, tartaric, and acetic.

Most investigators agree that at least two advantages are

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[1] Koch, R., 1881. Ueber Disinfektion. Mitth. aus dem Kaiserliche Gesundheitsamt, 1, 1-49.

derived from such additions, particularly the addition of the alkali chlorides and the acids, viz.: a lessening of the precipitation of the $HgCl_2$ by the albuminoids present, and greater solubility of the mercuric chloride. A pronounced increase in the toxic properties of these mixtures over that of the pure $HgCl_2$ solution has been claimed by several workers as a third and very important advantage. Laplace,[1] working with anthrax spores, found that hydrochloric and tartaric acids caused a very considerable increase in toxic properties when added to solutions of mercuric chloride of about 1:20,000. He recommends the use of the tartaric acid as being non-volatile and more stable than the hydrochloric. Later Behring,[2] in a very careful piece of work on various antiseptics, found substantial increases in the value of $HgCl_2$ as an agent of this class when certain salts were added to its solution. I copy a few of his results on this point. They were also with anthrax spores.

$HgCl_2$ alone	has a value of	1 : 10,000
$HgCl_2 + 10NaCl$	" " "	1 : 15,000
$HgCl_2 + 3NH_4Cl$	" " "	1 : 12,000
$HgCl_2 + 1KCN$	" " "	1 : 15,000

With Laplace's solution, $HgCl_2$ + tartaric acid, however, he got a somewhat lower value, viz., 1:8,000.

On the other hand, in one of the most recent and at the same time one of the most exact and exhaustive of the studies that have appeared, Krönig and Paul[3] have found that the addition to aqueous solution of $HgCl_2$ of any salt experimented upon had invariably the effect of lessening its toxic value under the conditions with which they worked.

It was with a view of determining the truth in regard to

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[1] Laplace, 1887. Saure Sublimat Lösung als desinficirendes Mittel. Deutsche Med. Wochenschrift, 1887, 866–867.

[2] Behring, 1889. Ueber die Bestimmung des antiseptischen Werthes chemischer Präparate mit bes. Berücksichtigung einiger Quecksilbersalze. Deutsche Med. Wochenschrift, 43, 884–887 (1889). See also Central. für Bakteriol, Bd. 1, 27–30 and 64–66 (1888).

[3] Krönig und Paul, 1897. Die chemischen Grundlagen der Lehre von der Giftwirkung und Desinfection. Zeit. f. Hygiene u. Infec. Bd. 25, 1-112.

this matter of toxicology that the present investigation was undertaken. It proved a large task, and at the end of six months of study I am for the present compelled by circumstances to discontinue the work. Inasmuch, however, as I have worked over the addition of the alkali chlorides quite thoroughly and done some satisfactory work on the addition of hydrochloric acid, it was thought well to publish my results at this time.

The work was largely done with the mold fungi. These plants, which have been so generally useful and so generally used in physiological investigations, were found to be especially well adapted for toxicological work, consequently of the more than seven thousand cultures made in this study, about sixty-three hundred were with the molds. The others were with yeasts, bacteria and phanerogams.

The fungi used were: *Aspergillus flavus*, *Sterigmatocystis nigra*, *Œdocephalum albidum*, *Botrytis vulgaris*, *Penicillium glaucum*, *Rhizopus nigracans*, and two yeasts, the species of which were undetermined. Of the phanerogams, I used seeds of wheat, sunflower, pea, lupine, and alfalfa. Of bacteria, *Bacillus colon* (from chick) and an undetermined Bacillus.

Culture Methods. — For a detailed account of my method of using the van Tieghem cell in toxicological work, the reader is referred to my article on "Electrolytic Dissociation and Toxic Effect."[1] This method of culture was used for the molds, yeasts, and bacteria. It will suffice to say here that when the precautions detailed in the above article were observed, especially that requiring the same solution in the bottom of the cell as was used in the culture drop, this method was found entirely satisfactory and reliable, and very well adapted for such studies.

Media. — The bulk of the results recorded here were from cultures grown in a decoction of sugar-beet. The root, sliced thin, in the proportion of 450 grams per liter, was heated in water in an autoclave for an hour at 120° C under a pressure of one atmosphere. The decoction was then filtered, poured into

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[1] Clark, J. F. Jour. Phys. Chem. 3, 263–316 (1899).

sterile flasks and again heated at the same temperature for about three hours, This second heating is intended to precipitate as completely as possible the proteid substances present. Immediately before use it was filtered, when cold, through seven filters to remove as completely as possible the precipitated albuminoids.

This medium is excellent for general work with nearly all saprophytic fungi, germination occurring quickly and regularly. Mercuric chloride, however, in any medium admitting of normal development of fungi or bacteria, is subject to serious deterioration from reduction to calomel. If the media be an infusion or decoction of a vegetable or animal substance, a second and even more serious factor causing deterioration is introduced by the presence of a varying quantity of proteid matter in suspension or solution.

The reduction to calomel is a rather *constant* factor, and being the result of the action of light and the presence of organic matter, it may be largely controlled by keeping the solutions of $HgCl_2$ in the dark and at a low temperature. The cultures as soon as prepared were grown in a light-proof thermostat, hence, the media containing $HgCl_2$ were exposed to light only during the preparation of the cultures and their examination from time to time. No media containing $HgCl_2$ was used later than 24 hours after the addition of the $HgCl_2$.

The deterioration due to precipitation by proteid substances was a more serious matter, inasmuch as the amount of proteids present in different batches of media was a variable and often considerable quantity. Long continued heating at 120° C, and the preparation of large quantities at a time were found the most reliable means of overcoming this source of error. The extent of the variation possible from this cause was illustrated by a number of cultures with *Rhizopus* in the pure juice of the beet extracted without boiling, and the same medium after heating for hours at 120° C. In the former case 0.0004 *n* $HgCl_2$ was required to inhibit germination, while in the latter case 0.00001 *n* was sufficient. This indicates that not more than 1/40 of the mercuric chloride was available for antiseptic purposes in the medium that had not been heated. It was also observed in practice that in working with a medium containing considerable proteid substance, the most of the deterioration took place within a few hours after the addition of the $HgCl_2$. This led to the precaution of adding the $HgCl_2$ to a sufficient quantity of beet decoction for the day's cultures six or eight hours before it was to be used. As already indicated, any solutions remaining unused when the cultures for the day were prepared were discarded. Inasmuch as the beneficial effect of adding compounds to $HgCl_2$ solutions has been attributed to the effect of these compounds in "protecting" the $HgCl_2$ from precipitation by albuminoids, it was thought desirable to use a medium which would be entirely free from such substances, accordingly several series of cultures were grown in the following well-known medium:

Cane Sugar	5 grams
$MgSO_4$	0.25 "
KH_2PO_4	0.5 "
Asparagin	0.5 "
Fe_2Cl_6	trace
Water to	100 cc.

In setting up a series of cultures with $HgCl_2$ to which some salt or acid had been added in varying quantity, checks were usually set up in pure $HgCl_2$ solutions *after* as well as before the cultures containing the compound whose effect was being tested. When the *precautions already mentioned were all observed*, however, these checks usually coincided very closely, showing that the deterioration during the setting up of a complete set — usually about five hours — could be disregarded.

By a complete set of cultures is meant a series of cultures in which the critical point (i. e., the point where germination is inhibited) is determined for the pure $HgCl_2$ solution, and as many other solutions, containing a varying addition to the $HgCl_2$ of the compound whose influence is being tested, as may be required to plot the curve giving the increase or decrease of toxicity, as the case may be, due to the addition of the compound. In my work I found that twenty-five such solutions covered the field satisfactorily. For example, suppose the effect of adding NaCl to $HgCl_2$ solutions is the problem. The toxic value of the pure $HgCl_2$ being determined, the next step is to determine that of a solution of $1HgCl_2 + 2NaCl$, $1HgCl_2 + 4NaCl$, . . ., $1HgCl_2 + 100NaCl$, and so on until a very injurious concentration of the NaCl itself is reached. In the case of *Aspergillus* this would be at approximately 15 percent NaCl, which inhibits germination. Measured in molecules it would mean the addition of about 36,000 molecules of NaCl for each molecule of $HgCl_2$ present. Considering this very great number it might be thought that 25 steps were far too few to cover the ground from + 2NaCl to + 36,000 NaCl, and it certainly would be, had one not in preliminary experiments determined approximately where the important points were. With *Aspergillus*, for instance, and with additions of NaCl (see Fig. 2) it will be noted that the important points are from + 2NaCl to + 1000 NaCl, near + 2000, and near + 15,000 NaCl.

At each of the twenty-five points selected, it was found necessary to make cultures covering a moderately wide range of $HgCl_2$ concentrations, as otherwise the critical concentrations might be missed. From six to twelve such cultures were prepared, the number varying according to the thoroughness with which the preliminary work was done. With *Aspergillus* these cultures should cover a range of from 0.0001 *n* to 0.00002 *n* with the pure checks in $HgCl_2$ and the smaller additions up to + 4000 NaCl, and from 0.00015 *n* to 0.00004 *n* with the stronger concentrations of NaCl. Reckoning ten cultures at each concentration of NaCl, and twenty-five concentrations as the number tested, it would require 250 cultures to develop a curve for a single fungus, as is shown for three in Fig. 2. As a matter of fact we must add at least forty or fifty more to this number for preliminary work.

A stock solution of mercuric chloride in distilled water containing 4.382 percent of the salt was prepared at first in sufficient quantity for the entire study, thus avoiding possible error from changes. A *normal* solution of $HgCl_2$ means in this paper the number of grams of the salt corresponding to the *full* molecular weight (270) dissolved in a liter of water; thus, 0.01 *n* equals 0.27 percent $HgCl_2$.

Except when otherwise stated, the *point of inhibition* of germination of the spores was taken as the critical point. This was taken in preference to the death-point on account of the greater ease and certainty with which it could be determined, and the fact that in *antiseptic* solutions the inhibiting-point is the point of practical importance. With *disinfecting* solutions, however, the death of the spore is the object, and the concentration at which it occurs the point to be determined. This was done when working with the $HgCl_2$ in disinfecting concentrations. The point of inhibition, however, must be understood to mean the concentration preventing the germination of 95 percent of the spores. The spores normally germinated practically 100 percent, and as the object was to test the effect of adding the salt, etc., on the toxicology of the mercury in solution, it was obviously safer to read the results from the intermediate 90 percent, disregarding the 5 percent most easily killed as well as the 5 percent abnormally resistant.

In many cases the spores from inhibited cultures were transferred to pure beet infusion and their vitality thus tested. In such transfers more or less of the deleterious agent is necessarily transferred with the spores. The general results of such transfers, however, indicated that with fungus spores a solution which inhibited germination would eventually kill if left in contact with the spores a sufficient length of time. Thus if a solution of a certain concentration just inhibited germination, a solution of four times this concentration might with some spores fail to kill in 24 hours; if left for ten days, however, the points of inhibition and death would usually nearly coincide, and with many forms this would be true in a much shorter time.

The temperature at which an antiseptic or disinfectant is applied has been shown to be very important.[1] The effectiveness

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[1] Henle, 1889. Ueber Creolin und seine wirksamen Bestandteile. Arch. f. Hyg. Bd. 9, Heft 2.

of the agent, other things being equal, increases with the temperature. In a number of experiments with *Aspergillus* I concluded that its greatest resistance to mercuric chloride was at a temperature near (apparently slightly below) the optimum for the germination and development of the fungus. Cultures above this point were killed because of the greater effect of the agent at the higher temperature. Cultures below this point were killed by the penetration of the poison before the spores had succeeded in the production of any considerable amount of proteid matter with which to neutralize the poison, thus cultures kept at 16° C were killed by a very small amount of $HgCl_2$, germination being so greatly delayed by the low temperature, time was given for the agent to have its maximum effect. In general, then, mercuric chloride may be said to be more effective either below or above the optimum temperature for the development of the organism or organisms to be checked; the lower temperature requiring the longer contact with the deleterious agent, the higher being effective in a shorter time. This is probably true of all antiseptics which, like mercuric chloride, check or destroy by precipitation of the contents of the living cell. It *may* be true of all toxic agents. The temperature at which my work was done was 28° C, a very favorable temperature for the development of the fungi with which I was working.

Sterile precautions were observed throughout the study. The spores used in the inoculation of the cultures were taken from pure cultures frequently renewed to insure high vitality. It is very important in any quantitative study of this kind to have as nearly uniform a number of spores in the various cultures to be compared as possible. It is equally important to avoid bunches of spores in making the inoculation. Oversight in regard to these two points leads to the most erratic results in working with a compound like $HgCl_2$, which in effecting its mission as a disinfectant, is itself precipitated in a harmless insoluble form. A moment's reflection will show how this is necessarily so. The amount of $HgCl_2$ required to kill say two hundred spores in a few hours may fail to kill ten out of a thousand in a medium where growth is possible before the poison has had time to have its effect. So, too, if a bunch of spores be introduced into a culture containing many single ones, the medium is relatively slow in reaching those bunched, especially when such a bunch contains air, as it almost invariably does. The result is that those floating singly are first killed, and the solution may be depleted of half or more of its toxic value before those enclosed in the bunch are reached. These then may germinate and grow almost as well as if no poison had been present. The difficulty was entirely overcome by soaking the spores for a longer or shorter time in sterile distilled water, with an occasional shaking. In some cases the soaking may be continued with advantage for days, in which case it is well to keep them at a low temperature to prevent germination. In all cases it was found advisable to inoculate from a mixture of spores in water, a uniform inoculation being approximated in that way without great difficulty.

The method of preparing the solutions of various concentrations of the added compound was briefly as follows: (to illustrate, I shall assume that *Aspergillus* is the form to be tested.) to a liter of beet decoction is added sufficient $HgCl_2$ to make 0.00015 *n*. To a portion of this enough NaCl (dry) is added to make the strongest concentration of NaCl desired. With these two solutions as a base any intermediate concentration may easily be prepared by using carefully graduated pipettes.

This method implies an error in the concentration of the $HgCl_2$ present, inasmuch as the *dry salt added* dilutes the $HgCl_2$ solution somewhat. This error, however, is *constant*, *easily calculated*, and *practically nil* until the concentration of the added salt reaches far into the thousands. At + 2000 NaCl it would be less than 0.3 percent of the total toxic value.

In preparing my results for publication, I have endeavored to present them in the briefest possible space. To this end I have decided to plot the general results in curves, giving as they do the significant facts without obscuring them with a mass of detail. The data have been further condensed by publishing only typical curves of the various classes. Thus, for example, while curves were worked out for seven fungi with sodium chloride, and five each for potassium and ammonium chlorides, only three of those for sodium chloride are herewith published, and none of those with either potassium or ammonium chloride, because they were practically the same as those with NaCl, and while invaluable in confirming that work, threw no new light on the problems involved. Complete sets were also run through with HCl with five fungi, but the results with *Sterigmatocystis* given in Fig. 5 give as much light on the subject as any other of the five or all the five, hence, only the one curve is given.

To give the reader an idea of the data from which these curves were developed, I shall insert here as Fig. 1 a page from my note-book, showing a short-checking series with *Aspergillus* in the non-albuminoid medium. On the left are the concentrations of $HgCl_2$ for the various cultures. Then arranged in order of preparation are a series of 11 sets, the last one being like the first, a set with $HgCl_2$ alone to test the deterioration of the solutions while the cultures were being prepared. The cultures are lettered and numbered, the letters referring to each set of twelve, the numbers to the cultures of that set, No. 12 being always the most concentrated. In order to prevent confusion in this limited space, I insert only the final estimate of germination in each culture. Cultures from *e* to *j* were much slower in germination than those containing but little salt. It will be noticed that 0.000025 *n* was the limiting culture with *Aspergillus* here. This was higher than was usual in a beet decoction, where the average was about 0.000075 *n* because of the albuminoids present. One batch of beet decoction, however, gave a value of practically the same as this, showing it to be almost free from proteid matter. It should be added that no curve was plotted without a repetition of the critical cultures on which it was based at some time other than when the entire series was set up. This method was adopted in place of duplicate cultures because it implied a checking in the computations and measurings as well as the observed germination.

Figure 2 gives the curves for three fungi, showing the toxic

Aspergillus flavus. Cultured December 31, 1900. Temperature 28° C.

Concentration of $HgCl_2$	No. of culture	+ 0 NaCl *a*	+ 10 NaCl *b*	+ 40 NaCl *c*	+ 400 NaCl *d*	+ 1000 NaCl *e*	+ 4000 NaCl *f*	+ 7000 NaCl *g*	+ 10,000 NaCl *h*	+ 15,000 NaCl *i*	+ 20,000 NaCl *j*	+ 0 NaCl *k*
.000008	1	normal	normal	normal	normal	40	40	normal	normal	normal	normal	normal
.000011	2	"	"	"	70	6	15	"	"	"	"	"
.000014	3	"	"	8	5	1	4	"	"	"	"	"
.000017	4	80	65	4	3	0	1	"	"	"	"	"
.000020	5	30	5	0	1	0	?	90	"	"	"	40
.000025	6	5	2	1	0	..	1	70	"	"	"	8
.000030	7	0	0	0	0	..	..	5	85	"	"	1
.000035	8	0	0	0	..	..	..	3	80	"	"	0
.000042	9	..	..	..	..	..	..	..	10	90	90	0
.000051	10	..	..	..	..	..	..	..	1	60	70	..
.000071	11	..	..	..	..	..	..	..	..	30	50	..
.000100	12	..	..	..	..	..	..	..	..	25	7	..

Fig. 1

values of the $HgCl_2$ solutions to which NaCl has been added. The ordinates give the concentration of the $HgCl_2$ in fractions of a normal solution, thus *Aspergillus* is inhibited by 0.000075 *n*.

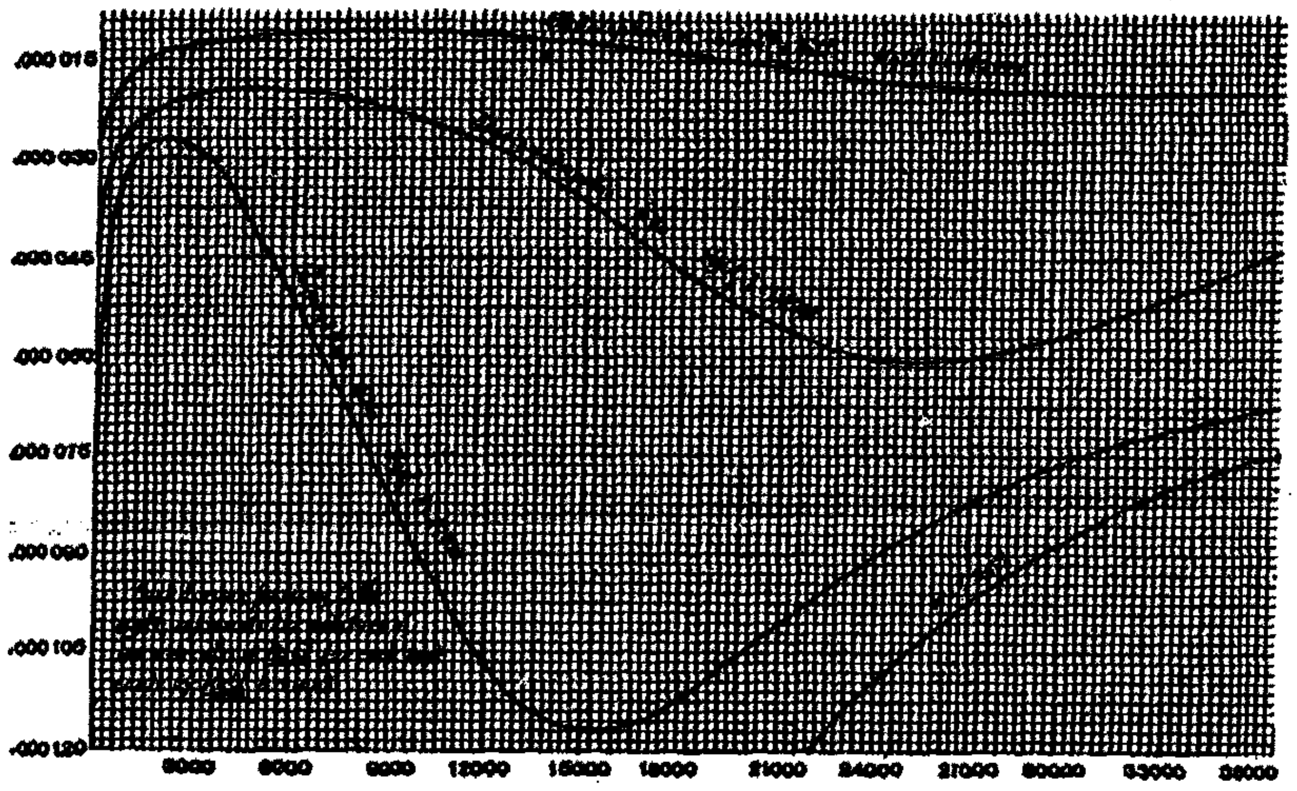

Fig. 2

The abscissæ give the additions of NaCl in molecules. Thus 3000 NaCl indicates a concentration of 3000 molecules of NaCl for each molecule of $HgCl_2$ present.

A very striking feature of this figure is the very rapid rise of the curves with the smaller additions of the NaCl. This is followed by a less rapid but equally marked fall with all forms. It is also to be noted that the maximum is reached with a relatively larger number of added NaCl molecules, as the fungi are more sensitive to $HgCl_2$. Thus, while *Aspergillus* reaches a maximum with about + 2000 NaCl, *Œdocephalum* reaches its maximum at about + 9000 NaCl. The actual percentage concentration, however, is not nearly so different on account of the fact that with *Aspergillus* it is + 2000 NaCl at a $HgCl_2$ concentration of about 1 : 200,000, while with *Œdocephalum* it is + 9000 NaCl at a $HgCl_2$ concentration of little more than 1 : 400,000. It is a significant fact, however, that the more dilute the $HgCl_2$ solution, the higher the percentage addition of NaCl required to give either an increase or decrease in the toxic value of the mixture. A glance at the falling of the curves will also show this. The upper curves fall neither so fast nor so far as that of *Aspergillus* in the more concentrated $HgCl_2$ solutions. The second rise in the lower two curves is due to the added NaCl, which is here present in injurious concentration. The short curve in the lower right hand corner indicates a 15.2 percent concentration of NaCl, which is sufficient alone to inhibit *Aspergillus* and *Sterigmatocystis.* Nine percent NaCl inhibits *Œdocephalum.* These curves then represent the combined inhibiting influence of the $HgCl_2$ and the NaCl present. In the more dilute concentrations of NaCl, say up to + 4000 NaCl, the influence of the NaCl as such is almost or altogether nil. With + 15,000 with *Aspergillus*, and + 25,000 with *Sterigmatocystis* it is appreciable.

In Fig. 3 the curve is that of *Aspergillus* in solutions of $HgCl_2$ + NaCl, but the theoretical value of the NaCl is subtracted. 30,000 molecules of NaCl are equal to 1 molecule of $HgCl_2$ as an inhibiting agent for *Aspergillus.* Theoretically, therefore, if 1000 molecules of NaCl be added for each molecule of $HgCl_2$ present in a certain solution the toxic value of that solution would be increased 1/30 of its original value. I say *theoretically*, for it is doubtful if that addition of NaCl would *as such* have any toxic value. To be on the safe side, however, the exact proportion of the toxic value for each addition of NaCl has been deducted in plotting this curve. Consequently the curve gives the toxic value of the *mercuric chloride as influenced by the presence of the NaCl.*

In this figure the ordinates represent units of toxicity. The value of mercuric chloride in the absence of NaCl is represented by unity.

The abscissæ represent the amount of NaCl added in fraction of normal solution and as a percentage.

The rise of the curve with additions of NaCl in small amounts up to 0.4 percent is very striking. At about 0.4 percent NaCl a maximum of about 160 percent increase is reached further additions presently cause a fall which reaches unity again at about 2.5 percent of NaCl. From this onward the decline is steady until at a 10 percent concentration of NaCl the mercury has not more than one-fifth its normal value when in the form of the bichloride.

It must always be borne in mind that this is for a fungus having a critical concentration for the pure $HgCl_2$ solution of about 1 : 50,000. As already noticed, and emphasized later, entirely different conditions obtain for solutions of greatly varying concentrations.

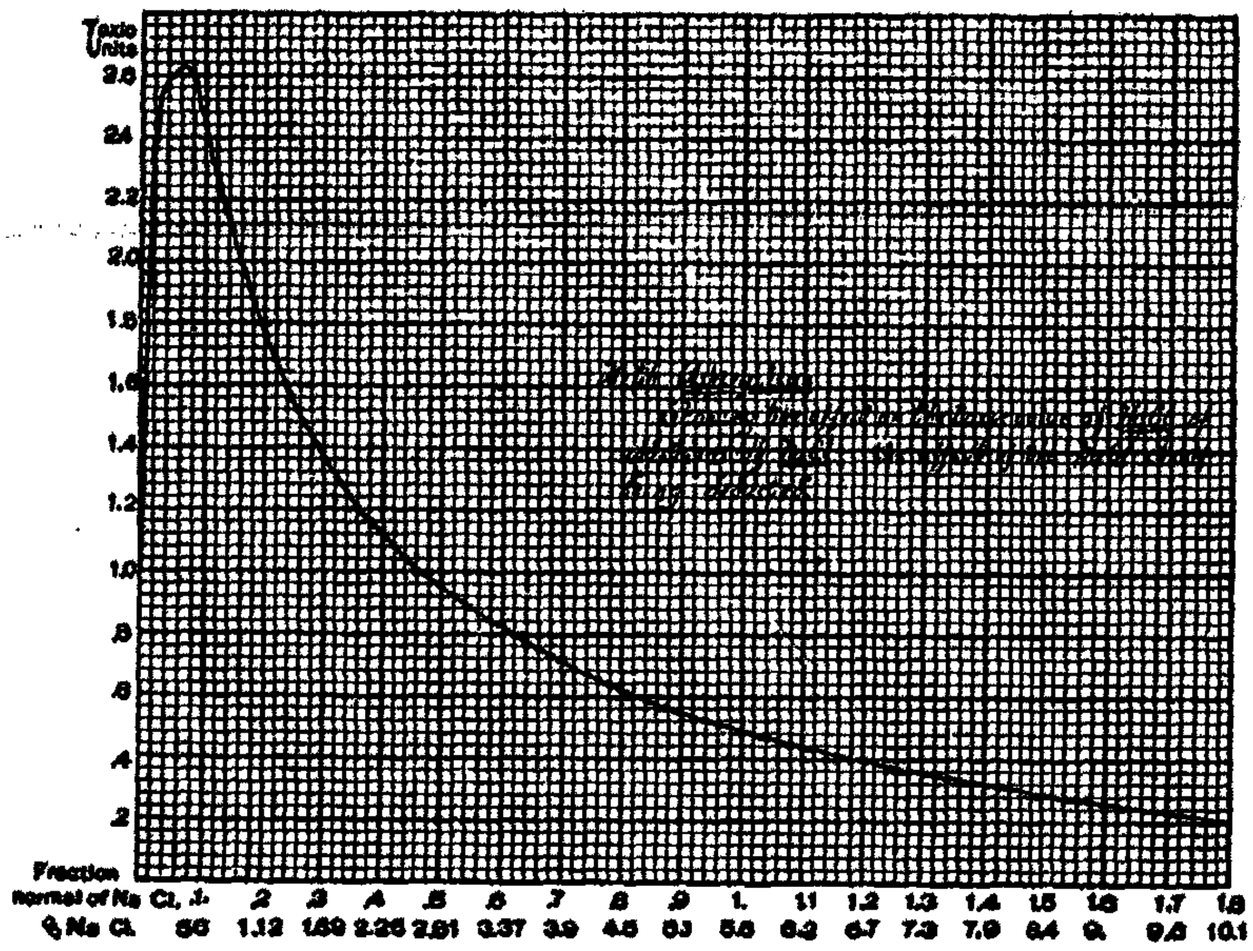

Fig. 3

After getting these results with beet decoction as a medium, the cultures were repeated, using the artificial medium compounded from salts and sugar already given. An entirely similar curve was gotten for *Aspergillus* and *Sterigmatocystis*, thus giving an emphatic negative to the theory so frequently advanced by bacteriologists that the value of the NaCl, used in connection with $HgCl_2$, has some relation to its "protective" powers in protecting the $HgCl_2$ from precipitation by the proteids present. Here there was of course no proteid. It is of interest to note in this connection that the presence of asparagin does not reduce the toxic value of $HgCl_2$. With copper sulphate and other copper compounds I have found it to cause a very striking decrease when present either in pure water solution or in connection with nutrient media.

While Figs. 2 and 3 show a very remarkable increase in toxic properties of the $HgCl_2$ solutions on the addition of small quantities of NaCl, Fig. 4 will show that this increase, while appreciable from the first, is by no means so sudden as might have been thought from Figs. 2 and 3. It is true that the first ten or twenty molecules added give a greater net increase than any ten or twenty added later, but this greater influence of the early additions is not such as to indicate any relation to the effect of the NaCl on the dissociation of the $HgCl_2$ as such. We will return to this point later.

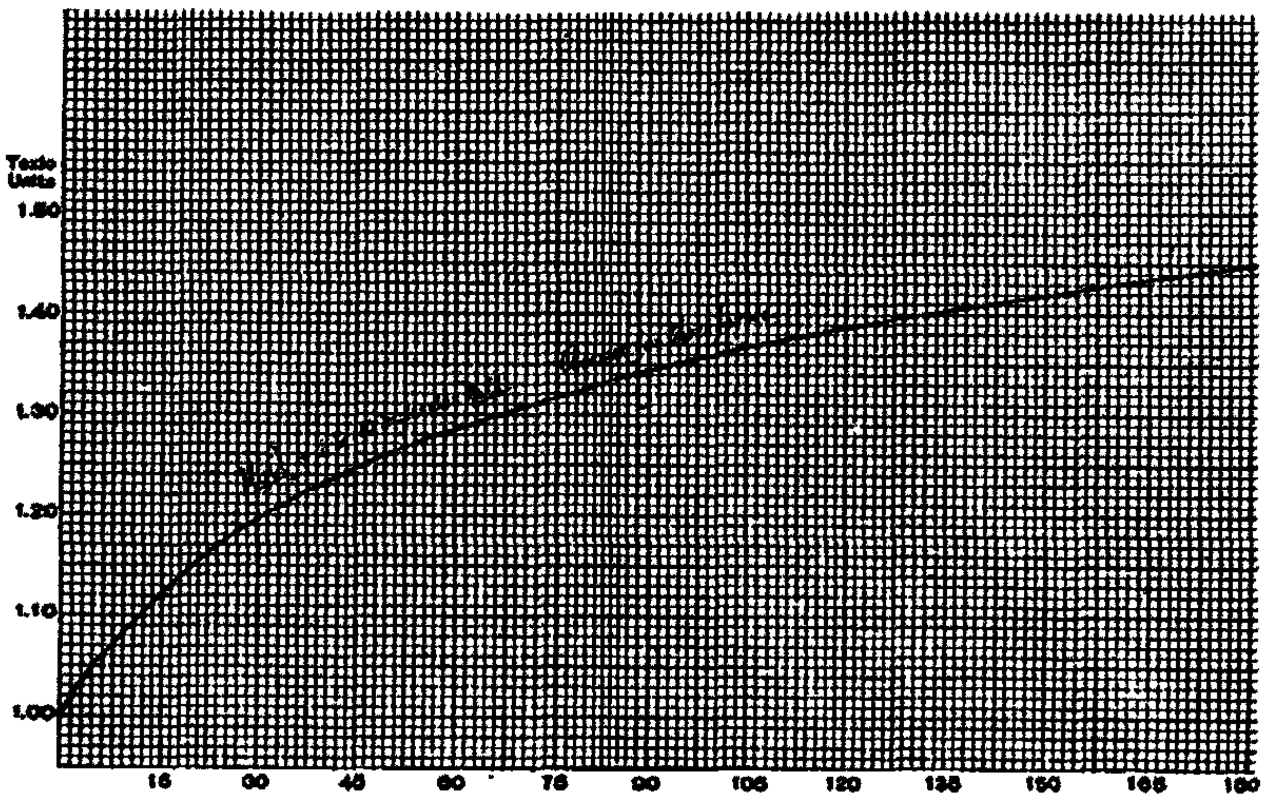

Fig. 4

Abscissæ here represent the number of NaCl molecules added for each molecule of $HgCl_2$ present

A very marked stimulation of mycelial development and some stimulation of germination was noted with *Sterigmatocystis* and *Œdocephalum* with the smaller additions of NaCl in cultures too dilute to be inhibited. This stimulation reached its maximum between + 5 and + 10 NaCl.

Figure 5 gives the result of adding varying quantities of HCl to $HgCl_2$ solutions. The second curve is inserted for comparison and gives the result of adding NaCl in similar proportions to similar solutions of $HgCl_2$ with the same fungus, *Sterigmatocystis*. The influence of the HCl and NaCl as such has been subtracted as in Fig. 3; hence the curves here indicate the toxic value of the mercury conbination only, when in the presence of the varying concentrations of hydrochloric acid and its sodium salt.

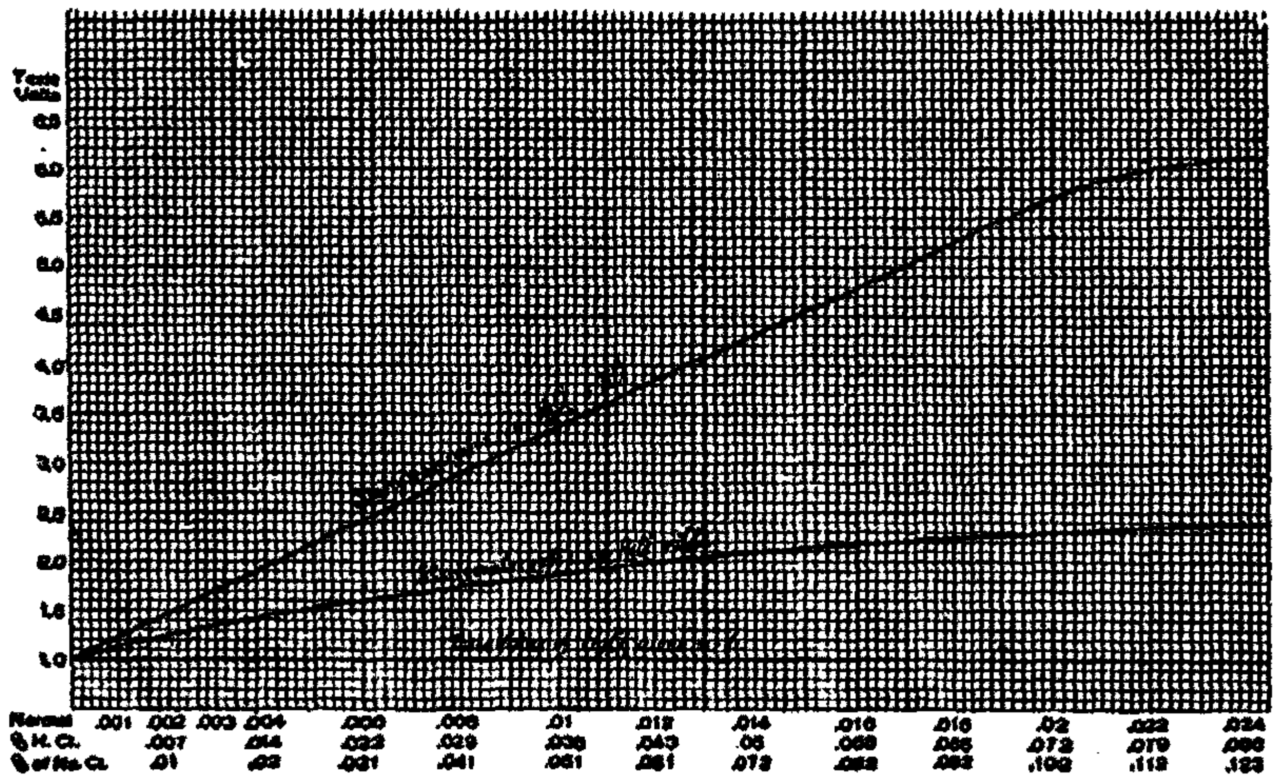

Fig. 5

The upper curve, which is a straight line for a considerable distance, shows a very great increase in toxic properties, amounting to about 500 percent with the addition of HCl in a concentration of 0.022 *n*, or less than 0.08 percent. *Aspergillus*, *Œdocephalum* and *Rhizopus* gave similar results, but their percentage increase was somewhat less than that of *Sterigmatocystis*. This is rather remarkable, inasmuch as *Sterigmatocystis* is much more *resistant* than pure HCl, and therefore to ionic $\overset{+}{H}$ than any of the other forms.[1]

The additions of HCl were not carried far enough to determine whether there would eventually be a decrease in the toxic value of the mercury compound or not. The toxic value remained practically constant from + 1100 HCl to + 3000 HCl (0.08–0.21 percent). The fact that the curve is at first a straight line indicates that within limits the increase in toxic properties is in direct proportion to the amount of acid added. It has already been noted that with the salts the first additions are always relatively more effective than the same quantity added later, thus giving a distinctly convex curve.

Thus far we have treated of solutions of $HgCl_2$ of no greater concentration than 1:50,000. Some tests were made to determine the effect of adding NaCl to *disinfecting* as opposed to *antiseptic* solutions. The method adopted was to shake up spores in comparatively concentrated solutions of $HgCl_2$ for a short time, then, after removing the $HgCl_2$ solution by filtering and washing, to germinate the spores in a favorable medium.

Rhizopus nigracans was selected for this study on account of the size of the spores, the ease with which they were evenly distributed throughout the solution, and their very dark color, enabling one to recognize them easily on the filter. The critical concentration for this form shaken up with $HgCl_2$ solutions for 75 seconds proved to be about 1:3700. The removal of the $HgCl_2$ from the spores before testing their vitality is the most difficult and important point. My method was to prepare a filtering cone having four times as many perforations on one side as on the other. The single ply of the folded filter was placed next this side. The filter was first wet with water and then connected with an air-pump. When the $HgCl_2$ solution was poured in, the fluid was almost instantly removed, leaving most of the

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[1] Clark, J. F. On the toxic effect of deleterious agents on the germination and development of certain filamentous fungi. Bot. Gaz. 28, 289 (1899).

spores evenly distributed over the single ply of the filter. A stream of water was then turned on and the washing continued until free from $HgCl_2$. This was tested by allowing the moist filters to lie for a few hours, and then by compression of those through which the most concentrated solutions were filtered a few drops of water were obtained. To this was added some beet decoction and a few fresh spores. The germination of these spores was accepted as evidence of thorough washing. In taking the washed spores from the filter, care was taken to test those in the most favorable position for thorough washing.

The results of these tests are plotted as curve No. 3 (from the top) in Fig. 6. The upper curve is derived from notes on *Rhizopus* grown in beet decoction, concentration of $HgCl_2$ 1 : 180,000. The second curve is the first part of the *Aspergillus* curve plotted in Fig. 2, $HgCl_2$ concentration being 1 : 50,000. The characteristic variation due to variation in concentration already remarked in discussing Fig. 2 is here very well brought out. The third curve is with the same fungus as the first, the difference being due to the greater concentration of the $HgCl_2$ in the

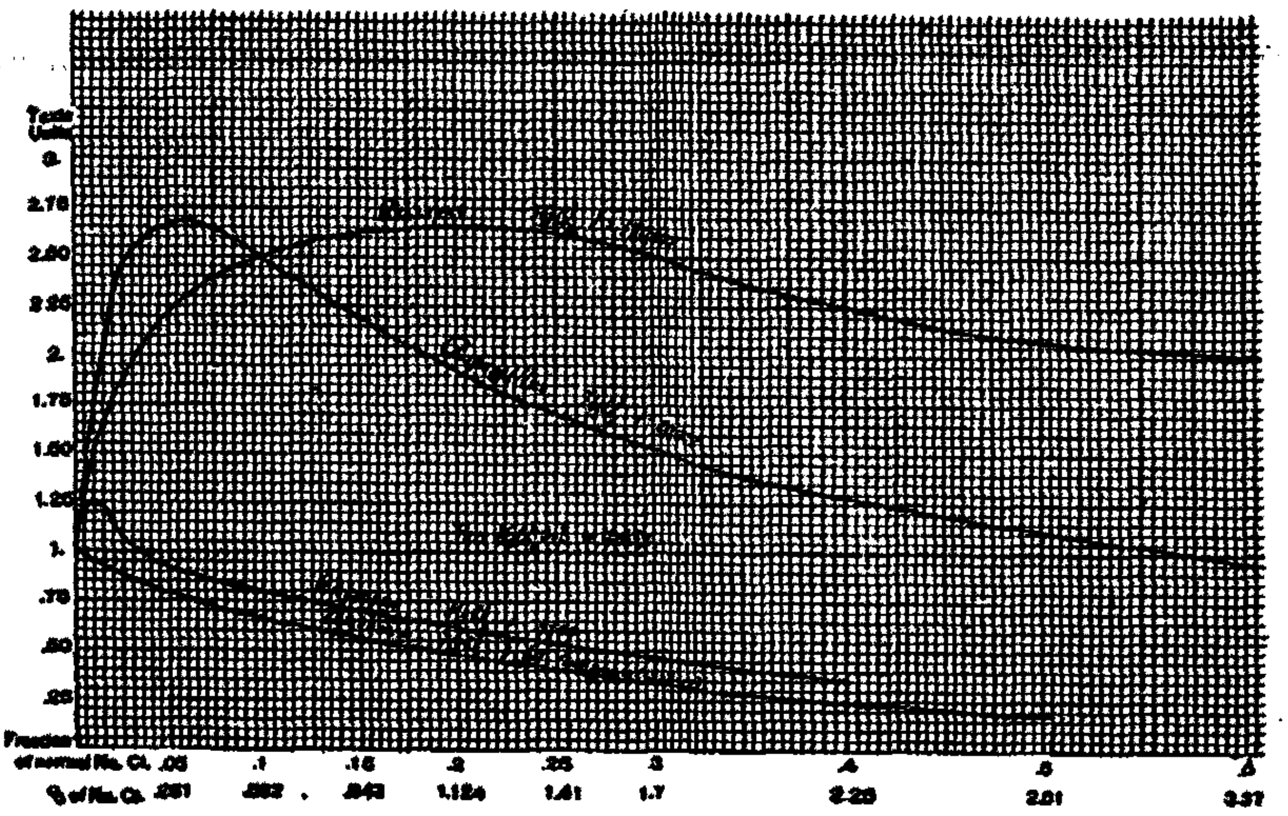

Fig. 6

former case. The increase in toxic properties resulting from additions of NaCl was only slight, and due to the adding of very small quantities of the salt. In a concentration of $HgCl_2$ of 1:180,000 *Rhizopus* shows a continued increase in toxic value for the solution on the addition of NaCl up to over 1 percent. When the $HgCl_2$ is present in 1:3700, however, the same plant shows that the mixture is already worth *less* as a toxic agent when but 0.2 percent NaCl has been added than the original pure $HgCl_2$ solution. The fourth curve here is from Krönig and Paul's work.[1] The data at my disposal do not enable me to draw a strictly quantitative curve, but it is drawn in such a way as to show two facts very clearly shown in their tables, viz., that there is a *lowering* of the toxic value of the mixture when any NaCl is added, and that the lowering is relatively greater with additions up to 1.5 percent than it is from that point to 3.3 percent NaCl. The smallest addition of NaCl they experimented with was 0.4 percent, and their concentration of $HgCl_2$ was 1:60. Their results, then, are in fullest accord with the general facts shown in the three higher curves. The four curves given here will, perhaps, throw a great deal of light on the apparently contradictory results of other workers. It will be remembered that those who found an increase in toxic properties on the addition of NaCl worked with the more dilute solutions of $HgCl_2$, while Krönig and Paul who found the contrary worked with very concentrated solutions.

A careful study of Fig. 6 shows that whether or not an increase or decrease is to be anticipated from an addition of NaCl to $HgCl_2$ solutions, depends altogether on two considerations:

(1) the concentration of the $HgCl_2$ present and

(2) the amount of the NaCl or other chloride added. A much higher percent of the salt must be added, however, if we would get a *decrease* of the toxic properties with the more dilute solutions of $HgCl_2$.

Fig. 7 illustrates a further peculiarity of concentrated $HgCl_2$ solutions to which NaCl has been added in considerable

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[1] Krönig and Paul. l. c., p. 49, Tables 26 and 28.

concentration. Here the abscissæ represent the concentration of $HgCl_2$ + a definite number of NaCl molecules. In the upper part of the figure it is $1HgCl_2 + 100NaCl$, in the lower part $1HgCl_2 + 10NaCl$. The ordinates represent the development of the fungus and the bacterium in the various concentrations. The two upper curves are from my notes on *Rhizopus* and are taken from the same series as curve No. 3 in Fig. 6, the ordinates representing the percent germinated. The lower are from Krönig and Paul's[1] Table 28, and the development of the cultures is represented on the ordinates by the number of spores of anthrax that survived immersion in the disinfecting solution for twenty minutes. The upper of the two curves represents in each case the $HgCl_2$ + the NaCl. The lower of each set represents the

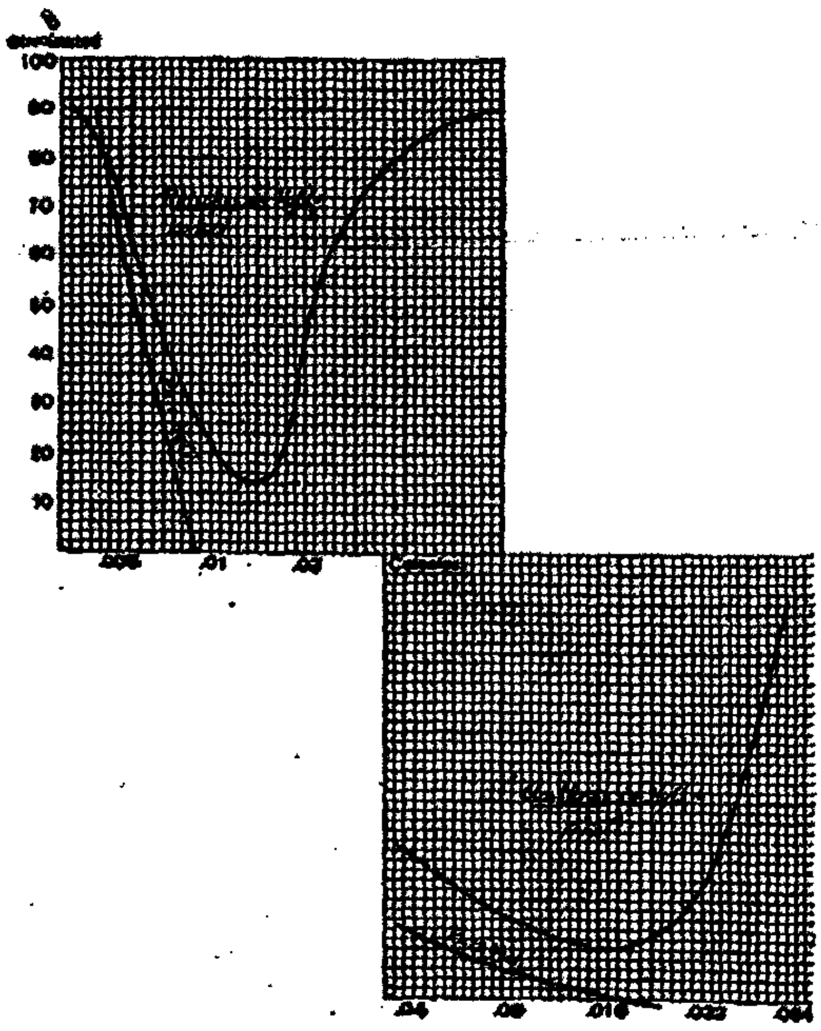

Fig. 7

Abscissæ represent the concentration of $HgCl_2$ in fractions of normal solution. The ordinates in the upper part give the percent of *Rhizopus* germineted, in the lower part the number of colonies of anthrax developed.

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[1] Krönig and Paul. l. c., p. 50.

effect of a pure $HgCl_2$ solution. The upper curves show that except in the very dilute solutions the pure $HgCl_2$ solution is the more toxic. The curves descend together with increasing concentration until about 0.8 percent is reached, when the $HgCl_2 + NaCl$ curve takes a sudden and very marked curve upward until it reaches a point indicating an extremely low toxic value where the NaCl is present in about 6 percent concentration. The lower curves are developed in a similar way. Here the $HgCl_2$ is present in about ten times the concentration used with *Rhizopus* because of the greater resistance of *Anthrax*, and the NaCl being ten to one of the mercury, instead of a hundred to one as before, is present in approximately the same percentage concentration in both cases. Here the $HgCl_2$ curve bends consistently downward with each increase of concentration of $HgCl_2$. The same is true of the $HgCl_2 + NaCl$ curve — although the mixture is uniformly less toxic — until it reaches a concentration of between 0.8 and 0.9 percent NaCl, when, like its mate above, it curves upward in an extraordinary manner.

Here we have a solution of 1.56 percent $HgCl_2$ + 9 percent NaCl, which may be increased markedly in toxic properties by simple dilution with pure water to four times its volume. The result with *Rhizopus* is entirely similar in kind, although it took place at a much greater dilution of the $HgCl_2$. That a toxic mixture may be made more toxic by simple dilution with water was so startling to me that the result was only accepted after a careful repetition of the work. With this in view, all available literature on the toxicology of $HgCl_2$ was reviewed to see if anything similar had been observed by other workers. The above example from Krönig and Paul was the only one found, and it seems to have been passed unnoticed by these workers, although it is quite clearly shown by their table No. 28.

The work with phanerogams was done by preparing 400 cc solutions of $HgCl_2$ of various concentrations and similar solutions of $HgCl_2$ + various additions of NaCl. The seeds, which were carefully selected, were put into these solutions in the dry state, and after soaking forty-eight hours at about 23° C, were removed, washed well in water, and germinated in sphagnum moss. I am not satisfied that this method is above criticism, and prefer not to say more than that the resistance of the phanerogams to $HgCl_2$ is in general very similar to that of the fungi, and that my experiments indicated clearly a similar relation to $HgCl_2$ solutions containing NaCl as that worked out for the fungi. The legumes, however, while showing an increase in toxic properties with the smaller additions of NaCl, apparently did not show any falling of the curve with increasing concentration of NaCl. More work, however, must de done on this point.

The yeasts and bacteria showed a remarkable difference in their resistance to $HgCl_2$. The two yeasts used were the most resistant of all plants tested, while the bacteria are, at least in the vegetative condition, extremely sensitive to very minute quantities of this agent. My cultures with the yeasts in $HgCl_2$ + NaCl solutions were somewhat erratic from some undetermined cause, and I propose to do further work before publishing. Few cultures were made with bacteria in solutiens to which NaCl was added, those which were made, however, showed that *Bacillus colon* was influenced by additions of NaCl in a way entirely similar to the fungi.

In concluding this review of my experimental data I wish to say that *Botrytis vulgaris* seems to be an exception to the rule established by the other molds. It is by far the most sensitive to $HgCl_2$ of the fungi tested. It is inhibited by about one-eighth the concentration required to inhibit *Œdocephalum*, itself a very sensitive form. *Botrytis* was tested nine times to test the effect of adding chlorides and hydrochloric acid to solutions of $HgCl_2$. And in no case, except possibly with HCl, did it show any evidence of increased toxic properties in the solution until the added compound was itself present in deleterious concentration.

In discussing the results of this work, it may not be out of place for even a botanist to express his opinion of the chemical significance of the facts observed. Krönig and Paul in summing up their work on mercuric chloride, especially their results with adding chlorides to the solutions, concluded that the lowering of the toxic value by such additions was due to the suppression of the dissociation of the $HgCl_2$. Were this view correct the additions of chlorides to more dilute solutions would result in a still more marked decrease in toxic value, inasmuch as the $HgCl_2$ would with greater dilution be more fully dissociated. We have found the contrary to be the case. Further they overlooked the fact that the $HgCl_2$ in the concentrations used by them (mostly 1.69 percent) would certainly not be appreciably dissociated. They explained the observation that the cadmium chloride reduced the toxic properties less than other chlorides on the basis of its less dissociation; hence its lessened ability to reduce the dissociation of $HgCl_2$. In view of what is now known regarding the toxicology of cadmium[1] the correct interpretation is doubtless to be found in the toxic effect of the cadmium itself.

It is established that the addition of chlorides to solutions of $HgCl_2$ results in the formation of double salts in which the $HgCl_2$ forms a part of a more complex molecule. A number of such double salts have been isolated in crystalline form. My interpretation of my results and the results of other workers is based on this fact, and on the probability that these complex salts dissociate readily, or at least comparatively readily into their ions. To illustrate this, we shall consider the case of NaCl only added to $HgCl_2$ solutions, and of the possible double salts only the well known Na_2HgCl_4 will be considered in detail. What is true of the formation and dissociation of this double salt is doubtless true with minor variations of all the double salts of the alkali chlorides. As already mentioned, quite a number of such salts have been isolated, and it may be that many occur in solutions with varying concentrations of the alkali chloride or the $HgCl_2$ which have not yet and perhaps cannot be isolated without decomposition.

When NaCl is added to $HgCl_2$ even in great dilution, we

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[1] Clark, J. F. Bot. Gaz. 28, p. 389.

must suppose that more or less of the double salt results. On its dissociation we would get two $\overset{+}{Na}$ and one $\overset{-\,-}{HgCl_4}$ ion. The addition of more NaCl within certain limits would increase the concentration of $\overset{-\,-}{HgCl_4}$ ions. That the replacing of the $HgCl_2$ molecule by the $\overset{-\,-}{HgCl_4}$ ions is likely to result in an increase of toxic properties, is, it seems to me, not only probable, but almost certain, being in harmony with all our knowledge of toxic agents which have the power of combining with chlorine in varying proportions. To quote from Davenport,[1] "Beginning with methane, CH_4, we find this substance — marsh gas — inocuous when mingled with air. As the H atoms become replaced by one or more chlorine atoms, the poisonous properties increase.

> CH_3Cl is slightly anesthetic.
> $CHCl_3$ = chloroform.
> CCl_4 is very dangerous, stupefying involuntary muscles."

This relation of chlorine to toxicology is quite well established, and is in fullest harmony with the upward curves of all my figures, when the solutions are dilute and the added chloride is not present in excess. With an increasing concentration of NaCl, however, there must come a time when the double salts can no longer readily dissociate on account of the high concentration of $\overset{+}{Na}$ ions present from the great excess of NaCl, which is not in combination with the $HgCl_2$, and also from the increased concentration of the $\overset{-\,-}{HgCl_4}$ ions. This continued increase of the NaCl would result then in three changes in the physical condition of the dissolved salts.

1. A lessening of the $HgCl_2$ molecules present, if all were not already combined to form the double salts.
2. A lessening of the $\overset{-\,-}{HgCl_4}$ ions.
3. An increase in the number of complex molecules containing mercury, e. g. Na_2HgCl_4.

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[1] Davenport, C. B., '97. Experimental Morphology, Part I.

Should these large and complex molecules—and it may be that in high concentrations they are very large and complex—have a lower toxic value than the pure $HgCl_2$ molecule, we have an explanation for the radical change occurring in the curve, indicating that the additions of NaCl no longer increase, but markedly decrease the toxic value of the mixture.

In this connection it is highly significant, as has already been hinted, that in all cases tested the concentration of the $HgCl_2$ at the critical points was the determining factor as to whether an increase or decrease of toxic value was to be expected from any given addition of a chloride. This is true alike for antiseptic and disinfecting concentrations. In the latter case we should expect that the greater concentration of $HgCl_2$ would facilitate the formation of the double salts, and the formation of these salts would presently prevent their own dissociation in the relatively concentrated solution. Fig. 6, Curve No. 3, shows that with an addition of only 0.08 percent NaCl the toxic properties of the $HgCl_2$ solution are being already reduced. It must be noted that this is but *one-fifteenth* the concentration of NaCl required to cause a falling of the curve with the same fungus but in a very much greater dilution of the $HgCl_2$. (Compare curves 1 and 3, Fig. 6.)

Finally Krönig and Paul, working with very concentrated solutions, found that salt added to such in 0.4 percent or greater concentration invariably lowered the toxic value. Here we must suppose, according to our theory, that the concentration of the $HgCl_2$ is too great to admit of the dissociation of the double salts formed.

I regard the results given in Fig. 7 as further evidence in favor of the view that in the molecular form these complex molecules are of a lower toxic value than $HgCl_2$, but of higher value when ionized. Here with different forms, different methods, different concentrations, and different workers, it is shown that solutions of $HgCl_2$ + NaCl when the salts—particularly the NaCl—are present in great concentration, *a great increase in the toxic properties of the mixture may be obtained* *by the simple diluting with water* to four or more volumes. It would appear that the most reasonable explanation is that the greater dilution enabled the double salts to dissociate, thereby giving us highly toxic $\overset{-\,-}{\mathrm{HgCl}_4}$ ions instead of the comparatively harmless $\mathrm{Na_2HgCl_4}$ molecule.

Just why *Botrytis vulgaris* proved an exception to the rule established by the other molds is unknown. There is, however, undoubtedly such a factor in biology as *specific resistances* of the protoplasm of certain organisms to certain agents. *Botrytis* itself has such a specific resistance to $\mathrm{AgNO_3}$ as compared with *Penicillium*.[1] One-eighth the concentration of mercuric chloride required to kill *Penicillium* is fatal to *Botrytis*. With silver nitrate the exact converse is the case four times the concentration fatal to *Penicillium* is required to inhibit *Botrytis*. I offer it merely as a suggestion that *Botrytis* may have a specific resistance to the complex $\overset{-\,-}{\mathrm{HgCl}_4}$ ion.

Just why HCl should be so much more effective than NaCl (see Fig. 5) in increasing the toxic properties of $\mathrm{HgCl_2}$ solutions is also hard to understand. It does not appear, *a priori*, that we have any reason to suppose that it unites more readily with $\mathrm{HgCl_2}$ than its sodium salt, or being united, that the resulting complex molecule would dissociate much more readily, as would be required were we to account for the increased toxicity of the mixture in the same way as we have done with the sodium salt. It may be that here we have an example of increased toxicity due to the catalytic action of the $\overset{+}{\mathrm{H}}$ ions on the very toxic ion, $\overset{-\,-}{\mathrm{HgCl}_4}$.

Whatever the chemical or physical conditions in these mixtures may be, it is demonstrated beyond doubt, that the recommendations of additions of NaCl to solutions of mercuric chloride for disinfecting purposes in practical sanitation have been without sufficient experimental basis. Every formula recommending the additions of NaCl for this purpose which has come to my notice has prescribed NaCl in a proportion that is

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[1] See my Bot. Gaz. article, p. 311.

undoubtedly a very considerable detriment to the usefulness of the disinfectant.

The fact that it renders the $HgCl_2$ more soluble, and the claim that it is not so readily precipitated by albuminoids will not offset this loss of toxic properties.

Mercuric chloride is ***readily soluble in hot water***, and the cold saturated solution retains about 5 percent of the salt in solution, a concentration vastly stronger than is required for any sanitary purpose. The claim that in the presence of NaCl the $HgCl_2$ is not so readily precipitated by proteids in solution is, in view of all work done on the subject, probably entirely correct. I would emphasize, however, that this is but another way of saying that the double salts of $HgCl_2$ + NaCl ***have less affinity for proteid substances than the pure*** $HgCl_2$ ***solution.*** Let us see where this leads us. The whole value of mercuric chloride as a toxic agent whether as an antiseptic or as a disinfectant, is due to this very remarkable affinity for proteid matters. It kills the living cell by chemical union with proteids necessary for the continuance of life. In this chemical union the $HgCl_2$ is necessarily precipitated as well as the proteid of the cell in the form of a quite insoluble mercury albuminate. Now it is patent that any treatment that "protects" $HgCl_2$ from being precipitated by the proteids must conversely protect proteids from precipitation by the $HgCl_2$, and must therefore be a positive and very serious detriment to the carrying on of the work of disinfection.

In the use of mercuric chloride as a fixing agent for tissues in biological studies, we find another case where an apparent advantage has been accepted as a real one without sufficient experimental work. It is the custom in many laboratories to recommend that the $HgCl_2$ for fixing purposes be dissolved in a "normal" salt solution, by which is meant a 0.6 percent solution of NaCl. Ten percent of $HgCl_2$ is easily dissolved in such a salt solution and the presumption is that a solution containing 10 percent $HgCl_2$ would necessarily be a much more rapid fixer than a saturated solution of the pure $HgCl_2$ where but 5 percent of the $HgCl_2$ is in solution. The probability is that there is a sufficient toxic power in either of these solutions to cause almost instant fixation, but there can be no doubt but that the pure $HgCl_2$ solution is the better in regard to toxic properties. And I have not known anyone who has used both who has had any other reason than the *amount of* $HgCl_2$ *present* for believing the contrary.

In conclusion I beg to acknowledge my indebtedness to Dr. B. M. Duggar, professor of plant physiology, and to Professor Geo. F. Atkinson, professor of botany in Cornell University, for every courtesy and assistance in the prosecution of this study. My best thanks are also due to Professor W. D. Bancroft for invaluable suggestions on the chemical aspects of the work.

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Cornell University.

NEW BOOKS

Die wissenschaftlichen Grundlagen der analytischen Chemie. *Elementar dargestellt. Von W. Ostwald. Dritte, vermehrte, Auflage. 13 × 21 cm; pp. xi + 221. Leipzig: Wilhelm Engelmann, 1901. Price: bound, 7 marks.* — The third edition follows the general lines laid down in the first. One-half the book is devoted to a statement of general theory, the other half to special applications. Under the head of theory we find five chapters: the recognition of substances, the separation of substances, physical methods of separation, chemical separations, measurement of substances. The divisions of the second part are: hydrogen and hydroxyl as ions; the group of the alkali metals; the metals of the alkaline earths; the metals of the iron group; the metals of the copper group; the metals of the tin group; the non-metals. A final chapter deals with the calculation of analyses, while an appendix contains a number of well-chosen lecture experiments.

This being the third edition there are naturally very few errors of fact remaining. One or two have escaped elimination. On page 36 it is not true that the distillate from two partially miscible liquids is always inhomogeneous. That is true only when the boiling-point does not lie between those of the two components. On page 92 the chief advantage of the mercury electrode is that the metals dissolve in it. On page 73 the reader would never guess that an increase of solubility sometimes followed the addition of an electrolyte having an ion in common with the solute. This about covers the list of slips and the rest of the book is excellent. Though there is as yet little outward sign of the good influence which this book must have had, that will come with time, and we shall have then yet another instance where Ostwald has been both pioneer and leader. *W. D. Bancroft*

Ausgewählte Methoden der analytischen Chemie. *By A. Classen. Erster Band. Unter mitwirkung von H. Cloeren. 14 × 21 cm; pp. xx + 940. Braunschweig: Friedrich Vieweg und Sohn, 1901. Price: bound, 20 marks.* — This comprehensive work is rather a handbook for experts than a textbook for elementary students. It contains no general descriptions of method, but starts directly with detailed statements concerning the modes of determining a particular metal. The present volume deals only with inorganic basic analysis; presumably the second volume will discuss acids. It supplies in some measure a lack which every one must have felt, — namely, the lack of a guide among the manifold methods of analytical chemistry, to point out those which long experience has shown to be practically satisfactory. Many modern papers are quoted, and in general the discussion of them shows the effect of wide reading about analytical topics, and much practical acquaintance with them. The references are given in full. One cannot but wish that the theoretical treatment were as complete as the practical; for in this work the vast mass of acceptable analytical data remains a mass of disconnected individual facts, without rhyme or adequate reason. The modern point of view is invaluable to the congested mind, simply as an assistance to the memory, apart from its inherent interest; but here the dissociation hypothesis is ignored, and the law of pressure-action ("mass-action") is not mentioned.

The volume under discussion covers much ground, although a book of chosen methods. The rare metals are given more space than ever before in a book of this kind, and even the analysis of the Welsbach "mantle" is briefly discussed. The abandonment of the old Gay-Lussac method of determining silver volumetrically, and the substitution of the Stas modification involving the use of bromides instead of chlorides, is an example of the wise practical discrimination which is sometimes seen. On the other hand, it is odd that the solubility of argentic chloride is not mentioned in its gravimetric relations also. In general, the accuracy sought is rather of the commercial than of the very precise scientific sort. As usual, the difference of electromotive force observed during electrolysis between the two electrodes is recorded as if it did not involve one variable unknown quantity depending upon strength of current and electrolytic resistance, and another depending upon the conditions at the anode. A strange incongruity is to be found in the first table for the calculation of analyses at the end of the book. This table is based upon the erroneous and abandoned value O = 15.96; but in it at least one element is given a value which corresponds to O = 16,000. Fortunately a shorter table, consistent with itself, although entirely inconsistent with the preceding, and evidently based upon the report of the Committee of the German Chemical Society, is available in an appendix.

In spite of its deficiencies, the work is unquestionably valuable; it will probably supplant in large measure the outgrown classic of Fresenius.

T. W. Richards.

A Text-Book of Urine Analysis, *for students and practitioners of medicine. By John H. Long. 14 × 19 cm; pp. iv + 249. Easton: The Chemical Publishing Co., 1900. Price: $1.50* — In this book, the attempt is made to present the subject of urine analysis in a manner adapted to the requirements of the medical student, and also to the wants of the medical practitioner who has occasion to make something more than the usual simple qualitative tests in urine examinations. The book contains much of the matter which appeared some years ago in the author's "Chemical Physiology and Urine Analysis" and which is now out of print. Two chapters are devoted to the microscopic examination of urinary sediments.

As the author states in his preface, "While the book is essentially one of analysis, not of diagnosis, numerous references are made throughout the test to the clinical significance of what is found by the various tests, and in the appendix a section is devoted to a tabular statement of the relation of pathological conditions to the chemical composition of the urine." *W. R. Orndorff*

REVIEWS

The object of this department of the Journal is to issue, as promptly as possible, critical digests of all Journal articles that bear upon any phase of Physical Chemistry.

General

Argon and its companions. *W. Ramsay and M. W. Travers. Proc. Roy Soc.* **67**, *329* (*1900*). — What was called metargon is now believed to be due to impurities caused by removing the oxygen with phosphorus containing carbon. On allowing liquid air to evaporate quietly, krypton and xenon are left behind. Since the vapor contains much more krypton than the liquid, krypton can be separated from xenon by fractional distillation. By fractional distillation a mixture of helium and neon can be separated from argon. By cooling the mixture thus obtained in liquid hydrogen, it was possible to distil off the helium, leaving neon practically pure. Helium, neon, argon, krypton, and xenon are all monatomic. The densities (O = 16) are 1.98, 9.97, 19.96, 40.88, and 64 respectively, so that these substances fit into the periodic table just after H, F, Cl, Br, and I. The critical temperatures and pressures are: Ne $< 68°$; A 155.6 and 40.2 m; Kr 210.5° and 41.24 m; Xe 287.7° and 43.5 m. On compressing the gases at 11.2° C the pressure-volume product increases with hydrogen, decreases, and then increases with nitrogen, increases with helium more rapidly than with hydrogen, decreases with argon followed at very high pressures by a gentle increase, decreases markedly with krypton and suddenly with xenon.

W. D. B.

Radio-activity of uranium. *W. Crookes. Proc. Roy. Soc.* **66**, *409* (*1900*). — On fractioning crystallized uranium nitrate with ether, the part insoluble in ether becomes more radio-active. By repeated crystallization from ether it is possible to get an inactive uranium nitrate. The radio-active substance is called provisionally UrX. On adding ammonia to an aqueous solution of uranium nitrate, the active substance is entirely in the precipitated yellow ammonium uranate. The brown precipitate obtained by adding ammonium carbonate is even more intensely radio-active, its action on a photographic plate being as marked in five minutes as that of ordinary uranium nitrate in twenty-four hours. Experiments are given to show that UrX is certainly not polonium and probably not radium. *W. D. B.*

Apparatus for determining the density and mass of very small quantities of a solid. *G. Guglielmo. Rend. Accad. Lincei,* (*5*) **9**, *II*, *261* (*1900*). — By measurements with the author's submersed areometer (**4**, 545) in two different liquids it is possible to determine fairly accurately the density of a few milligrams of a solid. *W. D. B.*

Thermal radiation in absolute measure. *J. F. Bottomley and J. C. Beattie. Proc. Roy. Soc.* 66, *269* (*1900*). —Reviewed (5, 90) from Phil. Mag. [5] 49, 543 (1900).

One-Component Systems

Change in temperature by solidification of melted organic compounds. *B. Pawlewski. Ber. chem. Ges. Berlin*, 33, *3727* (*1901*).— Fifty organic compounds were investigated to find anomalous melting-points similar to those observed with *p*-nitrochlorbenzene and *p*-dibrombenzene. The fall in temperature and time interval were plotted and curves constructed. Three types of curves are given. The third type gives a marked rise in solidification due to supercooling. Among the substances belonging to the last class are benzil, benzoin, monochloracetic acid, vanillin, and resorcin. Shaking or other mechanical disturbance will greatly vary the character of the curve.

C. G. L. W.

Effect of high pressures and temperatures on carbon. *Q. Majorana. Rend. Accad. Lincei*, (*5*) 9, *II*, *224* (*1900*.) — An apparatus was constructed in which carbon, enclosed in an insulating mass of magnesite, could be submitted to an estimated pressure of about eleven thousand atmospheres and also be heated to about 2000° by an alternating current of 2500 amperes. The carbon was converted into graphite with a density of 2.395. The experiment would have been more instructive if a little diamond dust had been added to the carbon in order to promote the desired crystallization.

W. D. B.

A reply. *B. Woringer. Zeit. phys. Chem.* 35, *724* (*1900*). — A reply to Winkelmann (5, 200).

W. D. B.

Critical temperatures of some organic sulphur compounds. *L. Ferretto. Gazz. chim. Ital.* 30, *I*, *296* (*1900*). —The method was that of Altschul. The following critical temperatures were obtained : C_2H_5SH, 228° ; $(CH_3)_2S$, 231.2° ; $(C_2H_5)_2S$, 284.7° ; $C_2H_5SCH_3$, 259.7°.

W. D. B.

The equation characteristic of water vapor. *O. Tumlirz. Nuovo Cimento*, (*4*) 11, *5* (*1900*). —The author finds that all of Battelli's results on water vapor can be expressed with remarkable accuracy by the formula $p(v + 0.008402) = 3.4348\,T$. This equation holds from −6° to +231°, but not quite to the point of saturated vapor.

W. D. B.

On Boyle's law at very low pressures. *A. Battelli. Nuovo Cimento*, (*5*) 1, *5* (*1901*). —The author has studied the pressure volume relations for air when the pressure varies from 6 mm to 0.02 mm. Slight variations from Boyle's law occurred whether the experiments were made with glass or with iron vessels. At pressures below 0.1 mm there are further variations with glass vessels which are probably to be attributed to surface action. The pressures were determined by a special differential manometer devised by the author. The liquids used in it were mercury, aniline and water ; it was one hundred times as sensitive as a mercury manometer.

W. D. B.

On the weight of hydrogen desiccated by liquid air. *Lord Rayleigh. Proc. Roy. Soc.* 66, *334* (*1900*). — Hydrogen was dried by cooling to the temperature of liquid air. The apparent weight was one to two-tenths of a milligram more than that of hydrogen dried with phosphorus pentoxide; but this slight excess is not considered of any significance. *W. D. B.*

Vapor-density of bromine at high temperatures. *E. P. Perman and G. A. S. Alkinson. Proc. Roy. Soc.* 66, *10, 489* (*1900*). — Reviewed (4, 546) from Zeit. phys. Chem. 33, 215, 577 (1900).

On the thermal conductivity of nitrogen peroxide with reference to changes of temperature and pressure. *G. Magnanini and V. Zunino. Gazz. chim. Ital.* 30, *I, 405* (*1900*). — A mass of data on the rate of cooling of nitrogen peroxide under different conditions of temperature and pressure (2, 65, 398). *W. D. B.*

An experimental investigation into the flow of marble. *F. D. Adams and J. T. Nicolson. Proc. Roy. Soc,* 67, *228* (*1900*). — The following is a summary of the results arrived at:

1. By submitting limestone or marble to differential pressures exceeding the elastic limit of the rock and under conditions described in this paper, permanent deformation can be produced.

2. This deformation, when carried out at ordinary temperatures, is due in part to a cataclystic structure and in part to twinning and gliding movements in the individual crystals comprising the rock.

3. Both of these structures are seen in contorted limestones and marble in nature.

2. When the deformation is carried out at 300° C, or better at 400° C, the cataclystic structure is not developed, and the whole movement is due to changes in the shape of the component calcite crystals by twining and gliding.

5. This latter movement is identical with that produced in metals by squeezing or hammering, a movement which in metals, as a general rule, as in marble, is facilitated by increase of temperature.

6. There is therefore a flow of marble just as there is a flow of metals, under suitable conditions of pressure.

7. The movement is also identical with that seen in glacial ice, although in the latter case this movement may not be entirely of this character.

8. In these experiments the presence of water was not observed to exert any influence. *W. D. B.*

The crystalline structure of metals. *J. A. Ewing and W. Rosenhain. Proc. Roy. Soc.* 67, *112* (*1900*). — If a cast lead plate be subjected to a severe strain and then heated to 200°, a marked change will take place in the crystalline structure even in the course of a few minutes. A similar change takes place at lower temperatures, though much more slowly. Similar phenomena were noticed with tin, zinc and cadmium. A hypothesis is advanced to account for the growth of crystals in solid metal. This assumes that a more fusible eutectic mixture due to impurities is essential. When a cold weld is made by pressure between two pieces of lead and the mass is brought to 200°, crystals always grow across the joint as if a more fusible mixture had been brushed over the fresh surfaces. *W. D. B.*

Two-Component Systems

On certain properties of the alloys of the gold-copper series. *W. Roberts-Austen and J. K. Rose. Proc. Roy. Soc.* 67, *105* (*1900*). — The freezing-point curve for gold and copper has been determined. Like that for silver and copper, it consists of two intersecting branches. The eutectic temperature is 905° (Au 1063°, Cu 1083°) and the liquid phase contains about 59.5 atomic percent of gold. As in the case of silver and copper, it seems probable that we are dealing with two series of solid solutions. *W. D. B.*

Solid solutions and isomorphous mixtures in saturated and unsaturated compounds with open chains, III. *G. Bruni and F. Gorni. Rend. Accad. Lincei,* (*5*) **9**, *II, 151* (*1900*). — A rise of freezing-point is observed when *p.p*-dimethyl stilbene is dissolved in *p.p*-dimethyl dibenzil. Both stilbene and dibenzil give normal values in diphenyl methane, as does stilbene diphenyl amine. The freezing-point constant for phenyl acetic acid was found to be about 90, using diphenyl, benzoic acid, salicyclic acid, cinnamic acid, and allocinnamic acid. While diphenyl, benzoic acid, and cinnamic acid are normal in *p*-nitrobenzaldehyde (K = 70), *p*-nitrobenzoic acid gives a molecular lowering of about 6). *W. D. B.*

On physical equilibrium in mixtures of isomorphous substances. *G. Bruni and F. Gorni. Gazz. chim. Ital.* 30, *II, 127* (*1900*). — Reviewed (4, 407) from Rend. Accad. Lincei, (5) **8**, II, 181 (1899).

Solid solutions and isomorphous mixtures. *G. Bruni. Gazz. chim. Ital.* 30. *II, 140* (*1900*). — Reviewed (4, 407) from Rend. Accad. Lincei, (5) 8, II, 212 (1899).

The cryoscopic behavior of nitro derivatives dissolved in formic acid. *G. Bruni and P. Berti. Rend. Accad. Lincei,* (*5*) **9**, *I, 273, 393; Gazz. chim. Ital.* 30, *II, 76, 31* (*1900*). — While the nitro derivatives of the fatty series give normal molecular weights in formic acid, the nitro derivatives of the aromatic series give results indicative of dissociation, the molecular weights coming out smaller than the normal and decreasing with decreasing concentration. This holds both for freezing-point and for boiling-point determinations. *W. D. B.*

Nitrogen peroxide as solvent. *G. Bruni and P. Berti. Gazz. chim. Ital.* 30, *II, 151* (*1900*). — Taking 41 as the freezing-point constant, normal values are obtained for nitro-methane, nitro-ethane and picric acid in nitrogen peroxide solutions, while acetic, butyric, trichloracetic and nitric acids give molecular weights one and one-half to three times the formula weight.

W. D. B.

The sodium salts of chromic acid. *F. Mylius and R. Funk. Ber. chem. Ges. Berlin,* **33**, *3686* (*1901*). — The following series of salts of chromic acid is described: $Na_2Cr_4O_{13}.4H_2O$; $Na_2Cr_3O_{10}.H_2O$; $Na_2Cr_2O_7.2H_2O$; $Na_2CrO_4.10H_2O$; 1/2($Na_4CrO_5.13H_2O$. The sodium salts show a marked increase in solubility with rise in temperature. *C. G. L. W.*

Calcium chromate. *F. Mylius and J. v. Wrochem. Ber. chem. Ges. Ber-*

lin, 33, *3689* (*1901*). — The solubility and crystallographic character of the following salts are described: $\alpha CaCrO_4.2H_2O$; $\beta CaCrO_4.2H_2O$; $CaCrO_4.H_2O$; $CaCrO_4.1/2H_2O$; $CaCrO_4$. The β-dihydrate shows an increase in solubility with rise in temperature. All other salts of this series give diminished solubility under similar conditions. *C. G. L. W.*

Sodium salts of some dibasic acids. *R. Funk. Ber. chem. Ges. Berlin*, 33, *3696* (*1900*). — The solubilities of sodium selenate, tellurate, molybdate, and tungstate are discussed. *C. G. L. W.*

On the vapor-pressure of binary liquid mixtures. *J. v. Zawidski. Zeit. phys. Chem.* 35, *129* (*1900*). — The experimental method employed was a modification of that used by Lehfeldt, the mixtures being distilled in a bath of fixed temperature, by adjusting the pressure; the composition of the distillate was determined by finding its index of refraction, and from this the partial pressures of the components were deduced. Boiling was brought about by an electrically heated platinum wire in the liquid. The object of the work was to test the validity of the formula of Margules for the relation between partial pressure and composition of the mixture:

$$\frac{d \log p_1}{d \log x} = \frac{d \log p_2}{d \log (1-x)},$$

where p_1 and p_2 are the partial pressures of the liquids A and B, x and $1 - x$ the concentrations in molecular percentages. The formula is confirmed for 13 binary mixtures, and a number of interesting cases brought forward. The author classifies his results as follows: (*a*) the simplest case, where the relative concentrations in the vapor phase stand in a constant relation with those in the liquid phase: benzene and ethylene chloride, propylene and ethylene bromides; (*b*) mixtures of liquids with normal vapor pressures: carbon tetrachloride with benzene, ethyl acetate, or ethyl iodide, ethyl acetate with ethyl iodide, carbon disulphide with methylal or acetone, acetone with chloroform; (*c*) cases of abnormal vapor densities, where one of the components appears partly associated in the vapor phase: acetic acid with benzene or toluene; (*d*) cases where chemical compounds are probably formed: pyridine with water or acetic acid. The results for all can be brought fairly well in line with the Margules formula.

It is only to be regretted that the actual observations were not confirmed by some independent method, since Taylor and others have found how little proof the constancy of results may afford of their correctness. *A. P. S.*

Note on an article by J. v. Zawidski, entitled: On the vapor-pressure of binary liquid mixtures. *P. Duhem. Zeit. phys. Chem.* 35, *483* (*1900*). — A claim for priority. *A. P. S.*

Correction. *J. v. Zawidski. Zeit. phys. Chem.* 35, *722* (*1900*). — An answer to Duhem (preceding review). *W. D. B.*

Dehydration of selenite and hydration of anhydrite. *V. Zunino. Gazz. chim. Ital.* 30, *I*, *333* (*1900*). — Hydrated calcium sulphate becomes anhydrous if heated long enough in the usual way at 188°. The author then passed water-vapor over the dehydrated salt at different temperatures and reports that under these circumstances all the water of crystallization is reabsorbed at 230°, seventy-five percent of it at 240°, and thirty-two percent at 250°. Unless calcium sulphate forms solid solutions with water, which is improbable, the results just cited must be due to experimental error. It is also noticed that hydrated calcium sulphate changes at least partially to anhydrite when boiled with concentrated sodium chloride solutions. Here again the author has either observed too much or too little. *W. D. B.*

Poly-Component Systems

Solid solutions in ternary mixtures, I. *G. Bruni. Rend. Accad. Lincei,* (*5*) 9, *II*, *232* (*1900*). — The author discusses the general forms of the boundary curves in three-component systems when one, two, or three pairs of components can form a continuous series of solid solutions. *W. D. B.*

Solid solutions in ternary mixtures, II. *G. Bruni and F. Gorni. Rend. Accad. Lincei,* (*5*) 9, *II*, *326* (*1900*). — The authors have made a systematic study of the freezing-points of mixtures of *p*-dichlorbenzene, *p*-chlorbrombenzene, and *p*-dibrombenzene. From these data they have constructed a number of isotherms. Since *p*-dichlorbenzene gives a continuous freezing-point curve passing through a minimum temperature both with *p*-chlorbrombenzene and with *p*-dibrombenzene (4, 1407) the form of the isotherms in the *p*-dichlorbenzene corner is especially interesting. *W. D. B.*

On the equilibrium between ester, water, acid, and alcohol. *H. Euler. Zeit. phys. Chem.* 36, *405* (*1901*). — In dilute aqueous solution, the final equilibrium varies with the nature both of acid and alcohol, the methyl esters being the least hydrolyzed, the ethyl esters the most, while the propyl esters give values lying between those for the other two. With the same alcohol and different acids, the hydrolysis of the ester is greater the stronger the acid. This leads the author to the conclusion that the cation of methyl acetate is $CH_3C\overset{+}{O}$ and the anion $C_2H_5\overset{-}{O}$. In other words, the alcohol is to be considered as an acid. As we say sodium ethylate and methylate, we should say acetic ethylate and methylate instead of ethyl acetate and methyl acetate. *W. D. B.*

On autoxidation. *F. Haber. Zeit. phys. Chem.* 34, *513* (*1900*). — The author seeks to harmonize the theory of van 't Hoff, Ewan, Jorissen, with that of Engler, Wild, Bach. He takes the following chemical equations as the basis for his thermodynamic considerations:

$$M + O_2 + 2H_2O = M(OH)_2 + H_2O_2.$$
$$M + H_2O_2 = M(OH)_2.$$

He considers that these processes apparently take place singly and independently of each other when the velocity of the one greatly exceeds that of the other. The first equation is an expression of Traube's idea of the rôle of water in the process, while the second represents the hydrogen peroxide hypothesis. The former is considered as the typical process in case autoxidation takes place in the presence of water. The double nick in the curve of the decomposition

potentials at 1.08 and 1.68 volts is thought to be due to the weak catalytic action of bright platinum toward H_2O_2, — the equilibrium $O_2 + 2H_2O \rightleftarrows 2H_2O_2$ taking place quickly at 1.08 volts and being, on the other hand, much retarded at 1.68 volts because of the decomposition of the peroxide. A number of chemical equations are given to illustrate the relation between wet and dry autoxidation.
L. K.

Autoxidation, II. *F. Haber and F. Bran. Zeit. phys. Chem.* 35, *81, 609* (*1900*). — The authors discuss the cases: sodium sulphite and sodium arsenite; sodium sulphite and nickelous hydroxide; indigo, with benzoic acid as catalytic agent, and benzaldehyde; triethyl phosphine and indigo; potassium ferrocyanide and benzaldehyde. In each case the first of the two substances is sensitive to hydrogen peroxide and the second is not. It is therefore reasonable to suppose that hydrogen peroxide is the intermediate substance formed during the simultaneous and equivalent oxidation of the two substances in presence of water. With indigo, benzoic acid and benzaldehyde alone, the oxidation of the indigo is relatively slight. *W. D. B.*

Crystallization of difficultly crystallizable compounds. *A. Rümpler. Ber. chem. Ges. Berlin,* 33, *3474* (*1900*). — With substances which are insoluble in alcohol and soluble in water, an aqueous solution is made and sufficient alcohol added just short of producing a turbidity. The solution is placed in a desiccator over lime which absorbs water and not alcohol. Crystals are produced in this way. *C. G. L. W.*

The course of the decomposition of a racemate by fungi. *C. Ulpiani and S. Condelli. Gazz. chim. Ital.* 30, *I, 382* (*1900*). — A careful study of the effect of oxygen, light, temperature, concentration, and acidity on the action of fungi on racemic substances. *W. D. B.*

The estimation of ozone. *O. Brunck. Ber. chem. Ges. Berlin,* 33, *2999* (*1900*). — A reply to Ladenburg (5, 81). *C. G. L. W.*

Osmotic Pressure and Diffusion

On the diffusion of gold in solid lead at the ordinary temperature. *W. Roberts-Austen. Proc. Roy. Soc.* 67, *101* (*1900*). — Discs of gold have been in contact with lead cylinders for four years. At the end of this time gold could be detected microscopically at a distance of seven millimeters from the gold plate, while at a distance of 0.5 millimeter it could be determined analytically. *W. D. B.*

Velocities

Theory of chemical catalysis. *H. Euler. Ber. chem. Ges. Berlin,* 33. *3202* (*1900*). — In the reaction

$$CH_3.COOH + C_2H_5OH = CH_3COOC_2H_5 + H_2O,$$

or

$$[CH_3CO][C_2H_5O] + [H][OH] = [C_2H_5O][H] + [CH_3CO][OH].$$

Equilibrium is reached when the ion product of the components reacting in one direction is equal to that of the components acting in the opposite direction, and the reaction velocity is equal to the difference between the ion product of the oppositely reacting components. The catalytic agent does not change the relations of the constants of the equilibrium formula, but the size of the numerator and denominator. Hence the special case of the van 't Hoff formula $A = RTln K_8$ is written

$$A = RTln \frac{K_1K_4}{K_2K_3} RTln \frac{K}{K_1} .$$

As $\frac{K}{K_1}$ is not influenced by the introduction of a catalyzing agent, the free energy of the reaction is unchanged.

It is possible by knowing the electrolytic dissociation constant to predict the velocity of a reaction and also from velocity measurements to estimate small amounts of dissociation which are not as yet measurable. *C. G. L. W.*

On the decomposition of organic halides in ethyl alcohol solution by dissolving sodium. *R. Löwenherz. Zeit. phys. Chem.* 36, *469* (*1901*). — This is a continuation of the preceding paper (4, 550). The general formula is confirmed and it is shown that the extent of the sodium surface has no effect. With some compounds the efficiency is greater in amyl alcohol solution, with others in ethyl alcohol solutions, so that it is important to select the right solvents in case of organic preparations. The presence of water in the alcohol decreases the efficiency very rapidly. *W. D. B.*

Saponification in organic solvents. *A. Cajola and A. Capellini. Gazz. chim. Ital.* 30, *I*, *233* (*1900*). — The reaction studied was the saponification of *n*/10 methyl acetate by a *n*/10 base. The reaction velocity is lowest in propyl alcohol, highest in isoamyl alcohol, and intermediate in isobutyl alcohol. A comparison of different bases in methyl alcohol solution showed the order to be NaOH, KOH, $(CH_3)_4NOH$, SrO_2H_2, BaO_2H_2, SrO_2H_2 NH_4OH, caustic potash saponifying about six times as fast as ammonia, while sodium hydroxide is nearly twenty times as effective as caustic potash. This comparison really has no value because the reaction is a bimolecular reversible one, and the authors have treated it as a bimolecular irreversible one counting from the equilibrium point. In propyl alcohol, isobutyl alcohol and isoamyl alcohol, the difference between the rates of saponification of potassium and sodium hydroxides scarcely exceeds the experimental error. The saponification proceeds least far with sodium hydroxide and farthest with barium hydroxide. *W. D. B.*

Reaction velocity for acids in organic solvents. *M. Geiger. Gazz. chim. Ital.* 30, *I*, *225* (*1900*). — Equivalent solutions of hydrochloric, hydrobromic, hydriodic, and nitric acids in methyl alcohol attack marble at practically the same rate. The rate of attack increases much less rapidly than the concentration and passes through a maximum. Acetic acid and the substituted acetic acids have practically no action on marble. The action of hydrochloric acid in methyl alcohol solution on malachite and on anhydrous sodium carbonate was also studied. Curiously enough, sulphuric acid in methyl alcohol solution does not attack either of these substances perceptibly at 25°. The action of hydrochloric acid on marble is much affected by the partial pressure of the carbonic acid. *W. D. B.*

The change of hyoscyamine into atropine under the influence of soda in alcoholic solutions. *A. Marzucchelli. Gazz. chim. Ital.* 30, *II*, *476* (*1900*).—The reaction is monomolecular, the sodium alcoholate acting as catalytic agent. The reaction velocity increases from methyl alcohol through ethyl alcohol to propyl alcohol. *W. D. B.*

Experiments on the sensitiveness to light of hydrogen peroxide in aqueous solutions on addition of potassium ferro- and ferricyanide. *W. Kistiakowsky. Zeit. phys. Chem.* 35, *431* (*1900*).—In dilute solutions, potassium ferrocyanide is slightly decomposed when exposed to light, a faint alkaline reaction resulting and potassium ferricyanide being formed. This reaction takes place much more readily when hydrogen peroxide is present. When filter-paper is treated with an aqueous solution of the ferrocyanide plus hydrogen peroxide and phenolphthalein and exposed to the light, the latter substance very soon indicates the presence of alkalinity. If instead the solution with which the paper is treated consists of the ferricyanide plus the peroxide and phenolphthalein slightly colored with alkali, the paper becomes colorless when exposed to light. If both cyanides are present in aqueous solution, together with hydrogen peroxide, the latter is rapidly decomposed in presence of light, free oxygen being formed. In the dark the reaction goes on very slowly, but an exposure of only a minute to light is enough to greatly accelerate the process, and the speed of the reaction once thus increased continues even after the mixture is again put into the dark-room. The progress of the reaction is represented by the logarithmic formula for monomolecular reactions. The increase of the speed of the reaction is ascribed to a catalytic agent formed from the two double cyanides in the presence of light. The experimental basis for this assumption is inadequate, however. *L. K.*

On a phenomenon observed during supercooling. *R. Moreschini. Gazz. chim. Ital.* 30, *I*, *339* (*1900*).—It is claimed that the rate of cooling changes suddenly as the temperature passes through the freezing temperature, even though no solid phase be formed. *W. D. B.*

Researches on modern explosives, II. *W. Macnab and E. Ristori. Proc. Roy. Soc.* 66, *221* (*1900*).—The authors noticed that a thin platinum wire fused when used to fire the explosive while a thicker wire did not. This showed that the maximum temperature was higher than the melting-point of platinum, but was held for a short time only. It occurred to them to observe the temperature recorded by thermopiles of different cross-sections and to extrapolate for the temperature to be obtained with an infinitely thin wire. In this note they describe their method. *W. D. B.*

Electromotive Forces

On electrode potentials. *N. T. M. Wilsmore. Zeit. phys. Chem.* 35, *291* (*1900*).—The difference of potential between metals—and also a few non-metals—and solutions which are normal with respect to the ions active in determining the particular potential in question, according to Nernst's theory, are tabulated. In part the data are taken from the work of previous observers and in part they are the results of new determinations made by the author. All voltages are compared with the potential of hydrogen under atmospheric pressure toward a solution normal with respect to hydrogen ions, which potential is arbitrarily placed equal to 0. On this basis the potential of the normal calomel electrode equals –0.283 volt. It is claimed that a hydrogen electrode of constant potential can readily be obtained. *L. K.*

Absolute potentials of metals with remarks on normal electrodes. *W. Ostwald. Zeit. phys. Chem.* 35, *333* (*1900*). — Wilsmore's introduction of the hydrogen electrode is criticized and the theoretical and practical advantages of the normal and more especially the *n*/10 normal calomel electrode are emphasized. Wilsmore's results are all recalculated on the basis of the normal calomel electrode whose E. M. F. is taken as 0.56 volt. The difference between the calomel electrode and the hydrogen electrode is taken as 0.283 volt. *L. K.*

Investigations on the electromotive activity of elementary gases. *E. Bose. Zeit. phys. Chem.* 34, *701* (*1900*) — A critical consideration of previous work on gas chains is first given, which contains a complete bibliography of the subject. An extensive theoretical and experimental investigation of the oxygen-hydrogen cell then follows. It is assumed that gases dissolved in metallic electrodes are in part or entirely dissociated into their atoms, the metals having high dissociating power. The electrolytic solution tension is considered to be the product of the osmotic pressure of these ions in the electrodes into a constant, depending on the nature of the solvent of the electrolyte. [These assumptions, which are hardly warranted by the facts, are used as a basis for theoretical considerations.] It is found that saturation of the electrodes with gas takes place exceedingly slowly, even where the metal is thin, and that previous observers have in consequence found too low a value for the E. M. F. of the Grove gas chain. The maximum value given is 1.106 volts which he, however, regards only as a lower limit. It is shown experimentally that the Grove gas chain is reversible. The higher decomposition potential, 1.67 volts, corresponds to an irreversible process. In the oxygen-hydrogen chain, water is formed at the hydrogen pole if the electrolyte is alkaline, and at the oxygen pole if the electrolyte is acid.

L. K.

The calculation of the degree of dissociation of strong electrolytes. *S. Arrhenius. Zeit. phys. Chem.* 36, *28* (*1901*). — The author points out the real connection between the Helmholtz and the Nernst formulas for concentration cells, showing that taking the concentration of the ions as the total concentration introduces errors which are fatal to Jahn's conclusions (4, 635). Attention is also called to a possible error in determining the electromotive force of concentration cells, due to the conductivity of the water. *W. D. B.*

The dissociation law for strong electrolytes. *O. Sackur. Zeit. Elektrochemie, 471* (*1901*). — A reply to Arrhenius (preceding review) in which the author claims that the Nernst formula is accurate, provided the dilution law holds. He overlooks the main point of the Arrhenius argument that we know that the undissociated portion of the salt does have an effect on the electromotive force and that any thermodynamic proof which brings out any other result is necessarily inaccurate. *W. D. B.*

On the Nernst formula for calculating the electromotive force of concentration cells. *H. Jahn. Zeit. phys. Chem.* 36, *453* (*1901*). — A reply to Arrhenius. The author merely shows that the Helmholtz and the Nernst formulas are identical for complete dissociation and looks upon that as a proof that the Nernst formula is absolutely exact. As a matter of fact the two formulas coincide only for complete dissociation, and the Helmholtz formula is the accurate one. It is interesting to notice that neither Nernst nor Planck originally claimed the accuracy of the formula as now applied by Jahn. Nernst says [Zeit. phys. Chem. 4, 144 (1899)]: "If we introduce, as is certainly more nearly right, the ratio of conductivities instead of the ratio of the concentrations...." This is admittedly a first approximation introduced because the strict calculation was too difficult. Planck is even more explicit [Wied. Ann. 40, 570 (1890)].

"When it comes to testing the theory here developed by experimental data, it is to be kept in mind that the assumption of complete dissociation which has been made is only approximately fulfilled and that the calculated values can therefore never agree absolutely with those found experimentally; they are rather the limits approached by the potential differences as the solutions are considered as more and more dilute. The influence of incomplete dissociation on the value of the potential difference is still further complicated by the degree of dissociation changing with the concentration in the intermediate layer...."

W. D. B.

Electromotive force and osmotic pressure. *R. A. Lehfeldt. Zeit. phys. Chem.* 35, *257* (*1900*). — The E. M. F. of concentration chains is calculated by means of a formula deduced from a cyclic process. The attempt is made to show that the total osmotic pressure of the salt and not simply that of the metallic ions is to be considered in calculating the E. M. F. When the potential is assumed to be proportional to $\int Pdv$ the solution tension of Zn equals 10^{19} atmospheres; when, however, it is regarded as proportional to $\int Vdp$ the solution tension is only 20,000 atmospheres.

L. K.

Thermodynamical comments on papers by Mr. R. A. Lehfeldt and Mr. H. Jahn. *H. J. S. Sand. Zeit. phys. Chem.* 36, *499* (*1901*). — The first part of this paper contains another attempt to prove that Nernst's formula is absolutely accurate even for partially dissociated electrolytes. It makes one wonder how people study thermodynamics. It is not surprising that mistakes should be made at first, because an implicit assumption is difficult to avoid; but it is not clear why people should persist in making mistakes when the thing was done right the first time and when the later assumptions have been pointed out.

The second part of the paper bears on Jahn's conclusions, but is vitiated by the flaws in the first part.

W. D. B.

Electromotive behavior of substances with several oxidation stages, II. *R. Luther. Zeit. phys. Chem.* 36, *385* (*1901*). — It is shown that when the intermediate oxidation stage decomposes spontaneously into the other two, it must be a stronger oxidizing agent than the highest oxidation stage, and a stronger reducing agent than the lowest oxidation stage. If the two end stages react spontaneously to form the intermediate stage, the reverse is true. If the concentrations are so chosen that the different stages are in equilibrium any metal which would normally become cathode as against the metal in question, may be considered an unattackable electrode and all such metals will give the same value when measured in the solution against a normal electrode. This was actually tested for silver, mercury, gold, and platinum with the equilibrium between copper, cuprous sulphate, and cupric sulphate. From electromotive measurements the author calculates the dissociation constant of mercuric chloride as 6.5×10^{-14}, while a calculation from Stas's solubility determinations gave 0.8×10^{-14}. *W. D. B.*

On the effects of strain on the thermoelectric qualities of metals, II. *M. Maclean. Proc. Roy. Soc.* **66**, *165* (*1900*). — "It seems (1) that for small longitudinal strain in copper or in iron the direction of the current through the hot junction is the same, whether the force which produced the permanent strain is on or off; (2) that as the permanent elongation is increased by increased longitudinal forces, a stage is reached which gives zero current when the forces are removed, and (3) that for greater longitudinal forces and permanent elongations the direction of the current is opposite, with the pulling forces off and on. It seems, in fact, that the permanent elongation must exceed a definite limit, to produce reverse thermoelectric effects with the longitudinal force on and removed."

With copper, platinoid, German silver and magnanin wires the current passed through the hot junction from the stretched to the unstretched wire, a reversal with greater permanent elongation being obtained for copper only. With reostene and iron the current passed through the hot junction from unstretched to stretched wire and was reversed for iron by a permanent elongation with the weights off. *W. D. B.*

On the relation between polarization and current density in solid and molten salts. *A. Gockel. Zeit. phys. Chem.* 34, *529* (*1900*). — By means of a method similar to that used by Le Blanc (Zeit. phys Chem. 5, 467 (1890)) experiments were made with the following salts: $NaNO_3$ (290°), $NaNO_3$ (308°), PbI_2 (385°–406°), CdI_2 (300°–325°), $PbBr_2$ (364°–478°), $PbCl_2$ (420°–436°), $BiBr_3$ (234°–302°), HgI_2 (229°–250°). In part, carbon electrodes were used and in part metallic wires. The voltages obtained are compared with those calculated by means of the formula of Wiedeburg, and that of Planck. The logarithmic formula of the latter gives results which agree better with those found, in many cases at least. In the case of the bromide of bismuth, the experimental values agree better on the whole with those calculated according to Wiedeburg's formula. *L. K.*

On difference of potential between a solid salt and its solution. *A. Campetti. Rend. Accad. Lincei,* (*5*) **9**, *II*, *27* (*1900*). — The author considers the case of a salt dissolving in an unsaturated solution and concludes that the sign of the potential difference will depend on the relative migration velocity of the two ions. It is not clear from the article how he tested this experimentally or what results he obtained; but he claims to have verified his hypothesis. *W. D. B.*

On the electrical effects due to evaporation of sodium in air and other gases. *W. C. Henderson. Proc. Roy. Soc.* 66, *183* (*1900*). — Marked electrification was observed when sodium was vaporized in air; but none when coal gas was substituted. The electrification is probably due, therefore, to oxidation of the sodium. *W. D. B.*

On the Volta effect and a new method of measuring it. *Q. Majorana. Rend. Accad. Lincei*, (*5*) 9, *II*, *132* (*1900*). — A silvered quartz thread is suspended between two different metallic spheres and the deflection determined under different conditions of charge for the three metals. *W. D. B.*

Influence of state of surface and of low temperature on the Volta effect. *Q. Majorana. Rend. Accad. Lincei*, (*5*) 9, *II*, *162* (*1900*). — The method was the one devised by the author (4, 413). The potential difference between zinc and gold may vary from 0.5 to 0.9 volt, depending on the degree to which the gold is polished. At the temperature of liquid air, the effect is 0.05 volt as against 0.88 volt at ordinary temperatures. The original potential is not restored by coming back to the original temperature, presumably owing to a change in the state of the surface Standing twenty-four hours in an atmosphere of hydrogen has, however, more of a disturbing effect than cooling to — 180°. *W. D. B.*

On the attraction between heterogeneous metals. *Q. Majorana. Rend. Accad. Lincei*, (*5*) 9, *II*, *199* (*1900*). — In order to measure the Volta effect the author has constructed a balance sensitive to 0.00001 mg. This sensitiveness is obtained by measuring the displacement of the arms by means of interference fringes. *W. D. B.*

Electrolysis and Electrolytic Dissociation

Electrolysis of hydronitric acid. *A. Peratoner and G. Oddo. Gazz. chim. Ital.* 30, *II*, *95* (*1900*). — Attention is called to the fact that the authors had anticipated Szarvasy (5, 152) and that they then proved qualitatively the occurrence of secondary reactions. *W. D. B.*

Electrolytic reduction of barbituric acid. *J. Tafel and A. Weinschenk. Ber. chem. Ges. Berlin*, 33, *3383* (*1900*). — Malonyl urea is easily reduced in dilute sulphuric acid to trimethylene urea and hydouracil. The hydrogen efficiency is less at low temperatures than at 40°–50°. *C. G. L. W.*

Electrolytic production of ozone. *G. Targetti. Nuovo Cimento*, (*4*) 10, *360* (*1899*). — A lead anode should be used and the important points are high current density, low temperature and introduction of air at the electrodes. Even then the yield is only 2.7 g per horse-power-hour. *W. D. B.*

Note on the electrical resistivity of electrolytic nickel. *J. A. Fleming. Proc. Roy. Soc.* 66, *50* (*1900*). — The nickel studied was prepared electrolytically from a hot solution of very carefully purified nickelous chloride. The electrolytic metal was annealed by heating in an atmosphere of hydrogen, after having been drawn into wire through a die. At 0° the resistance per centimeter cube is 6935 C. G. S. units and the mean temperature coefficient between 0° and 100° is 0.00618. The value obtained by Matthiessen was 12357 C. G. S. units, but

Matthiessen states explicitly that he was not certain of the purity of his nickel.
W. D. B.

On the connection between electrical properties and the chemical composition of different kinds of glass, II. *A. Gray and J. J. Dobbie. Proc. Roy. Soc.* 67, *97* (*1900*). — The specific resistance in ohms × 10^{10} of lime glass is 0.2 at 149°; of a lead glass containing potash and soda, 8.5 at 150°; of a lead soda glass, 136.5 at 142°; of a barium potash glass, 6.5 at 138°; of an unannealed lead-potash glass, 1329 at 142°; of the same glass when annealed $>$ 29000 at 140°.
W. D. B.

On the change of resistance in iron produced by magnetization. *A. Gray and E. T. Jones. Proc. Roy. Soc.* 67, *208* (*1900*). — It was found empirically that the change of resistance of soft iron is approximately proportional to the fourth power of the magnetization over the range covered by the experiments.
W. D. B.

Investigations on platinum thermometry at Kew observatory. *C. Chree. Proc. Roy. Soc.* 67, *3* (*1900*). — A most interesting report on the behavior of six platinum thermometers during the five years since 1895. It should be read by every one using or proposing to use platinum thermometers. *W. D. B.*

Energy of some acids dissolved in mixtures of organic solvents and water. *A. Morello. Gazz. chim. Ital.* 30, *I*, *257* (*1900*). — The author has determined the rate of inversion of sugar by hydrochloric acid and the substituted acetic acids when these acids are dissolved in water, in seventy percent acetone and in eighty-six percent methyl alcohol. He has compared the relative dissociations as thus obtained with the values calculated from conductivity measurements. The two sets of results are entirely discordant. *W. D. B.*

On the energy of some metallic hydrates deduced from the hydrolysis of the salts. *G. Carrara and G. B. Vaspignani. Gazz. chim. Ital.* 30, *II*, *35* (*1900*). — From the rate of catalysis of methyl acetate and from the conductivity the authors conclude that aluminum hydroxide is a stronger base than ferric hydroxide and that the order of the bases is Mg, Cu, Zn, Cd, Al, Fe.
W. D. B.

On the energy of some organic acids containing no carboxyl groups. *G. Coffetti. Gazz. chim. Ital.* 30, *II*, *235* (*1900*). — From the rate of inversion of cane sugar and from conductivity measurements it is shown that the strength of the acid decreases from hydrochloric acid through nitranilic and bromanilic acids to chloranilic acid. It was also shown that croconic acid is stronger than rhodizonic acid while this latter is stronger than leuconic acid. *W. D. B.*

Contribution to the study of dilute solutions. *N. Tarugi and G. Bombardini. Gazz. chim. Ital.* 30, *II*, *403* (*1900*). — The authors have determined the dissociation of the sulphates of cobalt, iron, cadmium, nickel, manganese, copper, zinc, and magnesium by means of freezing-point, boiling-point and conductivity measurements. The values obtained from the conductivity measurements do not coincide at all with those obtained from the other two methods.
W. D. B.

Relations between heat of solution and solubility in the case of electrolytes. *J. J. van Laar. Zeit. phys. Chem.* 35, *11* (*1900*). — The formula of van 't Hoff is practically the same as the author's. Both formulas contain errors, hence the author gives a new formula, the errors in which are negligible, viz:

$$L_{s} = \frac{RT_1T_2 \log(1-a_2)s_2 - \log(1-a_1)s_1}{T_2-T_1},$$

L' is the total molecular heat of solution at the saturation concentration, s_1 and s_2 the solubilities at T_1 and T_2, a_1 and a_2 the degrees of dissociation, and R the gas constant. By means of this formula a better agreement between found and calculated values is obtained in the case of silver acetate and silver propionate than with the old formulas. *L. K.*

Dissociation in colloidal solutions. *M. G. Levi. Gazz. chim. Ital.* 30, *II* *64* (*1900*). — The author has determined the conductivity of different concentrations of potassium iodide in water, in gelatine, in agar-agar, and in silicic acid. The presence of the colloid has only a very slight effect. The freezing-points of potassium iodide and potassium chloride solutions are the same whether the solvent is water or water thickened with gelatine. The presence of a silicic acid jelly has practically no effect on the rate at which hydrochloric acid inverts cane sugar. *W. D. B.*

On electrostriction of ions in organic solvents. *G. Carrara and M. G. Levi. Gazz. chim. Ital.* 30, *II*, *197* (*1900*). — Density determinations have been made for a number of substances in methyl alcohol, in ethyl alcohol, in acetone and in water. As a general statement it is true that the apparent molecular volume of the solute as calculated from these data varies most with the concentration when the dissociation also varies markedly; but the quantitative relations are not those deduced by Nernst and Drude. *W. D. B.*

Conductivity measurements as a test for hydrolytic dissociation. *R. Salvadori. Rend. Accad. Lincei.* (*5*) 9, *II*, *177* (*1900*). — In the case of a salt undergoing hydrolytic dissociation, the change of conductivity with dilution will be due to the change of dissociation plus the change in hydrolysis. If we dilute with a solution of an acid or a base as the case may be instead of with water the hydrolysis will not change. The two sets of results will run parallel in case the salt is not hydrolyzed and will not if the salt is hydrolyzed. The accuracy of the prediction is illustrated by experiments with barium nitrate, copper nitrate, lead nitrate and potassium carbonate. *W. D. B.*

Electrochemical abbreviations. *M. A. Hollard. Zeit. Elektrochemie*, 7, *139* (*1900*). — The following abbreviations have been proposed at the International Congress for Applied Chemistry held at Paris: p, osmotic pressure; P, solution pressure; j, heat of ionization; λ_v, molecular conductivity; γ, specific conductivity; v_a, migration velocity of the anion; v_k, migration velocity of the cations; e, electromotive force of polarization; ϵ_a, polarization at the anode; ϵ_k, polarization at the cathode; V, molecular volume; Λ, molecular concentration; Δ, dissociation constant; δ, degree of dissociation; n, transference number; v, valence of an element. *W. D. B.*

The electric plant in the chemical laboratory of the mining school at Clausthal. *F. W. Küster. Zeit. anorg. Chem.* 26, *167* (*1901*). — A very interesting description of the storage battery system in the chemical laboratory and of the way in which connections are made. *W. D. B.*

On the treatment of Cupron cells. *E. Jordis. Zeit. Elektrochemie*, 7, *469* (*1901*). — The author has used a battery of Cupron cells for four years in making electrochemical analyses, etc. He makes several useful suggestions as to the method of handling such cells. *W. D. B.*

An electrical platinum furnace. *W. Nernst. Zeit. phys. Chem.* 7, *253* (*1900*). — A platinum iridium wire is wound on an infusible tube and the whole protected from radiation by an outside insulating jacket. The apparatus will give a temperature of 1400° inside the tube when connected with a 110 volt circuit and uses only 2.4 amperes. It is made by Mohr and Loehrs of Rudolstadt in Thüringen and costs about forty marks. *W. D. B.*

On the requirements to be met by carbon as electrodes. *F. Winteler. Zeit. Elektrochemie*, 7, *356* (*1900*). — The author discusses what qualities are essential for carbon electrodes in the electrolysis of chlorides in the aluminum industry, and in the preparation of carbides. He concludes that in aqueous solutions where chlorine is set free, retort graphite must be used; that artificial carbon electrodes may be used in the aluminum industry, and that anthracite or anything else may be used for the preparation of carbide, provided only that it contains no phosphorus. *W. D. B.*

Stirrers and electrodes with hermetic seal. *W. Löb. Zeit. Elektrochemie*, 7, *117* (*1900*). — A glass cup is fused round the stem of a Witt stirrer and filled with mercury into which dips the end of the stationary glass guiding tube. When it is desired to stir with the electrode itself, the stirrer has a hollow stem down which a wire passes, sealed in top and bottom. *W. D. B.*

Stirrers with hermetic seal. *B. Neumann. Zeit. Elektrochemie.* 7, *350* (*1900*). — This stirrer differs from the one devised by Löb (preceding review) in that the mercury seal is outside and not inside the cathode chamber. This has the advantage that the stationary guiding tube can be used as a gas-delivery tube, simply by putting on a side arm. *W. D. B.*

The ampere-manometer. *G. Bredig and O. Hahn. Zeit. Elektrochemie*, 7, *259* (*1900*); *453* (*1901*). — Two nickel electrodes and a caustic soda solution are placed in a flask with a glass delivery tube connecting with a manometer and a capillary tube leading to the air. The pressure readings are a function of the rate at which the gas is evolved and the size of the capillary. By changing the capillary and standardizing for each capillary, the instrument becomes an ammeter with a number of scales and an accuracy of about five percent. *W. D. B.*

The ampere-manometer and its application in electrochemistry. *A. Job. Zeit. Elektrochemie*, 7, *421* (*1901*). — The author has invented independently an apparatus similar to that of Bredig and Hahn (preceding review). He points out that a modification of it might be used in following a reaction gas analytically. *W. D. B.*

Correction. *W. Ostwald. Zeit. Elektrochemie*, 7, *448* (*1901*). — A statement as to dates in regard to the ampere manometer (preceding review). *W. D. B.*

On a laboratory pump. *E. Jordis. Zeit. Elektrochemie*, 7, *464* (*1901*). — An apparatus for a continuous flow of solution through an electrolytic cell. *W. D. B.*

Dielectricity and Optics

On the dielectric constants of pure liquids. *B. B. Turner. Zeit. phys. Chem.* 35, *385* (*1900*). — Nernst's apparatus is tested and improvements are made in various details. These improvements make it possible to measure dielectric constants from five to ten times more accurately than would the original apparatus. The following dielectric constants were determined very accurately at 18°: benzol 2.288; nitrotoluene 27.7; water 81.1; ether 4.368; aniline 7.31; *m*-xylene 2.376; nitrobenzene 36.45. The first three substances are recommended for calibration purposes. Ether and aniline are found to be too changeable for such purposes. The purity of the last two substances was not so thoroughly investigated. The temperature coefficients of two of the above substances (*o*-nitrotoluene and nitrobenzene) were also determined; and preliminary measurements of the dielectric constants of fourteen other liquids were made, the results obtained being as follows: ethylene bromide 4.865 at 18°; carbon tetrachloride 2.246 at 18°; ethyl alcohol 26.8 at 14.7°; chloroform 5.2 at 18°; α-bromnaphthalene 5.17 at 19°; bromoform 4.51 at 20.7°; ethyl bromide 9.7 at 18°; methyl iodide 7.1 at 20.4°; acetophenone 18.6 at 20°; methylene iodide 5.5 at 19°; thiophene 2.76 at 16°; isobutyl alcohol 18.9 at 18°; quinoline 8.9 at 20°; phenylhydrazine 7.15 at 23°. *L. K.*

On the resistance and the residual charge of liquid dielectrics at different temperatures. *A. Naccari. Nuovo Cimento*, (4) 11, *50* (*1900*). — Increase of temperature causes increase of conductivity. The residual charge is greatest in the dielectrics with the highest resistance. *W. D. B.*

Experimental investigation of the variation of the dielectric constant of some gases and vapors with the temperature. *K. Bädeker. Zeit. phys. Chem.* 36, *305* (*1901*). — The method employed is a modification of that of Philip (2, 74). The gases and vapors studied were CS_2, SO_2, NH_3, H_2O, CH_3OH, C_2H_5OH, N_2O_4. It was found that the Clausius-Mossotti formula and the Maxwell law either both hold or both fail, the latter being the more usual case. With gases which are not described by the two equations, rise of temperature makes the dielectric constant approach the square of the index of refraction. *W. D. B.*

The birotation of *d*-glucose. *G. Osaka. Zeit. phys. Chem.* 35, *661* (*1900*). — The author finds that *d*-glucose must be considered as a weak acid; that the rate of change of the rotation is approximately proportional to the concentration of hydroxyl as ion and approximately proportional to the square root of the concentration of hydrogen as ion. Neutral salts increase the catalytic action of hydroxyl as ion, but have no measurable effect on that of hydrogen as ion. The catalytic action of acids is very much less than that of bases. The diamines were included among the weak bases. *W. D. B.*

On the molecular rotation of *n*-acidyl-*l*-ethyl malate. *H. Reiller. Zeit. phys. Chem.* 36, *129* (*1901*). — The values increase from the acetyl to the butyryl compound and then decrease with increasing carbon content. The results are not in harmony with Guye's calculations based on the "asymmetry product." *W. D. B.*

The determination of the index of refraction as a means of investigating the composition of coexisting vapor and liquid phases. *E. H. J. Cunaeus. Zeit. phys. Chem.* 36, *232* (*1901*). — The index of refraction of a mixture of two gases agrees only approximately with the value obtained by applying the rule of mixtures to the indices of refraction of the single gases. The variation from the rule of Amagat for the density of a gas mixture is sufficient to account for the discrepancy. For mixtures of ether and acetone, the formula of van der Waals for the compositions of the coexistent phases holds only so long as the solutions are very dilute. The author thinks the discrepancy may be due to errors of observation. *W. D. B.*

On the rotation and dispersion of malic acid. *B. Woringer. Zeit. phys. Chem.* 36, *336* (*1901*). — The following conclusions are drawn :

The changes in the specific rotations with the most different rays and with varying concentrations of malic acid are continuous.

For no concentration is there complete achromatism.

Partial achromatism occurs in dilute solutions containing over seventy-eight percent of water.

The anomaly in the rotation is to be represented by a fold in the surface of the specific rotations. *W. D. B.*

Asymmetry and vitalism. *C. Ulpiani and S. Condelli. Gazz. chim. Ital.* 30, *I*, *344* (*1900*). — A résumé of the discussion started by Japp. The authors also cite experiments of their own bearing on the subject. *W. D. B.*

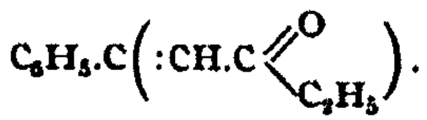
The refractive index of tellurium in some of its compounds. *G. Pellini and R. Menin. Gazz. chim. Ital.* 30, *II*, *165* (*1900*). — By the Gladstone formula the atomic refraction for tellurium becomes 32.5 from the tetrachloride in benzene solution ; 33 8 from the tetrabromide in benzene; 26.1 from potassium tellurite in water ; 24.6 from telluric acid in water ; 32.0 from liquid tellurium diphenyl. The freezing-point depression for tellurium tetrachloride in benzene solution points to a reacting weight double the normal. *W. D. B.*

Ultra-red absorption spectra of liquids. *L. Pucciani. Nuovo Cimento,* (*4*) 11, *241* (*1900*). — Liquid compounds containing carbon united directly with hydrogen show a maximum absorption for the wave-length 1.71 μ.V. *W. D. B.*

On the fluorescence of aluminum and magnesium in water and in alcohol through the action of currents from an induction coil. *T. Tommasina. Nuovo Cimento,* (*4*) 11, *47* (*1900*). — With aluminum or magnesium electrodes in water or alcohol, there is a marked anodic fluorescence. The other metals, zinc, cadmium, tin, brass, copper, silver and platinum do not show it. The fluorescence appears more rapidly and is more intense with slightly oxidized electrodes than with electrodes that have just been cleaned. *W. D. B.*

On the behavior of the Becquerel and Röntgen rays in a magnetic field. *R. J. Strutt. Proc. Roy. Soc.* 66, *75* (*1900*). — The author confirms the observation of Giesel (4, 420) that Becquerel rays can be deflected in a magnetic field and shows that the deflection of Röntgen rays under the same circumstances must be less than a ten-thousandth part of that observed in the case of the Becquerel rays and is probably zero. There is therefore an essential difference between the two classes of rays. *W. D. B.*

Arrangements for observing fluorescence and opalescence. *M. Tswett. Zeit. phys. Chem.* 36, *480* (*1901*). — A test-tube containing the solution is suspended in a black box opposite an opening through which the observer looks. The light from a Welsbach lamp comes in through an opening near the bottom of the box, and is thrown vertically upwards by means of a mirror. If there is any turbidity in the solution a cone of light will be seen near the bottom of the test-tube. *W. D. B.*

The chemical action of light. *G. Ciamician and P. Sieker. Ber. chem. Ges. Berlin,* 33, *2911* (*1900*). — The compounds which de Coninck and Devrien obtained by the action of light on an alcoholic solution of benzophenone is not the condensation product  $C_6H_5.C\left(:CH.C\begin{smallmatrix}\diagup O\\ \diagdown C_2H_5\end{smallmatrix}\right).C_6H_5$, but the pinacone. Acetophenone also forms a pinacone under similar circumstances.

C. G. L. W.

On lamps for spectra, I. *Ernst Beckmann. Zeit. phys. Chem.* 34, *593* (*1900*). — Luminous flames are produced by blowing air into solutions under a non-luminous burner. The spray thus formed reaches the flame and colors it. To produce this fine spray, it was found that the air is best blown into the liquid through the pores of a small tube of unglazed porcelain. By first saturating the porcelain tube with alcohol, acetone, acetic acid, ether, or benzene, better results are obtained, i. e., a finer, more copious spray is formed. Ether and benzene are apt to create foam and so are not as good as the other liquids mentioned.

The fine spray of sulphuric acid that forms on charging storage cells led the author to devise an apparatus to form the spray of solutions of metallic salts by evolving hydrogen by electrolysis of such solutions. For a detailed description of the apparatus, the original must be consulted in which the required cuts will be found. *L. K.*

On lamps for spectra, II. *Ernst Beckmann. Zeit. phys. Chem.* 35, *443* (*1900*). — An apparatus is described for cooling the liquid to be transformed into spray (see previous review). The liquid, being near the lamp, is apt to become too hot or to evaporate, and hence the necessity of a device for cooling it. Apparatus for washing the porous tube with alcohol, for creating and regulating the gas pressure are also described. When the carbon lines of the ordinary gas flame are objectionable, a hydrogen flame is used. An apparatus for producing the spray by electrolytic means is also described. Details must be looked up in the original which contains full descriptions, together with nine illustrations. *L. K.*

On lamps for spectra, III. *E. Beckmann. Zeit. phys. Chem.* 35, *682* (*1900*).—A universal lamp is described which can be used with all kinds of flames. For demonstration purposes the author recommends a round flame, the spraying to be done either by compressed gases or electrolytically. *W. D. B.*

Crystallography, Capillarity and Viscosity

On the viscosity of argon as affected by temperature. *Lord Rayleigh. Proc. Roy. Soc.* 66, *68* (*1900*).—The change of the viscosity of argon with the temperature is not radically different from that of the diatomic gases, the value of the exponential constant *n* being 0.812 for argon, 0.754 for dry air, 0.782 for oxygen, and 0.681 for hydrogen. The measurements were made by diffusion through a capillary heated to 15° and to 100.27°. *W. D. B.*

On the viscosity of gases as affected by temperature. *Lord Rayleigh. Proc. Roy. Soc.* 67, *137* (*1900*).—Experiments with helium at ordinary temperature and at 100° gave a value of 0.681 for the exponential factor *n* in the equation connecting change of viscosity with change of temperature. This is identical with the value for hydrogen (preceding review). *W. D. B.*

ERRATUM.

By inadvertence Fig. 3 in Mr. Kahlenberg's article (5, 223) was printed upside down.

CONTENTS

[*Continued from second page of cover*]

CONTENTS

THE THEORY OF ELECTROLYTIC DISSOCIATION AS VIEWED IN THE LIGHT OF FACTS RECENTLY ASCERTAINED[1]

BY LOUIS KAHLENBERG

(With the cooperation of ARTHUR A. KOCH and ROY D. HALL)

INTRODUCTION

The theory of electrolytic dissociation as advanced by Arrhenius[2] in 1887 is based primarily upon the facts that the molecular conductivity of solutions increases with the dilution, that substances which when dissolved conduct electricity, also have abnormally low molecular weights in such solutions when tested by osmotic or freezing- or boiling-point methods, and that the so-called degree of dissociation may be calculated from the electrical conductivity or the results of the molecular weight determinations. In his original article Arrhenius states that the phenomena of electrolysis, when viewed from the standpoint of thermodynamics, require the assumption of the presence of free ions, as was pointed out by Clausius, and that the heats of neutralization of acids and bases in dilute solutions and the various physical properties of salt solutions, which are well known to be additive in character, support the electrolytic dissociation hypothesis. The effect which the publication of that memorable article of Arrhenius had, need not to be dwelt upon at length here. Suffice it to recall that its author sought to save van 't Hoff's theory of solutions from having but a limited application, and at the same time to bring into correlation facts that had hitherto been entirely isolated. Chemists and physicists alike

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[1] Published also in the Bulletin of the University of Wisconsin, Science Series No. 4, 2, 247 (1901).

[2] Zeit. phys. Chem. 1, 629 (1887).

were astonished by the audacity of the assumption made by this investigator of recognized ability. The theory at once met with great opposition, notably in England, and it was by no means received with open arms on the continent. But the hypothesis inspired experimental investigation, and the results of this phenomenal activity (which at first centered in Ostwald's laboratory at Leipzig, but spread rapidly to other parts of Germany, to various other countries of Europe and to America) soon silenced opposition in Germany, and gradually diminished it also in England. It must not be supposed, however, that this silence meant that all were convinced. The silence seemed to result on the one hand because of a recognition of the futility of the debate with the knowledge of existing facts, and because of a recognition of, if not an admiration for, the enthusiasm displayed by the adherents of the theory,—enthusiasm that bore fruitful results in experimental investigations of various physical, chemical and physiological properties of solutions, which results were ingeniously interpreted in the light of the new theory.

It was at first only in the case of aqueous solutions of the ordinary acids, salts and bases that van 't Hoff's theory of solutions met its difficulties; and when Arrhenius pointed out that these solutions are conductors of electricity, and assumed that the dissolved substances are electrolytically dissociated into free ions, these solutions were on this basis shown to support the theory. Arrhenius calculated the troublesome factor i (which van 't Hoff had found it necessary to introduce to make the behavior of the above mentioned solutions conform to the gas equation) from the electrical conductivity on the one hand and from molecular weight determinations on the other, the resulting figures showing an agreement to within 5 to 15 percent, according to his estimation. In view of the few experimental data at hand in 1887, and the fact that many of them had not been determined with accuracy, the poor agreement, of a goodly number of values at least, was readily overlooked in view of the generalities that the theory sought to bring, generalities which were soon incorporated without proper qualifications into text-books. The electrolytic solutions with which Arrhenius made his comparisons and deductions were without exception aqueous solutions. The non-aqueous solutions known at that time were practically non-conductors of electricity; and in dilute solutions at least, they generally conformed fairly well in their behavior to van 't Hoff's theory of solutions. (Indeed it was not until Raoult began his famous work on the freezing-points of non-aqueous solutions that it was discovered that molecular weights could be calculated from the lowering of the freezing-point.) In view of the facts then known, the idea gradually gained ground in the minds of those holding van 't Hoff's theory and Arrhenius' auxiliary hypothesis concerning the nature of electrolytes, that non-aqueous solutions in general yield "normal" molecular weights for the solutes, and that they are "of course" non-conductors of electricity. This notion took root with surprising rapidity and the natural result was that investigations of electrical conductivity, of electromotive forces and of electrolysis in non-aqueous solutions was entirely neglected.[1] When in 1895 I had the great privilege of working in the inspiring atmosphere of Ostwald's laboratory, I upon one occasion asked the genial director of the institute why the electrical conductivity of non-aqueous solutions was not studied; the reply was, "*Die nichtwässerigen Lösungen leiten ja nicht.*" So it was hardly a surprise when in 1899 the new edition of Ostwald's Grundriss der allgemeinen Chemie appeared, containing on pages 390 and 391 the sweeping, unqualified, italicized statement, "*Jedesmal wenn ein gelöster Stoff von den Lösungsgesetzen in solchem Sinne abweicht, dass sein osmotischer Druck (oder die diesem proportionale Gefrierpunkts- oder Siedepunkts-änderung) grösser ist, als seinem Molekulargewicht entspricht, so zeigt er auch elektrolytische Leitfähigkeit und umgekehrt.*" It is to be noted that Reychler's book on physical chemistry, a much less compendious volume, the English translation of which appeared early in 1899,

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[1] On the other hand it was at once assumed that free ions exist whenever a substance conducts electricity with accompanying chemical decomposition, be that substance a gas, a molten salt, or a solid.

nevertheless contains a very fair consideration of the work that had at that time been accomplished in the study of non-aqueous solutions.

Behavior of non-aqueous electrolytic solutions

Before entering upon the experimental part of this paper, I desire to call attention briefly to the import of some of the work on non-aqueous conducting solutions as bearing upon the theory of electrolytic dissociation. In the first place many cases have been found in which the molecular conductivity decreases with increased dilution. This is true for instance of solutions of NaI and NaBr in benzonitrile,[1] of $AgNO_3$ in piperidine,[2] of $FeCl_3$ in pyridine,[3] of $FeCl_3$ in benzaldehyde[3] and of CoI_2 in $POCl_3$.[4] In other cases the molecular conductivity at first increases and then again decreases with the dilution, as for instance in solutions of $FeCl_3$ in paraldehyde,[1] of CBr_3COOH in $POCl_3$.[2] Again many solutions have been found in which the solute according to molecular weight determinations is undissociated, and which nevertheless possess excellent power of conducting electricity. So $AgNO_3$ has a normal molecular weight[5] in pyridine and benzonitrile, and yet it conducts[6] fairly well in these solvents. According to Dutoit and Friderich,[7] CdI_2, LiCl, NaI, $HgCl_2$ and NH_4CNS have normal molecular weights in acetone, and yet these solutions are conductors of electricity. Walden[8] has found that KI, NaI, RbI, NH_4I and KCNS conduct well in liquid SO_2 and yet have abnormally large molecular weights in this solvent; while $S(CH_3)_3I$, $N(CH_2)_4I$ have molecular weights in this solvent which hardly differ from the theoretical more than do the molecular weights of non-electrolytes examined in SO_2. Walden himself says concerning this, "*ganz*

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[1] Euler. Zeit. phys. Chem. 28, 619 (1899).
[2] Lincoln. Jour. Phys. Chem. 3, 457 (1899).
[3] Kahlenberg and Lincoln. Ibid. 3, 12 (1899).
[4] Walden. Zeit. anorg. Chem. 25, 213 (1900).
[5] Werner. Ibid. 15, 1 (1897).
[6] Kahlenberg and Lincoln. l. c. Also Lincoln. l. c.
[7] Bull. Soc. Chim. Paris, (3). 19, 334 (1898).
[8] Ber. chem. Ges. Berlin, 32, 2862 (1899).

unerwartet ist jedoch die doppelte Molekulargrösse für die Elektrolyte 4–7, was ganz aus dem Rahmen des Geforderten herausfällt und nicht ohne Weiteres mit der üblichen Auffassung vereinbar ist." Franklin and Kraus[1] have found that while NH_4NO_3, $NaNO_3$ and KI dissolved in liquid ammonia are excellent conductors of electricity, the boiling-points of the solutions, like those observed by Walden in SO_2, are not nearly as high as they ought to be on the basis of the assumption that electrolytic dissociation takes place. Again lately Nicolo Castoro[2] found by means of the freezing-point method that $AgNO_3$, $CdCl_2$, $HgCl_2$, and $ZnCl_2$ have normal molecular weights in urethane. I have made a few preliminary tests on the first three of these salts which showed that their solutions in urethane are conductors of electricity. Very recently Innes[3] found the molecular weights of succinic, salicylic and tartaric acids to be normal in pyridine according to the boiling-point method. These acids undoubtedly form salts which redissolve in the excess of the solvent. Preliminary tests have assured me that all three of these solutions are fairly good conductors of electricity. The tartaric acid solution conducts best, as might have been expected.

While in many cases the molecular conductivity of non-aqueous solutions increases with the dilution, this increase is generally relatively slight. It has generally been impossible to calculate the degree of dissociation of substances in non-aqueous solutions from the conductivity, because in these solutions the molecular conductivity commonly either diminishes with the increase of dilution, or it increases slightly with the dilution exhibiting no tendency to reach a maximum, or it remains practically constant, or soon reaches a maximum with so low a value that completeness of dissociation can not consistently be assumed. These facts will become evident to the reader by a perusal of the figures contained in the original articles above cited. I have

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[1] Amer. Chem. Jour. 20, 836 (1898).
[2] Gazz. chim. Ital. 28, II, 317 (1898).
[3] Jour. Chem. Soc. 79, 261 (1901).

already discussed at some length the difficulty of calculating the degree of dissociation in non-aqueous solutions,[1] and shall therefore simply add here that the calculation of the degree of dissociation from molecular weight determinations is in the case of non-aqueous solutions also impracticable, because the molecular weights are, as a rule, normal or greater than normal in spite of the fact that the solutions conduct well, and that the boiling-point constant of the solvent is so high that dissociation certainly ought to be indicated, if it were present.

It is a well known fact also that molecular weights determined according to cryoscopic or ebullioscopic methods at times increase with the dilution, again at other times they do not change much with the dilution, and at still other times they decrease as the dilution increases. The latter behavior only is in harmony with the theory of solutions and the theory of electrolytic dissociation. Furthermore, occasionally simple substances show abnormally low molecular weights and yet their solutions are not conductors of electricity. This I have found to be true, for instance, in the case of solutions of diphenylamine in methyl cyanide,— results as yet unpublished.

The osmotic theory of the galvanic cell, which uses the dissociation hypothesis as a basis, also naturally meets great difficulties when applied to chains containing non-aqueous solutions.[2]

In the face of these facts the theory of electrolytic dissociation is untenable in the case of non-aqueous solutions. While chemists have frequently in conversation admitted this to be true, I have also often been told, " But in the realm of aqueous solutions the theory concords with the facts so well." This led me to investigate the behavior of aqueous solutions somewhat further.

Experimental part

The general plan of the investigation was to determine the boiling-points of aqueous solutions of typical, common, chemical compounds from low to very high concentrations, in order to see

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[1] Jour. Phys. Chem. 3, 379 (1899).

[2] See Kahlenberg. Jour. Phys. Chem. 3, 395 (1899). Ibid. 4, 709 (1900).

how the molecular weight changes with the concentration, and at the same time to measure the electrical conductivity of such solutions at or near their boiling-points. This would enable one to make much more accurate comparisons between the values of the degree of dissociation as calculated from conductivity and molecular weight, than by the but too common practice of comparing coefficients deduced from conductivity results obtained at room temperature with those reckoned from boiling- or freezing-point experiments. The work of making the conductivity measurements at high temperatures and the corresponding boiling-point determinations was undertaken by Mr. Arthur A. Koch, to whose diligence and care the numerous tables (2 and 12 to 31 inclusive) given below are due. Again it was part of the plan to measure the conductivity of such solutions at 0° and at the same time to make molecular weight determinations by the cryoscopic method, and then to compare the degrees of dissociation found according to the two methods.[1] All the conductivity determinations at 0° were made by Mr. Roy D. Hall, the results of whose work are contained in Table 1 below.

The conductivity determinations were made by means of the usual Kohlrausch method, a telephone being employed. An Arrhenius resistance cell was used for the dilute solutions and a U-shaped cell with platinized electrodes sufficiently far apart was employed for the concentrated solutions. All of the solutions were carefully made up to the proper volume at the temperature indicated. The measurements at 0° were made in a bath of melting ice surrounded by another very large bath of the same nature. In the immediate vicinity of the resistance cell a

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[1] But few conductivity determinations at or near 100° could be found in the literature. For seven of the salts named in Table 2, Krannhals [Zeit. phys. Chem. 5, 250 (1890)] determined the conductivity at 99.4°. He did not, however, as a rule, begin with as concentrated solutions as those represented by the corresponding salts in Table 2, and his series are frequently incomplete. As far as conductivity determinations at 0° are concerned, only a few scattered determinations could be found in the literature, which would not have been adequate for the purpose in hand. Molecular weight determinations of a goodly number of the salts under consideration are to be found in the literature, but they do not cover a sufficient range of concentration for the present purpose.

delicate thermometer was kept which remained very constant at 0°. At first it was attempted to measure the conductivity of solutions at 100°, but it was soon observed that small gas bubbles are so apt to form on the electrodes at this temperature as to introduce considerable error. It was found that at 95° this particular difficulty is not so prominent, and so the conductivity measurements at the higher temperature were made at 95° instead of at 100°. The resistance cell was immersed in a large paraffine bath whose temperature was carefully regulated at 95°.

The freezing-point determinations were made with a regular Beckmann's apparatus of large size, about 40 grams of water being used in each case. The solutions were cooled only from two to three-tenths of a degree below their freezing-points, and the crystallization was each time inaugurated by means of a point of ice. The boiling-point determinations were made with a Beckmann's apparatus of about double the ordinary size. Unless otherwise stated, appropriate Beckmann's thermometers graduated to 0.01° (made by F. O. R. Goetze in Leipzig) were used. It was at first thought best to surround the thermometer with a platinum cylinder in the boiling tube, as recommended by Jones, but it was soon found that this at times causes slight fluctuations in the boiling-point, apparently due to the fact that the solution within the cylinder is apt to be slightly more concentrated than that without.

The water used in the experiments was distilled water condensed in a block tin condenser. By drawing air freed from carbon dioxide through it for a long time its conductivity was reduced to 2×10^{-6} (or somewhat less) at room temperature. The conductivity of the water has been deducted in each case, after having been determined at the proper temperature of course. The substances used were all of the C. P. variety of standard makes, generally either Kahlbaum's or Schuchardt's. They were tested as to their purity, and as a rule were recrystallized. When the salt contained water of crystallization, the amount of this was ascertained, and the salt was weighed in the crystallized form for the molecular weight determination, the crystal water being added to the solvent in making the computations, so that the latter are all based on the amount of anhydrous salt in the solutions. For the conductivity determinations the appropriate quantities of salt (also calculated on the basis of the anhydrous substance) of course simply had to be made up to the required volume at the proper temperature.

In Table 1 are given the results of the conductivity measurements at 0°, while in Table 2 the values obtained at 95° are presented. The numbers in each case indicate the equivalent conductivity (Λ_v) in reciprocal ohms. The value of v indicates the volume in liters in which a gram-equivalent is contained.

An inspection of Tables 1 and 2 shows that in each case Λ_v increases with the dilution, which fact has also been observed by other investigators[1] who determined the conductivity of these salts at 18° and 25°. The general manner in which the equivalent conductivity increases with the dilution can best be seen by charting the results in the form of curves. For the salts here under consideration, it is true in general that Λ_v increases with increase of v in a similar manner in the case of salts that are chemically analogous. Thus if curves be charted in which ordinates represent the volumes and abscissas the conductivities, these curves will have a similar trend in the case of the chlorides; the same will be true for the nitrates as a group; and again for the sulphates as a group. At the same time, the curves for the nitrates are very similar to those of the chlorides, but the sulphates have curves with more of a characteristic trend of their own. It was deemed unnecessary to present here the curves for all the salts in Tables 1 and 2. While they have all been plotted, it will suffice for the present purpose to reproduce curves of the various types of salts contained in the tables. As such typical salts have been selected NaCl, $BaCl_2$, $MgSO_4$ and $AgNO_3$. Figures 1 and 2 show the trend of the curves at 0° and at 95° respectively, the ordinates representing the cube roots of the volumes and the abscissas the equivalent conductivities. The

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[1] Compare for instance the tables in Kohlrausch und Holborn, — Das Leitvermögen der Elektrolyte.

TABLE I

Electrical Conductivity at 0°

(Figures represent Λ_v in reciprocal ohms)

v.	NaCl	KCl	KI	$BaCl_2$	KClOl	$NaNO_3$	•KNO_3	$AgNO_3$	$Ba(NO_3)_2$	$Sr(NO_3)_2$	K_2SO_4	MgSO	$ZnSO_4$	$MnSO_4$	$CdSO_4$	$NiSO_4$	$CoSO_4$	$FeSO_4$	$CuSO_4$
1/4	31.0	..	..	..	..	24.5	..	27.2	..	..	..	7.0	7.1	..	6.7	..	..	..	..
1/2	41.8	63.9	69.3	38.7	..	34.7	..	35.3	..	23.5	..	13.0	12.6	12.1	11.4	13.1	..	12.1	12.3
1	47.4	65.6	69.5	44.0	..	46.5	52.1	44.5	..	32.1	..	17.6	16.3	15.8	15.0	17.8	15.5	16.3	15.9
2	50.8	67.3	69.7	47.0	..	48.0	56.5	48.3	..	38.4	48.4	21.2	21.7	19.2	18.3	21.6	18.7	19.6	19.0
4	53.3	69.0	69.9	50.6	55.4	49.0	60.6	53.3	41.9	43.2	52.6	25.2	24.7	23.4	21.3	25.3	22.0	23.0	22.4
8	55.7	70.6	71.5	53.8	60.2	52.8	63.8	57.8	45.6	47.8	56.7	29.5	28.3	26.1	25.0	28.9	25.7	28.1	26.2
16	57.9	73.0	73.5	57.0	63.2	55.7	66.6	60.1	50.4	51.3	61.8	33.7	32.2	31.2	29.5	33.9	30.2	31.4	31.0
32	59.5	75.0	76.5	60.0	65.6	57.6	70.2	63.7	55.2	55.5	65.2	38.7	37.0	35.8	34.3	39.0	34.7	36.3	35.9
64	60.9	76.6	77.7	63.5	67.7	59.7	72.7	66.6	59.3	58.4	68.8	43.3	41.9	41.0	40.3	44.8	40.0	41.7	41.2
128	62.3	77.7	78.9	65.9	69.0	61.1	73.9	67.8	62.6	61.0	71.5	47.9	47.5	46.3	45.6	50.8	45.6	47.2	46.8
256	64.2	78.9	79.4	71.0	70.3	62.3	75 5	68.8	64.9	63.1	74.8	52.7	52.9	51.4	50.5	56.0	50.6	52.1	51.9
512	65.3	79.6	79.8	72.3	71.5	63.5	75.9	69.7	66.7	64.5	75.6	56.6	56.8	56.3	56.2	59.6	55.2	56.0	56.3
1024	67.7	80.5	80.7	..	72.1	64.3	76.8	70.2	67.9	66.1	76.9	60.5	61.0	59.4	59.4	63.0	58.4	59.5	60.7
2048	67.8	80.9	..	..	72.5	65.2	77.7	70.7	68.0	67.9	78.0	63.6	64.4	62.8	62.4	64.6	61.7	62.0	63.2
4096	67.7	..	..	..	..	..	78.4	70.5	..	68.0	79.0	66.2	65.4	65.6	63.4	65.9	64.3	63.4	66.4
8192	..	..	..	..	..	..	..	..	..	..	..	67.8	65.9	65.5	..	..	64.7	64.9	67.3

TABLE 2

Electrical Conductivity at 95°

(Figures represent Λ_v in reciprocal ohms)

v.	NaCl	KCl	KBr	KI	$MgCl_2$	$BaCl_2$	$HgCl_2$	$KClO_3$	KNO_3	$AgNO_3$	$MgSO_4$	$ZnSO_4$	$MnSO_4$	$CdSO_4$	$NiSO_4$	$CoSO_4$	$FeSO_4$	$CuSO_4$
1/4	115.9	169.1	121.9	114.3	....	....	....	....	....	....	....	....	....	....	....	....	....	....
1/2	156.1	213.2	222.8	216.3	....	....	....	....	....	....	....	....	....	....	....	....	....	....
1	206.7	261.0	245.4	252.8	158.7	146.3	....	185.9	198.1	180.5	75.6	64.2	58.2	52.5	70.8	64.8	60.6	58.8
2	215.5	271.9	265.3	261.7	183.4	171.1	1.93	208.3	216.6	205.0	91.1	76.7	70.0	63.6	84.5	74.7	74.3	67.9
4	236.3	284.8	286.0	274.3	197.5	193.9	2.12	235.6	251.3	228.7	103.7	87.8	84.7	74.6	98.7	87.8	89.2	76.8
8	267.5	289.5	296.4	296.3	222.6	218.5	3.98	248.7	269.4	244.4	121.0	104.0	100.4	88.6	114.2	107.8	103.5	92.2
16	271.5	313.2	317.7	305.4	235.1	240.4	5.24	266.2	288.2	252.4	142.7	123.2	119.6	109.7	133.4	123.9	125.5	108.7
32	277.2	334.4	325.8	315.1	257.7	276.1	8.78	284.1	304.6	286.8	169.7	149.4	141.4	131.2	157.7	144.7	144.2	133.8
64	288.9	360.3	338.1	331.6	272.1	297.1	14.40	300.0	320.4	293.7	194.7	172.0	171.2	152.2	183.2	178.0	173.0	150.5
128	302.6	363.9	340.4	341.4	278.6	308.1	18.60	310.3	323.1	303.0	227.4	202.9	197.3	185.6	213.0	209.6	211.5	180.8
256	310.0	373.5	343.9	348.2	285.2	326.0	28.77	320.8	330.1	309.0	259.6	232.1	236.4	225.1	253.4	241.0	250.3	218.9
512	318.8	401.8	351.5	357.5	290.9	338.9	45.90	327.7	338.7	319.3	295.4	257.4	275.4	261.7	298.6	282.7	275.9	246.8
1024	328.3	419.8	360.5	368.2	319.3	352.8	77.07	333.6	349.9	322.3	335.4	268.4	309.8	300.2	316.8	321.2	319.9	275.9
2048	339.1	433.3	375.0	389.8	317.1	363.1	106.2	337.9	349.6	343.4	387.6	277.6	338.6	357.0	359.6	383.4	413.1	298.3

shape of the curves of KCl and KI is similar to that of NaCl; the shape of the curves of $ZnSO_4$, $MnSO_4$, $CdSO_4$, $NiSO_4$, $CoSO_4$, $FeSO_4$ and $CuSO_4$ closely resemble that of $MgSO_4$, while KNO_3 and $NaNO_3$ have curves much like that of $AgNO_3$. The great similarity between the curves of the chlorides and those of the nitrates has already been alluded to; this similarity is clearly shown by the curves represented in the figures. A comparison of Figs. 1 and 2 shows that at 95° the $MgSO_4$ curve is practically a straight line, and that the curves of NaCl, $BaCl_2$ and $AgNO_3$ also exhibit a marked tendency to straighten out at the higher temperature. It should be stated in this connection, that the curve for $CdSO_4$[1] preserves more of its convexity toward the axis of abscissas at 95° than do the curves for the other sulphates. Curves that were chartered from data obtained for the same salts at 18° and at 25° showed a marked similarity[2] to those in

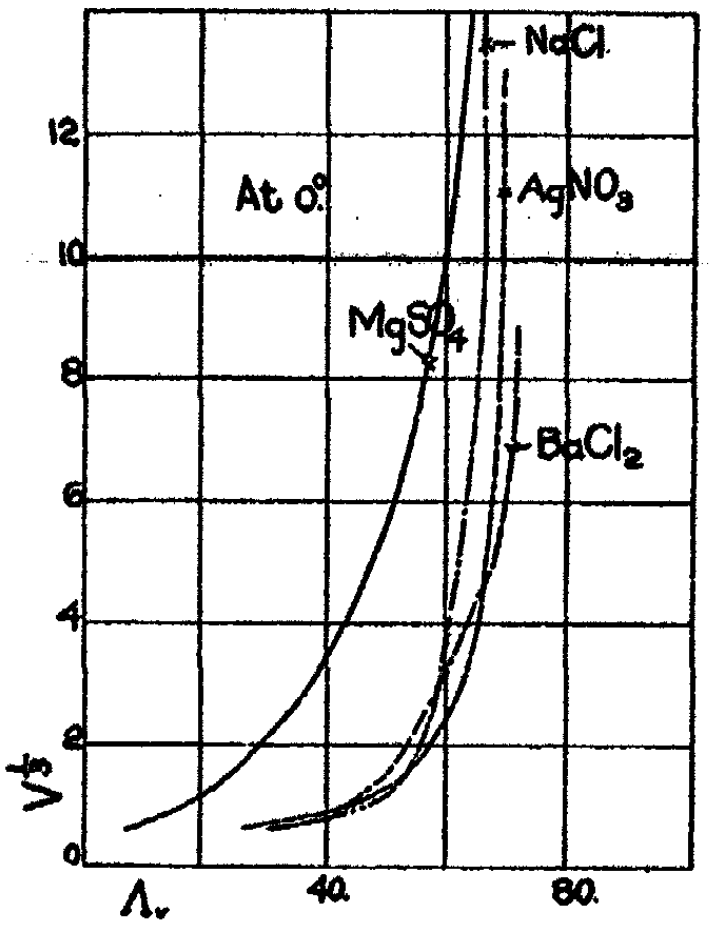

Fig. 1

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[1] This curve is not represented in the figures. The curve for $HgCl_2$—also not represented — is practically a straight line at 95°.

[2] Such similarity has also been pointed out at various times by other observers.

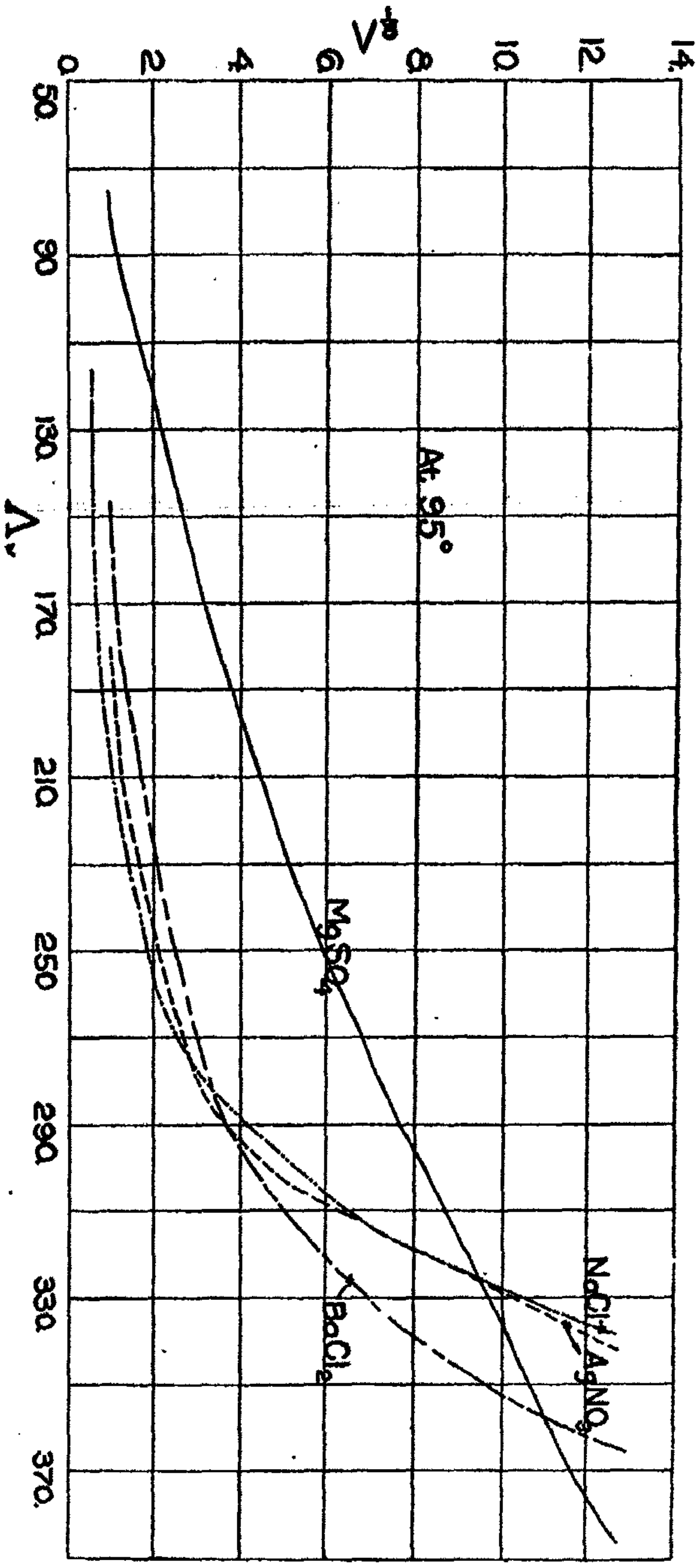
$V^{\frac{1}{3}}$
0
2
4
6
8
10
12
14
50
90
130
170
210
250
290
330
370
Λ_v
At 95°
$MgSO_4$
$NaCl$
$AgNO_3$
$BaCl_2$

Fig. 2

Fig. 1 at (at 0°), and indicate that the change in the shape of the curves at 0° and at 95° takes place gradually as the temperature rises. It should be clearly borne in mind that the curves for even very closely analogous salts are not perfectly parallel; all that can be said of them is that they are similar in trend.

The results of the freezing-point determinations are given in Tables 3 to 11. The headings of the tables are self-explanatory. In calculating the molecular weights 18.9° was assumed as the lowering of the freezing-point caused by the presence of one gram-molecule in 100 grams of water.

Tables 3 to 11 do not contain all the salts represented in Table 1. The freezing-points of barium chloride solutions have lately been determined by Jones and Chambers[1] between approximately the concentrations 0.1 and 0.6 normal, as have also those of the chlorides and bromides of other alkaline earths. Table 3, giving the results obtained with NaCl, indicates that for the concentrations investigated (0.2 to 1.0 normal approximately) the molecular weight is practically constant. For about 0.2 normal the molecular weight was found to be 32.6, which corresponds to a dissociation of 79.4 percent; for an approximately normal solution the molecular weight was found to be 31.7, which corresponds to a dissociation of 84 percent. These two results represent the extreme variations of the values in Table 3. For the average value of the six determinations, 32.2, the dissociation is 81 percent. According to Table 1 the degree of dissociation $\left(\text{calculated according to the usual formula } \frac{A_v}{A_\infty}\right)$ is about 79 percent for the 0.2 normal solution and 70 percent for the normal solution.[2] The degrees of dissociation 79 percent and 70 percent correspond, respectively, to the molecular weights

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[1] Amer. Chem. Jour. 23, 89 (1900).

[2] In calculating the degrees of dissociation from the conductivity the values of the conductivity at infinite dilution were taken either directly from the highest values given in the table of conductivities; or when the trend of the curve (which was in all cases charted) required it, from the careful extrapolation of the curve.

TABLE 3[1]

Sodium Chloride (NaCl). Mol. wt. 58.5

Amount NaCl in 100 g. water	Lowering of the freezing-point	Molecular weight
1.195	0.693	32.6*
2.550	1.512	31.9
2.970	1.750	32.1*
3.927	2.300	32.3*
4.914	2.866	32.4
5.741	3.395	31.7*

TABLE 4

Magnesium Sulphate ($MgSO_4$). Mol. wt. 120.4

Amount $MgSO_4$ in 100 g. water	Lowering of the freezing-point	Molecular weight
0.699	0.154	85.8
1.517	0.314	91.3
2.550	0.480	100.4
5.994	1.006	112.6
6.961	1.165	112.9
9.246	1.527	114.5

TABLE 5

Zinc Sulphate ($ZnSO_4$). Mol. wt. 161.5

Amount $ZnSO_4$ in 100 g. water	Lowering of the freezing-point	Molecular weight
1.602	0.258	117.4
5.026	0.625	152.0
8.962	1.030	164.5
10.930	1.246	165.8
13.675	1.493	173.1
16.935	1.922	166.5

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[1] The four determinations marked * in this table were made in this laboratory by Mr. G. M. Wilcox. The other two determinations were made by the writer.

TABLE 6

Manganous Sulphate ($MnSO_4$). Mol. wt. 151.1

Amount $MnSO_4$ in 100 g. water	Lowering of the freezing-point	Molecular weight
1.941	0.293	125.2
2.502	0.361	131.0
5.120	0.687	140.9
10.843	1.399	146.5
18 572	2.591	135.5

TABLE 7

Cadmium Sulphate ($CdSO_4$). Mol. wt. 208.1

Amount of $CdSO_4$ in 100 g. water	Lowering of the freezing-point	Molecular weight
3.071	0.313	185.5
8.608	0.742	219.3
15.640	1.322	223.6
22.647	1.968	217.5
26.120	2.330	211.9

TABLE 8

Nickelous Sulphate ($NiSO_4$). Mol. wt. 154.8

Amount $NiSO_4$ in 100 g. water	Lowering of the freezing-point	Molecular weight
1.077	0.189	107.8
2.364	0.351	127.3
4.332	0.557	147.0
5.896	0.779	143.1
10.443	1.284	153.7
16.030	1.984	152.7

TABLE 9

Cobaltous Sulphate ($CoSO_4$). Mol. wt. 155.1

Amount $CoSO_4$ in 100 g. water	Lowering of the freezing-point	Molecular weight
1.457	0.209	131.8
2.982	0.390	144.5
4.927	0.600	155.2
9.657	1.067	171.2
14.143	1.587	168.5

TABLE 10

Ferrous Sulphate ($FeSO_4$). Mol. wt. 152.1

Amount $FeSO_4$ in 100 g. water	Lowering of the freezing-point	Molecular weight
2.270	0.316	135.8
2.651	0.376	133.3
6.502	0.794	154.8
8.980	1.072	158.4
13.849	1.655	158.2

TABLE 11

Copper Sulphate ($CuSO_4$). Mol. wt. 159.7

Amount $CuSO_4$ in 100 g. water	Lowering of the freezing-point	Molecular weight
1.835	0.300	115.6
3.312	0.405	154.6
6.443	0.743	163.9
9.242	0.996	175.4
14.210	1.569	171.2

32.7 and 34.4. It is clear then, that the degree of dissociation for the most dilute solution tested is found to be the same by freezing-point and conductivity methods to within the experimental error of the former method. But the disssociation increases rapidly with the dilution according to the conductivity, whereas the freezing-point results show, that it at least remains constant, if it does not diminish with the increase of the dilution, within the limits tested. C. Dieterici[1] has shown by his very careful measurements of the diminution of the vapor tension of NaCl solutions at 0° that between the limits 0.1 and 1.0 normal the molecular diminution of the vapor tension decreases as the dilution increases. R. W. Wood[2] found that the degree of dissociation of KCl, while nearly the same by cryoscopic and conductivity methods at a concentration slightly above 0.1 normal, increases more rapidly with the dilution according to the latter than according to the former method.

In the case of $MgSO_4$ (Table 4) the solutions examined varied in concentration from about 0.1 to 1.5 normal, the degree of dissociation for the most dilute solution being 40 percent and for the most concentrated only 5 percent. According to the conductivity determinations (Table 1) the corresponding degrees of dissociation are 44 and 22 percent respectively. The discrepancy between the dissociation as determined by the two methods then, while relatively rather small at first, increases enormously with the concentration within the limits investigated.

Zinc sulphate (Table 5) shows no dissociation according to the freezing-point determinations when the solutions contain a gram-equivalent or more of the salt per liter, and yet zinc sulphate solutions have an electrical conductivity nearly the same as that of the equivalent solutions of $MgSO_4$ (Table 1). The most dilute solution represented in Table 5 yielded a molecular weight of 117.4, corresponding to a dissociation of 38 percent; the conductivity method yields about 40 percent. For the normal solution, where the dissociation is nil according to the cryoscopic work, it is 24 percent according to the conductivity.

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[1] Wied. Ann. 62, 616 (1897).

[2] Zeit. phys. Chem. 18, 522 (1895).

Manganous sulphate (Table 6) at first shows an increase of molecular weight with the increase of concentration and then a decrease. This also appears in the case of $ZnSO_4$ (Table 5), though less markedly. Again $CdSO_4$ (Table 7) shows this behavior in a marked degree, while $NiSO_4$ (Table 8), $CoSO_4$ (Table 9) and $CuSO_4$ (Table 11) show it slightly, and possibly also $FeSO_4$ (Table 10). The electrical conductivity of $MnSO_4$ solutions increases regularly with the dilution, as does that of solutions of all the other sulphates investigated. It is clear that according to conductivity determinations the dissociation constantly increases with the dilution in the case of the particular sulphates, just enumerated, whereas according to the cryoscopic determinations there is at first a decrease of dissociation with increase of concentration and then an increase of dissociation with increase of concentration. The most dilute solution of $MnSO_4$ tested (about 0.25 normal) gave a molecular weight of 125.2, corresponding to 21 percent dissociation, the conductivity method yields about 35 percent. When the molecular weight is 146.5 the dissociation is 3 percent, — the conductivity indicates 20 percent.

It is practically useless to make the comparison in the case of $CdSO_4$ (Table 7) for the cryoscopic determinations show no dissociation except in the most dilute solution tested; whereas, as stated above, the conductivity of the solutions is excellent and increases regularly with the dilution. The most dilute solution, in which a molecular weight of 185.5 was found, would contain the salt dissociated to the extent of 12 percent; the conductivity results yield about 30 percent.

Nickel sulphate is practically undissociated according to cryoscopic determinations (Table 8) when the solution is about 10 percent strong. The conductivity at about this strength indicates 22 percent dissociation. The molecular weight of the most dilute solution investigated corresponds to 43 percent dissociation; the conductivity indicates 42 percent.

In the case of $CoSO_4$ the freezing-point indicates no dissociation in a solution about 5 percent strong or stronger (Table

9), whereas the conductivity determinations show about 26 percent dissociation when the observed molecular weight is 155.2. In the most dilute solution the molecular weight found is 131.8 corresponding to 18 percent dissociation; the conductivity indicates about 34 percent.

According to cryoscopic determinations $FeSO_4$ also is undissociated in about 6 percent solutions or over (Table 10). When the observed molecular weight is 154.8 the conductivity nevertheless indicates 24 percent dissociation. The most dilute solution shows a molecular weight of 135.8, or 12 percent dissociation; the conductivity indicates 30 percent.

Copper sulphate is also undissociated in 5 percent solutions or over (Table 11). When the molecular weight observed equals 163.9, which corresponds to no dissociation, the conductivity indicates about 22 percent dissociation. In the most dilute solutions tested, the molecular weight found, 115.6, corresponds to 38 percent dissociation; the conductivity indicates about 32 percent.

From the foregoing it is evident that with the exception of a few instances (and these at certain special concentrations) the agreement between the value of the degree of dissociation as calculated from the freezing-point of the solutions and that deduced from their conductivity must in general be pronounced poor, even in the case of the most dilute solutions tested; while in the somewhat stronger solutions there is no agreement at all, many of the cryoscopic determinations showing no dissociation, whereas the conductivity indicates quite appreciable dissociation.

Arrhenius[1] in his original tables presents figures from cryoscopic data indicating no dissociation for $MgSO_4$, $FeSO_4$, $CuSO_4$, $ZnSO_4$ and $CdSO_4$, whereas the electrical conductivity (he used the results obtained at room temperatures) showed considerable dissociation, which substantially agrees with the results above recorded for the stronger solutions. Cadmium iodide, as Arrhenius shows, exhibits a similiar behavior. Arrhenius seeks to explain away the discrepancy in the case of the sulphates men-

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[1] l. c.

tioned by assuming that the inactive or undissociated molecules in the solutions are polymerized; and he seeks to base this assumption on the fact that Hittorf[1] found that the migration numbers of $MgSO_4$ and $ZnSO_4$ show a considerable variation with the concentration, which was also found to be true — though much more markedly — in the case of CdI_2, for which Hittorf assumed double molecules in the solution in order to explain the phenomena he observed. The latter also clearly states that he applies the same explanation to the other salts of the magnesia series, for their migration numbers also vary considerably with the concentration. This at first seems to justify perfectly the position taken by Arrhenius. However, the latter has not applied the explanation to all the salts of the magnesia series as he ought to, but he has simply assumed polymerized molecules in the case of those salts that did not behave according to his theory. He ought to assume polymerized molecules in the case of $MgCl_2$ for instance, for Hittorf found the migration numbers of this salt strongly dependent upon the concentration as he did those of $MgSO_4$. But it happens that to assume polymerized molecules in the case of $MgCl_2$ would be very inconvenient for Arrhenius' theory, as his calculations of the factor *i* show; and so he did not make the assumption which he, in order to be consistent, ought to have made. In the case of $CaCl_2$, $BaCl_2$, $Ca(NO_3)_2$, $Ba(NO_3)_2$ Hittorf likewise found the migration numbers strongly dependent upon the concentration, yet Arrhenius does not assume polymerized molecules for these as he ought, to be consistent, for these salts agree better with his theory when such an assumption is not made. To assume polymerization of the molecules of such salts as $MgCl_2$, $CaCl_2$ and $BaCl_2$ would lead to the greatest difficulty also in harmonizing the freezing-point results obtained by Jones and Chambers[2] with the dissociation theory; for they have found that the molecular lowering shows a minimum between the

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[1] Pogg. Ann. 106, 547 (1859).

[2] Amer. Chem. Jour. 23, 89 (1900). Compare also in this connection Chambers and Frazer. Ibid. 23, 512 (1900).

strengths 0.1 and 0.2 normal, and that in concentrated solutions the lowering is as great or greater than the theoretical lowering, if the compounds were completely electrolytically dissociated. Jones and Chambers seek to harmonize their "abnormal" freezing-point lowerings by assuming that the salts form hydrates in the solutions. There can hardly be any doubt that the salts in question unite with water to form hydrates; but when the authors seek to use this to explain the "abnormally" low freezing-points of solutions, it might be well to remind them that the dissociation theory itself was promulgated to explain "abnormally" low freezing-points of solutions, and that since they have found the theory unable to do this and have reached out to the hydrate theory for help, it might be well in the face of the facts to acknowledge freely the weakness of the dissociation theory, and to proceed to explain the facts on the basis of the hydrate theory alone. If it be urged that the solutions conduct electricity and therefore the salts must be electrolytically dissociated,—the answer is, they must be, only if the dissociation theory be assumed.

Attention must now be directed especially to the careful determinations of C. Dieterici,[1] who measured the lowerings of the vapor tensions of a series of aqueous solutions of electrolytes and non-electrolytes at 0°. He found that for $CaCl_2$ the molecular lowering of the vapor tension diminishes strongly with the increase of dilution, and then at about 0.1 normal it again increases with the dilution. He also emphasizes the fact that the very careful freezing-point work of Loomis[2] and of Ponsot[3] shows a minimum of the molecular lowering of the freezing-point at nearly the same concentration. The work of Jones and Chambers above cited also corroborates this. Between the concentrations 0.1 and 1.0 normal, to which Dieterici's work is really limited, he found that for the substances tested (H_3PO_4, H_2SO_4, NaCl, $CaCl_2$, cane sugar, dextrose and urea) the molec-

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[1] l. c.

[2] Wied. Ann. 51, 500 (1894); Ibid. 57, 495 (1896); Ibid. 60, 523 (1897).

[3] Recherches sur les congélations Gauthiers-Villars, Paris (1896).

ular lowering of the vapor tension diminishes as the dilution increases, which is the opposite of that which the theory of Arrhenius requires. In view of this fact Dieterici rightfully refrains from even attempting to make a further comparison between the degree of dissociation as calculated from the vapor tension measurements on the one hand and the conductivity on the other. The reader is also referred to the able critical consideration of the very careful freezing-point determinations of various investigators, which is contained in Dieterici's article.

Attention is now called to the results of the boiling-point determinations (Tables 12 to 29). For a number of the most important salts represented in these tables, two, and in a few instances three or four series of determinations were made by Mr. Koch, in order to be perfectly sure of the facts.

In Table 12, giving the results for NaCl, it appears that the molecular weight decreases steadily with the increase of concentration,[1] becoming in the strong solutions less than half the theoretical molecular weight. The facts then indicate that the dissociation of common salt would increase with the concentration and that in solutions above about 20 percent the molecule would break up into more than two parts, which is impossible on the basis of the atomic theory as generally accepted. The behavior of NaCl is clearly diametrically opposed to that which we should expect according to the theory of electrolytic dissociation. The electrical conductivity of NaCl solutions increases regularly with the dilution as Table 2 shows. From the character of the boiling-point results, it is clearly out of the question to make even an attempt to compare the dissociation as calculated from the molecular weight determinations with the dissociation as deduced from the electrical conductivity measurements.

What has been said concerning NaCl applies also to KCl (Table 13), KBr (Table 14) and KI (Table 15). The molecular weights of these salts continually diminish with increase of concentration, finally becoming less than half the theoretical,

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[1] The same fact is also demonstrated by the determinations of Landsberger and Biltz. Zeit. anorg Chem. 17, 452 (1898).

TABLE 12

Sodium Chloride (NaCl). Mol. wt. 58.5

(Series 1)

Amount NaCl in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
1.139	0.197	747.7 mm	33.4
4.167	0.744	747.1	32.4
5.524	1.002	747.0	31.9
8.254	1.553	"	30.0
11.010	2.157	746.9	29.5
15.910	3.304	"	27.8
20.520	4.495	746.8	26.4
(Series 2)			
2.900	0.499	743.6	33.6
6.006	1.082	743.5	32.1
7.103	1.690	"	30.6
12.625	2.514	"	29.0
15.640	3.231	"	28.0
18.530	4.032	"	26.7
20.130	4.471	"	26.0
(Series 3)[1]			
1.256	0.195	754.0	33.5
2.500	0.390	"	33.3
3.793	0.598	"	32.5
5.046	0.820	"	32.0
6.299	1.031	"	31.8
8.792	1.474	"	31.0
11.409	1.970	"	30.1
(Series 4)			
10.090	1.68	743.7	31.5
12.902	2.23	"	30.4
15.631	2.77	"	29.6
19.043	3.70	743.4	27.0
22.950	4.56	"	25.8
25.320	5.28	"	25.2
28.697	6.17	"	24.4
31.242	6.82	"	24.1

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[1] The results in Series 3 are those of Mr. G. M. Wilcox. In Series 4, a thermometer graduated to tenths, which readily permitted the hundredths to be estimated with the aid of a lens, was used, the temperature range being greater than that of the Beckmann's thermometer.

TABLE 13

Potassium Chloride (KCl). Mol. wt. 74.59

(Series 1)

Amount KCl in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
2.122	0.293	737.6 mm	41.9
5.124	0.700	"	42.3
9.012	1.247	"	41.8
13.990	2.004	"	40.4
20.170	2.975	"	39.2
24.160	3.653	"	38.2
27.720	4.266	"	37.7
31.840	5.009	"	36.8
(Series 2)			
1.911	0.255	744.0	43.3
4.052	0.554	"	42.3
7.225	0.986	"	42.4
11.620	1.625	743.9	41.3
16.520	2.406	744.0	39.4
21.350	3.206	"	39.5
26.130	3.911	744.2	38.5
30.370	4.756	744.1	37.1
(Series 3)[1]			
5.676	0.65	736.1	45.4
7.427	0.91	"	42.4
10.001	1.25	"	41.6
12.447	1.59	736.2	40.7
15.949	2.05	"	40.5
19.676	2.60	"	39.6
23.937	3.18	"	39.1
27.174	3.75	736.3	37.7
30.868	4.30	"	37.3
34.901	5.00	"	36.2
38.491	5.60	736.2	35.7
42.268	6.28	"	35.0
45.862	6.88	"	34.7
48.935	7.60	"	34.2

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[1] In Series 3 the thermometer graduated to tenths was used.

TABLE 14

Potassium Bromide (KBr). Mol. wt. 119.1

(Series 1)

Amount KBr in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
2.614	0.206	740.2 mm	66.0
5.504	0.433	"	66.1
9.593	0.763	"	65.4
16.503	1.351	"	63.7
23.393	1.968	"	61.8
28.177	2.413	"	60.7
33.278	2.899	"	59.7
38.497	3.425	"	58.4
43.418	3.932	"	57.4
47.065	4.312	"	56.8
51.204	4.778	"	55.7
	(Series 2)		
3.380	0.244	739.5	72.0
5.656	0.449	"	65.5
9.422	0.725	"	67.6
13.488	1.066	"	65.8
17.978	1.437	"	65.0
22.310	1.854	"	62.6
26.485	2.249	"	61.2
30.440	2.677	"	59.1
34.760	3.115	"	58.0
39.785	3.656	"	56.6
45.367	4.267	"	55.3
49.066	4.735	"	53.9

TABLE 15

Potassium Iodide (KI). Mol. wt. 166

(Series 1)

Amount KI in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
2.803	0.155	736.1 mm	94.0
7.032	0.397	"	92.1
10.801	0.620	"	90.6
14.923	0.870	"	89.2
19.782	1.184	"	86.9
24.537	1.494	736.0	85.4
29.244	1.812	"	83.9
33.666	2.134	"	82.0
39.059	2.511	"	80.9
47.611	3.159	"	78.4
	(Series 2)[1]		
4.174	0.23	740.6	94.3
6.177	0.33	740.4	97.3
12.929	0.72	"	93.3
19.024	1.10	"	89.8
26.237	1.58	740.0	86.4
35.003	2.14	"	85.0
43.059	2.74	739.4	81.6
66.253	4.67	"	73.4
77.17	5.55	739.5	72.1
85.71	6.36	"	70.0
92.73	7.02	"	68.6
104.80	8.02	"	67.9

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[1] The thermometer graduated to tenths was used in this series.

TABLE 16

Magnesium Chloride ($MgCl_2$). Mol. wt. 95.26

Amount $MgCl_2$ in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
3.371	0.416	750.1 mm	42.1
6.199	0.850	750.0	37.9
9.156	1.351	749.0	35.2
13.869	2.380	750.0	30.3
16.802	3.164	749.8	27.6
20.422	4.243	749.8	25.0
22.056	4.720	749.6	24.3

TABLE 17

Barium Chloride ($BaCl_2$). Mol. wt. 208.3

(Series 1)

Amount $BaCl_2$ in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
4.078	0.242	742.8 mm	89.7
8.777	0.525	"	86.9
13.422	0.825	"	84.7
18.619	1.174	742.9	82.5
24.076	1.586	"	78.9
32.025	2.243	"	74.2
40.468	2.970	"	70.9
47.879	3.625	"	68.7
54.519	4.157	"	68.2
	(Series 2)		
3.397	0.208	752.8	84.9
8.290	0.496	"	86.6
13.612	0.839	"	84.4
19.868	1.293	"	79.9
27.071	1.909	"	75.5
35.036	2.517	"	72.4
38.843	2.877	"	70.2
44.255	3.362	"	68.5
48.130	3.737	"	67.0
53.863	4.157	"	67.3

TABLE 18

Mercuric Chloride ($HgCl_2$). Mol. wt. 270.9

Amount $HgCl_2$ in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
3.341	0.056	751 mm	310.1
8.580	0.143	"	312.0
15.463	0.248	750.9	324.2
24.858	0.376	"	343.8
34.90	0.496	750.8	366.4
45.87	0.600	750.6	397.6
52.59	0.645	750.5	423.1

TABLE 19[1]

Potassium Chlorate ($KClO_3$). Mol. wt. 122.6

Amount $KClO_3$ in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
3.743	0.34	738.8 mm	57.2
8.121	0.65	"	66.4
12.837	1.01	738.6	66.0
17.116	1.31	"	67.9
23.484	1.72	738.4	70.9
29.689	2.10	"	76.7
35.42	2.49	738.1	73.9
42.96	2.98	"	74.9
48.92	3.43	737.6	74.1

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[1] This series of determinations was made with the thermometer graduated to tenths.

TABLE 20

Potassium Nitrate (KNO_3). Mol. wt. 101.2

(Series 1)

Amount KNO_3 in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
2.789	0.248	741.1 mm	58.5
6.058	0.518	"	60.8
9.727	0.822	"	61.5
14.798	1.207	"	63.8
21.333	1.706	741.2	65.0
27.095	2.123	"	66.4
33.80	2.577	"	68.2
41.54	3.079	"	70.2
49.42	3.570	741.3	72.0
57.20	4.027	741.4	73.9
62.83	4.357	"	75.0
(Series 2)			
4.286	0.378	744.5	59.1
8.434	0.725	744.6	60.5
13.068	1.101	"	61.7
19.740	1.603	"	64.0
28.056	2.212	"	66.0
35.54	2.710	744.8	68.2
44.53	3.275	744.9	70.7
53.37	3.795	"	73.1
61.64	4.309	"	74.4
70.76	4.677	"	78.7

TABLE 21

Silver Nitrate ($AgNO_3$). Mol. wt. 170.0

(Series 1)

Amount $AgNO_3$ in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
3.893	0.197	739.4 mm	102.8
11.926	0.570	“	106.3
23.342	1.066	“	113.9
35.08	1.523	“	119.8
45.89	1.915	“	124.6
56.30	2.249	“	129.9
68.68	2.636	“	135.5
83.38	3.047	“	142.3
99.74	3.521	“	147.3
110.22	3.755	“	152.6
122.33	4.060	“	156.7
136.26	4.398	“	161.1
	(Series 2)		
8.315	0.422	738.8	102.4
16.289	0.772	738.7	109.7
25.137	1.091	“	119.8
30.61	1.526	“	131.3
45.39	1.887	“	125.4
54.32	2.178	“	135.9
65.40	2.516	“	135.2
74.52	2.790	“	138.9
86.43	3.143	738.5	143.0
99.71	3.496	738.4	148.3
115.23	3.900	“	153.7
136.46	4.431	“	160.2

TABLE 22

Magnesium Sulphate ($MgSO_4$). Mol. wt. 120.4

Amount $MgSO_4$ in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
2.733	0.097	739.3 mm	146.5
7.236	0.281	"	168.6
27.58	0.524	"	273.7
36.91	0.925	"	207.5
43.47	1.455	"	155.4
52.77	1.984	"	138.3
60.52	3.220	"	97.7
64.39	3.316	739.4	101.0
72.28	3 630	"	105.9

TABLE 23

Zinc Sulphate ($ZnSO_4$). Mol. wt. 161.5

Amount $ZnSO_4$ in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
2.886	0.080	743.0 mm	187.6
6.647	0.169	"	204.5
10.139	0.266	"	198.2
13.389	0.372	"	201.1
17.713	0.461	"	199.8
22.202	0.591	"	190.5
25.199	0.690	"	189.9
28.249	0.811	"	181.1
30.47	0.899	742.0	176.3
32.89	0.995	"	171.9
35.18	1.122	"	163.0
37.36	1.240	"	156.7
39.83	1.381	"	150.0
41.30	1.459	"	147.2
44.56	1.671	"	138.7

TABLE 24

Manganous Sulphate ($MnSO_4$). Mol. wt. 151.1

Amount $MnSO_4$ in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
3.713	0.114	739 mm	169.4
7.132	0.193	"	192.2
10.250	0.282	"	194.1
14.464	0.373	"	201.7
19.349	0.520	"	193.5
24.209	0.678	"	185.7

TABLE 25

Cadmium Sulphate ($CdSO_4$). Mol. wt. 208.1

Amount $CdSO_4$ in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
4.563	0.105	741.3 mm	225.8
10.972	0.215	"	265.4
15.090	0.287	"	273.5
20.662	0.356	"	301.7
24.76	0.385	"	334.4
27.77	0.494	"	292.3
32.93	0.604	"	283.5
36.76	0.699	"	273.4
41.28	0.820	"	261.8
47.38	0.988	"	249.3
53.47	1.164	"	239.4

TABLE 26

Nickelous Sulphate ($NiSO_4$). Mol. wt. 154.8

Amount $NiSO_4$ in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
2.766	0.096	737 mm	149.8
5.255	0.169	"	161.7
7.676	0.230	"	173.5
11.196	0.336	"	173.3
15.135	0.448	"	175.7
17.943	0.536	"	174.1
20.847	0.641	"	169.1
23.143	0.738	"	163.1
25.525	0.841	"	157.8
27.159	0.939	"	150.4
29.021	1.042	"	144.8
31.144	1.190	"	136.1
32.705	1.302	"	130.6
34.461	1.389	"	129.0
35.165	1.576	"	118.7
37.735	1.734	"	113.2

TABLE 27

Cobaltous Sulphate ($CoSO_4$). Mol. wt. 155.1

Amount $CoSO_4$ in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
2.107	0.068	736 mm	160.8
4.446	0.110	"	205.3
8.744	0.201	"	226.1
9.596	0.262	"	190.5
12.936	0.346	"	194.3
16.134	0.449	"	186.3
20.600	0.568	"	188.6
22.151	0.626	"	184.0
24.070	0.694	"	180.8
26.150	0.772	"	175.7
28.745	0.876	"	170.8
32.841	1.055	"	161.9

TABLE 28

Ferrous Sulphate ($FeSO_4$). Mol. wt. 152.1

Amount $FeSO_4$ in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
3.245	0.093	738 mm	181.4
6.704	0.182	"	191.6
9.222	0.243	"	197.3
13.087	0.343	"	198.4
15.810	0.412	"	199.5
17.962	0.483	"	193.4
22.806	0.545	"	212.6
24.452	0.633	"	200.9
26.645	0.713	"	194.3
28.788	0.805	"	185.6
30.692	0.899	"	181.7
32.768	0.994	"	171.4
35.346	1.099	"	167.2

TABLE 29

Cupric Sulphate ($CuSO_4$). Mol. wt. 159.7

Amount $CuSO_4$ in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
3.356	0.091	742.9 mm	191.8
7.811	0.189	742.7	214.9
12.208	0.186	"	221.5
15.952	0.374	742.6	221.8
22.914	0.571	"	208.7
27.466	0.708	742.5	201.8
32.356	0.874	"	192.5
36.449	1.042	742.4	181.9
39.57	1.192	742.2	172.6
44.03	1.414	"	158.4
48.63	1.692	741.9	149.5
52.02	1.916	741.8	140.9
56.95	2.283	741.7	129.7
64.14	2.903	"	114.9
68.98	3.363	"	106.7
73.77	3.768	"	101.8

whereas the conductivities increase regularly with the dilution (Table 2). It is interesting to note the similarity of the behavior of the haloid salts of the alkalies, to which attention has been previously directed in a general way.

The molecular weight of $MgCl_2$ too decreases with the increase of concentration (Table 16), finally becoming less than one-third the theoretical value. This salt would then have to dissociate into more than three ions and that in concentrated solutions. On the other hand the conductivity increases with the dilution. It is again clearly useless to attempt a comparison of the degree of dissociation as computed from the observed molecular weights and the conductivity.

What has been stated concerning $MgCl_2$ applies exactly to $BaCl_2$ (Table 17), so that further comments about the behavior of the latter salt are superfluous. It is interesting to note that these two salts of analogous composition exhibit a similar behavior, which resembles closely that of the haloid salts of the alkalies.

Mercuric chloride (Table 18) shows no dissociation by the boiling-point method. The behavior of mercuric chloride differs from that of the salts last mentioned in that its molecular weight increases with the concentration. Of course, with this behavior polymerization of the molecules with increase of concentration could consistently be assumed; it could further be assumed that some of the molecules not yet polymerized are electrolytically dissociated and thus the observed phenomena could, with these assumptions, be brought into harmony with existing conceptions, at least qualitatively. The electrical conductivity of the solutions of this salt (Table 2) though relatively low, increases regularly with the dilution.

The boiling-point determinations for $KClO_3$ (Table 19) were made with a thermometer graduated to tenths, so that the measurements are relatively less accurate than those in which the Beckmann thermometer was used. The results are sufficient to indicate, however, that in the case of this salt the molecular weight increases with the concentration, which is at least qualitatively in harmony with that which the dissociation hypothesis requires. The degree of dissociation corresponding to a molecular weight of 66 is 88 percent, whereas for the same strength of solution the conductivity results (Table 2) indicate a dissociation of not more than 70 percent. No special stress is laid upon this comparison, however, because the Beckmann instrument was not employed in making the determinations.

In the case of KNO_3 (Table 20) we again have an increase of molecular weight with increase of concentration, which agrees qualitatively with the requirements of the dissociation theory. For the most dilute solution tested the molecular weight is 58.5, which corresponds to 73 percent dissociation; from the conductivity results (Table 2) the dissociation for this concentration is about 72 percent, — a satisfactory agreement. For a normal solution the molecular weight found is about 61.7, corresponding to 64 percent dissociation; the conductivity results yield 56 percent.

Silver nitrate (Table 21) also shows an increase of molecular weight with increase of concentration, which behavior agrees qualitatively with the dissociation theory. The most dilute solution tested yielded a molecular weight of 102.8, corresponding to a dissociation of 65 percent; the conductivity results yield about 67 percent, — an acceptable agreement. For a normal solution the molecular weight is about 110, corresponding to 54 percent dissociation; the conductivity determinations indicate 52 percent, — again a very fair agreement. It happens then, that the behavior of potassium and silver nitrate agrees much better with the demands of the dissociation theory at the boiling-point of the solutions than at the freezing-point.[1] It will be noted that these nitrates behave alike and that solutions of $KClO_3$ apparently exhibit a behavior similar to that of the nitrates.

The sulphates (Tables 22 to 29) again show great similarity in their general behavior. In the case of $MgSO_4$ (Table 22) the molecular weight begins with a value somewhat above the theoretical, — which indicates no dissociation; then it increases

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[1] Compare for instance Arrhenius' table. l. c.

at first with the concentration, and finally it decreases with increase of concentration after having passed through a maximum, the values in the strongest solutions becoming less than the theoretical. There is clearly no irregularity in the conductivity values (Table 2) to even suggest such a behavior. What has been said about $MgSO_4$ applies also to $ZnSO_4$ (Table 23), $NiSO_4$ (Table 26), and $CuSO_4$ (Table 29). The same general behavior is also exhibited by $MnSO_4$ (Table 24), $CdSO_4$ (Table 25), $CoSO_4$ (Table 27), and $FeSO_4$ (Table 28), except that the molecular weights of these salts, while first increasing and then decreasing with the increase of concentration, always remain above the theoretical values. As Table 2 shows there is nothing in the conductivity results to lead one to expect such a behavior. A comparison of the freezing-point results (Tables 4 to 10) with those obtained by the boiling-point method (Tables 22 to 29) shows that the molecular weight of the sulphates is less by the former than by the latter method in the case of corresponding concentrations. So that if it be assumed that these sulphates are polymerized in their solutions, it follows that this polymerization is greater at the boiling-points of the solutions than at their freezing-points, which seems unlikely.

It was thought to be of interest in this connection to investigate the behavior of a non-electrolyte. Cane sugar was selected, the results obtained with which by the boiling-point method are given in Table 30. The results indicate clearly that the molecular weight diminishes appreciably as the concentration increases. Strong sugar solutions, however, do not — as is well known — conduct electricity in consequence thereof. The solution was finally tested with Fehling's solution to see whether any sugar had become inverted during the process of boiling, but no invert sugar was found. On the other hand, a series of boiling-point determinations of solutions of H_3BO_3 (Table 31) shows that the molecular weight remains practically constant for very considerable changes in the concentration of this substance, considering its low molecular weight. The freezing-points of solutions of H_3BO_3[1] show that the molecular weight is lower at 0°

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[1] Compare Kahlenberg und Schreiner. Zeit. phys. Chem. 20, 548 (1896).

TABLE 30

Cane Sugar ($C_{12}H_{22}O_{11}$). Mol. wt. 342

Amount $C_{12}H_{22}O_{11}$ in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
20.75	0.30	736.6 mm	360
29.51	0.42	"	366
36.15	0.55	"	342
42.69	0.70	"	310
49.38	0.75	"	335
57.35	0.91	"	328
65.97	1.13	"	304
77.77	1.41	"	280
92.97	1.77	737.1	273
103.4	2.06	737.4	261
113.4	2.20	737.6	268
114.9	2.32	"	258
125.1	2.57	"	253
137.8	2.90	"	247
149.1	3.20	"	242
159.9	3.48	"	239
167.5	3.70	"	236
175.1	3.84	737.9	237
187.1	4.25	"	229
197.7	4.56	738.5	226
207.1	4.80	"	225
222.0	5.20	739.0	222
236.9	5.60	"	220
248.0	5.92	"	218
259.1	6.11	"	221
266.7	6.41	"	216
276.2	6.71	739.1	214
289.4	7.10	739.0	212

than at 100°; and its solutions at the lower temperature really ought to be somewhat better conductors of electricity (according to the dissociation hypothesis) than they are.

Discussion

The difficulties which the theory of electrolytic dissociation encounters in explaining the phenomena in aqueous solutions are really insurmountable. We have seen that there are solutions which are excellent electrical conductors, and yet the molecular weight determinations show a normal molecular weight of the dissolved substance. It is clear that while in some cases the molecular weight increases with the concentration, thus according at least qualitatively with the theory, in other cases the molecular weight decreases with the increase of the concentration, finally becoming less than what it ought to be even on the assumption that electrolytic dissociation is complete. Again, in other cases, the molecular weight at first increases with the concentration and then it diminishes as the concentration increases. And these phenomena are observed in solutions, the conductivity of which steadily increases with the increase of the dilution. I have not given any examples of aqueous solutions in which the molecular conductivity does not increase regularly with the dilution; but such cases do exist. So for instance the molecular conductivity of aqueous solutions of the alkaline hydroxides first increases with the dilution and then decreases as the dilution increases.[2]

TABLE 31[1]

Boric Acid (H_3BO_3). Mol. wt. 62

Amount H_3BO_3 in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
3.161	0.26	743 mm	63.2
5.264	0.42	"	65.2
8.746	0.72	"	63.0
12.040	1.01	"	62.2
14.098	1.18	"	62.1
16.600	1.41	"	61.2
19.956	1.67	"	62.1
23.896	2.00	"	62.1
26.500	2.13	742.5	64.5
29.295	2.41	"	63.2
33.793	2.82	"	62.3
36.407	3.01	"	62.9

From the facts here presented in the case of aqueous solu-

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[1] In this series, which was really only a preliminary one, the thermometer graduated to tenths was used.

[2] The determinations of Kohlrausch show this phenomenon. See also the measurements of Kahlenberg and Lincoln. Jour. Phys. Chem. 2, 87 (1898).

tions and those detailed above in the case of non-aqueous solutions, it follows that there is no such connection between the freezing-points and boiling-points of solutions on the one hand, and their electrical conductivity on the other, as is claimed by the theory of electrolytic dissociation of Arrhenius. In numerous cases not even a qualitative agreement exists. A careful scrutiny of Arrhenius' original table reveals the fact that while in a certain number of instances the agreement of the values of the factor *i*, as computed from cryoscopic measurements and from conductivity determinations is acceptable, in many cases it is poor, and again in others it is entirely wanting. To be sure Arrhenius bases this table upon measurements which he deemed might in some cases contain large errors; but later experimental work has really only served to emphasize the presence of such discrepancies. Further we have seen that investigations of non-aqueous and of aqueous solutions have in reality yielded a host of facts which even the most ardent adherents of the dissociation theory have not been able to harmonize with it. For some facts, to be sure, explanations have been offered upon the basis of auxiliary assumptions which frequently had no root in facts, having been created simply to save the dissociation theory from being pronounced untenable.

The attempt has been made to explain all of the various properties of electrolytic solutions upon the basis of the theory of electrolytic dissociation. To these efforts attention must now be directed. The various additive properties of salt solutions as mentioned by Arrhenius and as detailed by Ostwald and by Nernst in their text-books are presented as supporting the dissociation theory. But it is clear that even if these additive properties could be explained on the basis of the dissociation theory, the theory could not be based on this alone, since additive properties are well known to exist in the case of true chemical compounds, where since there are no solutions under consideration, and since there is no electrical conductivity observable, the possibility of electrolytic dissociation is entirely out of the question. In the realm of physiology, where it at first seemed that the theory of electrolytic dissociation would be particularly helpful, it has after all appeared that it can not cope with the facts.[1]

The heats of neutralization of acids and bases in dilute solutions have been heralded as an argument in favor of the dissociation theory; but Crompton[2] has shown that the dissociation hypothesis is not only unnecessary to explain the heats of neutralization, but that it is really inadequate, for it does not bring the behavior of electrolytes, as far as heat changes that accompany the formation of salts in aqueous solution are concerned, into line with the behavior of non-electrolytes. It is unnecessary to dwell further upon the insurmountable difficulties which the dissociation theory meets in general in the realm of thermal chemistry. These difficulties have been sufficiently discussed by Reychler,[3] whose conclusion is that, "above everything else we notice that *the hypothesis of free ions is in opposition to thermochemical observations.*"[4]

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[1] In this connection the reader is referred in particular to the following articles and to the additional references that they in turn contain: L. Kahlenberg, The Taste of Acid Salts and Their Degree of Dissociation. Jour. Phys. Chem. 4, 33 (1900). T. W. Richards, The Relation Between the Taste of Acids and Their Degree of Dissociation. Ibid. 4, 207 (1900). L. Kahlenberg, The Taste of Acid Salts and Their Degree of Dissociation, II. Ibid. 4, 533 (1900). J. F. Clark, Electrolytic Dissociation and Toxic Action. Ibid. 3, 263 (1899). L. Kahlenberg and R. M. Austin, Toxic Action of Acid Sodium Salts on *Lupinus Albus.* Ibid. 4, 553 (1900). In reviewing the above articles for the Jour. Amer. Chem. Soc. and the Zeit. phys. Chem., Arthur A. Noyes has made the attempt to bring the facts into harmony with the dissociation theory. I will simply state here that I have no desire whatever to enter upon a discussion of these "explanations" of Mr. Noyes, the weakness of which is sufficiently apparent upon the face of them. The facts are before the reader and he can safely be left to judge for himself. I must request the reader, however, to refer to the original of the third article in the above list, or at any rate to use the review of it given in the Chemisches Centralblatt or the Jour. Chem. Soc. (London), since Noyes has omitted to mention an essential part of the very simple experiment upon which the argument is based and has then claimed that the experiment is irrelevant. Evidently Mr. Noyes, in his ardor to uphold the dissociation theory, did not see the full import of the experiment in question.

[2] Jour. Chem. Soc. 71, 951 (1897). See also Crompton's interesting article on Rotations of Optically Active Salts. Ibid. p. 946.

[3] "Outlines of Physical Chemistry." (Translated by McCrae). Whittaker and Co. (1899), p. 214.

[4] The italics are Reychler's.

The attempts to harmonize the theory of electrolytic dissociation with the law of mass action have signally failed in the case of the electrolytes *par excellence* as is well known, in spite of the fact that very earnest endeavors have been made in this direction for over a decade. In the case of weak organic acids to be sure a tolerable agreement between the law of mass action and the dissociation theory has been found by Ostwald. The fact that the dissociation hypotheses cannot be brought into harmony with the law of mass action is one of the strongest arguments against the theory. It is really unfortunate that in discussing problems of equilibrium into which strong electrolytes enter (their solubility for instance) the adherents of the dissociation theory should go right ahead with their mathematical equations and deductions as though the theory were in full accord with the law of mass action.[1]

The chemical reactiveness of electrolytes has been explained by attempting to ascribe to the ions a peculiarly strong chemical activity on account of the electrical charges that are supposed to reside upon them.[2] The fact that a goodly number of substances will not react with each other when water is not present, and that they do react in aqueous solution, or at any rate when moist, has been called into requisition in this connection. While this behavior may be claimed to agree with the dissociation theory, it cannot be used as an argument to support the latter; for it is clear that many pure substances and mixtures of substances in which there are no grounds whatever for assuming the presence of ions, are nevertheless exceedingly reactive chemically, — take for instance many well known explosives as a striking example.

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[1] Compare for instance the general and unqualified statements concerning the so-called solubility product contained in Ostwald's "Scientific Foundations of Analytical Chemistry," which the author applies to electrolytes to most of which it certainly does not apply unqualifiedly.

[2] A recent statement of H. C. Jones illustrates the extreme views that are entertained by some regarding this matter. He concludes a review of the work done on the dissociating power of solvents [Amer. Chem. Jour. 25, 232 (1901)], with the statement, "The chemistry of atoms and molecules has thus given place to the chemistry of ions".

And on the other hand, it is a well recognized fact that, in many cases at least, salts, acids, and bases unite chemically with water and other solvents, and that any reaction which then takes place in solution is one between these new products; and that therefore such reactions might easily occur in presence of water, whereas the anhydrous substances might not react at all. It might be helpful to some to use the language of the dissociation theory and to say, for example, — the analytical test for chlorine ions is silver ions; instead of saying, — the analytical test for chlorine in the form of a soluble chloride is silver nitrate or any other soluble silver salt in which silver is the base; but that the new terminology, coupled with an attempt to apply the law of mass action to electrolytes in a way in which it certainly does not apply, forms a scientific foundation for analytical chemistry, is a position that is clearly untenable. The very fact that analytical chemistry has not received much benefit from Professor Ostwald's little book on "The Scientific Foundations of Analytical Chemistry", in the way of improving existing analytical methods and discovering new ones speaks for itself.

In connection with the dissociation hypothesis the solvent has been considered as having a peculiar "dissociating power". Water, then, yielding such excellent conducting solutions as it does, would have a very high degree of this dissociating power. The effort has been made by Nernst and by J. J. Thomson, practically simultaneously, to ascribe this strong dissociating power of water to its high dielectric constant which is about 80 at room temperatures. At the time when this was done relatively few solvents had been investigated that yielded solutions having considerable conductivity, and so it was perfectly easy to show that in the case of water, formic acid, alcohol, ether, and benzol, for example, the conductivity of the solutions in which these liquids are the solvents diminishes with the dielectric constant of the solvent.[1] The idea underlying the attempt to bring this hypothetical dissociating power into correlation with the

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[1] Compare for instance Nernst's table, on page 365, of the third edition of his book, "Theoretische Chemie," F. Enke, Stuttgart (1900).

dielectric constant of the solvent is, that a high dielectric constant of the latter would make it more difficult for the electrically charged ions to neutralize their charges by reason of the electrostatic attraction existing between them. It is not claimed that the dissociating power is proportional to the specific inductive capacity of the solvent, but simply that it increases and diminishes with it, the exact mathematical relation being as yet unknown. Since the Nernst-Thomson rule has been put forth the electrical conductivity of various salts in a goodly number of solvents has been investigated.[1] While the dielectric constants of all the solvents tested were not known at the time so that a comparison could be made in all cases, in the majority of instances where the dielectric constants were known, the Nernst-Thomson rule was indeed corroborated.[1] At the same time a few striking exceptions were present. The relatively low dielectric constant of liquid ammonia[2] and the high conductivity[3] of solutions of salts in it, speak powerfully against the Nernst-Thomson rule. It can hardly be argued that this high conductivity in liquid ammonia is due largely to the high rate with which the ions move because the conductivity of the solutions has been examined at the boiling-point of the solvent, – 38°; for liquid ammonia has a specific inductive capacity lower than that of alcohol and yet alcoholic solutions at their boiling-point have incomparably lower electrical conductivity than that observed in liquid ammonia solutions. Another striking exception to the Nernst-Thomson rule has recently been pointed out by H. Schlundt,[4] who found the dielectric constants of butyronitrile and pyridine to be 20.3 and 12.4, respectively, and pointed out that nevertheless the solutions in the latter solvent are known to be the better conductors. Again liquid SO_2 which Walden[5] has shown to yield excellent conducting solutions, has

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[1] Compare Kahlenberg and Lincoln. l. c. Also Lincoln. l. c., and the additional articles referred to in these papers.

[2] Goodwin and Thompson. Physical Review, 8, 38 (1899).

[3] Franklin and Kraus. l. c.

[4] Jour. Phys. Chem. 5, 157 (1901).

[5] l. c.

a low dielectric constant[1] that would not lead one to expect such a behavior. The dielectric constant of liquid HCN was found by Schlundt[2] to be 95; this would lead one to expect this solvent to have a dissociating power greater than that of water. Preliminary tests which Mr. Schlundt and I have made show that solutions in liquid HCN are very much poorer conductors of electricity than corresponding aqueous solutions.[3] On the other hand I have found that amyl amine with a specific inductive capacity of the order of that of chloroform[4] yields fairly good conducting solutions. More striking proofs that the Nernst-Thomson rule is untenable could hardly be produced.[5] The fact that the Nernst-Thomson rule can not be maintained takes away another pillar upon which the dissociation theory has been resting.

That the "dissociating power" of solvents is dependent upon the polymerization of their molecules, as claimed by Dutoit and Aston, is not in harmony with the facts in many cases, has clearly been shown by Kahlenberg and Lincoln.[6] Again it has

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[1] The exact value has been determined in this laboratory by Mr. Schlundt, who will report upon the same in connection with numerous measurements made on other solvents, among which are practically all the solvents investigated by Walden, l. c. Some older determinations of the dielectric constant of SO_2 have been found in the literature by Mr. Schlundt, which he will present in connection with his own work. Mr. Schlundt's article will appear in the October number of this Journal.

[2] l. c.

[3] We hope soon to be able to publish exact conductivity measurements of solutions in liquid HCN and also of solutions in liquid cyanogen.

[4] The exact value of the dielectric constant of amyl amine will be reported by Mr. Schlundt, whose list of determinations includes a fairly complete series of the substituted ammonias of both the fatty and aromatic series.

[5] Nernst himself ("Theoretische Chemie," 3d Edition, p. 365) has realized the difficulty of harmonizing his rule with the far less striking instance that NaCl, KBr, etc., in formic acid (dielectric constant 62) solutions conduct almost as well as the corresponding aqueous solutions,—in which connection he remarks that other "specific influences" come into play. He states: "*Wahrscheinlich steht hier in erster Linie eine Association der Ionen mit Molekülen des Lösungsmittels.*" It is interesting to compare in this connection the treatment which the hydrate theory receives at the hands of the same writer, page 491.

[6] l. c.

been maintained by Brühl[1] that "dissociating power" is possessed by such solvents as are unsaturated in character. It has been shown in this connection[2] that Brühl's position is untenable inasmuch as some solvents, which according to Brühl's view are unsaturated, and of which Brühl had predicted that they would yield conducting solutions, were found to yield solutions of high resistance. Later Brühl[3] has entered the objection that he did not mean to assert, that whenever a solvent possesses spare valences it must necessarily yield conducting solutions. In other words, he claims that he did not mean to assert the converse of his original statement. Brühl cites in this connection that the statement, that whenever a compound is optically active it possesses an asymmetric carbon atom, is also not necessarily true when taken conversely. He apparently forgets, however, that in our knowledge of racemic mixtures and meso compounds, we have reasons why the converse of the latter statement is not necessarily true. A corresponding reason as to why his own statement should not hold in the converse has, however, not been furnished by Brühl.

The theory of electrolytic dissociation is at present at its best in explaining the phenomena of actual electrolysis. But it must nevertheless be admitted, that there are important phenomena of electrolysis which the theory does not explain satisfactorily. Thus if when for example a silver solution is electrolyzed, the process consists in each case of neutralizing the positive charge residing on silver ions (as far as the process at the cathode is concerned) as the theory claims, why do we always get poorly adhering crystalline deposits from certain solutions and dense, well-adhering deposits from others, the potential and the current density being the same. The writer has also observed certain phenomena which appear to him to be incompatible with the idea that during the process of electrolysis there is

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[1] Zeit. phys. Chem. 18, 514 (1895). Ibid. 27, 317 (1898). Ber. chem. Ges. Berlin, 30, 163 (1897).

[2] Kahlenberg and Lincoln. l. c.

[3] Zeit. phys. Chem. 30, 1 (1899).

a regular procession of charged, oriented, material particles in the solution. The study along this line is being pursued further, and it is hoped that the results may be ready for publication at some date in the near future. The study of the changes of concentration that take place around the electrodes in the electrolysis of non-aqueous solutions promises to yield results of unusual interest, especially as bearing upon the value of the dissociation theory in interpreting electrolytic phenomena. Since the time when Hittorf[1] determined the migration numbers of CdI_2, ZnI_2, and $ZnCl_2$ in absolute alcohol, and those of CdI_2 in amyl alcohol this field has not been cultivated. Now we know of a number of fairly good, and some cases of excellently conducting non-aqueous solutions in which the migration numbers await determination. This work has been begun in this laboratory.

It might not be superfluous to recall in connection with the claim that thermodynamics requires the dissociation theory, that Clausius who showed the discrepancy between the Grotthus theory and thermodynamics did not find it necessary to put forth such a radical hypothesis as that of Arrhenius. Again, Hittorf, on the basis of his studies of the migration of the ions, evidently did not think it necessary to frame a theory giving the term ion the meaning that it now has. Finally let the reader try to recall any real marked improvements or discoveries in the realm of electrolysis which are directly traceable to the influence of the dissociation theory. The function of E. M. F. in electrolysis, especially in electrolytic separations has been more strongly emphasized, but that is really about all. The importance of current density has early been pointed out by Bunsen, and as far as the influence of the temperature of the electrolyte upon the mechanical and chemical character of the deposit is concerned, we are still upon an empirical basis as before. It is very significant for instance, that in the latest edition of his work on quantitative analysis by electrolysis, Classen has devoted about four pages of the introductory part of the book to the ionic theory, and after that in the main body of the book we read

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[1] l. c.

nothing more of that theory; the preparation of the solutions from which to get suitable deposits is very much upon the same empirical basis as ever. And it is also safe to say that electrolysis as used in the arts has not received much help from the theory of Arrhenius.

The dissociation theory has led to Nernst's theory of the E. M. F. of galvanic cells, which has already been referred to above. This theory is an attempt to explain the difference of potential between two electrolytes and to account for the difference of potential between an electrode and an electrolyte, and this not only qualitatively, but also quantitatively. Nernst's theory assumes that metals have a certain tendency to pass into the ionic condition, which tendency is termed the electrolytic solution tension of the metal. That which operates against this tendency is supposed to be the osmotic pressure of the ions of the metal already present in the solution, and the difference of potential between the metal and the electrolyte is the result of the action of these two forces; on the other hand, the difference of potential between two electrolytes is ascribed to the different rates with which the charged ions move. Nernst's formula really involves the assumption that the law of mass action is applicable to electrolytes in the sense required by the dissociation theory. That the law of mass action does not hold, however, in the case of electrolytes *par excellence*, has already been mentioned. By maintaining the correctness of Nernst's formula and thus assuming that the law of mass action does hold for such electrolytes, Jahn has arrived at the conclusion (as clearly he must) that $\frac{A_v}{A_\infty}$ does not correctly represent the degree of dissociotion, and that the ionic velocities vary in dilute solutions. The latter is not, in many cases at least, in harmony with the facts. Arrhenius on the other hand stoutly defends his original $\frac{A_v}{A_\infty}$, which of course leads to a denial of the validity of the mass law as applied to the electrolytes in question. Ostwald, too, in the new addition of his Grundriss (p. 406) clearly inclines toward maintaining the time-honored $\frac{A_v}{A_\infty}$ formula. The polemical discussion between Arrhenius and Jahn is still going on in the Zeit. phys. Chem., and recently Nernst has also taken a hand in the debate. It seems at first rather deplorable that so much valuable energy is being expended in trying to decide which is the correct way to calculate the degree of dissociation, of which there are such excellent reasons to believe that it has no counterpart in reality. Naturally, then, insurmountable obstacles must arise in determining the value. These polemical discussions, however, are doing considerable good in that they emphasize how inadequate the dissociation theory really is, — they represent the beginning of the end of that theory.

It is true that as soon as the theory of electrolytic dissociation is declared invalid the original difficulty with the van't Hoff theory of solutions[1] recurs, namely the theoretical interpretation of the factor *i*. Whenever the factor *i* in the equation $PV = iRT$, is unity, we have the gas equation in its simplicity, as it holds for dilute solutions of the now classical cane sugar. When in any case *i* is less than unity and diminishes as the concentration increases, the assumption that polymerization of the dissolved molecules takes place can be made; but when *i* is greater than unity dissociation must be assumed. Arrhenius assumed so-called electrolytic dissociation; from which it followed that whenever a solution conducts electrolytically it requires a corresponding factor *i* greater than unity, — that this is by no means always the case has been sufficiently set forth above. Again, it has been shown above that in the case of cane sugar, for instance, a factor *i* which increases with the concentration must be introduced. There is no other logical theoretical significance to put upon this behavior than to assume that the stronger the sugar solution is the more the solute dissociates. This conclusion is absurd, — let alone the additional fact that sugar solutions do not conduct. And cane sugar is by no means the only

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[1] Compare in this connection Crompton's explanation. Jour. Chem. Soc. 97, 925 (1897).

non-electrolyte that behaves thus. Attention has been directed to the fact that Dieterici found that the molecular lowering of the vapor tension of dextrose and urea also increases with the concentration like that of cane sugar.

I am well aware that the gas equation is supposed to hold strictly only for infinitely dilute solutions, just as it holds only for ideal gases, and that the solutions with which Dieterici worked varied between 0.1 and 1.0 normal, and that those used in experiments detailed above frequently were much stronger than normal. That a normal solution is nevertheless for many of the practical purposes of life a rather dilute solution will hardly be disputed. No one expects the gas equation to hold strictly for a normal solution or even for one considerably more dilute; but what one has a right to expect from the modern theory of solutions is, that with increasing concentration a solution should behave at least qualitatively as a gas does with increase of pressure. And this requirement is clearly not met, since while all gases behave alike under increase of pressure (so that van der Waals has been able to express their behavior by means of his well known equation) solutions as has been shown, often behave in the opposite manner in which a gas does, and this too, frequently in solutions that can not be termed concentrated. This demonstrates then that the van 't Hoff law is at best only approximate and must be applied with great care. As Dieterici well says: "*Raoult hat seine Gesetze der Dampfspannungs- und Gefrierpunktsdepression durchaus nicht als absolut streng gültige Naturgesetze aufgestellt, sondern als nahezu zutreffende Erfahrungssätze, welche für die Zwecke der Molekulargewichtsbestimmung genau genug sind*".

We have seen above (and the literature is replete with records of facts illustrating the same point) that substances of similar chemical composition, when dissolved in the same solvents behave similarly, as far as the changes of the boiling- or freezing-points are concerned; this clearly shows that the influence of the chemical nature of the dissolved substance enters into the determination of the molecular rise of the boiling-point and the molecular lowering of the freezing-point.

In pressing the analogy between gases and solutions (which undoubtedly exists and from which at times valuable suggestions may be derived) it has often been forgotten that this is after all simply an analogy; and like other analogies it fails when carried too far. It is so easy to compare the process of dissolving a lump of sugar in a beaker of water with the expansion of a gas; — the analogy is at once apparent. In seeing it with the mind's eye one abstracts from the water and centers the attention entirely on the sugar. But it must be remembered that a gas will expand readily in vacuo, and that it will mix with any other gas or mixture of gases, while on the other hand, the lump of sugar will not dissolve when for instance benzene or absolute alcohol is poured over it. The process of solution of a substance and the expansion of a gas then, while possessing analogy, are in reality very different processes. And right here lies the difficulty with the theory of solutions. It neglects the all important rôle of the solvent. It fails to emphasize the fact that the process of solution takes place because of a mutual attraction between solvent and dissolved substance, and that this mutual attraction which is a function of the chemical nature of both solvent and dissolved substance, is the essence of the so-called osmotic pressure.[1] It is true that the thermodynamic considerations of van 't Hoff will hold whether the osmotic pressure be considered as the outcome of a mutual attraction of solvent and dissolved substance or as resulting from the bombardment of the molecules of the dissolved substance against the semipermeable membrane. But if we choose to use the gas equation in working with solutions, it is very evident that the factor *i* must never be placed equal to unity (unless direct experimental evidence justifying this step is at hand) if exact results are desired, no matter whether we work with electrolytes or non-electrolytes. The dissociation theory, as has been shown, does not furnish a satisfactory explanation of the significance of *i* in

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[1] Compare here the warning words of Lothar Meyer, in his article — Das Wesen des osmotischen Druckes. Zeit. phys. Chem. 5, 23 (1890). Also the reply of van 't Hoff. Ibid. p. 174 (1890).

the case of electrolytes. This value of *i* varies in all cases with the nature of the solvent and also in general, with the strength of the solution ; and it does not always vary to the same extent nor even in the same sense in different solutions. It is clear then, that when the simple equation $PV = RT$ is applied to a solution, only approximate results are obtained at best, unless experimental data are at hand showing that in the particular case and for the particular concentration under consideration *i* is actually equal to unity.

It must be fully and freely admitted that the dissociation theory has done much good in stimulating research in many lines. It has been fruitful in proportion to the amount of truth contained in it. Like other theories founded upon too narrow a basis of induction, it has gradually been outgrown, — the facts are too much for it. It would be difficult of course to say of any theory — even of one long ago discarded — that it is entirely worthless, and so the writer has no inclination to make such a statement concerning the dissociation theory. And further, he would not be understood as having the remotest intention to belittle in any way the work done by the enthusiastic adherents of the theory of electrolytic dissociation, for this will no doubt always form a bright page in the history of the development of chemistry and of science in general.

It is solely because of the rapid growth of the erroneous idea that the deductions drawn from the indiscriminate application of the simple gas equation to solutions and from the notion that all well-known facts harmonize with the theory of electrolytic dissociation, that I have felt compelled to call attention to the real status of the experimental facts underlying these deductions. It is hoped that this will stimulate to renewed experimental activity, for surely our theory of solutions leaves much to be desired. The analogy between gases and solutions does not help us to understand even moderately concentrated solutions; and whenever experimental work on such solutions is done, the assumption that there is chemical union between solvent and dissolved substance calls for recognition. That there is chemical union between solvent and dissolved substance, in many cases at least, there can be no doubt; and as for the osmotic pressure, the outcome of that mutual attraction between solvent and dissolved substance, its various eccentricities and caprices, as exhibited even in moderately concentrated solutions, show clearly that it is closely related to, if not essentially identical with chemical affinity. Our hope in the study of solutions lies in the recognition of this. The problem of solutions is preeminently one for the chemist. Each solution will have to be examined separately, and then it will appear that chemically analogous solutes in the same solvent will have a similar behavior, the closeness of the agreement being determined by the degree of the analogy; and finally from such a study of solutions, which can and should begin with the most concentrated, the behavior of the most dilute solutions will appear as a limiting case, — and then we shall see the present theory of solutions in its true relation to the facts. And finally as far as the answer to the question, — What must be the relation between solvent and dissolved substance in order that the resulting solution may conduct electricity[1] is concerned, we are unfortunately as yet in the dark; just as we do not know why certain solids conduct electricity and others do not. The essence of electrical conduction in electrolytes and in metals is after all not so radically different as is frequently supposed. The further experimental investigation of the general problem of electrical conduction will, let us hope, ere long give us the true key to the situation.

Laboratory of Physical Chemistry,
University of Wisconsin,
Madison, Wis.,
May 1901.

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[1] The investigations of D. Konowalow [Wied. Ann. 49, 733 (1893)] are of special interest in this connection.

ON THE GENERALIZATION OF CLAPEYRON'S EQUATION

BY PAUL SAUREL

Various simple demonstrations of Clapeyron's equation for univariant systems have been given, but as yet no simple demonstration of the extension of this equation to the indifferent points of bivariant and multivariant systems has appeared in an easily accessible publication. The object of the present note is to offer such a demonstration.

Before giving the demonstration it is necessary to recall the characteristic properties of univariant systems and also those of the indifferent points of bivariant and multivariant systems.

The temperature and the pressure of a univariant system in equilibrium are functions one of the other. At a given temperature and under the corresponding equilibrium pressure, the equilibrium concentrations of the phases are determinate, but the volume and the entropy of the system may be varied.

The indifferent points of a bivariant or multivariant system form a continuous series analogous to the series of states of equilibrium of a univariant system. At a given temperature, the pressure of the corresponding indifferent point and the concentrations of the phases at that point are determinate. The ratios of the masses of the independent components are also determinate, but the volume and the entropy of the system may be varied. In passing from one indifferent point to an adjacent indifferent point, the temperature, the pressure, the concentrations of the phases and the masses of the independent components of the system vary.[1]

Let us denote the temperature by T, the pressure by Π, the

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[1] Jour. Phys. Chem. 5, 47 (1901).

volume by V, the entropy by H, and the energy by E. We shall also make use of the functions F, G and Φ defined by the equations

$$F = E - TH, \tag{1}$$

$$G = E + \Pi V, \tag{2}$$

$$\Phi = E - TH + \Pi V. \tag{3}$$

F is the free energy and Φ the total thermodynamic potential.

It can be shown[1] that for the i-th phase of the system, the following equation holds

$$d\Phi_i = -H_i dT + V_i d\Pi + \sum_{j=1}^{n} F_{ij} dM_{ij}. \tag{4}$$

H_i, V_i and Φ_i are respectively the entropy, the volume and the thermodynamic potential of the phase, M_{ij} is the mass of the j-th component which is present in the i-th phase, F_{ij} is what what may be called the chemical potential of the j-th component in the i-th phase, and n is the number of independent components.

When the system of r phases is in equilibrium, we have,[2]

$$F_{1j} = F_{2j} = \cdots = F_{rj} = F_j, \qquad j = 1, 2, \ldots, n.$$

If then we add the various equations of the form 4 and if we recollect that

$$\sum_{i=1}^{r} \Phi_i = \Phi, \quad \sum_{i=1}^{r} H_i = H, \quad \sum_{i=1}^{r} V_i = V, \quad \sum_{i=1}^{r} M_{ij} = \mathfrak{M}_j,$$

$\mathfrak{M}_j$ being the total mass of the j-th component, we get

$$d\Phi = -H dT + V d\Pi + \sum_{j=1}^{n} F_j d\mathfrak{M}_j. \tag{5}$$

From this equation and equations 1, 2 and 3, we obtain without difficulty

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[1] Jour. Phys. Chem. 5, 49 (1901).

[2] Jour. Phys. Chem. 5, 49 (1901).

$$dE = TdH - \Pi dV + \sum_{j=1}^{n} F_j d\mathfrak{M}_j, \tag{6}$$

$$dF = -HdT - \Pi dV + \sum_{j=1}^{n} F_j d\mathfrak{M}_j, \tag{7}$$

$$dG = TdH + Vd\Pi + \sum_{j=1}^{n} F_j d\mathfrak{M}_j. \tag{8}$$

Each of these equations will enable us to establish Clapeyron's equation for the indifferent points of bivariant or multivariant systems as well as for univariant systems.

Consider a univariant system, or a bivariant or multivariant system at an indifferent point. Keeping the temperature, the pressure and the masses of the independent components constant we may vary the entropy and the volume of the system. If we denote the initial and the terminal states of equilibrium by the subscripts 1 and 2, the four equations just written give us

$$\Phi_2 - \Phi_1 = 0, \tag{9}$$
$$E_2 - E_1 = T(H_2 - H_1) - \Pi(V_2 - V_1), \tag{10}$$
$$F_2 - F_1 = -\Pi(V_2 - V_1), \tag{11}$$
$$G_2 - G_1 = T(H_2 - H_1). \tag{12}$$

Suppose now that the pressure and temperature are changed. The states of equilibrium 1 and 2 will change into two new states of equilibrium. The equations last written give us

$$d(\Phi_2 - \Phi_1) = 0, \tag{13}$$
$$\begin{aligned} d(E_2 - E_1) = {} & Td(H_2 - H_1) - \Pi d(V_2 - V_1) \\ & + (H_2 - H_1)dT - (V_2 - V_1)d\Pi, \end{aligned} \tag{14}$$
$$d(F_2 - F_1) = -\Pi\, d(V_2 - V_1) - (V_2 - V_1)d\Pi, \tag{15}$$
$$d(G_2 - G_1) = Td(H_2 - H_1) + (H_2 - H_1)dT. \tag{16}$$

If we are considering the change from one indifferent point to another, the changes in the temperature and the pressure must, in general, be accompanied by changes in the masses of the independent components. If, on the contrary, the system considered is a univariant system, the masses of the independent components need not change. In both cases, however, equations 5, 6, 7 and 8 give us

$$d(\Phi_2 - \Phi_1) = -(H_2 - H_1)dT + (V_2 - V_1)d\Pi, \qquad (17)$$

$$d(E_2 - E_1) = Td(H_2 - H_1) - \Pi d(V_2 - V_1), \qquad (18)$$

$$d(F_2 - F_1) = -(H_2 - H_1)dT - \Pi d(V_2 - V_1), \qquad (19)$$

$$d(G_2 - G_1) = Td(H_2 - H_1) + (V_2 - V_1)d\Pi. \qquad (20)$$

If we substitute these values in equations 13, 14, 15 and 16, we get in each case the equation

$$\frac{d\Pi}{dT} = \frac{H_2 - H_1}{V_2 - V_1}. \qquad (I)$$

This equation may of course be written in the familiar Clapeyron form

$$\frac{d\Pi}{dT} = \frac{Q}{T(V_2 - V_1)}, \qquad (II)$$

if we denote by Q the heat absorbed by the system during the reversible change at constant temperature and under constant pressure.

If the system under consideration be a univariant system it is not necessary to consider changes in the masses of the independent components. Equations 5, 6, 7 and 8 then take the more familiar forms

$$d\Phi = -HdT + Vd\Pi, \qquad (21)$$

$$dE = TdH - \Pi dV, \qquad (22)$$

$$dF = -HdT - \Pi dV, \qquad (23)$$

$$dG = TdH + Vd\Pi. \qquad (24)$$

From these equations we can derive simple proofs of Clapeyron's equation for univariant systems. To do this we shall make use of the fact that for a system of constant mass we may choose the entropy and the volume as independent variables which fix the state of the system, or we may take as independent variables either of the above variables and the temperature or the pressure.

Equation 9 shows that for a univariant system Φ is a function of T alone. If then we write equation 21 in the form

$$d\Phi = \left(-\mathrm{H} + \mathrm{V}\frac{d\Pi}{d\mathrm{T}}\right)d\mathrm{T},$$

it follows that the coefficient of dT is a function of T alone. If we take, as our second independent variable, the volume, we must have

$$\frac{\partial}{\partial \mathrm{V}}\left(-\mathrm{H} + \mathrm{V}\frac{d\Pi}{d\mathrm{T}}\right) = 0.$$

This reduces to

$$\frac{d\Pi}{d\mathrm{T}} = \left(\frac{\partial \mathrm{H}}{\partial \mathrm{V}}\right)_{\mathrm{T}}. \qquad \text{(III)}$$

Consider next equation 22 and take, as independent variables, the volume and the entropy. Expressing the fact that the right-hand member of the equation is a perfect differential, we get

$$\left(\frac{\partial \Pi}{\partial \mathrm{H}}\right)_{\mathrm{V}} = -\left(\frac{\partial \mathrm{T}}{\partial \mathrm{V}}\right)_{\mathrm{H}}.$$

In virtue of the well-known relation

$$\left(\frac{\partial \mathrm{T}}{\partial \mathrm{H}}\right)_{\mathrm{V}}\left(\frac{\partial \mathrm{H}}{\partial \mathrm{V}}\right)_{\mathrm{T}}\left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{H}} = -1,$$

this becomes

$$\left(\frac{\partial \Pi}{\partial \mathrm{H}}\right)_{\mathrm{V}} = \left(\frac{\partial \mathrm{T}}{\partial \mathrm{H}}\right)_{\mathrm{V}}\left(\frac{\partial \mathrm{H}}{\partial \mathrm{V}}\right)_{\mathrm{T}},$$

or, finally,

$$\left(\frac{\partial \Pi}{\partial \mathrm{T}}\right)_{\mathrm{V}} = \left(\frac{\partial \mathrm{H}}{\partial \mathrm{V}}\right)_{\mathrm{T}}, \qquad \text{(IV)}$$

In deriving this formula we have not made use of the fact that the system under consideration is a univariant system.

Consider next equation 23 and take as independent variables the temperature and the volume. Expressing the fact that the right-hand member of the equation is a perfect differential, we get

$$\left(\frac{\partial \Pi}{\partial \mathrm{T}}\right)_{\mathrm{V}} = \left(\frac{\partial \mathrm{H}}{\partial \mathrm{V}}\right)_{\mathrm{T}}. \qquad \text{(V)}$$

Similarly, if we take as independent variables the pressure and the entropy, equation 24 will give us

$$\left(\frac{\partial T}{\partial \Pi}\right)_H = \left(\frac{\partial V}{\partial H}\right)_\Pi. \qquad \text{(VI)}$$

In deriving equations V and VI we have not made use of the fact that the system under consideration is univariant.

For a univariant system the pressure is a function of the temperature alone; we may therefore omit the subscript which appears in the left-hand members of equations IV, V and VI. Moreover, for a univariant system, we may write

$$\left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial H}{\partial V}\right)_\Pi = \frac{H_2 - H_1}{V_2 - V_1}.$$

Equations III, IV, V and VI thus reduce to the form

$$\frac{d\Pi}{dT} = \frac{H_2 - H_1}{V_2 - V_1}.$$

The demonstration by which we obtained equation V seems to be due to van der Waals.[1]

The demonstrations just given can be modified so as to apply to the indifferent points of bivariant or multivariant systems, but the demonstrations lose their simplicity. For the sake of completeness, however, we shall indicate the more important steps in the work.

We shall denote the total mass of the system by $\mathfrak{M}$, and we shall suppose this total mass to remain constant. Moreover, we shall write

$$\mathfrak{M}_j = m_j \mathfrak{M},$$

so that m_j may be called the mean concentration of the j-th component in the system. Although $\mathfrak{M}$ is to remain constant, $\mathfrak{M}_j$ and m_j may vary.

Equations 5, 6, 7 and 8 now become

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[1] Bakhuis Roozeboom. Sur les conditions d'équilibre de deux corps dans les trois états, solide, liquide et gazeux d'après M. v. d. Waals. Recueil des travaux chimiques des Pays-Bas, 5, 336 (1886).

$$d\Phi = -H\,dT + V\,d\Pi + \mathfrak{M}\sum_{j=1}^{n} F_j\,dm_j, \tag{25}$$

$$dE = T\,dH - \Pi\,dV + \mathfrak{M}\sum_{j=1}^{n} F_j\,dm_j, \tag{26}$$

$$dF = -H\,dT - \Pi\,dV + \mathfrak{M}\sum_{j=1}^{n} F_j\,dm_j, \tag{27}$$

$$dG = T\,dH + V\,d\Pi + \mathfrak{M}\sum_{j=1}^{n} F_j\,dm_j. \tag{28}$$

It is to be remembered that for univariant systems every dm_j is equal to zero, and that for the indifferent points of bivariant and multivariant systems F_j and m_j are functions of the temperature alone or, if we please, of the pressure alone. We may also say that F_j is a function of m_j.

The four demonstrations given above now take the following forms:

Equation 25 yields

$$\frac{\partial}{\partial V}\left(-H + V\frac{d\Pi}{dT} + \mathfrak{M}\sum_{j=1}^{n} F_j\frac{\partial m_j}{\partial T}\right) = 0.$$

From this we get, as before

$$\frac{d\Pi}{dT} = \left(\frac{\partial H}{\partial V}\right)_T. \tag{III}$$

Equation 26 yields

$$\frac{\partial}{\partial V}\left(T + \mathfrak{M}\sum_{j=1}^{n} F_j\frac{\partial m_j}{\partial H}\right)_H = \frac{\partial}{\partial H}\left(-\Pi + \mathfrak{M}\sum_{j=1}^{n} F_j\frac{\partial m_j}{\partial V}\right)_V.$$

Since F_j is a function of m_j,

$$\frac{\partial F_j}{\partial V}\,\frac{\partial m_j}{\partial H} - \frac{\partial F_j}{\partial H}\,\frac{\partial m_j}{\partial V} = 0,$$

and the preceding equation reduces, as before, to

$$\left(\frac{\partial T}{\partial H}\right)_H = -\left(\frac{\partial \Pi}{\partial H}\right)_V.$$

This may again be reduced to the form

$$\left(\frac{\partial \Pi}{\partial T}\right)_V = \left(\frac{\partial H}{\partial V}\right)_T. \qquad \text{(IV)}$$

Equation 27 yields

$$\left(\frac{\partial \Pi}{\partial T}\right)_V = \frac{\partial}{\partial V}\left(H - \mathfrak{M}\sum_{j=1}^{n} F_j \frac{dm_j}{dT}\right)_T.$$

This gives

$$\left(\frac{\partial \Pi}{\partial T}\right)_V = \left(\frac{\partial H}{\partial V}\right)_T. \qquad \text{(V)}$$

Finally, equation 28 yields

$$\left(\frac{\partial T}{\partial \Pi}\right)_H = \frac{\partial}{\partial H}\left(V + \mathfrak{M}\sum_{j=1}^{n} F_j \frac{dm_j}{d\Pi}\right)_\Pi,$$

from which

$$\left(\frac{\partial T}{\partial \Pi}\right)_H = \left(\frac{\partial V}{\partial H}\right)_\Pi. \qquad \text{(VI)}$$

By the same reasoning as before, these equations may be reduced to the form of equation I.

New York, March 5, 1901.

ON THE PHASE RULE

BY PAUL SAUREL

The very simple demonstration which Wind has given[1] of the phase rule is based upon a theorem which may be stated as follows:[2] If a system of phases is in equilibrium at a given temperature and under a given pressure, then, to each of the independent virtual changes which the system can undergo at that temperature and under that pressure, there corresponds a relation between the following variables: the concentrations of the phases, the temperature and the pressure.

As the demonstration of the phase rule follows immediately from this theorem, it may be of interest to show that this theorem may be regarded as one way of stating the conditions of equilibrium which we have given in a previous paper.[3]

Consider a system of r phases formed by means of n independent components. Denote by M_{ij} the mass of the j-th component which appears in the i-th phase; there will be nr such quantities. To determine the number of independent virtual changes of which the system is capable at the given temperature under the given pressure and with the given masses of the independent components, we must determine how many of the masses M_{ij} are independently variable.

In the first place, the variations of the masses M_{ij} are subject to the conditions that the total mass of each component in the system remain invariable; these conditions are expressed by the n equations

$$\sum_{i=1}^{r} \delta M_{ij} = 0, \qquad j = 1, 2, \ldots, n. \tag{1}$$

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[1] Zeit. phys. Chem. 31, 390 (1899).
[2] Zeit. phys. Chem. 31, 391 (1899).
[3] Jour. Phys. Chem. 5, 31 (1901).

Moreover, it may happen that certain of the components cannot enter into certain of the phases. We thus have a certain number of equations of the form

$$\delta M_{ij} = 0. \tag{2}$$

We shall suppose that there are p equations of this form. Finally, it may happen that certain of the components can enter certain of the phases only when associated with other components in definite proportions. Accordingly there will be a certain number of conditions of the form

$$\delta M_{ij} = \lambda \delta M_{uv}, \tag{3}$$

in which λ is a constant. We shall suppose that there are q conditions of this form. The system accordingly admits of only $nr - n - p - q$ independent virtual changes.

Denote by m_{ij} the mass of the j-th component which appears in the unit of mass of the i-th phase. This quantity may be called the concentration of the j-th component in the i-th phase. In the paper referred to above we have shown[1] that the conditions of equilibrium of the system are expressed by the equations

$$F_{1j} = F_{2j} = \dots = F_{rj}, \qquad j = 1, 2, \dots, n, \tag{4}$$

in which the functions F_{ij} are functions of the temperature, the pressure and the nr concentrations. The above equations apparently furnish $n(r - 1)$ equations between these $nr + 2$ variables. But in the demonstration by which these equations were established it was shown that p of the functions F_{ij} corresponding to the p equations 2 are identically equal to zero and are to be omitted from equations 4. Moreover, q of the equations 4 corresponding to the q conditions 3 are mere identities and do not furnish relations between the variables. The conditions of equilibrium 4 thus furnish $nr - n - p - q$ relations between the temperature, the pressure and the concentrations. We have thus established the theorem that the number of equations 4 is the same as the number of independent virtual changes of the system. Moreover, by referring to the demonstration by means

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[1] Jour. Phys. Chem. 5, 31 (1901).

of which equations 4 are established, it is not difficult to see that to each of the independent virtual changes there may be made to correspond one of the equations of equilibrium.

The phase rule follows immediately from equations 4. For, from the definition of the concentrations and the definition of the system, it follows that the nr concentrations are not independent, but are subject to the r conditions

$$\sum_{j=1}^{n} m_{ij} = 1, \qquad i = 1, 2, \ldots, r, \tag{5}$$

to p equations to the form

$$m_{ij} = 0, \tag{6}$$

corresponding to the p equations 2, and to q equations of the form

$$m_{ij} = \lambda m_{ik}, \tag{7}$$

corresponding to the q equations 3. Thus, from the definition of the system, the temperature, the pressure and the concentrations are subject to $r + p + q$ conditions; from the conditions of equilibrium 4 these variables are subject to $nr - n - p - q$ additional conditions. There are thus $nr - n + r$ conditions among the $nr + 2$ variables in question; in other words, only $n + 2 - r$ of these variables are independent.

New York, April 2, 1901.

NEW BOOKS

Prime Nozioni fondamentali di Elettrochimica. *By Alfonso Cossa. 9 × 14 cm; pp. viii + 113. Milan: Ulrico Hoepli, 1901.* — The headings of the chapters are: electrical energy; electrolysis; osmotic theory of the cell; energetics of the cell; applications of electrolysis. The pages are small and relatively few in number; but it is an interesting little book, though not free from mistakes. It is certainly confusing to the reader to postulate the intermediate formation of anhydrous zinc sulphate and the hydrated salt (p. 4) when zinc is acted on by dilute sulphuric acid. The author has read his Ostwald well, but not too intelligently. Electrolytic cell, p. 9, and voltameter are not interchangeable terms. The Daniell cell, p. 27, is not strictly reversible. A normal cell, p. 29, is not necessarily one in which there is a paste. The theories of Le Blanc and of Liebenow, p. 32, are not identical and the author has not stated either of them, though he seems to think he has. A voltmeter, p. 37, does not give electromotive forces; it gives potential differences. In the table on page 65, there is a misprint in the grams of gold deposited per ampere-hour. Neumann, p. 85, did not measure single potential differences. He deduced them from his measurements by means of the assumption that the value of the normal calomel electrode is 0.560 volt. *Wilder D. Bancroft*

Les Matières colorantes naturelles. *By V. Thomas. (Encyclopédie scientifique des Aide-Mémoire) 11 × 18 cm; pp. 180. Paris: Gauthier-Villars. Price: paper, 2.5; boards, 3 francs.* — This is a monograph on the yellow coloring matters belonging to the ketone, xanthone and flavone groups. Occurrence, preparation and properties are given. *Wilder D. Bancroft*

Analisi chimica qualitativa di Sostanze minerali ed organiche e Ricerche tossicologiche, ad uso dei Laboratori de Chimica in genere e in particulare delle Scuole di Farmagia. *By P. E. Alessandri. 9 × 14 cm; pp. xii + 384. Milan: Ulrico Hoepli, 1901.* — In this book the author tries to strike the happy mean between the elementary books which lead to a purely mechanical way of testing and the more advanced books which are too elaborate for the beginner. The book also contains four interesting chapters on qualitative analysis of organic mixtures. *Wilder D. Bancroft*

REVIEWS

The object of this department of the Journal is to issue, as promptly as possible, critical digests of all Journal articles that bear upon any phase of Physical Chemistry.

General

Samarium. *E. Demarçay. Comptes rendus,* 130, *1185* (*1900*). — The author describes the properties of some salts of samarium, the method of purification being the fractional crystallization of the double magnesium nitrates in nitric acid (5, 151). The combining weight is believed to be nearer 148 than the value 150 given by Clève, *W. D. B.*

On a new method of determining the atomic weights of uranium. *J. Aloy. Comptes rendus,* 132, *551* (*1901*). — The author determines the amount of nitrogen and of UO_2 in uranium nitrate. In this way he obtains a value of 239.4 for uranium. *W. D. B.*

Method of determining atomic weights based on the transparency of matter to X-rays. *L. Benoist. Comptes rendus,* 132, *772* (*1901*). — The permeability of the acetylacetonate of indium to X-rays is of the same order as that for the compounds of silver and cadmium. The author therefore concludes that the atomic weight of indium is 113.4 and not 75.6. *W. D. B.*

The true atomic weight of boron. *G. Hinrichs. Comptes rendus,* 130, *1712* (*1900*). — The author concludes from Gautier's experiments (4, 219) that the atomic weight of boron is exactly 11.00. *W. D. B.*

The standard atomic weight, IV. *B. Brauner. Zeit. anorg. Chem.* 26, *186* (*1901*). — A further discussion of the advantage of taking oxygen as sixteen. *W. D. B.*

The unit atomic weight. *H. Erdmann. Zeit. anorg. Chem.* 27, *127* (*1901*). — A reply to Brauner (preceding review). *W. D. B.*

Deduction and application of a general equation for free energy and physical equilibrium. *G. N. Lewis. Zeit. phys. Chem.* 32, *365* (*1900*). — The author deduces a single equation which should enable one to predict anything; but which does not lead the author to anything new. He even discusses the distribution of a substance between two liquid phases without any reference to the increased miscibility of the two phases. What we need in physical chemistry is a closer adherence to facts and less approximation theory. *W. D. B.*

Permanent changes and thermodynamics, V-VIII. *P. Duhem. Zeit. phys. Chem.* 33, *641*; 34, *312*, *683* (*1900*); 37, *91* (*1901*). — The fifth paper of the series contains a theoretical study of systems depending on two variables, of which one is not affected by hysteresis. The sixth paper applies the theory to steel and the nickel steels. The seventh deals with the secular hardening of metals, while the eighth is devoted to a discussion of the Clausius entropy equation in its bearing on hysteresis phenomena. *W. D. B.*

Heat, energy, entropy. *O. Wiedeburg. Zeit. phys. Chem.* 29, *27* (*1899*). — The author claims that special peculiarities have been improperly attributed to the entropy and he would like to see the entropy defined as one entropy = one erg per degree Centigrade. *W. D. B.*

Remarks on a paper by K. Wesendonck. *M. Planck. Drude's Ann.* 1, *621* (*1900*). — The author replies to certain criticisms offered by Wesendonck in a previous paper to his proof of the second law of thermodynamics. *H. T. B.*

On the significance of the symbolic theory of invariants in chemistry. *W. Alexejew. Zeit. phys. Chem.* 36, *741* (*1901*). — This is a reply to a criticism of the original paper (5, 265). *W. D. B.*

On a peroxide of lithium. *R. de Forcrand. Comptes rendus*, 130, *465* (*1900*). — Thermochemical data.

On anhydrous calcium peroxide and the composition of its hydrates. *R de Forcrand. Comptes rendus*, 130, *1388* (*1901*). — Thermochemical data.

On the dihydroxides. *R. de Forcrand. Comptes rendus*, 130, *1555* (*1900*). — Thermochemical data.

Heat of solution of hydrogen peroxide. *R. de Forcrand. Comptes rendus*, 130, *1620* (*1900*). — Thermochemical data.

Investigations on the formation of organic sulphur compounds. *M. Berthelot. Comptes rendus*, 132, *55* (*1901*). — Thermochemical data.

New investigations on the isomerism of sulphocyanic ethers. *M. Berthelot. Comptes rendus*, 132, *57 1901*). — Thermochemical data.

Heat of formation of acetals compared with that of isomers. *M. Delépine. Comptes rendus*, 132, *777* (*1901*). — Thermochemical data.

Deformation by warming as the cause of the thermal change of the sensitiveness of a balance. *T. Middel. Drude's Ann.* 2, *115* (*1900*). — On account of the slight decrease in sensitiveness, noted by Richary and Krigar-Mengel in their balance, with rise of temperature, the author makes a special investigation of the cause and finds it due to a slight difference in structure of the material composing the beam of the balance on the upper and under side. By repeated heating and cooling it was found that the effect could be much reduced. Constructing a balance with a beam composed of materials showing the same structural differences the same effects were noticed. *H. T. B.*

Tubular furnace for constant temperature work. *A. Gautier. Comptes rendus*, 130, *628* (*1900*). — A modification of a combustion furnace. The temperature is kept approximately constant by keeping the gas pressure constant. *W. D. B.*

One-Component Systems

Physical chemical studies on tin, IV. *E. Cohen. Zeit. phys. Chem.* **36**, *513* (*1901*). — Historical references. It is shown that the allotropic change of tin was known in the time of Aristoteles. Montaigne's citation is really from Plutarch, who refers to the change of lead in cold weather. It is possible however that Plutarch meant tin. *W. D. B.*

Change in volume of rubidium by melting. *M. Eckardt. Drude's Ann.* **1**, *790* (*1900*). — The increase in volume of rubidium was found to be 0.01657 cc for one gram, the melting-point being 37.80°. For caesium the change in volume amounts to 0.01393 cc. *H. T. B.*

Investigations on the pressures of saturated mercury vapor. *L. Cailletet, Colardeau and Rivière. Comptes rendus,* **130**, *1585* (*1900*). — The authors have determined the boiling-point curve of mercury from 400° to 880°. *W. D. B.*

Determination of the latent heats of vaporization of some organic substances. *W. Louguinine. Comptes rendus,* **132**, *88* (*1901*). — The author has determined the specific heats and the heats of vaporization of aniline, methyl ethyl acetoxime, anisol and butyronitrile. *W. D. B.*

Specific heat and heat of fusion of ethylene glycol. *R. de Forcrand. Comptes rendus,* **132**, *569* (*1901*). — The mean specific heat per gram is 0.6268 between 13° and 139°, 0.5848 between 13° and 59.6°, 0.5365 between −22.8° and +9°. The specific heat of the solid near its melting-point is probably 0.265. The heat of fusion is −2.66 per reacting weight. *W. D. B.*

Vaporization and hydration of ethylene glycol. *R. de Forcrand. Comptes rendus,* **132**, *688* (*1901*). — The author has determined the boiling-point curve for ethylene glycol from 44–760 mm. From the heats of solution he concludes that a dihydrate exists in solution. *W. D. B.*

The critical point of pure liquids and mixtures. *R. v. Hirsch. Drude's Ann.* **1**, *655* (*1901*). — A discussion of the conditions which influence the determination of the critical point. The disappearance and appearance of the separation line taking place at slightly different temperatures, the mean result must be taken as the true point. The height in the tube of the separation line also influences the result. The author considers that the anomalies noted by previous investigators in the determination of the critical point, may all be adequately explained. *H. T. B.*

Liquefaction of hydrogen. *M. W. Travers. Zeit. phys. Chem.* **37**, *100* (*1901*). — A description of the apparatus used by Ramsay and Travers in preparing relatively large quantities of liquid hydrogen. *W. D. B.*

Generalization of Trouton's law. *R. de Forcrand. Comptes rendus,* **132**, *879* (*1901*). — For non-polymerized liquids we find that $Q/T = 20\text{–}21$ (Trouton's law), where Q is the heat of vaporization and T the absolute temperature at which the vapor-pressure equals one atmosphere. For the dissociation of ammoniacal compounds, etc., it is found that $Q_1/T = 30\text{–}31$, where Q_1 equals the

heat of dissociation. The author proposes to bring these two rules under one head by postulating $(Q_2 + Q_3)/T = 10$, where Q_2 equals the heat of liquefaction of the dissociating gas and Q_3 the heat of combination of the two solids.
W. D. B.

Formulas giving the volumes and pressures of saturated vapors. *H. Moulin. Comples rendus*, 130, *1454* (*1900*). —The author deduces reduced equations for volume and temperature and for pressure and temperatnre, which he says are very satisfactory. *W. D. B.*

Some isotherms and isochores for ether. *E. Mack. Comples rendus*, 132, *952, 1035* (*1901*). —Thirteen isotherms were determined between 100° and 206°; one isobar at 256 kg/cm², and isochores between 1 cc and 1.85 cc *W. D. B.*

On two remarkable groups of geometrical loci. *E. Mathias. Comples rendus*, 130, *1748* (*1900*). —The author claims that the diameter, for points at which, with unit mass of substance, liquid and vapor each occupy the same volume, cannot be a straight line, though it may approximate one very closely. The only straight line is the 'rectilinear diameter.' [Cf. however Amagat (5, 200)]. *W. D. B.*

A remarkable point in connection with the Joule-Kelvin effect. *D. Berthelot. Comples rendus*, 130, *1379* (*1900*). —From Amagat's data for nitrogen it appears that there must be a reversal of the sign of the Joule-Thomson effect at about 40° under a pressure of 310 m Hg. The formula of van der Waals predicts this change at about 108° C and 228 m Hg. *W. D. B.*

On the thermal conductivity of gases and the dependence on the temperature. *P. A. Eckerlein. Drnde's Ann.* 3, *120* (*1900*). —The work has to do entirely with air, hydrogen and carbon dioxide at low temperatures. In addition to the thermal conductivities for these gases, their temperature coefficients are obtained as low as —150° C. The calculation of the results for 0° C shows a good agreement with previous determinations. The ratio of the conductivities for hydrogen to air for the three temperatures. 0°, —59°, and —150° C is 6.8, 6.6 and 5.6, but according to theory the ratio should be 7.1.

The temperature coefficient for air, hydrogen and carbon dioxide is found to be

Air,	0.00362
H,	0.00422
CO_2	0.00352

H. T. B.

On the laws of the specific heats of liquids. *E. H. Amagat. Comples rendus*, 130, *1443* (*1900.*) —The author shows how conclusions in regard to specific heats may be drawn from a study of the graphical representation of the p, v, T relations. *W. D. B.*

On the specific heats of liquids whose elements are subject to their mutual actions. *P. Duhem. Comples rendus*, 132, *292* (*1901*). —The author shows that "all the laws, which one deduces in elementary thermodynamics for a liquid subjected to a normal and uniform pressure, apply to a liquid whose parts exert any reciprocal action, Newtonian or otherwise." *W. D. B.*

Study of the viscosity of sulphur at temperatures above that of the maxi-

mum viscosity. *C. Malus. Comptes rendus*, 130, *1708* (*1900*).—Sulphur heated three hours at 360° and then cooled to 100° or any intermediate temperature remains fluid. Sulphur which has been heated ten minutes at 360° and then cooled to 100° is viscous at first, but becomes fluid after five or six hours. It is then apparently like the sulphur that has been heated for several hours at 360°; but differs in that it becomes viscous on reheating, which the other does not. *W. D. B.*

Is there a law for solids corresponding to Avogadro's for gases? *C. Benedicks. Zeit. phys. Chem.* 36, *529* (*1901*).—The following conclusions are drawn:

The hardness of simple substances is proportional to the number of atoms in a given space.

The hardness of solid solutions increases with the increase of the osmotic pressure. *W. D. B.*

Allotropic forms of silver. *M. Berthelot. Comptes rendus*, 132, *234* (*1901*).—The author employs the crude method of dissolving different samples of silver in mercury and measuring the heat effect. He distinguishes amorphous silver from crystalline silver. Silver precipitated from compounds is usually different from these other two and may vary with nearly every form of precipitation. *W. D. B.*

The expansion of amorphous silica. *H. Le Chatelier. Comptes rendus*, 130, *1703* (*1900*).—The mean coefficient of expansion of amorphous silica between 0° and 1000° is 0.0000007, by far the smallest coefficient of any of the common substances. *W. D. B.*

On the elasticity and hardness of crystallized, amorphous and hydrated silica. *F. Auerbach. Drude's Ann.* 3, *116* (*1900*).—The new kind of glass formed by melting quartz in the electric furnace, which has been prepared at Jena and other glass works, is the subject of the present investigation in its relation to pure quartz crystal and opal. The elasticity and hardness of the amorphous quartz are both less than for the crystallized form, and for opal they are not much more than half as great. *H. T. B.*

On the hardness of metals. *F. Auerbach. Drude's Ann.* 3, *108* (*1900*).—By the method devised by the author of testing the hardness of a material by applying pressure through a lens-shaped body, and so noting the pressure at which the material gives way, a number of metals are determined containing impurities. The work is mostly of technical interest. *H. T. B.*

On the additive properties of the atomic heats. *St. Meyer. Drude's Ann.* 2, *135* (*1900*).—It is found that in general the estimation of the molecular heats from the atomic heats can be expected from those substances which obey, at least approximately, the additive relation of the atomic volumes. *H. T. B.*

On the molecular heat of mixtures and the Neumann-Joule-Kopp law. *E. van Aubel. Jour. de Phys.* 10, *36* (*1901*).—Referring to the paper by Stephan Meyer (see review) on the relation of the additive properties of the atomic heats to the atomic volumes, the author points out that taking the exact work of Hagemann on the change of volume of solid and fluid substances by chemical processes, and Regnault's work on molecular heats in connection with the recent values given for the atomic heats by Ostwald that for AgBr, KI, Hg_2I_2 and HgI_2 the law does not hold. The first two both show a large contraction of volume when compared to the volume calculated from the atomic volumes, while the molecular heat is considerably larger than the sum of the atomic heats. With the last two salts the reverse is the case. *H. T. B.*

Two-Component Systems

On the angular points in solubility curves. *H. Le Chatelier. Comptes rendus,* 130, *1606* (*1900*).—The author shows that at a eutectic point "the trigonometric tangents of the two curves are a measure of the heats of solution of weights of the two substances equal to those in the saturated solution." *W. D. B.*

The cryoscopic method in dilute solutions. *M. Wildermann. Zeit. phys. Chem.* 30, *508* (*1899*).—A description of experiments carried out in 1895. The author discusses the form in which ice crystallizes, the question of dissolved gases, the temporary changes in the thermometer, the effect of pressure, the rate at which the mercury column reaches equilibrium under change of hydrostatic pressure, the matter of roughnesses in the capillary, the divisions of the scale, the method of reading, and many other points. In addition, there are replies to various criticisms. Whether one accepts the author's estimate of the accuracy of his method or not, there can be no question but that he has paid more attention to the influence of conditions than any one else. *W. D. B.*

Cryoscopic studies. *P. Crousichoff. Comptes rendus,* 132, *955* (*1901*).—The author finds that concordant results with a platinum thermometer can be obtained only in case a heavy plate of ebonite covered with paraffin is used where the leads are fastened. *W. D. B.*

On the determination of the work corresponding to affinity. *E. Cohen. Zeit. phys. Chem.* 36, *517* (*1901*).—A redetermination of the dissociation pressures of $MgSO_4 7H_2O$ leads to a calculated value for the heat of dissociation of 3712 cal while Thomsen found 3700 experimentally. Below 46.5° $MgSO_4 7H_2O + FeSO_4 6H_2O$ is the stable system; above this temperature, $MgSO_4 6H_2O + FeSO_4 7H_2O$. *W. D. B.*

Dissociation and thermal study of $Al_2Cl_6 18H_2O$. *E. Baud. Comptes rendus,* 132, *690* (*1901*).—The author has determined some of the dissociation pressures for $Al_2Cl_6 18H_2O$ and also the heat of dissociation. *W. D. B.*

On the combinations of metallic iodides with sulphur dioxide. *E. Péchard. Comptes rendus,* 130, *1188* (*1900*).—Solid potassium iodide combines with sulphur dioxide forming $KISO_2$. The dissociation pressures at 0°, 10°, 20° and 30° are 60, 93, 146, 238 cm Hg respectively. The compound appears to be more or less stable in solution. Other iodides behave similarly. *W. D. B.*

Compounds of lithium bromide with ammonia. *J. Bonnefoi Comptes rendus,* 130, *1394* (*1900*).—Lithium bromide crystallizes with one, two, three and four of ammonia. The variations of the entropy (Q/T) are practically the same for all four (4, 226). *W. D. B.*

Compounds of ammonia with aluminum chloride. *E. Baud. Comptes rendus*, 132, *134, 553* (*1901*). — Aluminum chloride, Al_2Cl_6, has been made to crystallize with two, ten, twelve and eighteen of ammonia. The author has also determined heats of dissociation and of solution. *W. D. B.*

On the volatility of boric acid with water vapor. *F. Skirrow. Zeit. phys. Chem.* 37, *84* (*1901*). — From the corresponding compositions of the liquid and vapor phases the author concludes that the volatile components in the system boric anhydride and water are water and H_3BO_3. This conclusion is based on the distribution law and on the accuracy of experiment, neither of them above suspicion in the present case. *W. D. B.*

Vapor-pressures of binary mixtures. *P. Kohnstamm. Zeit. phys. Chem.* 36, *41* (*1901*). — In this paper, the author calls attention to some of the laws derivable from the van der Waals theory for mixtures of two volatile components, and tests experimentally the one which requires that the partial pressure curves shall possess but one maximum or one minimum when the vapor-phase is dilute and the components perfectly miscible. The two apparent exceptions — propionic acid and water, benzene and carbon tetrachloride — he finds normal (Cf. Phase Rule, p. 119). With this continuity theory as his guide, he examines the pressure curves given by Ostwald, Bancroft, and Nernst; his criticisms are partially answered by a foot-note inserted by Ostwald.

He shows (as had previously been done by Hartman) that the Margules formula is merely a rearrangement of one given by van der Waals, for whom he claims priority as well as a more general mathematical development. The relation of the form of the partial pressure curve to the critical pressure is tested, while the bearing of associating molecules on the form of curve is also examined. A brief résumé gives the type of curves possible.

The reviewer would call attention to the facts that the D curve (Fig. 2) is ascribed to hydrobromic acid and water; that without comment there are introduced (B, Fig. 2) four volumes for a two-liquid-layer system, requiring a modified equation for the consolute temperature; and that the curves shown in Figs. 3 and 4 will probably obtain no acceptance until it is shown that the theorems of van der Waals which prove their correctness do not conflict with those of Gibbs which bear on the conditions necessary that both phases be identical. *H. R. C.*

On the vaporization of binary mixtures. *P. Duhem. Zeit. phys. Chem.* 36, *605* (*1901*). — Kohnstamm (preceding review) deduced from the theorem of van der Waals that no pair of consolute liquids can give one mixture with a maximum pressure and another with a minimum pressure at the same temperature. To this the author replies that such a case has already been described by Caubet (5, 202) for methyl chloride and sulphur dioxide. *W. D. B.*

On the liquefaction of gaseous mixtures. *F. Caubet. Comptes rendus*, 132, *128* (*1901*). — A discussion of some of the isotherms in the concentration-pressure diagram, masses constant, for CO_2 and SO_2. For the particular case under consideration, vapor and liquid have the same composition at 86°. *W. D. B.*

Contribution to the study of indium. *C. Chabrié and E. Rengarde. Comptes rendus,* 131, *1300* (*1900*) *;* 132, *472* (*1901*). — Boiling-point experiments show that indium is trivalent in the acetylacetonate of indium, but iron and aluminum are also trivalent in the corresponding compounds. This fact, together with the composition of the rubidium indium alum, makes the authors believe that the formula for indium chloride should be In_2Cl_6 if the formula for ferric chloride is to be written Fe_2Cl_6. *W. D. B.*

Study of uranium nitrate. *Oechsner de Coninck. Comptes rendus,* 132, *90* *204* (*1901*). — The author has determined the densities of some solutions of uranium nitrate in dilute nitric and sulphuric acids; also the solubility in methyl alcohol, ordinary ether, ethyl acetate and concentrated formic acid. Several modifications of the oxide appear to be formed depending on the rate of decomposition of the heated nitrate. *W. D. B.*

The compounds of silver with mercury. *M. Berthelot. Comptes rendus,* 132, *241* (*1901*). — The only method of attack is the thermochemical which leads to the conclusion that silver and mercury form mix-crystals. It seems incredible that any one can base such conclusions on such experiments. No one has done more than Berthelot to bring thermochemical methods into disrepute. *W. D. B.*

Compressibility of solutions. *Guinchant. Comptes rendus,* 132, *469* (*1901*). — For non-electrolytes and pressures up to four atmospheres the author finds that the total change in volume is due to the solvent and not the solute. This applies of course only to dilute solutions *W. D. B.*

On a new method of preparing the hydrates of sodium peroxide. *G. F. Jaubert. Comptes rendus,* 132, *86* (*1901*). — When sodium peroxide and water are placed in two beakers under a bell glass, water distils from one beaker to the other, forming the successive hydrates, the highest being $Na_2O_2 8H_2O$. *W. D. B.*

Some properties of sodium peroxide. *R. de Forcrand. Comptes rendus,* 132, *131* (*1901*). — A claim of priority against Jaubert (preceding review). *W. D. B.*

Poly-Component Systems

Action of hydrogen on bismuth sulphide. *H. Pélabon. Comptes rendus,* 132, *78* (*1901*). — The author has studied the reaction

$$BiS + H_2 \rightleftarrows Bi + H_2S.$$

At 610° equilibrium is reached in twenty minutes. When hydrogen sulphide acts upon bismuth below the melting-point of bismuth sulphide, there is apparently a false equilibrium due to the fact that the reaction is brought practically to a standstill by the film of sulphide formed on the surface of the bismuth. *W. D. B.*

Action of hydrogen on realgar. *H. Pélabon. Comptes rendus*, 132, *774* (*1901*). — The author has studied the effect of pressure and temperature on the reversible reaction

$$AS_2S_2 + 2H_2 = 2H_2S + As_2.$$

W. D. B.

Certain conditions of reversibility. *A. Colson. Comptes rendus*, 132, *467* (*1901*). — The decomposition of silver carbonate is reversible only when traces of moisture are present. Carbon monoxide reduces yellow mercuric oxide quite rapidly while it is almost without action on the red modification. *W. D. B.*

Action of water on mercurous sulphate. *A. Gouy. Comptes rendus*, 130, *1399* (*1900*). — At 20° there is equilibrium between mercurous sulphate, a basic sulphate, solution and vapor, when the aqueous solution contains about 0.4 g Hg and 0.16 g SO_3 per liter. In presence of saturated zinc or cadmium sulphate solutions the hydrolysis is practically zero, but the solubility is increased, there being 0.8 g Hg in the zinc sulphate solution and 1.1 g in the cadmium sulphate solution. *W. D. B.*

On the equilibrium between different oxidation stages of the same metal. *E. Abel. Zeit. anorg. Chem.* 26, *361* (*1901*). — A general discussion of equilibrium relations followed by a special study of copper and mercury. In mercurous nitrate the mercury is bivalent; but no definite conclusion was reached with cuprous salts. A solution of cuprous chloride in hydrochloric acid probably contains the anion $\overset{-\,-}{Cu_2Cl_4}$, and the author believes in the existence of complex ions in solutions containing cuprous sulphate. Foerster and Seidl showed that when copper and an acidified solution of copper sulphate are heated at 100°, cuprous sulphate is formed and that metallic copper precipitates on cooling. The author confirms this and shows that when insufficient acid is present, cuprous oxide precipitates owing to the hydrolysis of the cuprous sulphate. The author has further determined the conditions under which the copper voltameter can be used as a moderately accurate instrument for low currents.

W. D. B.

Investigations on the action of hydrogen peroxide on silver oxide. *M. Berthelot. Comptes rendus*, 132, *897* (*1901*). — When hydrogen peroxide and silver oxide are brought together the first reaction may be represented by the equation

$$Ag_2O + H_2O_2 = Ag_2O_2 + H_2O.$$

Part of the silver peroxide decomposes at once, according to the equation

$$Ag_2O_2 = 2Ag + O_2,$$

while another part changes more slowly according to the equations

$$Ag_2O_2 = Ag_2O + O$$

$$Ag_2O_2 + Ag_2O = Ag_4O_3.$$

W. D. B.

On the formation and decomposition of acetal. *M. Delépine. Comptes rendus*, 132, *331* (*1901*). — The author shows that the reaction

$$RCHO + 2ROH \rightleftarrows RCH(OR)_2 + H_2O$$

is reversible. *W. D. B.*

Specific heat of a gaseous mixture of substances in chemical equilibrium. *A. Ponsot. Comptes rendus*, 132, *759* (*1901*). — The system occupying the larger volume has the higher specific heat and is the one which alone tends to remain when the temperature becomes infinite, whether the system be kept at constant pressure or at constant volume. [This theorem is not necessarily true for finite temperatures]. *W. D. B.*

Direct production of crystallized mercuric and mercurous iodide. *F. Bodroux. Comptes rendus*, 130, *1632* (*1900*). — Crystallized mercuric iodide, usually yellow, separates in half an hour from a solution of methyl iodide and mercuric acetate in water. When mercurous nitrate is substituted for mercuric acetate, crystallized mercurous iodide is formed. *W. D. B.*

Amorphous and crystallized dimercuric ammonium iodide. *M. François. Comptes rendus*, 130, *571*, *1023* (*1900*). — Dimercuric ammonium iodide, NHg_2I, is quite stable and can be made by the action of ammonia on mercuric iodide. It is easier to make it by the action of concentrated sodium hydroxide solution on $HgI_2 2NH_3$. When the formation from ammonia and mercuric iodide is so carried out as to take place very slowly, purple crystals are obtained. The intermediate compound, $NHgH_2I$, was also prepared. *W. D. B.*

Studies on the reducing power of calcium carbide. *F. v. Kügelgen. Zeit. Elektrochemie*, 7, *541*, *557*, *573* (*1901*). — Lead oxide is reduced by calcium carbide according to the equation

$$5PbO + CaC_2 = 5Pb + CaO + 2CO_2.$$

The calcium reduces much more intensely than the carbon, so that the reaction really runs in two stages. With lead chloride and calcium carbide the reaction is too intense but can be moderated by addition of lead oxide. The lead is pretty nearly pure. Similar results were obtained with copper and other metals, though the difficulty in obtaining a good regulus of the reduced metal increases with rise of melting-point. *W. D. B.*

On the separation of yttria, ytterbia, and the new erbia. *G. and E. Urbain. Comptes rendus*, 132, *136* (*1901*). — By fractional crystallization of the ethyl sulphates, yttrium, ytterbium, and erbium are separated from the other substances in gadolinite. Ytterbium was separated from the other two by fractional decomposition of the fused nitrates. Its atomic weight is 172.6, while the yttrium, as finally obtained, gives a value of 88.6. *W. D. B.*

Hydrogenization of acetylene in presence of reduced iron or cobalt. *P. Sabatier and J. B. Senderens. Comptes rendus*, 130, *1628* (*1900*). — With iron at 215° there is marked condensation of the acetylene but very little addition of hydrogen. When cobalt is substituted for iron there is much formation of ethane. *W. D. B.*

Hydrogenization of acetylene in presence of copper. *P. Sabatier and B. Senderens. Comptes rendus*, 130, *1557* (*1900*). — Above 130° finely divided copper causes hydrogen and acetylene to combine to a certain extent. If acetylene be present in excess, the specific action of copper on acetylene becomes the predominant one. *W. D. B.*

Hydrogenization of ethylene in presence of different metals. *P. Sabatier and J. B. Senderens. Comptes rendus*, 130, *1761* (*1900*). — The effects of finely divided metals on a mixture of ethylene and hydrogen is very similar to the effects of the same metals on a mixture of acetylene and hydrogen. With nickel there is a continuous formation of ethane even when cold; with cobalt there is a brief reaction when cold and the metal eventually becomes inactive when hot. There is no reaction with copper below 180°, but above that temperature the reaction is continuous. Iron and cobalt are not very satisfactory since the reaction is slow even at high temperatures and soon comes to an end. *W. D. B.*

Preparation of hexahydrobenzene. *P. Sabatier and J. B: Senderens. Comptes rendus*, 132, *210* (*1901*). — Heated nickel powder causes benzene and hydrogen to combine with formation of hexahydrobenzene. *W. D. B.*

General method of preparing naphthenes *P. Sabatier and J. B. Senderens. Comptes rendus*, 132, *566* (*1901*). — By heating almost any benzene compound at 170°–200° in presence of hydrogen and reduced nickel, the hydrogen addition compound can be formed. Cobalt, platinum, and iron have little or no effect and cannot be substituted for nickel. *W. D. B.*

Oxidation or dehydrogenization by means of ferricyanides. *A. Étard. Comptes rendus*, 130, *569* (*1900*). — The ferricyanides appear to have specific oxidizing powers, removing hydrogen from substances containing nitrogen. The author concludes that a division into weak or powerful oxidizing agents is inaccurate, each oxidizing agent having its own special field. *W. D. B.*

Osmotic Pressure and Diffusion

On osmosis through copper ferrocyanide membranes. *G. Flusin. Comptes rendus*, 132, *1110* (*1901*). — The method was that of Pfeffer. Osmotic pressures agreeing well with the theory were obtained with saccharose, amygdaline and antipyrine. Low values were found with urea, but it was shown that this substance passed through the membrane. The author also studied the rate of flow of water into the cell and found that, with the same cell, the rate of flow was proportional to the osmotic pressure. *W. D. B.*

Experimental studies on the development of the lamprey. *E. Bataillon. Comptes rendus*, 130, *1413* (*1900*). — Isotonic solutions of calcium chloride, sodium chloride and cane sugar have the same effect on the development of the eggs of the lamprey. Solutions containing less than 0.8 g NaCl, or its equivalent, per liter, cause the egg to swell through absorption of water and either prevent or retard growth. *W. D. B.*

On the sensibility of the higher vegetables to low concentrations of toxic substances. *H. Coupin. Comptes rendus*, 132, *645* (*1901*). — The author has determined the concentrations at which twenty-seven salts have a toxic effect on wheat. *W. D. B.*

Influence of the osmotic pressure of the medium on the form and structure of vegetables. *J. Beauverie. Comptes rendus*, 132, *226* (*1901*). — The roots of sprouting peas tend to grow out of pure water while they grow more and more nearly straight down, the more concentrated the solution is. *W. D. B.*

On the permeability of amorphous silica to hydrogen. *P. Villard. Comptes rendus* 130, *1752* (*1900*). — Amorphous silica at a red heat is quite permeable to hydrogen though the rate of diffusion is not so great as with platinum.
W. D. B.

An addition. *V. v. Turin. Zeit. phys. Chem.* 36, *524* (*1901*). — The author explains and amplifies some points in the preceding paper (5, 81).
W. D. B.

Velocities

On the theory of catalytic reactions. *H. Euler. Zeit. phys. Chem.* 36, *641* (*1901*). — The author upholds the view that all reactions are ion reactions and that all catalytic agents increase the concentration of the reacting ions. In order to carry out this view, it is of course necessary to assume ions of unknown concentrations, the change in these unknown concentrations being then assumed to be that required by the theory. *W. D. B.*

Velocity and catalysis in inhomogeneous systems. *K. Drucker. Zeit. phys. Chem.* 36, *693* (*1901*). — Experiments are cited to show that the rate of solution of a solid is not a question of diffusion alone. The rate of solution of arsenic trioxide in dilute sulphuric acid is chiefly a function of the concentration of the catalytic agent, and is only slightly affected by the amount of arsenic already in solution. *W. D. B.*

On the decomposition of ammonium nitrite. *R. Wegscheider. Zeit. phys. Chem.* 36, *543* (*1901*). — It is pointed out that the qualitative fact of an increase in the rate of decomposition of ammonium nitrite on addition of salts with a common ion does not prove that it is the undissociated substance which decomposes. The reaction may be one between ions and the increased velocity due to increased concentration of one of them. *W. D. B.*

On the spontaneous decomposition of thiosulphuric acid. *A. F. Holleman. Zeit. phys. Chem.* 33, *509* (*1900*). — It is pointed out that the experiments of v. Oettingen (4, 549) do not prove that it is not the undissociated thiosulphuric acid which decomposes. *W. D. B.*

Studies on inversion. *E. Cohen. Zeit. phys. Chem.* 37, *69* (*1901*). — The author has determined the rate of saponification of ethyl acetate by sodium hydroxide in aqueous solutions with varying amounts of mannit, cane sugar, *d*-glucose, *d*-fructose, invert sugar. These decrease the reaction velocity, mannit having the least effect and invert sugar the greatest. *W. D. B.*

Inorganic ferments. *G. Bredig and K. Ikeda. Zeit. phys. Chem.* 37, *1* (*1901*). — The authors have made a long series of experiments bringing out the analogy between the catalytic action of platinum, of ferments, and of red blood corpuscles on hydrogen peroxide. The most intense poisons for colloidal platinum are HCN, CNI, I_2, $HgCl_2$, H_2S, $Na_2S_2O_3$, CO, P, PH_4, AsH_3, $Hg(CN)_2$, CS_2. Less intense but still powerful poisons are aniline, hydroxylamine, bromine, hydrochloric and oxalic acids, amyl nitrite, arsenious acid, ammonium chloride. Phosphorous acid, sodium nitrite, nitrous acid, pyrogallol, nitrobenzene, hydrofluoric acid, and ammonium fluoride are only slightly poisonous. Ethyl and amyl alcohols, ether, glycerol, turpentine, chloroform and dilute potassium chlorate are all practically indifferent while the reaction is accelerated by formic acid, hydrazine and dilute nitric acid. In about two-thirds of the cases there is a very marked analogy between the action of blood and of colloidal platinum on hydrogen peroxide in presence of these different substances. *W. D. B.*

The diastasic action of colloidal platinum and other metals. *G. Bredig. Comptes rendus*, 132, *490, 576* (*1901*.) — A brief statement is given of the author's work on "inorganic ferments." *W. D. B.*

The development and propagation of the explosion wave. *H. Le Chatelier. Comptes rendus*, 130, *1755* (*1900*). — The author describes some results obtained by photographic registration of explosion waves. *W. D. B.*

Limits of combustion with heated copper oxide of hydrogen and carbonaceous gases diluted with large amounts of air. *A. Gautier. Comptes rendus*, 130, *1353* (*1900*). — Hydrogen diluted with 5000 volumes of air is completely burned to water when the mixture is passed over 0.7 m of red-hot copper oxide at the rate of 2–3 liters per hour. With methane instead of hydrogen only about 71 % of the hydrogen and 59 % of the carbon was burned, these values falling to 45 % and 36 % on increasing the dilution threefold. Methane does not therefore burn as a whole under these conditions. Experiments were also made with mixtures of methane and hydrogen. *W. D. B.*

The formation of nitric acid during combustions. *M. Berthelot. Comptes rendus*, 130, *1345, 1430, 1662* (*1900*). — When carbon or sulphur is burned in oxygen containing nitrogen, a small amount of nitric acid is also formed, the quantity varying with the conditions of the experiment. When zinc or iron is burned under similar conditions, no acid is formed. With hydrogen, acid is formed only when oxygen is present in excess. *W. D. B.*

Electromotive Forces

Electrocapillary properties of some organic compounds in aqueous solutions. *A. Gouy. Comptes rendus*, 132, *822* (*1901*). — It is found that the addition of almost any organic substance to Eq/100 solution of sodium sulphate decreases the maximum surface tension, the amount of change being a function of the nature and concentration of the added substance. *W. D. B.*

On capillary electrical phenomena. *W. Palmaer. Zeit. phys. Chem.* 36, *664* (*1901*). — The author gives his reasons for preferring the Nernst theory of the Lippman electrometer to the Warburg theory; but is forced to admit, that, as yet, there is no satisfactory explanation of the different maximum surface tensions. It does not seem to have occurred to the author to ask himself whether the so-called single potential differences might not be decomposition voltages between mercury electrodes. *W. D. B.*

On the effect of a salt with a common ion on the electromotive force of con-

centration cells and on the rate of diffusion. *R. Abegg and E. Bose. Zeit. phys. Chem.* 30, *545* (*1899*). — The authors deduce formulas for electromotive force and rate of diffusion when we take two solutions with the same electrolyte in different concentrations and add the same quantities of a neutral salt with a common ion to the two solutions. The deductions involve the assumption of complete dissociation. *W. D. B.*

Electromotive force of Clark and Weston cells. · *W. Marek. Drude's Ann.* 1, *617* (*1900*). — The author publishes two tables giving numerically the interpolated values for the Clark and Weston cells, from the formulas of Kahle and Jaeger between 0° and 30° C. *H. T. B.*

The thermoelectric properties of various alloys. *E. Steinmann. Comptes rendus*, 131, *34* (*1900*). — A 36.1 % nickel steel gives a value of —2461 microvolts between 0° and 100° and not a 28 % steel as stated in a previous paper (5, 152, attributed by an oversight to A. Cornu). *W. D. B.*

Addition. *K. Schaum. Zeit. Elektrochemie*, *7*, *523* (*1901*). — It now seems probable that the author was measuring the reducing power of benzyl alcohol (5, 270) rather than that of the reversible reaction sulphite into sulphate. *W. D. B.*

Electrochemical relations of allotropic states. *M. Berthelot. Comptes rendus*, 132, *732* (*1901*). — The author finds that different forms of silver show qualitative differences when made electrodes in a silver nitrate solution. We are told that amorphous silver is anode, but no further information is vouchsafed. *W. D. B.*

On the modification of metallic surfaces by light. *H. Buisson. Comptes rendus*, 130, *1298* (*1900*). — Aluminum, zinc, copper, tin, lead, antimony, bismuth, brass, amalgamated zinc become more electronegative after being illuminated, the differences sometimes amounting to a tenth of a volt. Platinum becomes more positive, while, gold, silver and iron show only slight variations. A red or yellow glass prevents the effect, a colorless glass gives the whole effect, while the ultraviolet rays by themselves reverse the sign of the effect. *W. D. B.*

Reply to some remarks of Messrs. Arrhenius, Kohnstamm, Cohen, and Noyes. *W. Nernst. Zeit. phys. Chem.* 36, *596* (*1901*). — A very petulant reply to a series of criticisms. *W. D. B.*

Electrostatic influence on the electrical discharge through a rarefied gas. *J. Stark. Drude's Ann.* 1, *430* (*1901*). — The influence of a charge or conductor near a tube containing a gas through which a discharge from a large number of primary cells is passed shows that if this tends to increase the electric tension the discharge passes more easily, while the reverse is the case when it acts in the contrary way. The effect of an unsteady or intermittent discharge is studied with reference to acoustic and electrical waves set up on the cathode. The author elaborates on the difference in discharge from positive and negative electrodes. *H. T. B.*

On the influence of temperature on the fall of potential in rarefied gases.

G. C. Schmidt. Drude's Ann. 1, *625* (*1900*). — This is a somewhat extensive paper describing a number of miscellaneous experiments on vacuum discharge, the gas used being nitrogen. The effect of temperature on the distribution of light around the two electrodes is studied, as well as the effect on the potential gradient. The effect of an increase of temperature on the total potential between the electrodes is to cause it to decrease at first slowly, then more rapidly, until, passing through a minimum, it increases again. The potential minimum for the same tube is at a lower temperature the smaller the initial pressure.

H. T. B.

Determination of a magnetization number. *St. Meyer. Drude's Ann.* 1, *664* (*1900*). — Solutions of vanadium chloride of five different concentrations are treated, and the magnetization number for each solution determined for field strengths of from 10,000 to 17,000 lines. In addition two rare earths are also determined Gd_2O_3 and $Sa_2(SO_4)_3$. *H. T. B.*

On atomic and molecular magnetism. *St. Meyer. Drude's Ann.* 1, *668* (*1900*). — The general result obtained by the author's study of the relation of the additive property of the atomic magnetism to the same property for the atomic volume, is that where volume contraction ensues the paramagnetic properties are enhanced, and where dilatation results the diamagnetic properties are increased. A precise formula connecting the molecular susceptibility with the voluminal changes cannot be given. *H. T. B.*

Resistance of bismuth in a variable magnetic field. *W. Eichhorn. Drude's Ann.* 3, *20* (*1900*). — Owing to the use of a bismuth spiral in the apparatus of Hartmann and Braun for the determination of magnetic field strength, the author undertakes to study the behavior of this material under different conditions with respect to temporary hysteresis. It is found that moving from a weak to a strong field, the resistance is less than should be expected, and moving from a strong to a weak, the resistance is greater, the amount depending on the rate of change of field. The use of a bismuth spiral is completely justified, however, in a constant magnetic field. The effect is simplest explained on the assumption of the existence of a kind of viscous hysteresis of the resistance.

H. T. B.

Electrolysis and Electrolytic Dissociation

On the rate of the electrolytic precipitation of copper in presence of sulphuric acid. *J. Siegrist. Zeit. anorg. Chem.* 26, *273* (*1901*). — The author considers that the rate of precipitation of copper from an acid sulphate solution under constant current and current density is to be expressed by the formula

$$dx/dt = k(A - x)^n,$$

where $A - x$ is the concentration of the copper sulphate. The exponent n is zero when no hydrogen precipitates. With increasing relative acidity the exponent varies between zero and unity, the reaction finally becoming monomolecular. The absolute value of k increases with increased stirring. The change of this constant is approximately proportional to the change of the current, though a hyperbolic function would be necessary to express it accurately.

The reaction velocity constant increases approximately proportionally to the increase of temperature. *W. D. B.*

The electrolytic preparation of benzidine. *W. Löb. Zeit. Elektrochemie,* 7, *597* (*1901*). — Seventy percent yield of benzidine can be obtained by working with a nickel cathode and a hydrochloric acid solution to which stannous chloride has been added. Cathodes of other metals cannot be substituted profitably for nickel.

While dimethyl aniline is not oxidized in sulphuric acid solution with a platinum anode, it is changed to tetramethyl benzidine when a little chromic acid is added to the solution. *W. D. B.*

Electrochemical reduction of aromatic mono-nitro substances to amines. *K. Elbs and F. Silbermann. Zeit. Elektrochemie,* 7, *589* (*1901*). — Nitrobenzene can be reduced electrolytically to aniline in aqueous alcoholic hydrochloric acid solution by using a zinc cathode. Any cathode may be used if zinc chloride be added to the solution. The yield is 66–75% of the theoretical. *W. D. B.*

Electrolytic preparation of periodates. *E. Müller. Zeit. Elektrochemie,* 7, *509* (*1901*). — Potassium periodate can be formed electrolytically by working in alkaline solutions. In neutral solutions this is possible only when other oxidizing agents tend to be formed, such as chlorine, persulphates, etc. *W. D. B.*

The electrolysis of phenol in presence of haloid acids. *H. Zehrlant. Zeit. Elektrochemie,* 7, *501* (*1901*). — Phenol is oxidized during the electrolysis of normal hydrochloric or hydrobromic acid. With concentrated hydrobromic acid bromine substitution products are formed. With hydriodic acid iodine is set free. *W. D. B.*

Investigations on alkali preparation by the bell process. *G. Adolph. Zeit. Elektrochemie,* 7, *581* (*1900*). — The experiments show that the use of a bell-shaped vessel instead of a diaphragm does not affect the theory of the electrolytic preparation of alkali and chlorine. For the same electrical energy it seems possible to get a higher concentration of alkali with the bell apparatus than when using a diaphragm. *W. D. B.*

The impossibility of primary electrolytic formation of potassium chlorate. *A. Brochet. Comptes rendus,* 130, *1624* (*1900*). — No potassium chlorate is formed during the electrolysis of alkaline potassium chloride if cobalt oxide be added to the solution. *W. D. B.*

Electrolysis of oxyacids. *J. Hamonet. Comptes rendus,* 132, *259* (*1901*). — When a solution of β-amyl-oxy proprionate of potassium is electrolyzed, two acid radicals combine with loss of CO_2. *W. D. B.*

Electron theory of metals. *P. Drude. Phys. Zeit.* 1, *162; Drude's Ann.* 1, *566* (*1900*). — The speculative enquiry which was first begun by Weber and then by Giese that metallic conduction could be interpreted in the light of the ionic theory or the transportation of the electric current by material particles has been the basis upon which the author has developed a theory which in its entirety brings together in a remarkable way the various phenomena connected with the passage of electric current through conductors. It offers an explanation, if not complete in all particulars, yet so suggestive as to indicate that it may become the basis upon which sound electrical theory of matter may be founded. The fundamental conception of an electron, nucleus, or kernel as the author prefers to call it rather than use the word ion which he reserves for the carrier in electrolysis, and which he considers made up of a bundle or aggregation of electrons, is that of a point in space from which proceed $4\pi e$ lines of electric force. Every moving electron represents an electric current differing from the ion in electrolysis in not possessing a transport number. Under the influence of electric force these electrons vibrate about positions of rest and hand on as it were the charge from electron to electron by collision. The author finds it simpler not to consider that these particles possess ponderable mass, but that the apparent mass should be interpreted as self induction which would depend on their charge and spacial relation. Different classes of electrons are supposed to exist with different charges, but such that those of a higher class possess charges even multiples of those of the lower class. Positive and negative electrons exist and a double nucleus is a point in space from which $8\pi e$ lines are supposed to spring. With simple nuclei of the same sign the apparent mass may differ in different metals, since the extent of a nucleus that is the divergence or convergence of the electric lines would be influenced by the ponderable molecules. In a charge-free space if e_1 n_1 and e_2 n_2 etc. represent the charge and the number of nuclei per unit of vol for the different classes of electrons, then $e_1 n_1 + e_2 n_2 + \cdots = 0$. In the case this is not fulfilled, bound nuclei exist along with the free, these being supposed bound to the ponderable molecules. Cathode rays are a stream of free negative electrons, while canal rays of free and bound positive particles. The bound positive nucleus tears the molecule to which it is fastened and hence conveys with itself ponderable mass, moving thereby much more slowly than the free nuclei. Applying the kinetic theory of gases to the case of the moving electrons, the author considers besides the electrical conductivity the heat conductivity, and deduces the Wiedemann-Franz law and shows by reference to the recent observations of Jaeger and Diesselhorst that it is completely fulfilled on the assumption of the existence of simple nuclei.

The Thomson effect, contact potential, thermoelectricity and the Peltier effect are all explained in the light of the present theory, which, taken together with the explanation offered of the optical properties of metals, gives exceedingly strong evidence in favor of the existence of these particles, which must be at the same time considered very much smaller than the atom. *H. T. B.*

The conductivity produced in gases by the motion of negatively charged ions. *J. S. Townsend. Phil. Mag.* [*6*] 1, *198* (*1901*). — It was shown elsewhere by the author that negatively charged ions moving through a gas generate fresh ions. The relation between current and electromotive force, which is characterized at ordinary pressures by a maximum value of the current however the electromotive force may be increased, is found not to be so simple at low pressures. The author finds that there are three stages: the first where there is an increase in the value of the current with E. M. F.; the second where the current remains nearly constant, and third, where the current again increases with the

E. M. F. On reversing the E. M. F. a difference in conductivity was noticed depending on the character of the electrodes. It is shown that only negative ions produce fresh ones by collision, moving through the gas with very much greater velocity than the larger positive ions, and it is to the negative ions that the rapid increase in conductivity is due. If it is accepted, as is justified by previous work, that the negative ions are very much smaller than a molecule and that the positive ions are of molecular dimensions, then the author shows that the velocity of agitation of the negative ions is 80 times the velocity of agitation of the molecules of air and between two points differing in potential by four volts the velocity of these ions would be 800 times the velocity of agitation of the molecules of air.

Mathematical deductions from the author's experimental results lead to conclusions as to the number of ions which would be generated by a single ion moving through a gas, the mean free path and number of collisions compared with the same values for molecules of air.

In conclusion the author treats the results of Stoletow on the conductivity produced by ultraviolet light and shows that they may be explained in the light of the collision theory. *H. T. B.*

An investigation into the hypothesis of the electrolytic conductivity in Geissler tubes. *H. Morris-Airey. Drude's Ann.* 1, *466* (*1900*). — The work was undertaken to test the explanation, given by J. J. Thomson, for the phenomena in a hydrogen tube containing a small quantity of chlorine that the chlorine spectrum was apparent only at the electrode which was made the anode. A reversal of the current caused the chlorine to appear at the new anode. A specially constructed double tube was made and filled with hydrogen containing 7 % of chlorine. While the discharge was passing from one tube to the other, the connecting tube was fused off. Should Thomson's explanation be correct, that the appearance of chlorine was caused by a conveyance of the particles through the hydrogen to the anode, then the tube connected with the cathode before sealing should not show the presence of chlorine. On sending a discharge through this tube, however, the chlorine was visible at the new anode with the same intensity as was shown by passing the discharge through the other tube. No explanation is offered by the author. *H. T. B.*

On the electric conductivity of compressed powders. *F. Streintz. Drude's Ann.* 3, *1* (*1900*). — This is the first communication on the subject from the author, and deals with the conductivity of platinum black, amorphous carbon and graphite, the two former being in the form of powder or small particles compacted under pressure. The temperature coefficient of each material is determined, extending as low as — 78° C. The specific resistance of the platinum black is found to be 6 1/2 times as great as solid platinum, and to possess a temperature coefficient less than one-half. For amorphous carbon it is found that the resistance is very much higher than for graphite, and that the general character of the conductivity in the former resembles more that of an electrolyte, while that of the latter approaches more closely pure metallic conduction. The decrease in resistance of carbon with temperature is supposed to result from the material being converted from an allotropic modification at low temperatures to the pure metal at high temperatures, being there free from latent heat. The calorimetric bomb experiments of Berthelot and Petit show that the heat of combustion of amorphous carbon is greater than for graphite, and the conclusion is therefore reached that amorphous carbon is that allotropic form possessing greatest latent heat. *H. T. B.*

On the determination of the thermal conductivity in metals and the ratio to the electrical conductivity. *E. Grüneisen. Drude's Ann.* 3, *43* (*1900*). — The object of the present work is more especially to determine the effect of impurities on the thermal conductivity and ratio to the electrical conductivity. In addition the constants for the pure materials are also obtained. The method adopted is that of Schulze (3, 170). Copper, with a small and large trace of arsenic, and iron, with different amounts of impurities, are the materials most carefully studied. The effect of the impurities is more pronounced in decreasing the electrical than the heat conductivity, a strong analogy in the two cases is shown. *H. T. B.*

Permanent modifications in metallic wires and variations of electrical resistance. *H. Chevallier. Comptes rendus*, 130, *120*, *1612* (*1900*). — When a wire is subjected to oscillations of temperature, its resistance varies with the time, approaching a definite limit for each set of oscillations. The author has studied these hysteresis phenomena over a range of temperatures. The results all harmonize with the theory of Duhem. *W. D. B.*

Relation between the dissociation constant and the degree of dissociation of an electrolyte in presence of other electrolytes. *Y. Osaka. Zeit. phys. Chem.* 36, *539* (*1901*). — "The degree of dissociation of a very weak electrolyte is equal to its dissociation constant divided by the total concentration of all anions or cations in the solution." *W. D. B.*

Amphoteric electrolytes and internal salts. *G. Bredig. Zeit. Elektrochemie*, 6, *33* (*1900*). — A preliminary account of Winkelblech's work (next review). *W. D. B.*

Amphoteric electrolytes and internal salts. *K. Winkelblech. Zeit. phys. Chem.* 36, *546* (*1901*). — Amphoteric electrolytes are substances which can act either as bases or as acids. If the basic and the acid parts neutralize each other to a certain extent, as in the amido acids, we have an internal salt. Only weak electrolytes can be amphoteric. The author has studied the sodium salts and the hydrochlorides of a number of amido acids, determining the hydrolysis by the conductivity method and also by the catalytic action on esters.

W. D. B.

Action of acids on carbonates of the alkaline earths in presence of alcohol. *C. Vallée. Comptes rendus*, 132, *677* (*1901*). — Even when a solution of sulphuric acid in alcohol is thoroughly shaken with an excess of calcium carbonate it takes three months before neutralization is complete. A solution of acetic acid in alcohol does react with calcium carbonate though the reaction is so small that one might easily overlook the change. *W. D. B.*

Dielectricity and Optics

The dielectric constant of hydrogen peroxide. *H. T. Calvert. Drude's Ann.* 1, *483* (*1900*). — It was found by Drude's method that hydrogen peroxide has a slightly larger dielectric constant than water. The constant, which the author considers to be about 1 percent too small, is 84.7. *H. T. B.*

On hysteresis and viscosity in dielectrics. *F. Beaulard. Comptes rendus*, 130, *1183* (*1900*). — The author's experiments confirm the view of Steinmetz and others that we have to deal with viscosity but not with hysteresis in dielectrics. *W. D. B.*

Refractive indices for normal salt solutions. *C. Bender. Drude's Ann.* 2, *186* (*1900*). — The refractive indices for KCl solutions from 0.5 to 3 gram equivalents per liter of solution are determined over a range of temperature from 10° to 70° C. Formulas for the three hydrogen lines are given similar to those for pure water (4, 64, 421). The molecular refraction at first increases and then decreases with the concentration, the results show also that temperature has little influence. *H. T. B.*

Note on the radiation from black bodies between 0° and 100° C. *O. Lummer and E. Pringsheim. Drude's Ann.* 3, *159* (*1900*). — The first results of the authors, reduced on the early temperature scale for the thermo-couple given by Holborn and Wien, show a slight variation from Stefan's law, but, reduced according to the scale given by Holborn and Day, the discrepancies disappear. Thus the truth of Stefan's law is verified. *H. T. B.*

On the action of ultraviolet light on gaseous bodies. *P. Lenard. Drude's Ann.* 1, *486* (*1900*). — The author points out that cathode rays were the first example of rays producing an electrical action on gases. The present paper is an experimental investigation into the similar action of various other sources of rays, including ultraviolet light. The whole question, as the author suggests, is one of very great interest in connection with the production of atmospheric electricity. *H. T. B.*

On the constitution of the yellow sodium rays. *C. Fabry and A. Pérot. Comptes rendus*, 130, *653* (*1900*). — It is found that the apparent doubling of the sodium D_1 and D_2 lines is due to a reversal owing to increased absorption by the vapor. *W. D. B.*

On the influence of heat on the electric glow of a gas at low pressures. *J. Stark. Drude's Ann.* 1, *424* (*1900*). — In view of a series of data as to the temperature of a glowing gas and the effect of a white hot body in diminishing the glow in its immediate neighborhood, the conclusion is arrived at that the electric discharge through a heated gas is dark. The high temperature causes, the author considers, a dissociation in the gas, which causes it to lose its power of glowing or phosphorescing. *H. T. B.*

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ON THE FIRST PLAIT IN VAN DER WAALS'S FREE ENERGY SURFACE FOR MIXTURES OF TWO SUBSTANCES[1]

BY CH. M. A. HARTMAN

(Physical Laboratory, Leiden)

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[1] The present paper is a translation of my dissertation for the doctorate (Leiden, June, 1899), to which are added data that have since come to my knowledge.

INTRODUCTION

The number of observations with reference to mixtures of liquids and gases has greatly increased in recent years: among the most important may be counted those which are directed toward the testing and further elucidation of van der Waals's theory of binary mixtures.

These have proved conclusively that the theory is adapted to explain in a simple manner the peculiarities of those mixtures of normal substances which have been investigated. The critical phenomena of mixtures have been examined, particularly by Kuenen, who has observed in this connection peculiarities of behavior which could be in every respect foreseen by means of the theory.

Being occupied with experiments designed to fill gaps in existing experimental material, Professor Kamerlingh Onnes induced me to arrange according to van der Waals's theory all the experiments which may be brought into relation with the first plait of the Ψ-surface. This compilation is given in Part III. of the present paper. In Part I. a review is given of *one* part of the theory of van der Waals, namely, that relating to the first plait, and in Part II. some special questions are considered. The systematic application which I have made in Part I. of the graphical conceptions consequent upon van der Waals's theory, to all the observations obtainable for the region selected, may, I hope, help to place in a clear light the significance of this theory in the study of mixtures.

PART I. THE Ψ-SURFACE AND THE CONCEPTIONS DERIVED THEREFROM

Chapter A.—The Ψ-surface

§ 1. The questions with which we shall be occupied, of equilibrium of phases in the case of mixtures of two substances, have been solved by van der Waals, by help of the Ψ-surface, in his "*Theorie moléculaire d'une substance composée de deux matières différentes*".[1]

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[1] Arch. Néerl. 24, 1-56; Ztschr. phys. Chem. 5, 133 (1900). This theory has been since further developed in his standard work: "*Die Continuität des Gasförmigen und flüssigen Zustandes*, 2te Theil: *Binäre Gemische*, Leipzig, 1900. Reference will usually be made to the original papers.

This surface is obtained for a definite temperature T, by plotting in a system of rectangular coordinates the free energy Ψ as a function of the molecular composition x and the volume V. This has been done by means of plaster models for mixtures of methyl chloride and carbon dioxide at 100° by Kamerlingh Onnes,[1] and at 9.5° by myself.[2] Ψ and V here refer to a mixture consisting of $1-x$ gram-molecules of the first and x of the second constituent.[3] This quantity is called a gram-molecnle of the mixture and V its molecular volume.

What phases can exist under a definite pressure P, apart from the question whether or no they are in stable equilibrium, is shown by the *pressure lines* (lines of equal pressure) on the surface. These lines are the loci of the points where the inclination of the intersections of the tangential plane with the VΨ-plane is the same with reference to the V-axis.

Whether a homogeneous mixture of a definite composition and volume can exist in a stable state will be determined by the answer to the question, whether the Ψ-surface, which, in general, is convex towards the x,V-plane, is so in the neighborhood of the point that represents the condition of the mixture.

If the Ψ-surface represents stable as well as labile states of equilibrium, these latter will be enclosed by the *spinodal line* on the Ψ-surface, which separates the concavo-convex parts from those that are concave in all directions. This line may consist of more than one branch. If so, a plait exists on the surface.[4]

Whether under a definite pressure P two phases can exist in stable equilibrium with each other, depends upon whether a tangential plane in moving along a pressure line touches

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[1] Zittingsversl. Kon. Akad. Amsterdam, June, 1900, p. 199; Proc. id. 3, 275; Comm. Phys. Lab., Leiden, No. 59*a*. Here elaborate drawings are given of sections of the surface by planes $v =$ constant (Plate II., Fig. 1) and by planes $x =$ constant (Fig. 2).

[2] Arch. Néerl. (2) 5, (Livre Jubilaire dédié à H. A. Lorentz) 636 (1900); Comm. Leiden, No. 64.

[3] Arch. Néerl. 24, 8.

[4] Van der Waals: l. c. 13 and 16.

the Ψ-surface in two separate points.[1] These two points of contact represent two coexisting stable states of equilibrium; and a point on the *tangent chord* which joins these two points represents a complex of both phases.

The locus of these points of contact is the *connodal line*, which lies outside the spinodal line; like the latter it can consist of more than one branch, and in general cuts the pressure-lines. The portions of the pressure lines between the points of intersection of these with the connodal and spinodal lines belong to metastable states.

§ 2. A conception of the plait is obtained by projecting the above-mentioned lines upon the x,V-plane. The accompanying diagram (Fig. 1) represents the case in which the plait has, in general, a direction parallel to the x-axis and is extended over the whole breadth of the Ψ-surface. a and a' then represent the projections of the liquid and vapor branches of the connodal line, ϕ and ϕ' in the same manner those of the spinodal line, π that of the pressure line for the two-phase pressure P, and HH′ that of the tangent-chord for the two phases H and H′ which coexist at this pressure. The projection of this tangent chord has, in general, in addition to its end-points, one other point in common with that of the pressure-line. In what follows, we shall refer to the projections of all these lines on the x,V-surface simply as pressure-line, tangent chord, etc.[2]

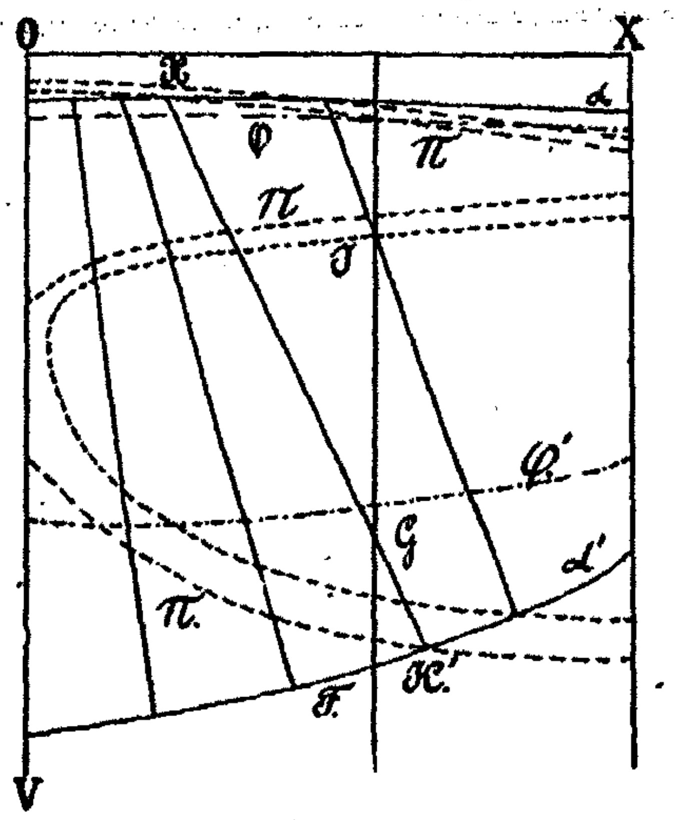

Fig. 1

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[1] The method of finding these points graphically is given by Kamerlingh Onnes, l. c.

[2] Comp. van der Waals. l. c. p. 55.

With the help of the pressure-lines in the labile region we can read off what pressure p must exist for a given mixture $x = x_1$ at any volume V in order that the mixture may remain constantly homogeneous. So we can construct in the usual V,p-diagram a *theoretical* isotherm for the homogeneous mixture. Likewise for the same mixture we can, by means of the tangent chord, read off what two-phase pressure P corresponds to the complex into which the mixture separates on compression to a definite volume V. In the same diagram, we can also construct an *experimental* isotherm. These two isotherms intersect one another in this diagram at least once. This happens at the volume where in the diagram (Fig. 1) the projections of a pressure line and the corresponding tangent chord cut one another in the line $x = x_1$ (Point J).

By arranging the isotherms for $x =$ constant according to the parameter T, or for a given value of T according to x as parameter, we obtain the infinite diagram (Fig. 2) or the finite diagram (Fig. 3).[1]

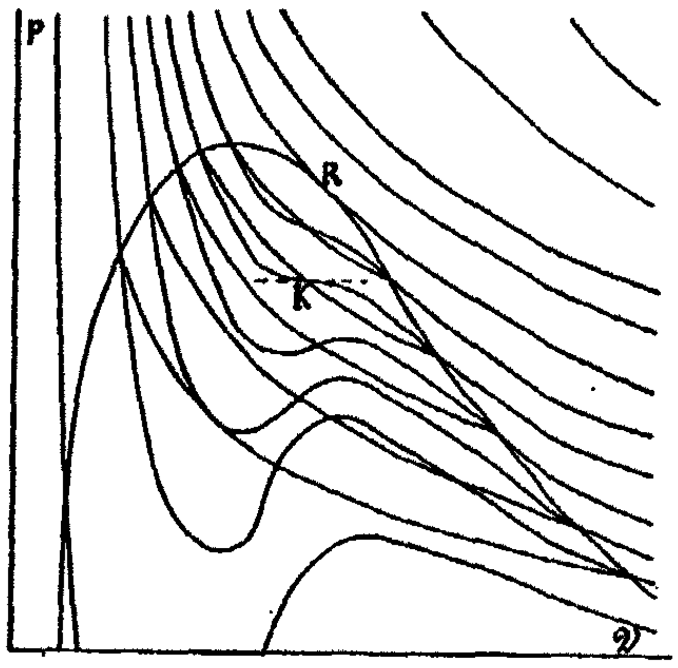

Fig. 2

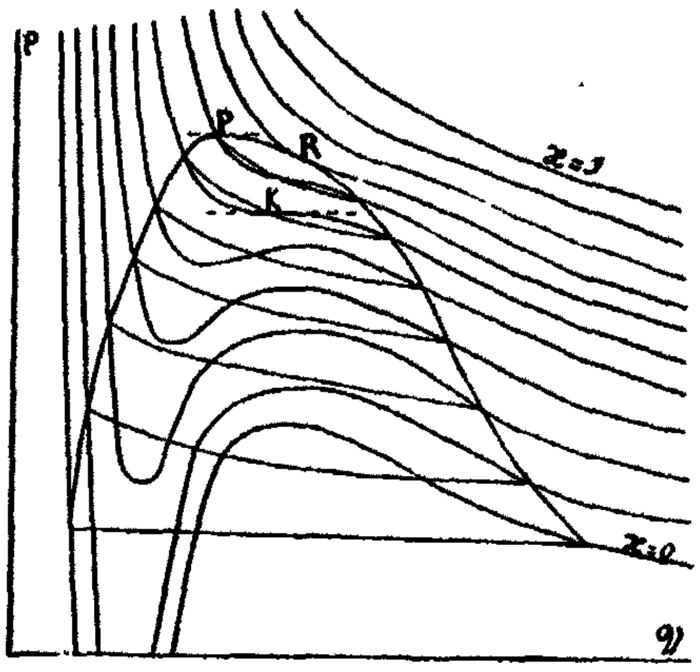

Fig. 3

If a gram-molecule of the mixture is compressed to the volume represented by F′ (Fig. 1), a liquid phase begins to separate. If the compression is continued to the volume represented by G the mass under consideration separates into two phases, H and

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[1] Compare last note, § 5 and § 20*b*.

H′, such that the molecular quantities in H and H′ are inversely proportional to the parts into which G divides the tangent-chord.[1]

The pressure which this complex then exerts will not however be represented by the pressure-line passing through G, but by that on which the points H and H′ lie. On compression the molecular quantity of the liquid will then steadily increase. This sequence can be called normal condensation.

§ 3. In this example, we consider the case of two coexisting phases. Whether three phases can likewise exist in equilibrium with one another depends on whether the tangent-plane touches the Ψ-surface in three points.

These three points represent in that case the three coexisting phases; a point within the plane triangle formed by the three points represents a complex of these three phases.

We shall not consider the case where a solid phase appears.

Of the three phases mentioned, one, the vapor, is situated on the side of greater volume; while the two coexisting liquid phases on the side of smaller volume show that in addition to the transverse plait a longitudinal plait exists.

In this review, we shall not consider the longitudinal plait any further, but only the transverse plait;[2] and here the liquid phase will be represented by x and V, the vapor phase by x' and V′.

§ 4. When the temperature rises, the region of labile equilibrium contracts, so that the projection of the connodal line on the x,V-plane disappears. Thus α and α' in Fig. 1 of Plates I., II., and III. represent both branches of the connodal line at a temperature far below the critical temperature of the components, β and β' at a temperature but little below this, while γ represents the connodal line where the transverse plait no longer extends over the whole breadth.

In this case the connodal line is continuous and is touched

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[1] Van der Waals. l. c. p. 26.

[2] Van der Waals has stated that a longitudinal plait will probably not occur with mixtures of normal substances. Zittingsversl. Kon. Akad. Amsterdam, March, 1899, p. 464; Proc. idem. 1, 385.

by a pressure-line (See Plate I., Fig. 5) in such a manner that both are curved toward the same side;[1] the common tangent is here in general not parallel to the v,Ψ-plane.

This point of contact is the *plait point* P (See also Fig. 3) at which the two coexisting phases are identical.

Of special importance, moreover, is the point of contact R (See Figs. 2 and 3) of the connodal line, with a plane parallel to the v,Ψ-plane. The separation into two phases no longer takes place for a mixture of higher concentration than corresponds to this point, while at lower concentrations separation occurs.[2]

This point is the critical point of contact.[3] The transition from the lines β to γ forms the plait for the critical temperature of the second component. Then the connodal line touches the plane $x = 1$, and critical point of contact and plait point coincide with the critical point for the pure substance.[4] The locus of the plait points for rising temperature is given in projection by the line δ, that of the points of contact by the line λ (Fig. 1 of Plates I., II., and III.).

§ 5. At the temperature to which γ refers (Fig. 5, Plate I.) if a mixture is compressed, the composition of which lies between the concentrations corresponding to the plait point P and the critical point of contact R, then the condensation is no longer normal.

If the plait point lies on the side of smaller volume, then on continuing the condensation after the pressure of the critical point of contact is reached, the quantity of the phase with smaller molecular volume diminishes and simultaneously the concentrations of both phases approach each other. The phase

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[1] See in this connection Korteweg, "Ueber Faltenpunkte." Wiener Sitzungsber, 98, 1154; Arch Néerl. 24, 57 and 295.

[2] Van der Waals. l. c. p. 56. Long before this van der Waals had indicated how this point can be found in the isothermal diagram. (See Continuität, Roth. 1881, p. 145, note). This is represented in Fig. 2, Point R.

[3] See Kuenen. Zittingsversl. Kon. Akad. Amsterdam, 25 June, 1892, p. 15; Comm. Phys. Lab., Leiden, No. 4, p. 9.

[4] In opposition hereto is the incorrect conception formed by Blümcke (Ztschr. phys. Chem. 8, 554, (1890)), according to which the projection of this line consists of two portions intersecting on the V-axis.

with greater molecular volume has then acquired completely the character of a liquid, and in the end is alone left. This is called by Kuenen *retrograde condensation of the first kind.*[1]

If, however, the plait point lies on the side of greater volume, then on condensation a phase with greater molecular volume is at first formed, and afterwards diminishes and disappears. The original vapor-phase then takes on imperceptibly the character of a liquid. This is *retrograde condensation of the second kind* (Kuenen).

In order to understand the course of the pressure line in the region of retrograde condensation near the plait point, it is important to notice that the pressure line which passes through the critical point of contact touches the tangent chord, as will be more fully discussed in §§ 20 and 20*a*. (See Fig. 5, Plate I.)

The point K[2] where, at the point of inflection of the pressure line in the x,V-plane, the tangent is at the same time parallel to the V axis, also deserves mention. This point represents the composition of a mixture which, while remaining homogeneous, just exists in the critical state, at the volume represented by K and at the temperature considered. (See also Figs. 2 and 3.)

§ 6. The sense in which the two-phase pressure changes with the composition at constant temperature, is determined by the course of the pressure lines and of the connodal line on the Ψ-surface, with which the mutual position of the tangent chords is connected. Here the connection may be noticed, that in each point of the connodal line the tangent chord and the labile portion of the pressure line always lie on the same side of the plane $x = x_r$.

In the case of normal condensation, since the concentration of the second substance in the vapor phase (x') is greater than in the liquid phase (x), the two-phase pressure increases with

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[1] Zittingsversl. Kon. Akad. Amsterdam, June 25, 1892; Comm. Phys. Lab. Leiden, No. 4, p. 8.

[2] It is quite accidental that point K in this figure coincides with the point of intersection of the tangent chord and pressure line and in Figs. 2 and 3 with that of the experimental and theoretical isotherms.

this concentration. The same holds for the concentrations of the other component.[1] (See Fig. 1.)

In retrograde condensation of the first kind, on the other hand, the two-phase pressure diminishes with increase of the concentration of the second substance in the phase with greater molecular volume, if this concentration is greater than that in the phase with smaller molecular volume (See Fig. 5, Plate I.); and similarly in retrograde condensation of the second kind, the pressure diminishes with the increase of the concentration of the second substance in the last-mentioned phase, if this concentration is smaller than that in the former phase. The figure here is quite analogous to the last-mentioned figure.[2]

§ 7. If the special case occurs that a tangent chord is parallel to the v,Ψ-plane (Fig. 5, Plate II.), then the two-phase pressure for the mixture to which this tangent chord refers has a maximum or minimum value, compared with the value of this pressure for neighboring mixtures. The figure gives a diagrammatic representation of the course of the pressure lines on the Ψ-surface in this case.

The fan-shaped arrangement of the other tangent chords is then approximately symmetrical with reference to this chord.

If they approach one another on the side of greater volume then the mixture so represented shows a maximum vapor-pressure. If they approach one another on the side of the liquid phase the vapor-pressure has a minimum value.

In the case of the maximum (or minimum) mixture the connodal line touches the pressure line both in the liquid and in the vapor phase. (Point E and E').

This leads us to classify the fluid pairs[3] into types[4] according as the vapor-pressure in the neighborhood of the critical

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[1] This property was derived as early as 1881 by Konowalow. Wied. Ann. 14, 48.

[2] This departure from Konowalow's law has been pointed out by van der Waals (See Kuenen, Arch. Néerl. 26, 379, note).

[3] By "fluid pair" we mean the system of all possible mixtures of any two given fluids.

[4] Konowalow. l. c. p. 49.

state changes, with increasing concentration of one of the components at constant temperature, in one and the same sense (first type, Plate I.), or reaches a maximum value (second type, Plate II.), or a minimum value (third type, Plate II.).

If the temperature is reduced from the critical temperature, the composition of this maximum (or minimum) mixture generally changes. It can even happen that the fluid pairs show a maximum or minimum pressure at a lower temperature though they do not possess this property at the critical state. The relation between this composition and the volume of the vapor and liquid phases at different temperatures is represented by the line ϵ (Fig. 1, Plate III.). In Fig. 1, Plate II., the line ϵ coincides with the line parallel to the V-axis and thus with the maximum tangent chord.

§ 8. Fluid pairs possessing a maximum mixture never show a maximum, but usually a minimum, critical temperature.[1] At this temperature the plait separates into two and the connodal line is composed of two intersecting curves.[2] (The point of intersection is denoted by A in Fig. 1, Plate II.). For the mixture to which the point of intersection belongs, the temperature of the plait point and that of the critical point of contact coincide.

At higher temperatures, the plait for this type consists of two parts; the one represents retrograde condensation of the first kind, the other, to which the maximum mixture belongs, that of the second kind.

If in this type the tangent to the connodal line at the plait point is parallel to the v,Ψ-plane (line γ_0 and point B, Fig. 1, Plate II.) then no retrograde condensation takes place at the temperature under consideration. For the mixture to which this plait point then refers, the plait point temperature is then likewise the temperature of the critical point of contact. In this plait point the connodal line γ_0, the pressure line π, and the line ϵ touch one another. (Comp. the close of § 7).

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[1] Van der Waals. Zittingsversl. Kon. Akad. Amsterdam, May and June, 1895, pp. 20 and 82; Arch. Neérl. 30, 266 and 278.

[2] Van der Waals. See Kuenen, Comm. Leiden, No. 16, p. 24.

At still higher temperatures, both portions of the plait represent only retrograde condensation of the first kind.

§ 9. For fluid pairs with a mixture of minimum pressure, on the other hand, critical temperatures higher than those of both components usually occur.

Then the connodal lines are closed curves with two plait points (line γ, Fig. 1, Plate III.). The other characteristics in the neighborhood of the plait point, are entirely analogous to those of the former type. (Comp. above for line γ_0.)

At the maximum critical temperature the whole plait contracts to one point, A.

§ 10. In the case of fluid pairs of the second and third types, the point K (Comp. the end of § 5) is very near to the points P and R; and for the maximum and minimum mixtures all three coincide.

Chapter B.—The x,T,P-surface

§ 11. If the Ψ-surfaces and the pressure lines and connodal lines thereon, are known for all temperatures, then, with the help of the data which they represent, the connection between concentration, temperature, and pressure for coexisting phases can be represented graphically in rectangular coordinates by the x,T,P-surface.[1] This surface consists of two connected sheets lying the one above the other. They are bounded on both sides by the vapor-pressure lines of the pure components.

The surface has to a certain extent the form of a flat cushion extended towards the side of the X-axis.

The distance between the two sheets determines the increase of pressure the mixture will show on condensation, or — what is almost the same thing — the elevation of boiling-point on evaporation.

To the important and oft considered question whether and under what circumstances separation of two substances by fractional distillation is more or less easily attained, the theory of

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[1] Comp. Kuenen. Phil. Mag. [5] 40, 190 (1895); Comm. Leiden, No. 16, p. 26; Zeit. phys. Chem. 24, 689 (1897).

van der Waals gives a very simple answer. If the distance between the two sheets is great, then separation of two components by fractional distillation can be readily effected.

The coexisting phases reappear on this surface in the two points of intersection with a line parallel to the x-axis. Points on this line between the points of intersection then represent complexes of both phases. Similarly, points outside the x,T,P-surface in the space between the surfaces $x = 0$ and $x = 1$ represent homogeneous gas or liquid phases. The plait point curve moreover, which we shall hereafter call line d, is the line on this surface joining the plait points; in these points the tangent plane is parallel to the x-axis.

Similarly the critical points of contact are connected by the *critical contact point curve* l;[1] in its points the tangent plane is parallel to the P-axis.

For maximum and minimum mixtures, which condense or evaporate under constant pressure, the two sheets touch each other. The locus of these points of contact on the surface is formed by the *maximum* (or *minimum*) *curve*, line e. The tangent plane to the surface is, in these points, parallel to the x-axis.

We obtain a conception of the nature of this surface by the projections of the lines d, l, and e on the planes of the coordinates, and by sections of the surface perpendicular to the axes.

We shall in these projections represent points that are similar for different types by the same letters.

§ 12. While in the T,P-diagram (Fig. 3, Plates I., II., and III.) the connection between T and P for pure substances was represented by the lines f_1 and f_2 convex towards the T-axis and ending in the critical point, in the case of mixtures loop-shaped border curves f occur.

The point R farthest to the right on the border curve gives the temperature of the critical point of contact of the mixture.

Another particular point on the border curve is the highest

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[1] The significance of these lines was first pointed out by Kuenen. Zittingsversl. Kon. Akad. Amsterdam, June 25, 1892.

point M, representing the two-phase pressure, which we shall call the maximum coexistent pressure, i. e., the greatest pressure under which a given mixture exists in equilibrium with another.

On the x,T,P-surface the points M reappear in the points where the tangent plane is parallel to the T-axis (line m).

The intersection of two border curves shows under what circumstances two mixtures of given composition can coexist.[1]

The intersection of two border curves differing infinitely little in composition is the plait point.

The border curves f are therefore enveloped by the plait point curve d_x. The form of this line depends upon the type of the fluid pair; moreover the position of the plait point on the border curve and on the plait point curve depends upon the composition.

In general, the border curves lie between the two vapor-pressure curves. For fluid pairs, with mixtures of maximum or minimum pressure, some of the border curves lie above or below these. If the composition of these mixtures of maximum or minimum pressure changes with the temperature, then the mutual tangency of the vapor and liquid branches of the same border curve shows under what circumstance a liquid and a vapor-phase of the same composition are in equilibrium. The locus of these tangent points is the line e_x (Fig. 3, Plates II., and III.).

At the minimum (or maximum) critical temperature the lines d_x and l_x touch each other. (See detail drawing in Fig. 3, Plate II.).

For the mixture which at its critical point is also a maximum (or minimum) mixture, the border curve ends in a cusp B. Here the vapor and liquid branches touch each other and also the lines d_x, l_x, m_x and e_x. (See detail drawing in Fig. 3, Plate II.).

If the maximum (or minimum) pressure always corresponds to the same composition, then the course of the condensation for

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[1] The intersection of three border curves in one point does not occur in the cases we are considering, in which only a transverse plait is present on the ψ-surface.

this mixture is determined graphically by a simple vapor-pressure curve, which then coincides entirely with l_x.

§ 13. In the x,P-diagram (Fig. 2, Plates I., II., and III.) the connection between the composition of the liquid and vapor-phases and the two-phase pressure, in other words, between the composition and the evaporation pressure P and the condensation pressure P′, is represented graphically at constant temperature.

For a temperature below the critical temperature of the mixtures considered, the lines a and a' are the liquid and vapor branches corresponding to one another, and similarly the lines b and b'. These are quite distinct and intersect only in their terminal points; if the plait of the Ψ-surface possesses the peculiarity of a tangent chord parallel to the v,Ψ-plane, then they also possess a common highest or lowest point. (Point E, Fig. 2, Plates II., and III.)

If there is a temperature at which the plait divides, then the x,P-curve consists at the minimum critical temperature of two branches intersecting in the point A. (Line b_0, detail drawing in Fig. 2, Plate II.). If at higher temperatures the plait does not extend over the whole breadth, then the x,P-curve has the form of a loop (line c, Fig. 2, Plates I., II. and III.).

The plait-point then reappears in the highest or lowest point of this loop, according to whether we are dealing with retrograde condensation of the first or of the second kind; the critical point of contact, likewise, reappears in the point farthest to the right or left.

Through these points passes the plait point line d_T (Fig. 2, Plates I., II., and III.), and similarly, the critical contact point curve l_T (Fig. 2, Plate I.).

At the critical temperature of the mixture of maximum (or minimum) pressure, the loop ends in a *cusp* (line c_0, Fig. 2, Plates II., and III.). The line e_T, the locus of the highest point E, also ends in this point B.

The loops are enveloped by the curve of maximum co-existent pressure, that is, the locus of the points M (line m_x),[1]

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[1] This has probably been overlooked by Kuenen (Zeit. phys. Chem, 24, 690), where he says: "This point M has no simple geometrical significance in the x,P-diagram." On the contrary, the point M plays the same part therein as the plait point in the T,P-diagram.

(this line is, in Fig. 2 of Plates I., II., and III., not distinguished from the line *d*. Compare the detail drawing in Fig. 2, Plate II.).

§ 14. Entirely analogous considerations hold for the x,T-diagram (Fig. 4, Plates I., II., and III.), in which is represented the dependence of the boiling-point T and condensation temperature T′ under constant pressure upon the composition.

If the plait extends over the whole breadth, this relation is determined by the two lines *g* and *g*′, and for higher pressures by *h* and *h*′ (Fig. 4, Plates II. and III.), the first, the liquid branch, being nearest to the x-axis.[1]

Since the mixture with the maximum (or minimum) vapor-pressure is likewise that of minimum (or maximum) boiling-point, the two branches will in this case touch at the vertex, that is in the point E nearest to the x-axis (Fig. 4, Plate II.) or furthest therefrom (Fig. 4, Plate III.).

For pressures greater than the critical pressure of one of the components, the x,T-curve is a loop, at the apex of which the plait point is situated.

For liquid pairs of the first type this loop is at high pressures a closed curve with two plait points including neither of the pure components (line *k*, Fig. 4, Plate I.); for those of the second and third types on the other hand the loop usually extends to one of the components (line *k*, Fig. 4, Plates II. and III.). The plait point curve d_P in this diagram passes through the tops of the loops *k* (Fig. 4, Plate I.). The curve in this diagram enveloping the loops is the projection of the critical contact point curve (line l_P, Fig. 4, Plates, I., II., and III.).

Part II.—Consideration of some special questions

§ 15. With the object of deducing relations between two-phase pressure, composition, and molecular volume, van der Waals expresses the conditions for the coexistence of two phases by means of the free energy Ψ, putting the quantities

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[1] Bancroft (The Phase Rule, p. 124) is wrong in considering that the line *g*′ may lie partly above and partly below the line *g*.

$$\left(\frac{\partial\Psi}{\partial V}\right)_x, \quad \left(\frac{\partial\Psi}{\partial x}\right)_V \text{ and } \Psi - V\left(\frac{\partial\Psi}{\partial V}\right)_x - x\left(\frac{\partial\Psi}{\partial x}\right)_V$$ [2]

equal in both phases, the temperature being taken as constant.

From this it follows that the increase of the two-phase pressure P with the composition of each of the phases must fulfil the following conditions:

$$\left.\begin{aligned} &\left\{\frac{V'-V}{x'-x} - \left(\frac{\partial V}{\partial x}\right)_P\right\} \cdot \frac{dP}{dx} = \frac{f(\Psi)}{\frac{\partial^2\Psi}{\partial V^2}} \\ &\text{and} \\ &\left\{\frac{V'-V}{x'-x} - \left(\frac{\partial V'}{\partial x'}\right)_P\right\} \cdot \frac{dP}{dx'} = \frac{f(\Psi)'}{\frac{\partial^2\Psi}{\partial V'^2}} \end{aligned}\right\} \cdots\cdots\cdots A^{[3]},$$

where x, V and Ψ refer to the liquid and x', V' and Ψ' to the vapor-phase, and

$$f(\Psi) = \frac{\partial^2\Psi}{\partial V^2} \cdot \frac{\partial^2\Psi}{\partial x^2} - \left(\frac{\partial_2\Psi}{\partial V . \partial x}\right)^2.$$

If we call the thermodynamic potential for the same molecular quantity ζ, then

$$\frac{f(\Psi)}{\frac{\partial^2\Psi}{\partial V^2}} = \left(\frac{\partial^2\zeta}{\partial x^2}\right)_p.$$

Every attempt to express analytically, with the aid of special assumptions, the relations between composition, volume, and two-phase pressure must be based on these equations of van der Waals, as indeed they have been repeatedly used by him to deduce various rules.

§ 16. By assuming that the two constituents in the vapor mixture obey the gas laws, the second equation A can be further developed.

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[1] Zittingsversl. Kon. Akad. Amsterdam, Feb. 23, 1889.

[2] Curves on the ψ-surface where these quantities are constant, are called by Kamerlingh Onnes *pressure curves*, *substitution curves* and *potential curves*. Comm. Leiden, No. 59*a*: § 5 and Plate II., Figs. 3 and 4.

[3] Arch. Néerl. 24, 15.

Then $\left(\frac{\partial V'}{\partial x'}\right)_p = 0$, while the value of the second term follows from

$$\Psi' = -MRT\log V' + MRT\,[(1-x')\log(1-x') + x'\log x'].$$

This last equation, if $\pi_1 = (1-x')P$ and $\pi_2 = x'P$ (π_1 and π_2 being the partial pressures of the constituents in the mixture), may also be written:

$$\zeta' = MRT[(1-x')\log\pi_1 + x'\log\pi_2] + MRT(1-\log MRT),$$

or

$$\zeta' = (1-x')\zeta_1'(\pi_1) + x'\zeta_2'(\pi_2),$$

or, expressed in words:

The thermodynamic potential of a perfect gaseous mixture in a given volume is equal to the sum of the potentials which the two constituents would have if each occupied the same volume.

From this form for ζ' follows

$$\frac{\partial^2\zeta'}{\partial x'^2} = \frac{MRT}{x'(1-x')} = \frac{PV'}{x'(1-x')}.$$

The first equation A thus becomes

$$\left(1-\frac{V}{V'}\right)\frac{1}{P}\,\frac{dP}{dx'} = \frac{x'-x}{x'(1-x')} \quad \ldots\ldots\ldots\ldots\ldots \text{B}'$$

This same relation, but simplified by neglecting the volume of the liquid in comparison with that of the vapor, has been again deduced by Lehfeldt,[2] and nearly at the same time by Margules.[3]

§ 17. Equation B contains only quantities which can be directly measured, and hence can be readily tested by experiment in all cases where the observations include both the lines a and a' in the x,P-diagram and a and a' in the x,V-diagram.

In particular, laws may be derived therefrom which hold for dilute solutions, since for small values of x and x' we may put

$$\frac{dP}{dx'} = \frac{P-P_1}{x'}.$$

---

[1] Compare Kohnstamm. Zeit. phys. Chem. 36, 49 (1901).

[2] Phil. Mag. [5] 40, 397 (1895).

[3] Wien. Sitz. Ber. Dec., 1895, p. 1243.

This has more recently been pointed out by Lehfeldt.[1]

Thus we get in the case where the solute is non-volatile the well known formula for the molecular diminution of vapor-pressure

$$\frac{P_1 - P}{P_1} = x,$$

which proof van der Waals has already pointed out.[2] Similarly there follows from B the formula given by Planck[3] for dilute solutions,

$$\frac{P - P_1}{P_1} = x' - x.$$

This formula, in which all quantities refer to the same temperature T, may be transformed into another, given by him, which connects the composition of both phases, the absolute boiling-points T and T_1 of the mixture and the solvent, and the heat of vaporization of the latter, all under the same pressure P.

From Clausius's formula

$$T\frac{dP}{dT} = \frac{Q}{V},$$

applied to the solvent, there follows:

$$P - P_1 = \frac{1}{T_1} \cdot \frac{Q_1}{V_1}(T_1 - T).$$

Inserting this value of $P - P_1$ in Planck's first formula and noting that PV_1' is equal to the absolute temperature T_1, there follows

$$x' - x = \frac{Q_1}{T_1^2}(T_1 - T).$$

For non-volatile dissolved substances, this gives the formula for the elevation of boiling-point.

Lastly, from equation B we may derive the formula given by Nernst,[4]

$$\frac{P_1 - \pi_1}{P_1} = x,$$

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[1] Phil. Mag. [5] 48, 215 (1899).

[2] l. c. p. 44.

[3] Zeit. phys. Chem. 2, 405 (1888).

[4] Zeit. phys. Chem. 8, 124 (1891).

in which $\pi_1 = (1 - x')P$ represents the partial pressure of the solvent in the vapor mixture. That this formula follows directly from van der Waals's equation B has been overlooked by Nernst. Clarence L. Speyers[1] has applied it incorrectly to solutions which are not dilute, in order to deduce the molecular weight of each component in the liquid state.

§ 18. In addition to equations A and B for the increase of the two-phase pressure, van der Waals[2] has derived an explicit formula for the two-phase pressure itself from thethree conditions of stable equilibrium; this is, however, to be regarded as an approximation. As before the vapor-phase is here assumed to obey the gas laws, and the temperature is always taken as constant.

In connection with the values which Ψ has in the gaseous state, van der Waals introduces the auxiliary function

$$\mu = \Psi + p.V - MRT[(1 - x)\log(1 - x) + x\log x],$$

and considers this as a function of x and p.

For the pure components, this μ is then equal to the thermodynamic potential; and in the gaseous state we then have

$$\mu' = MRT\log\frac{p}{MRT} + MRT, \text{ and } \left(\frac{\partial\mu'}{\partial x'}\right)_p = 0.$$

Introducing this, the conditions become

$$\frac{\partial\mu}{\partial x} + MRT\log\frac{x}{1-x} = MRT\log\frac{x'}{1-x'}$$

and

$$\mu - x\frac{\partial\mu}{\partial x} + MRT\log(1 - x) = MRT\log\frac{(1-x')P}{MRT} + MRT;$$

wherefore

$$(1 - x')P = \pi_1 = (1 - x)\cdot MRT\, e^{\frac{\mu - x\frac{\partial\mu}{\partial x}}{MRT} - 1},$$

and

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[1] Jour. Phys. Chem. 2, 347 (1898).

[2] Zittingsversl. Kon. Akad. Amsterdam, March, 1891, p. 409; Zeit. phys. Chem. 8, 188 (1891).

$$x'\mathrm{P} = \pi_2 = x \cdot \mathrm{MRT}\, e^{\frac{\mu + (1-x)\frac{\partial\mu}{\partial x}}{\mathrm{MRT}} - 1};$$

whence

$$\mathrm{P} = \mathrm{MRT}\left[(1-x)e^{\frac{\mu - x\frac{\partial\mu}{\partial x}}{\mathrm{MRT}} - 1} + x \cdot e^{\frac{\mu + (1-x)\frac{\partial\mu}{\partial x}}{\mathrm{MRT}} - 1}\right] \ldots\mathrm{C}.$$

Hence follows, for $x = 0$, and for $x = 1$,

$$\mathrm{P}_1 = \mathrm{MRT}\, e^{\frac{\mu_1}{\mathrm{MRT}} - 1} \quad \text{and} \quad \mathrm{P}_2 = \mathrm{MRT} \cdot e^{\frac{\mu_2}{\mathrm{MRT}} - 1},$$

in which μ_1 and μ_2 are equal to the values of the potentials, for the pure substances, respectively, at the two-phase pressures P_1 and P_2.

The form of P therefore becomes

$$\mathrm{P} = \mathrm{P}_1(1-x)\, e^{-\frac{1}{\mathrm{MRT}}\frac{x^2}{2}\frac{\partial^2\mu}{\partial x^2}\cdots} + \mathrm{P}_2 x\, e^{-\frac{1}{\mathrm{MRT}}\frac{(1-x)^2}{2}\frac{\partial^2\mu}{\partial x^2}\cdots} \cdot\mathrm{D},$$

since by approximation we may put

$$\frac{d\mu}{dx} = \frac{\partial\mu}{\partial x} \quad \text{and} \quad \frac{d^2\mu}{dx^2} = \frac{\partial^2\mu}{\partial x^2}.$$

The factor by which $\mathrm{P}_1(1-x)$ is completed, shows the alteration the vapor-pressure of the liquid undergoes when x molecules thereof are replaced by an equal number of another liquid.

In the adaptation of the formula for the solution of gases in liquids, P_1 may be neglected in comparison with P and x is small; thus we have

$$\frac{\mathrm{P}}{\mathrm{MRT}} = x \cdot e^{\frac{\mu + (1-x)\frac{\partial\mu}{\partial x}}{\mathrm{MRT}} - 1},$$

and, approximately, neglecting PV and $\frac{\partial \mathrm{V}}{\partial x}$ in comparison with MRT,

$$\frac{x}{\mathrm{P}} \cdot \frac{d\mathrm{P}}{dx} = 1 + \frac{x(1-x)}{\mathrm{MRT}} \cdot \frac{\partial^2\mu}{\partial x^2}.$$

According to Henry's law, $\frac{x}{P}\cdot\frac{dP}{dx}=1$; the variations from this law thus depend upon the magnitude of $\frac{\partial^2\mu}{\partial x^2}$.

Since $\frac{d^2P}{dx^2}$ and $\frac{\partial^2\mu}{\partial x^2}$ are of the same sign, the sign of $\frac{\partial^2\mu}{\partial x^2}$ determines whether the liquid branch in the x,P-diagram is concave or convex towards the x-axis.

§ 19. It should be possible to determine the two-phase pressure whenever, in equation B, x is known as function of x', and the volume of the liquid is neglected. A relation of purely empirical character which serves this purpose is proposed by Lehfeldt,[1] namely,

$$\frac{1-x'}{x'}=k'\cdot\left(\frac{1-x}{x}\right)^r,$$

in which k' and r are constants.

By the help of this relation equation B may be integrated; this gives for the pressure P the form

$$P=(1-x)^r\cdot P_1+x^rP_2,$$

and, furthermore,

$$k'=\frac{P_1}{P_2}.$$

A similar relation, but with $r=1$, had been previously put forward by Brown;[2] this would require the pressure to vary in direct proportion to the composition, which is not the case for most liquid pairs. If we put, with Lehfeldt, r smaller or greater than unity, then it follows from the relation obtained that the pressure should show a maximum or minimum value, which would exclude mixtures of the first type. The relation given certainly fulfils the conditions that x and x' assume the values 0 and 1 simultaneously, and that the character of the relation does not change when x and x' are replaced by $1-x$ and $1-x'$. It is, however, in view of the previous considerations, inadmissible.

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[1] Phil. Mag. [5] 40, 402 (1895).

[2] Jour. Chem. Soc. 35, 547 (1879).

Another empirical formula for the two-phase pressure has been proposed by Margules,[1] namely,

$$P = (1 - x)^{\alpha_0} \cdot P_1 \cdot e^{\alpha_1 x + \frac{1}{2}\alpha_2 x^2 + \cdots} + x^{\beta_0} \cdot P_2 \cdot e^{\beta_1(1-x) + \frac{1}{2}\beta_2(1-x)^2 + \cdots}$$

For normal substances then $\alpha_0 = \beta_0 = 1$ and $\alpha_1 = \beta_1 = 0$. This formula is applicable to all the three types of liquid pairs. It corresponds with van der Waals's formula D of § 18.

§ 20. From the equations A may moreover be derived certain properties already mentioned in Part I.

The equation holds at a given temperature only for the points of the Ψ-surface that lie upon the connodal line; therefore, the second term of this equation has usually a finite value which is either positive or zero. The latter is the case at the plait point, and hence, $\frac{dP}{dx} = 0$.

Moreover, both factors of the first term have the same sign, from which some conclusions may be drawn with regard to the mutual position at a point of the connodal curve, of the projections of the tangent chord and of the pressure line on the x,v-surface.

The inclination to the x-axis will be given for the tangent chord by the term $\frac{V' - V}{x' - x}$, for the pressure line by the term $\left(\frac{\partial V}{\partial x}\right)_p$.

For normal condensation, both inclinations having the same sign, the first is the greater. On the other hand, for retrograde condensation, both inclinations must have the same sign and the pressure line must be steeper than the tangent chord.

Thus at the critical point of contact, where $\frac{dP}{dx}$ is infinite, the projection of the tangent chord will touch the pressure line.[2]

Thus, too, for pressures between P_P and P_R the pressure lines in the labile region lie, in the projection, between the tan-

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[1] Wien. Sitz. Ber., Dec., 1895, p. 1266.

[2] Comp. van der Waals. Arch. Néerl. 24, p. 56.

gent chord and the connodal curve, so that the projections of tangent chord and pressure line for the same pressure between P_P and P_R cannot intersect.

For pressure slower than P_R, the tangent chord and pressure line will intersect in the projection only in one point S. The curve on which these points of intersection lie extends over the whole breadth of the plait and ends in the critical point of contact R.

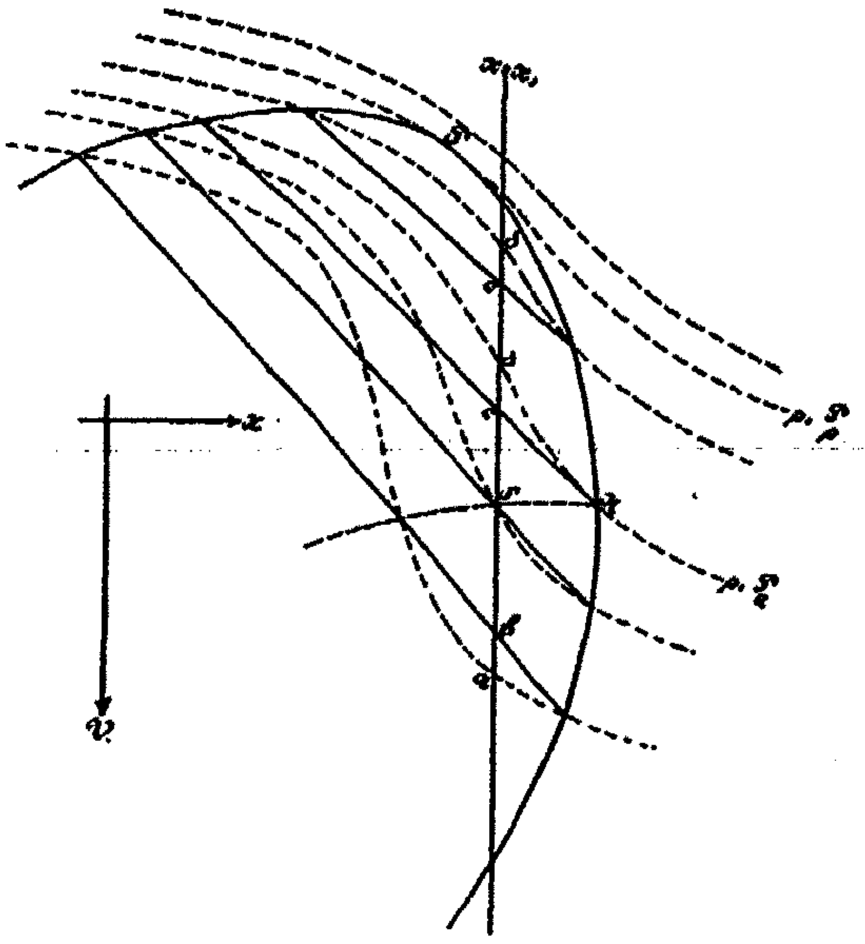

Fig. 4

§ 20(*a*).[1] From this it may be shown that Duhem[2] is incorrect in stating that the theoretical and experimental isotherms can intersect in two points.

For if we move along a line $x = x_1$ with diminishing volume, then the condensation phenomena may be ascertained from the accompanying Fig. 4.

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[1] §§ 20(*a*) and 20(*b*) are taken from a paper by the author, "On Condensation Phenomena of Mixtures near the Critical State." Zittingsversl. Kon. Akad. Amsterdam, May 26, 1900, p. 60; Comm. Phys. Lab., Leiden, No. 56.

[2] Procès-Verbaux des Séances de la Soc. des Sc. phys. et. nat. de Bordeaux, 1899.

At the beginning of the condensation, under a constant pressure, we shall first meet the pressure line at *a* and then the tangent chord at *b*; beyond S on the contrary, the tangent chord is first met at *c* and then the pressure line at *d*.

If now we transfer the connection between V and p to a V,p-diagram, then the point of intersection just mentioned, for all mixtures which show condensation, will reappear as the point of intersection of the experimental and theoretical isotherms, and will be the only point of intersection of these two curves. Likewise, at the beginning of condensation, the first-mentioned isotherm will always lie below the second, and, beyond the point of intersection, above it.

The method by which Duhem comes to his hypothesis is as follows: In the first place, he considers the way in which the total volume V_1 of a complex of two phases changes with the two-phase pressure P, the temperature remaining constant.

If the composition, molecular volume, and quantity of the first phase (liquid) are represented by x, V, and m, and similarly, those of the second phase (vapor) by x', V′, and $1-m$, and the mean composition of the complex by x_1, then

$$\left(\frac{\partial V_1}{\partial p}\right)_{x_1} = m\left\{\left(\frac{\partial V}{\partial p}\right)_x + \left(\frac{\partial V}{\partial x}\right)_p \cdot \frac{dx}{dP}\right\}$$

$$+ (1-m)\left\{\left(\frac{\partial V}{\partial p}\right)'_{x'} + \left(\frac{\partial V}{\partial x'}\right)'_p \cdot \frac{dx'}{dP}\right\} + (V-V')\frac{dm}{dP}\,.$$

Then Duhem considers the form this relation assumes at the plait point, where

$$x = x' = x_1,\ V = V',\ \left(\frac{\partial V}{\partial p}\right)_x = \left(\frac{\partial V}{\partial p}\right)_{x'} \text{ and } \left(\frac{\partial V}{\partial x}\right)_p = \left(\frac{\partial V'}{\partial x'}\right)_p.$$

Moreover he assumes that there $\frac{dx}{dp} = -\frac{dx'}{dP}$, and comes thus to the conclusion that

$$\left(\frac{\partial V_1}{\partial P}\right)_{x_1},\quad \left(\frac{\partial V}{\partial p}\right)_{x'},\ \text{ and }\ \left(\frac{\partial V'}{\partial p}\right)_{x'},$$

at the plait point are equal. However, he overlooks the fact that at the plait point $\frac{dx}{dP}$ is infinite, so that these quantities cannot be equal. Thus the experimental and theoretical isotherms in the V,p-diagram have not the same tangent at the plait point, as is incorrectly drawn by Duhem. His further conclusions thus fall to the ground.

§ 20(*b*). Professor van der Waals has kindly pointed out to me that the relative courses of the theoretical and experimental isotherms, and thus the incorrectness of Duhem's assertion, may be immediately deduced from the section of the Ψ-surface, and of the corresponding rule dsurface, by a plane x = const.

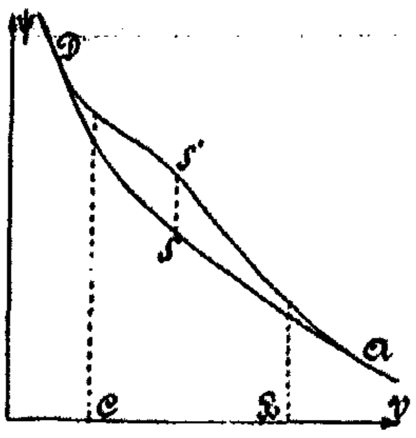

Fig. 5*a*

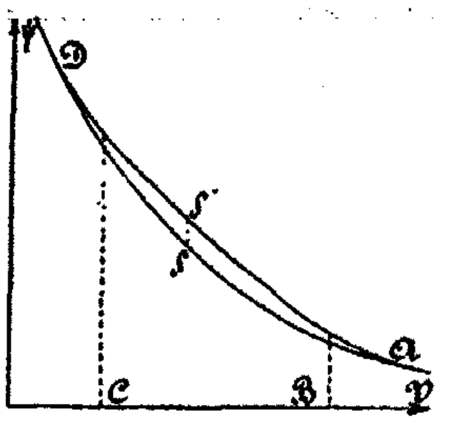

Fig. 5*b*

Professor van der Waals remarks in this connection:
1. That for a given composition the experimental Ψ-curve ASD must lie below the theoretical curve AS'D (See Fig. 5*a* and 5*b*) where Ψ is taken as ordinate and V as abscissa).[1]

2. That at the beginning and end of the condensation, at A and D respectively, the experimental and theoretical Ψ-curves have the same slope and touch each other in these points.

3. That therefore at a volume B, at the beginning of condensation, the slope of the theoretical Ψ-curve is greater than that of the experimental curve, or $P_{exp.} < P_{theor.}$.

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[1] Fig. 5*a* refers to the case where the critical temperature of the mixture which has not separated into two portions lies above the temperature for which the Ψ-surface is constructed, Fig. 5*b* for the case where the first temperature lies below the second. In other words Fig. 5*a* holds for values of x on the one side, and 5*b* on the other side, of a straight line passing through the point K. (Comp. end of § 5, and Fig. 5, Plate I.).

Equality of pressure for one and the same volume would be again attained where the tangents to the two Ψ-curves are parallel, that is, at the points S and S′ of the figures; while for a volume C, near the end of the condensation, the slope of the experimental Ψ-curve is greater than that of the theoretical curve, and thus $P_{exp.} > P_{theor.}$.

The points S and S′ correspond to the points of intersection of the two isotherms in the V,*p*-diagram (Figs. 6*a* and 6*b*), and to the point of intersection of the tangent chord and pressure line, in Fig. 4. Since no other cases are possible than Figs. 5*a* and 5*b*, only one such point exists.

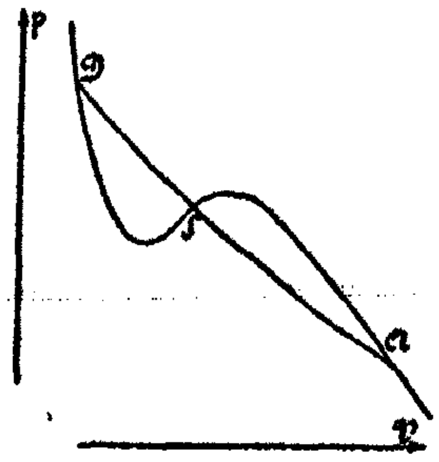

Fig. 6*a*

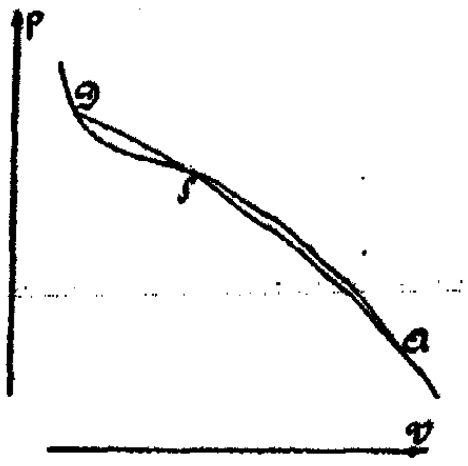

Fig. 6*b*

As for the course of condensation of mixtures, the following further statements may generally be made. In the V,*p*-diagram the experimental isotherm may be convex or concave toward the V-axis. The first is the case for a mixture that contains only a little of the more volatile component, as is the case in Verschaffelt's experiments.[1] (See Fig. 6*a*.) The second is the case for mixtures that consist chiefly of the more volatile substance; it occurs in Kuenen's experiments.[2] (See Fig. 6*b*.)

The experimental Ψ-curve will in the first case have its greatest curvature near the point D, and in the second case near A. (Comp. Fig. 5*a* with Fig. 6*a*, and Fig. 5*b* with Fig. 6*b*.)

§ 21. To derive numerical results from equation C of § 18,

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[1] Versl. Kon. Akad. Amsterdam, Dec. 24, 1898, p. 281; Proc. idem. Vol. I., p. 288; Comm. Phys. Lab., Leiden, No. 45.

[2] Proc. Roy. Soc., Edinb., 21, 433 (1897); Zeit. phys. Chem. 24, 672 (1897).

or from the equation derived therefrom, the exact form of the Ψ-surface must be known. Van der Waals, in his "*Theorie Moléculaire, etc.*," has proposed for p the form

$$p = \frac{\mathrm{MRT}}{\mathrm{V} - b_x} - \frac{a_x}{\mathrm{V}^2},$$

from which it follows that

$$\Psi = -\mathrm{MRT} \log (\mathrm{V} - b_x) - \frac{a_x}{\mathrm{V}} + \mathrm{MRT}\Big[(1 - x) \log (1 - x) + x \log x\Big].$$

For the quantity a_x, the molecular pressure in absolute measure, van der Waals obtains the form[1]

$$a_x = a_1(1 - x)^2 + 2a_{12}x(1 - x) + a_2x^2;$$

and a similar form, proposed by Lorentz,[2] is assumed by him for b_x.

The Ψ-surface for two known substances will thus be determined by a_{12} and b_{12}.

By means of these assumptions, van der Waals[3] derives by approximation, for example, the course of the plait point curve for mixtures of the second and third type, and the criterion for the occurrence of a minimum critical temperature.

Kamerlingh Onnes[4] has treated the problem of deducing values for a_{12} and b_{12} from isothermals for the gaseous state, in order to construct with these values Ψ-surfaces for lower temperatures, and to derive from the Ψ-surfaces obtained in this manner the equilibrium of liquid and vapor phases. Especially has he pointed out that the law of corresponding states can be applied to researches on the laws of mixtures. In subsequent papers, Kamerlingh Onnes and Reinganum,[5] Hartman,[6] and

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[1] l. c. p. 4.

[2] Wied. Ann. 12, 134 (1881).

[3] Zittingsversl. Kon. Akad. Amsterdam, Nov., 1897, p. 279; Arch. Néerl. (2) 2, p. 79. Comp. Note to § 8.

[4] Zittingsversl. Kon. Akad. Amsterdam, June, 1900, p. 199; Proc. idem. 3, 275; Comm. Leiden, No. 59*a*.

[5] Zittingsversl. Kon. Akad. Amsterdam, June, 1900, p. 213; Proc. idem. 3, 289; Comm. Leiden, No. 59*b*.

[6] Arch. Néerl. (2) 5, 636; Comm. Leiden, No. 64.

Verschaffelt[1] have applied these principles to mixtures of methyl chloride with carbon dioxide, and of carbon dioxide with hydrogen, and compared the calculated results with the observations.

In regard to the connection between the values of the constants a_{12} and b_{12}, with the values of a_1, a_2, b_1, and b_2, so far nothing certain is known. No answer can therefore be given to the questions as to which type a mixture of two given substances will belong, what influence the physical structure has, and whether fixed rules may here be laid down.

For substances the vapor-pressures of which are nearly equal at the same temperature, and hence the tangent chords are nearly parallel, it is indeed probable that the tangent chords somewhere in the middle of the Ψ-surface will belong to the second or third type; it is, however, *a priori* difficult to choose between the two types.

Lehfeldt,[2] without giving the grounds for the statement, has come to such an assumption. He has not, however, taken the possibility of the third type into consideration.

§ 22. Van der Waals's theory is developed for normal substances[3] which exert no chemical action upon each other. Different observers have made observations upon substances that depart more or less from this simple assumption.

Many of the phenomena they have observed can thus be referred to the association[4] or dissociation that already exists in the components, or to chemical interactions which occur on mixing.

Without doubt van der Waals's theory must undergo a revision and extension to include these cases. But it is certain that in their discussion of these cases, the observers have incorrectly laid too much stress upon this factor.

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[1] Arch. Néerl. (2) 5, 644; Comm. Leiden, No. 65.

[2] Phil. Mag. [5] 40, 408 (1895).

[3] The case of the association of a single substance is considered by van der Waals from the standpoint of his theory in § 14, of the "*Theorie Moléculaire.*"

[4] Experiments of Kuenen and Robson (Zeit. phys. Chem. 28, 342 (1899) have been interpreted in this way by van der Waals (Zittingsversl. Kon. Akad. Amsterdam, March, 1899, p. 464).

Thus Brown[1] attempted, without giving theoretical grounds, to predict that a minimum boiling-point will appear when one of the components contains a hydroxyl group, for example, water or one of the alcohols; and, similarly, Lehfeldt[2] predicted that the mixture would belong to the first type if both substances were normal.

They succeeded, however, neither in establishing rules nor in giving proofs; and it has obviously escaped Lehfeldt that the occurrence of a maximum pressure for mixtures of normal substances not only agrees with van der Waals's theory, but has also been proved experimentally by Kuenen.

Guthrie[3] has noticed that in fluid pairs of the second type mixing is generally associated with expansion and with absorption of heat. To explain this, he assumes that the composition which exists at maximum pressure belongs to a chemical 'anti-combination' or 'maximum effect of repulsion'; according to him these states are as numerous as ordinary combinations.

It is, however, possible, by means of the characteristics of the Ψ-surface alone, to explain the connection between the occurrence of a maximum pressure and an increase of volume on mixing.

For liquid pairs with a minimum critical temperature, the connodal line at this temperature consists of two intersecting branches (See § 8, p. 434); at a lower temperature it is to be expected that in the projection on the x,V-plane the liquid branch will be concave and the vapor branch convex toward the x-axis. The meaning of this is that in the first case expansion occurs on mixing, and in the second a maximum pressure exists.

This coexistence of minimum critical temperature and maximum pressure has been observed by Kuenen (See § 53) in the case of various mixtures, and has been explained by van der Waals (See pp. 434 and 451).

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[1] Jour. Chem. Soc. 39, 528 (1881).
[2] Phil. Mag. [5] p. 52, 1898.
[3] *Ibid.* [5] 18, 516 (1884).

Moreover, whenever increase of volume occurs on mixing gases at constant pressure, van der Waals[1] has pointed out that the quantity

$$A = \frac{a_1}{b_1^2} + \frac{a_2}{b_2^2} - \frac{2a_{12}}{b_1 b_2},$$

is positive, and similarly that whenever A is positive heat is absorbed by the mixture.[2]

Guthrie's assumption to explain the peculiarities of mixtures is thus superfluous. It has as a consequence that, in the new states, a simple relation must exist between the number of molecules of the two components; this is, however, contradicted by many investigations, in which the change of the composition of a maximum mixture with the pressure has been observed. (See Chapter 3, *c*.)

For fluid pairs of the first type, Guthrie[3] has observed that mixture is usually accompanied by contraction of the liquid and evolution of heat, particularly if, as in the case of chloroform-ether, the line *a* in the x,P-diagram is convex towards the x-axis (see Fig. 6, Plate I.).

This he ascribes to the formation of molecular compounds of the same nature as hydrates.

Here again, such a hypothesis is unnecessary. The contraction is to be explained by a great mutual attraction and the evolution of heat may be a necessary consequence of the contraction.

If one prefers to assume with Guthrie the existence of these molecular compounds, one has then to do with a mixture of three substances, of which one, the molecular compound, can be converted into either of the others and in the vapor is present probably only in very small amount.

The occurrence of a considerable increase of the vapor-density on mixing gives more ground than the phenomena

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[1] Zittingsversl. Kon. Akad Amsterdam, 26, 239 (1898). Proc. idem. I. p. 179.

[2] Arch. Néerl. 24, 52.

[3] l. c. p. 506.

already discussed for the supposition that chemical action plays a part in these phenomena.

Thus, there is much to say for the assumption of Friedel[1] that in the mixture of hydrochloric acid and methyl ether the liquid phase consists of a molecular compound, in which the gaseous components are dissolved. This hypothesis is based principally on the observation that the vapor-density of the mixture is considerably greater than corresponds to that of the components.

PART III. REVIEW OF THE INVESTIGATIONS REFERRING TO BINARY MIXTURES

§ 23. In this review shall be considered the accessible observations that relate to each of the curves of the figures examined in Part I. All fluid pairs will be discussed under type one, excepting those which can be definitely placed in types two or three. Plate I. refers to the first, Plate II. to the second, and Plate III. to the third type.

Although van der Waals's theory applies only to normal substances, I have in this review not wholly excluded fluid pairs in which one of the components shows association or dissociation. Often these deviations have little influence upon the character of the phenomena.

As far as possible, all the observations are included in the drawings. However, the range of temperature and pressure values is so great that not all the curves can be included in the same diagram on the same scale. To avoid this difficulty, the lines for a number of fluid pairs have been represented either by the side of the principal figure or upon an obviously different scale. The full lines represent observations plotted to scale; the dotted lines diagrammatically complete the observations.[2]

The methods of observation adopted are considered in a preliminary chapter, and a bibliography is added at the close

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[1] Comptes rendus, 81, 152 (1875).

[2] Some researches, of the existence of which the author was unaware when the plates were made, failed accordingly to appear in the figures. In this paper they are indicated by asterisks before the authors' names.

of this part. Different papers by a same author are distinguished, in their chronological order, by parenthesised numbers.

The composition of the mixtures is frequently given in weights per cent; these I have recalculated as molecular quantities, in order to discuss the observations from the standpoint of the Ψ and the x,T,P-surfaces.

In connection with the notation followed in Part I. the two-phase pressure is called P, the vapor-pressures of the pure substances P_1 and P_2; and x, V, T, P henceforth refer to the liquid, and x', V′, T′, P′ to the vapor phase.

Chapter A. Methods

§ 24. The investigation of vapor-pressures, boiling-points, critical temperatures, etc., of mixtures is made as in the case of simple substances. However, the fact that one has to do with mixtures necessitates special precautions in each method.

The discussion of some of these precautions is the object of this chapter, where a knowledge of the general methods of determining vapor-pressures, densities, critical constants, etc., for simple substances, is assumed.

§ 25. At pressures that do not exceed or only slightly exceed the barometric pressure, one of the first methods of investigation is to measure the pressure statically, for example, in an ordinary barometer tube.

This method has been adopted by Regnault, Wüllner, Dronke, Guthrie, Konowalow, Tammann, and Raoult (2).

It is essential in these experiments that the composition of the liquid phase shall be approximately that of the mixture introduced. For this purpose, the above investigators make the quantity of liquid introduced relatively great and the volume of the vapor small, by using short measuring tubes.

In general, this precaution is not sufficient. By evaporation from the liquid mixture, as Tammann noticed, different layers are formed, and it is the compositions of the two surface layers of vapor and liquid in contact that determine the pressure.

In certain cases gravitation can assist the process of mixing. In mixtures of the first type, for example, the above-mentioned liquid layer will contain more of the first substance than the original mixture. For most of the fluid pairs investigated, the second (more volatile) substance is at the same time the specifically lighter, and thus the surface layer has an increased density; convection currents then arise to establish stable equilibrium.

In mixtures of the second type, the same is the case, if the mixture of maximum pressure is specifically lighter than the component on the side on which the investigated mixture lies; in those of the third type, if the mixture of minimum pressure has a greater specific gravity.

Raoult (2) attempts to avoid the difficulty of the occurrence of layers of varying composition by shaking the tubes backward and forward about a horizontal axis fixed to the foot of the tube. Here, however, the volume of the vapor is constantly changing, so that a homogeneous mixture is not assured.

Another difficulty is that the presence of air is generally not completely excluded. Konowalow seeks to avoid this by giving the tube the form of a siphon barometer and arranging this so that the mixture is freed from the air which may be present before it is admitted to the closed end of the barometer.

§ 26. A second method of investigation is the dynamical method, so named by Regnault (2), in which the substance is boiled in a closed apparatus. Here Regnault obtains the desired pressure by connecting the flask with a reservoir filled with air of an arbitrary pressure. The vapor rises into a condenser and the liquid thus formed is again heated by the vapor to the boiling temperature before it flows back into the flask.

Lehfeldt (2) likewise uses a closed flask, but without bringing the vapor into contact with the air. Here, as in the first-mentioned method, the composition of the liquid is changed by the evaporation; but since the total weight of the vapor is small in comparison with that of the boiling liquid (in Lehfeldt's experiment it was 1/250), the influence thereof is likewise small.

The movements in the liquid caused by boiling help to keep the liquid mixture homogeneous.

Effects of superheating have been carefully eliminated by Taylor, Schreinemakers, and von Zawidski.

To test whether by the formation or escape of vapor the composition is noticeably changed, Lehfeldt determined the index of refraction of the liquid mixture before and after each experiment. The result was very satisfactory.

Boiling-point determinations with Beckmann's apparatus have been carried out by Nernst, Jackson, Young, and Thayer.

§ 27. The composition of the vapor mixture is determined by Brown, Lehfeldt, and others, by distilling it over; by Cunaeus from the index of refraction of the vapor itself.

When distilling, care must be taken not to allow the vapor to cool too quickly; for example, by first leading it through heated tubes above the flask (Brown), or by heating the flask itself from above (Lehfeldt, Taylor).

Above all, a narrow connection is here necessary between flask and receiver to prevent convection currents. The question, however, remains, whether the liquid distillate obtained agrees exactly in composition with the vapor. Certainty in this method it can be obtained only by preventing the vapor or a part of it from returning to the flask. This has been done by Schreinemakers in a very satisfactory manner.

The composition of the distillate is determined from the density by Brown and Ebersole; from the index of refraction by Lehfeldt and von Zawidski; from the boiling-point by Carveth, Pettit, and Taylor; and from analysis by Schreinemakers.

Winkelmann separated the vapor mixture either by drawing dry air slowly through the liquid, or by exhausting the space above the liquid, and thus causing a gentle ebullition. Both methods gave the same result. The liquid here had a temperature of 17° to 50°. The vapor was then condensed and the composition determined from the index of refraction. The temperature of the condenser (between $-70°$ and $-18°$) had no influence on the composition of the vapor obtained; we may thus very well assume that the vapor was here completely condensed.

§ 28. In experiments under greater pressure, a thorough mixture of the phases is no less necessary to obtain a stable state. Incomplete stirring has caused retardation both in the condensation and critical phenomena.

De Khanikoff and Louguinine, in the determination of the solubility of carbon dioxide in water under different pressures, employed for this purpose a thick-walled glass tube, the volume of which could be diminished by pouring in mercury, this being at the same time in connection with an open manometer. The apparatus was arranged in such a manner that the glass tube could turn on a horizontal axis, while the mercury was temporarily cut off. In this way complete mixture was insured.

Blümcke (4) too, has paid special attention to this retardation. He points out that retardation occurs more easily in condensation and evaporation of mixtures than in the case of pure substances, since not only the density, but also the composition of a part of the homogeneous substance may change. Retardation in evaporation is favored when the glass tube is not drawn out to a point; thus he succeeded in reducing the pressure of a liquid mixture 16 atmospheres below its vapor-pressure, which at the temperature of the experiment, was 35 atmospheres. Similarly, the vapor remains in a gaseous state on increasing the pressure 0.2 atmospheres.

Kuenen, having experienced the influence of retardation phenomena, came to the conclusion that observations with mixtures can give trustworthy results only when they are stirred. This he succeeded in effecting by moving the stirrer electromagnetically.

Since then this method has been adopted by van Eldik, Verschaffelt, van der Lee, Quint, and myself.

Incomplete mixture may be the reason that investigations by other observers give curves of irregular form. This is, for example, the case in the plait-point curve obtained from the experiments of Ansdell (Comp. § 33 and Fig. 2, Plate I.); and it is possible that Villard has observed much too high vapor and critical pressures for the same reason. (Compare § 35.)

§ 29. Determinations of the specific gravity of liquids under great pressure, such as solutions of carbon dioxide in water, have been carried out by Blümcke (1), (2), and (3) in a very peculiar manner.

The solutions were obtained by forcing a definite quantity of water into a reservoir which contained a known volume of gaseous carbon dioxide under pressure, whereupon the carbon dioxide dissolved to a greater or lesser extent, depending upon the speed of injection.

In the reservoir there was a float revolving on an axis and furnished with a mirror, and the displacements of the float were measured by the deflections of the mirror. To calibrate the float, standard liquids were used.

The quantity of carbon dioxide absorbed was deduced from the residual gas above the solution, the aqueous vapor present therein being neglected.

Coexisting phases were accordingly not obtained, so that no connection exists between the composition of the solutions and the pressure of the gas above it.

§ 29*a*. The method I adopted for determining the composition and volume of the coexisting phases of gaseous mixtures at given temperature and pressure, is as follows. After having obtained in a wide reservoir under high pressure a stable equilibrium of the phases, small samples of both were isolated between two cocks. They were then transferred to gas measuring tubes and analyzed.

Chapter B. Mixtures of the first type (Plate I.)

§ 30. In these mixtures, the component that has the smaller vapor-pressure at the same temperature, is always taken as the first substance. Since the vapor-pressure curves in the T,P-plane do not cut one another in the case of the fluid pairs investigated belonging to this type, this substance has the smaller vapor-pressure at all temperatures, and thus also has the highest boiling-point.

In addition, it is almost always the case that it has the highest critical temperature. The exceptions will be pointed out as they occur.

1. The x,P-diagram

§ 31. The curves represented diagrammatically in Fig. 2 by a and a' belong to mixtures that exist in the usual liquid state, that is, at a temperature and pressure far below the critical state of either component. From the following investigations these lines may be constructed more or less perfectly; they are represented to scale in Fig. 6.

Chloroform and ether. Guthrie: curve a at 19.02° is slightly convex towards the x-axis.

Acetone and ether. *Cunaeus: curves a and a' for 0° and 15°. Maximum difference, $x' - x = 0.3$.

Turpentine and ether. Raoult (2): curve a at 16.2° is nearly straight.

The same is the case for mixtures of *aniline*, *nitrobenzene*, and other slightly volatile substances with *ether*.

Benzene and methyl acetate. Lehfeldt (1) determined the corresponding values of x and x' at 18°, without, however, measuring the vapor-pressures. The divergent values of the vapor-pressures of the two components made him expect large values of $x' - x$. The maximum value was found to be 0.18.

Toluene and carbon tetrachloride. Lehfeldt (2): curves a and a' at 50°. Curve a is nearly straight, curve a' is convex towards the lower side. The greatest value of $x' - x$ is here 0.247.

Benzene and carbon tetrachloride. Lehfeldt (2): curves a and a' at 50° are both slightly curved and concave towards the x-axis. At the same pressure, the difference $x' - x$ is small, at most 0.036.

*Von Zawidski's curves a and a' at 49.99°, and *Kohnstamm's curve a at 34.5°, have corresponding forms.

In addition to these, Linebarger has determined the curves a and a' at a single temperature for a number of liquid pairs.

For the liquid pair *benzene* and *carbon tetrachloride* the curve *a* as determined by him shows both a maximum and a minimum, while according to the partial vapor-pressures of the constituents which he has given, the values of x' are always greater than those of x.

Since, according to Konowalow's rule, these facts are mutually contradictory, and, moreover, the simultaneous occurrence of a maximum and a minimum pressure is very improbable, these observations have no value for the construction of the curves *a* and *a'*.

Alcohol and ether. Wüllner: the curves *a* given for ten temperatures between 7.2° and 25.5°, derived from the border curves in the T,P-diagram for the mixtures $x = 0.617$, 0.763, and 0.865, are all slightly curved and concave towards the x-axis. The line for 25.5° is given in the diagram.

Ethylene dichloride and benzene. *Von Zawidski: curves *a* and *a'* for 49.99°, the first is straight, maximum value of $x' - x = 0.03$.

Propylene dibromide and ethylene dibromide. *Von Zawidski: curves *a* and *a'* for 85.05°, the first is straight, maximum value of $x' - x = 0.07$.

Glycerine and water. *Gerlach: curve *a* for 100° is convex.

Acetic acid and water. Konowalow: curves *a* for temperatures between 16° and 100°, derived from three border curves in the T,P-diagram are all slightly concave. That for 100° is given in the diagram.

Propionic acid and water. Konowalow: curves *a* for the same temperatures, likewise derived from three border curves, are very concave. That for 100° is given in the diagram.

That the curve *a* at 64° should show both a maximum and a minimum pressure, as follows from the somewhat rough figure given by Konowalow, is contrary to the observations recorded; if the curves *f* are constructed for the mixtures $x = 0.71$ and $x = 0.91$, then the T,P-curve for the first substance falls entirely below that for the second.

This Bancroft has overlooked in considering the first-mentioned course of line *a* as theoretically possible.

The last two liquid pairs have the peculiarity that while the critical temperature of the water is higher than that of the acids, the vapor-pressure curves of the latter lie below those of water. When in this case the critical temperature is approached, the mixtures must show, at temperatures above the critical temperature of the acid, retrograde condensation of the second kind for all compositions.

§ 32. The curves denoted by *b* and *b'* in Fig. 2 belong to states that, as regards the liquid branch *b*, no longer resemble ordinary liquids, while the vapor represented by *b'* can no longer be assumed to obey the gas laws approximately. The curves *c* refer to temperatures above the critical temperature of the second component; for these lines the following observations can be utilized.

Hydrochloric acid and carbon dioxide. Ansdell has investigated vapor-pressures for seven mixtures from 0° to the critical point, but it is here uncertain whether the pressures given refer to the beginning or to the end of condensation. Moreover, some of the mixtures were probably contaminated with air, so that too high pressures have been observed.

The lines *b* and *c* derived from the vapor-pressures are, accordingly, very irregular in shape and lead one to suppose that in some mixtures, for example, the pressures were observed at the end, in others at the beginning of condensation. As an example is drawn the line for 0° C, with which the observations that it represents are connected by short lines.

This experiment will be referred to when considering Fig. 3, § 38.

Sulphur dioxide and carbon dioxide. Blümcke (3) determined vapor-pressures for mixtures from $x = 0$ to $x = 0.38$, from which portions of curve *b* from $-15°$ to $35°$ may be derived. The composition of the twelve mixtures used was determined from the pressures at 0°. For the standard mixtures compared with these, the composition of the liquid phase was derived—just as with the ordinary liquids in the above-mentioned investigations of Wüllner and others—from the quantity of the components placed in the experimental tubes. Here it was overlooked that at the pressures occurring the quantity of vapor cannot be neglected in comparison with that of the liquid. Indeed Blümcke mentions that the pressure in the tube depends upon the total quantity of liquid introduced.

The points (x, P) from his observations lie therefore somewhat below line b. The portion of the loop for 35°, as far as it may be derived from his observations, is given as an example.

Recent researches of *Caubet (2) which give x,P-isotherms of very regular form, show that the pressures found by Blümcke are too low.

The circumstance that in reference to lines b and b', no investigations have been carried out extending over the whole breadth of Fig. 2 at one and the same temperature, caused me in 1897 to undertake such an investigation myself. Since, as we shall see, the most systematic investigations in this region are those of Kuenen, I have taken, as he did, *methyl chloride* and *carbon dioxide* as the component substances. From my observations it follows that at a temperature of 9.5°, the line b is nearly straight and line b' strongly curved. The greatest value of $x' - x$ is approximately 0.50. The lines b and b', drawn in Fig. 2, represent to scale my observations in this experiment.

*Caubet(1) has recently obtained border curves from which may be derived curves b and b' and loops c. The upper curve b and the upper branch of c have very irregular forms.

Sulphur dioxide and methyl chloride. *Caubet (3): curves b and b', derived from border curves, have for one and the same temperature a maximum and a minimum pressure. This phenomenon, which is the only one of its kind known, and which moreover can only with difficulty be brought into agreement with certain developments of van der Waals, requires further investigation, especially since Caubet's experiments are but incompletely communicated.

§ 33. The plait-point curve d_T, passing through the ends of the loops c, can in most investigations be derived only approximately from the observations.

Hydrochloric acid and carbon dioxide. The attempt to derive a plait point curve from Ansdell's experiments would lead us to ascribe to it an irregular form; which is to be expected, since retardation phenomena were not excluded.

For the same fluid pair, van der Waals determined the critical temperature and pressure for the mixture $x = 0.7$ to be 31.6° and 90 atm, values that differ greatly from those given by Ansdell. I have, however, drawn as well as possible a curve with which the different observations are connected by short lines.

Methyl chloride and carbon dioxide. Kuenen (1) has accurately determined the critical contact point temperatures with the corresponding pressures for three mixtures; the plait point pressures are probably about 2 to 3 atm. Assuming this, I arrived at an approximate plait point curve d_T. It is curved upwards, and has a maximum at about $x = 0.5$.

§ 34. The curves of Fig. 2 assume another shape, when $x' - x$ is very large and approaches unity. This is often the case when the critical temperatures of the components are far apart; for example, when the first substance retains the properties of an ordinary liquid at temperatures at which the second substance is already a gas. Fig. 8 shows for this case the form of the curves of the x,P-diagram. Here curve a shows in the beginning (that is, beginning with the first component), how at a constant temperature, lower than the critical temperature of the gas, the solubility of this in the liquid depends upon the pressure. According to the observations made thereupon, the pitch of this portion of curve a is very great.

According to Henry's law (see p. 29) this portion should be straight; however, exceptions to this law have been indicated for various solutions of gases.

Thus Pagliani and Emo find for mixtures of various alcohols with *ammonia* that the x,P-isotherm, in the neighborhood of P_1, is convex towards the x-axis.

For mixtures of *carbon disulphide* and of *chloroform* with *carbon dioxide*, Woukoloff finds that the curve a is concave towards the x-axis, so that the calculated coefficients of absorption show deviations of four percent.

For mixtures of *water* and of *sulphuric acid* with *carbon dioxide*, Setschenow finds at various pressures fairly constant values of the coefficient; the temperature in these observations was 15.2° and 17° respectively.

For higher pressures, however, the curve *a* for *water* and *carbon dioxide* is no longer straight. This is shown by the observations of de Khanikof and Louguinine, executed at 15° and under pressures up to 4 atm; the solubility increases faster than the partial pressure of the carbon dioxide.

Blümcke's experiments (1) and (2) on the density of these mixtures under high pressures furnish no material for the curve *a*, since it is quite uncertain whether at the pressure given the water was saturated with carbon dioxide or not.

Concerning mixtures of *alcohol* and *carbon dioxide*, the researches of Bohr on coefficients of absorption between — 67° and 45° may be mentioned.

Concerning the further course of the curve *a*, it is possible that at greater concentrations of the gas, the pitch becomes less, so that finally the curve *a* terminates with only a low pitch. But it is also possible that upon compressing a mixture, a pressure is reached at which two liquid layers occur, coexistent with the vapor. According to Dewar's researches, the former is the case for mixtures of *chloroform* and of *benzene* with *carbon dioxide*, and the latter for *carbon disulphide* and *carbon dioxide*.

The pressure at which the two liquid layers coexist with the vapor increases here with the temperature.

In Dewar's researches there is no doubt that retardation phenomena have influenced the results, since for the latter mixture Kuenen has found that even at a lower temperature the two liquid layers are transformed into one phase when thoroughly mixed.

The pressures given by Dewar are for this reason greater than correspond to a stable state of equilibrium. We need not therefore consider his values in this connection.

For *water* and *carbon dioxide*, a separation into two liquid layers is definitely established; the liquid carbon dioxide floats upon the water. We shall not go further into this matter, since we are exclusively occupied with the transverse plait.

With regard to the curves a' we may assume that they have a low pitch near $x = 1$; as here Dalton's law holds, according to which the partial pressure of the liquid in the vapor mixture is equal to the vapor-pressure of the pure substance itself, and this is small in comparison with the total pressure under which solution takes place. Finally, the curve a' will rise rapidly in the neighborhood of $x' = 1$.

§ 35. Coexisting phases are represented by the curve c in the case where the temperature of observation is higher than the critical temperature of the second substance. To this case refer the researches of Bunsen, Bohr and Bock, Timofejef, Carius, and others, on the solubility of different gases in water and in alcohol. From these experiments, which extend from 0° to 100°, it follows that the pitch of the curve c is at first very considerable, and increases with rising temperature.

A minimum coefficient of absorption, that is, a maximum pitch of the curve c, has been observed by Bohr and Bock for hydrogen in water at 60°; the formula derived by Timofejef from his experiments between 1° and 26° is in agreement with this.

Just as in the case of the curve a', we may assume that the curve c' is at first nearly horizontal, rises more rapidly as P approaches 1 atm, and thus changes into the portion c''. This portion, however, cannot extend to $x' = 1$, since the loop corresponds to a temperature higher than the critical temperature of the gas.

On the assumption that in the liquid state mixture is always possible, this curve on ascending further must bend over towards the left and pass into the portion c'''.[1]

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[1] The course of the vapor branch which follows from this reasoning, shows that a very slight addition of water to the air, certainly less than 0.5 percent, is sufficient to raise the critical contact point temperature of the latter to 0° C.

The farthest point toward the right then shows the conditions at the critical point of contact. The pressure under which the parts c and c''' meet each other in the plait point may be very considerable. If, as has been observed by Kuenen and Robson for mixtures of certain alcohols with ethane, separation into two liquid layers occurs, then the plait point may be expected at a lower pressure.

As a proof that the loop really possesses a portion represented by c''', the experiments of Villard on the solution of liquids and solids in gases, under high pressures, may be cited.

These experiments are in the direction of those of Kundt,[1] "in order to reach the critical state at ordinary temperatures." Van Eldik has correctly termed this "the formation of a mixture whose plait point temperature is the temperature of observation." While, however, van Eldik needed only low pressures to dissolve his liquid (methyl chloride) in his gas (ethylene above the critical point), Villard observed for more dissimilar substances far greater pressures before noticeable solution took place, and thus the peculiar course of b''' could be shown.

The data given by him are, it is true, mostly of a qualitative character, since the composition of the solutions obtained is seldom given, and was possibly not even observed; yet, by means of the properties of the Ψ-surface, certain conclusions may be drawn.

So, for example, he finds that at 17° bromine, dissolved in compressed oxygen, colors the latter to a noticeable degree even at 4 atm pressure, and at 300 atm gives it the color of bromine water, just as, according to Cailletet and Hautefeuille, iodine dissolves appreciably in carbon dioxide. In the first case, the molecular quantity of bromine is very probably smaller than in the second. The direction of the pressure line can therefore be given by b'''; and probably at this temperature, the plait point pressure, represented by the top of the loop, is much greater still.

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[1] Berl. Berlin., Oct. 21, 1880. At the same time van der Waals put forward the thesis that "all substances mix with one another when the pressure exceeds a certain value." Verhand. Kon. Acad. Amsterdam, Aug. 1880, p. 24.

At the same temperature, bromine dissolves appreciably in hydrogen at 200 to 300 atm, iodine in oxygen at 200 atm, and in methane at 300 atm (color deep violet); one volume of ethyl chloride in five volumes of methane at 200 atm; carbon disulphide in methane at 550 atm. The plait point pressure at 17° for the different mixtures is thus still higher.

It is quite possible that owing to incomplete stirring solution is retarded so that the pressures observed are greater than those which occur in the case of coexisting phases; yet the observations certainly show that the plait point pressure is much higher than the critical pressure of the components (see further § 2, p. 474).

This increased solubility at greater pressure is also indicated by Hannay and Hogarth for various metallic salts in alcohol, carbon tetrachlorid, etc., and by Schiller for the solutions of ether and chloroform in air (see further § 2, p. 474).

§ 36. For temperatures not far below the critical temperatures of the first substance, the size of the loop diminishes.

This may be deduced from the very careful observations lately carried out by Verschaffelt with mixtures of *carbon dioxide* and *hydrogen*. Thus, he obtains for the loop at 34.20° :

$x =$	0	0.05	0.10	0.13	(interpolated)
$P_1 =$	62.1	74.0	87.9	109.5 (Con. pt.)	"
$P =$		97.5	114.3 (Pl. pt.)		

The loop is thus narrow and rises rapidly.

Still smaller loops are obtained whenever a liquid is mixed with but extremely little gas.

The investigation of the critical phenomena of substances not absolutely pure has occasioned all sorts of assertions to the effect that liquids do not behave in accordance with the simple conceptions of Andrews and van der Waals. Pressure, density, and temperature of the critical point are held to depend on the volume into which a certain quantity of the substance investigated and considered as pure, is brought. All these observations can be looked upon as so many contributions to investigations of very small plaits on the Ψ-surface.

I shall not here enter upon a complete summary of these observations, which can as yet be only qualitatively explained by the properties of the Ψ-surface, and shall content myself with referring to Kuenen's investigation (3) in which it is convincingly shown that even in the best of these researches the substances dealt with are mixtures. To bring about the variations observed, only quantities as small, according to his investigation, as $x = 0.000138$ of gaseous impurities are necessary.

§ 37. Experiments on the change of vapor-density of a substance considered as pure when the volume in which it is contained is increased or diminished, or more or less of this substance is brought into the same volume, belong to a related class of phenomena. These also can as yet be only qualitatively explained, so that I again refrain from a review of these observations.

As regards vapors under ordinary conditions, Tammann and Julius have shown that the phenomena may be considered as due to admixture.

2. The T,P-diagram

§ 38. The portion of the liquid branch of the border curve f of Fig. 3, extending far from the plait point, may be derived from the observations of Wüllner and Konowalow for the mixtures which they have investigated. (See § 31.)

These lines all lie between the vapor pressure curves f_1 and f_2 of the components; as regards form they agree exactly with the latter, and are accordingly not represented in the figure.

The same has been observed by Regnault (2) for the following fluid pairs:

Carbon tetrachloride and *carbon disulphide;* curves f between 8° and 48° for the mixtures $x = 0.398$ and 0.616.

Benzene and *carbon disulphide;* curve f for $x = 0.591$ between 23.11° ($P = 225.19$ mm) and 142.17° ($P = 5827.14$ mm $= 7\frac{2}{3}$ atm).

We shall recur (§ 42) to these observations of Regnault.

Sulphur dioxide and *carbon dioxide*. Blümcke's experiments (3) refer to the portions of the liquid branch of *f* which lie nearer the critical region; these lines for the first component and for twelve mixtures have all a regular form; that for the mixture $x = 0.38$ is represented in the figure.

*Caubet (2) has determined for eight mixtures the complete border curves from 20° up to the plait point. (Compare § 32.)

Hydrochloric acid and *carbon dioxide*. The pressure lines for the mixtures investigated by Ansdell are, according to the table given by him, not so regular as would be assumed from the accompanying figure. The real border curve of a mixture must necessarily entirely enclose the corresponding observed pressure line; and the small difference in the vapor-pressure of the components being taken into account, the border curve is rather narrow.

The difference in pressure at the beginning and end of condensation probably does not greatly exceed 4 atm, if we may assume that the border curves of the mixtures all lie between the vapor pressure curves of the components.

On the other hand, van der Waals finds for a mixture $x = 0.7$ as beginning and end pressure:

At 0° $P' = 39$ atm $P = 150$ $P_2 = 34.3$
At 22.5° $P' = 69$ atm $P = 115$ $P_2 = 59.7$

and Dewar as beginning pressure for the mixture $x = 0.5$

At 0° $P' = 36.0$ atm $P_2 = 34.3$
At 34° $P' = 83.0$ atm
At 35.5° $P' = 90.0$ atm

According to these observations, the fluid pair belongs to the second type. However, it is just as probable that these high pressures are caused by the presence of air or by retardation of the condensation. The reason why I have considered this fluid pair to be of the first type is to be found in the regular course of the plait point curve in the x,T-diagram. (See Fig. 4, Plate I.)

Methyl chloride and *carbon dioxide*. The upper portion of the border curve for the mixture $x = 0.41$ follows from more recent observations by Kuenen (4). As pressures at the beginning and end of condensation for various temperatures he obtains among others:

Temperature,	70°	101.5°	103.0°	106.8°.
Pressure at beginning,	28.8	65.7	67.9	79.5
Pressure at end,	64.9	84.7	84.0	

The plait point curve *d* touching this border curve in the point T = 103.0°, P = 84.0 atm, and drawn through the end points lies, as might be expected, above the three observed critical points of contact (see § 33). The plait point curve begins to rise from both ends, so that like the plait point curve in Fig. 1 a maximum occurs at about $x = \frac{1}{2}$.

*Caubet (1) determined the border curves for ten mixtures; these do not quite agree with Kuenen's measurements.

Sulphur dioxide and *methyl chloride.* Caubet (3). The border curves experimented on indicate a maximum as well as a minimum pressure mixture, the plait point curve showing at the same time neither a minimum nor a maximum critical temperature (see § 32).

Acetylene and carbon dioxide. Kuenen (7) obtained as critical temperature and pressure of the mixture $x = 0.5$, 32.55° and 66.52 atm. Here the plait point temperature and contact point temperature approximately coincide. The border curve *f* for this mixture and therefore probably for mixtures of other compositions is decidedly narrow.

These data indicate that the line d_x for this fluid pair is nearly straight and possesses no maximum pressure nor maximum critical temperature at 41°, as Dewar asserts that he found for this composition.

Kuenen (6) has also determined the border curve *f* for two samples of *impure ethane.* On the basis of what might have been formed in the preparation of these samples, and of the determinations of their molecular weights, he estimates that this ethane contained 2½ and 5 pct of butane respectively. ($T_{cr.}$ ± 150°).

§ 39. In connection with the shape which the lines in the

x,P-diagram assume for mixtures of liquids and gases, the border curves of these mixtures also acquire a different shape, of which Fig. 9 gives an idea.

The lines f are here generally very broad loops, and in particular the top of the border curve, point M, is far removed from the critical contact point. This appears from the following observations.

Carbon dioxide and *nitrogen*. Andrews (2) and (1) determined the pressure at the commencement and end of condensation for the mixture $x = 0.2257$ at various temperatures.

The indications of the hydrogen manometer which he used are not, however, corrected in respect of the deviations from the gas laws. If this is done, according to the calculations of Galitzine, we obtain:

T	6.3°	9.9°	13.2°	T_c	14.0°
P′	72.1	81.9	97.8	P_c	105.1
P	122.8	116.5	111.0		

which data are utilized in the figure.

He here observed not so much a completion of the liquefaction as a flattening and disappearance of the meniscus. This he ascribes to a retardation in reaching equilibrium. The pressures P are therefore probably too high.

Furthermore, he found for the mixture $x = 0.1389$ at 3.5° $P' = \pm 49$, and $P = \pm 109$ atm. And for the mixture $x = 0.5714$ a critical temperature of $-20°$.

Carbon dioxide and *air*. With a mixture of $x = \frac{1}{6}$, the following observations have been made:

Compressing it at 5.5°, Cailletet found that at a pressure of 150 to 200 atm the liquid carbon dioxide was entirely dissolved in the gas; and on reducing the pressure slowly, the first quantity of liquid was observed at 132 atm. As corresponding temperatures and pressures he obtained:

T	5.5°	10°	13°	18°	19°	crit. temp. < 21°
P	132	124	120	113	110	

According to later observations carried out by him and reported by Jamin for the same mixture, the pressure steadily diminishes from 15° (P = 135 atm) to 25° (P = 79 atm), so that the critical temperature must lie above 25°. Wroblewski, also working with this mixture, obtained by compression at 0° two liquid layers in superposition; according to his own description this was, however, no state of stable equilibrium.

Kuenen (2), improving this experiment by means of his stirring apparatus, obtained as critical temperature of this mixture 19° and as plait point temperature 15.6°; while retrograde condensation was observed continuously between both temperatures. He justly concludes that the occurrence of two liquids seen by Wroblewski and the great difference between the various values given by Cailletet should be referred to retardation phenomena. On account of their inexactness, these observations are not included in the figures.

For the mixture $x = 0.1$ van der Waals obtained as critical point (probably the critical contact point was here observed) 25° at 77.5 atm. Here, too, the vapor-pressure continually diminishes from 2° (145 atm) to 23.5° (95 atm).

All these observations are hence related chiefly to the portion of the border curve between the points M and R. In these experiments, air and nitrogen may be considered alike in their influence on the condensation phenomena. If the observations are compared it is seen to be impossible to draw a plait point curve d_x that shall agree with all these border curves. It may well be concluded that the plait point curve rises rapidly from the critical point of carbon dioxide.

Moreover, we may assume that the pressures observed are too high, because of retardation of the condensation.

Ether and *air*. Schiller observed the disappearance of the meniscus at 167° and 50 atm, and hence a plait point is here found.

Carbon dioxide and *hydrogen*. The above considerations hold also for the observations of Cailletet (see Jamin) on a mixture of carbon dioxide and hydrogen, $x = 1/6$, which on the whole do not agree with the border curves determined by Verschaffelt for the mixtures $x = 0.05$, 0.10, and 0.20. Since these latter are very accurately determined, and above all attention was continually directed to the attainment of equilibrium, no value need be attached to Cailletet's numbers.

The plait point curve which envelopes these border curves determined by Verschaffelt, is at first convex toward them. These latter lines are recorded in the figure and schematically completed; the course of the curves *d* and *m* is also schematically indicated.

Villard's observations were all carried out at the same temperature, and contribute thus nothing to Fig. 9. He mentions only that *carbon disulphide* and *methane* are entirely miscible at 17° under a pressure of 550 atm, and at 150° under 250 atm. Presumably plait points were here observed.

§ 40. An indirect method of finding the plait point pressure for any temperature is employed by van Eldik. Knowing the dependence of the capillary rise, when two phases coexist, upon the two-phase pressure, which dependence was investigated by him, one can deduce the plait-point pressure from observations of the change of this capillary rise with the pressure. In this way, van Eldik has deduced from his experiments on the capillary rise in the case of coexisting phases of *ether* and *hydrogen*, that at ordinary temperatures the capillary rise will probably vanish only at pressures above 750 atm. The plait point pressure at the ordinary temperature is thus of this magnitude.

Through these observations we obtain a conception of the course of the first portion of the plait point curve for ether and hydrogen. If we compare these observations with those of Verschaffelt on carbon dioxide and hydrogen, we obtain, keeping also in view Villard's observations, the diagrammatical representation of the lines *d*, *l*, and *m* which is given in Fig. 9.

§ 41. Concerning the influence of small admixtures on the critical pressure and temperature, refer back to § 36 and § 37.

3. The x,T-diagram

§ 42. In Fig. 4 the connection between composition and boiling-point and condensation temperature at constant pressure is represented for ordinary liquid mixtures by the curves *g* and

g'. The following observations included in Fig. 7 refer to these points:

Benzene and *carbon disulphide*. Brown (1) determined the curves g and g' at 760 mm; curve g is convex towards the x-axis, and g' is nearly straight; the greatest value of $x' - x = 0.313$ at $x = 0.35$.

Carveth determined the same curves; the results compared with the former are slightly different. The maximum value of $x' - x = 0.27$ at $x = 0.35$.

The curve f determined by Regnault (2) for the mixture $x = 0.59$ (see § 38) does not agree with these observations. Since Regnault adopted the dynamical method, an alteration of the composition during the experiment is quite possible.

Carbon tetrachloride and *carbon disulphide*. Brown (4) determined the curves g and g' at pressures of 430 and 760 mm. The curves are similar in form to those of the former fluid pair; the composition of the vapor from the same liquid mixture seems here to be independent of the pressure. The greatest difference $x' - x = 0.263$ obtained at $x = 0.37$.

The curves f determined by Regnault for the mixtures $x = 0.398$ and 0.616 (see § 38) confirm the values of the boiling-points obtained by Brown.

Benzene and *hexane*. Jackson and Young determined the curve g at the ordinary barometric pressure, finding it strongly curved; addition of 10 pct of benzene to hexane has very little influence on the boiling-point; an addition of 10 pct hexane to benzene, however, lowers the boiling-point 3°.

Alcohol and *acetone*. Thayer (2) likewise obtains for curve g at a pressure of about 741 mm a slightly curved form.

Alcohol and *ether*, *acetone* and *ether*, *carbon tetrachloride* and *chloroform*. *Haywood (1) determined for each of these combinations a curve g at the ordinary barometric pressure. All these curves are convex to the x-axis.

Mixtures of *ethyl alcohol* with *methyl alcohol*, and of *benzene* with *ether*, *chloroform*, and *carbon tetrachloride*, experimented on by *Haywood (2) have a boiling-point curve of the same form.

Benzene and *acetone.* *Ebersole obtained a curve g slightly convex, and g' nearly straight; *Haywood (2) a curve g fairly corresponding.

Methyl alcohol and *ether.* *Haywood (2) and *Pettit both found curve g to be convex towards the x-axis.

Water and *acetone.* *Carveth obtained a convex curve g and a concave curve g'. *Haywood (1) found a similar curve g and *Taylor the same curves g and g', all these fairly corresponding.

Glycerine and *water.* *Gerlach: curve g for 760 mm is convex.

Acetic acid and *water.* *Roscoe (2): curve g between $x = 0$ and $x = 0.5$ is convex.

For liquid mixtures of *oxygen* and *nitrogen* evaporating at low temperatures under barometric pressure, the corresponding values of x and x' are given by Linde without observing the boiling-points, and cannot therefore be included in the diagram. The greatest difference between x' and x reaches 0.27 when $x = 0.50$.

*Baly determined complete curves g and g', agreeing fairly well with the former observations.

§ 43. For mixtures of liquids and gases the curves g may be derived from experiments on the relation between temperature and solubility of the gas; these are not included in the drawing.

Such investigations have been carried out by Bakhuis Roozeboom for mixtures of water with sulphur dioxide and with chlorine. These results, completed by the end-points of the curve g, are:

Water—sulphur dioxide P = 760 mm

Boiling-point $t =$	100°	20°	10°	5°	0°
Composition $x =$	0	0.0285	0.0415	0.0518	0.0623

Water—chlorine P = 760 mm

$t =$	100°	12°	9°	6°	0°
$x =$	0	0.00221	0.00241	0.00274	0.0037

§ 44. The dependence of the critical temperature on the composition had been investigated by various observers before Kuenen indicated the difference between plait point temperature and critical contact point temperature.

From the manner of the investigation, it is seen that in most cases the plait-point has been observed.

Pawlewski, from his experiments on mixtures of homologous substances, such as alcohols, reaches the conclusion that a linear relation exists between the critical temperature and the percentage composition by weight.

Since, in general, the substance with the greater molecular weight has also a higher critical temperature the curve d_P is thus usually concave towards the x-axis.

In the following fluid pairs, the line d_P according to the observations is convex towards the x-axis.

Alcohol + ether, Strauss.

$x =$	0.022	0.107	0.189	0.358	0.617	0.776
$T_{cr.} =$	239.9	233.9	227.5	218.8	208.8	202.8

Ramsay and Young, $x = 0.370$, $T_{cr.} = 219.5°$. The agreement is here satisfactory.

Benzene + ether, Ramsay, $x = 0.513$, $T_{cr.} = 240.7$.

On the other hand, d_P is concave in the case of *acetone + ether*, Galitzine.

$x =$	0.052	0.114	0.258
$T_{cr.} =$	230.1	227.3	218.7

§ 45. For the mixtures of *methyl chloride* and *carbon dioxide* investigated by Kuenen (1) and (4), the contact-point temperatures are observed as follows:

$x =$	0	0.25	0.41	0.50	0.75	0.89	1
$T_{cr.} =$	143.0°	123.0°	106.8°	97.1°	65.4°	46.0°	31.25°

The line l_P derived therefrom is likewise concave toward the x-axis. Here, too, we have deviation from Pawlewski's law.

For the mixtures of *hydrochloric acid* and *carbon dioxide*, investigated by Ansdell, contamination with air seems to have been of influence on the vapor-pressures, but little, however, on the contact-point temperatures observed; the points (x, T), which represent these states, lie on opposite sides of a curve that is convex toward the x-axis. The variations from this are at most 1.°

§ 46. Altschul observed a fall of the critical temperature on addition of small quantities of *alcohol* to *chloroform;* this fall amounted to 3.8°, while the boiling-point changed 0.1° to 0.2°. Similarly a rise in the critical temperature is observed on addition of *alcohol* to *chlorethyl*, and of various liquids and solid substances to *ether;* so, for example, a mixture of *borneol* and *ether*, $x = 0.24$, has a critical temperature of 296°. In this investigation, plait point temperatures were observed. Furthermore, as to the change of critical temperature on the addition of very small quantities of other substances, and also as to the accompanying phenomenon of change of the critical temperature with the volume into which a given quantity is introduced, see § 37.

4. The x,V-diagram

§ 47. In Fig. 1, curve *a* refers to the molecular volume of ordinary liquid mixtures; the properties of this curve are deduced immediately from the curve given by most observers, which represents the connection between the composition in parts by weight and the specific volume (referred to water at 4°).

If the first line is straight, the second is so also. Both curves too are alike convex or concave towards the x-axis. However, the one line can show a maximum or minimum volume while the other does not.

For the convexity or concavity of the curves *a* we have for liquid mixtures the following observations, which extend over the whole breadth, but are not included in the figure:

(Contraction is indicated by +.)

	Maximum change of volume	
Glycerol and *water*	+0.011	(Gerlach)
Acetic acid and *water*	+0.03	(Oudemans)
Benzene and *carbon tetrachloride*	+0.00024	(Brown)[3]
Toluene and *carbon tetrachloride*	+0.00024	"
Carbon tetrachloride and *carbon disulphide*	—0.0043	"
Benzene and *carbon disulphide*	—0.0082	"
Dichlorethane and *benzene*	—0.0029	"
Dibromethane and *benzene*	—0.0026	"
Benzene and *hexane*	—0.04	(Jackson and Young)

Moreover Bussy and Buignet and also Guthrie have observed changes of volume in the following cases:

Chloroform and *ether*	$+ 0.01089$ at $x = 0.44$ (G.)
Chloroform and *amylene*	$+ 0.00151$ at $x = 0.57$ (G.)
Alcohol and *ether*	$+ 0.00689$ at $x = 0.36$ (G.) $+ 0.0091$ at $x = 0.60$ (B. and B.)
Benzene and *ether*	$+ 0.00346$ at $x = 0.46$ (G.)
Carbon disulphide and *amylene*	$- 0.00311$ at $x = 0.37$ (G.)
Benzene and *amylene*	$- 0.00108$ at $x = 0.45$ (G.)
Benzene and *chloroform*	$- 0.00184$ at $x = 0.52$ (G.)

Guthrie's observations refer to mixtures of equal volumes of the constituents.

The line α' gives the molecular volume of the vapor mixture. Since we have here assumed that the gas laws are obeyed, this volume may be derived from the corresponding vapor-pressure, which is given by the curve a' of Fig. 2. If a' is straight, then α' is a hyperbola, and vice versa.

Concerning the possibility of a and α' being simultaneously straight, I may refer to the theoretical discussions of van der Waals.[1]

§ 48. For mixtures of *sulphur dioxide* and *carbon dioxide* Blümcke has observed the density at 0° and 30°; the observations include proportions from $x = 0$ to $x = 0.6$. The curve β derived therefrom, but not included in the figure, shows a minimum molecular volume at approximately $x = 0.3$. In the case of the mixtures of *methyl chloride* and *carbon dioxide* investigated by me at 9.5°, the curves β and β' are nearly straight; β moreover is parallel to the x-axis.[2] The corresponding values of P and V′ for the vapor phase no longer follow the relation $PV' = RT$, since the conditions of observation are too near the critical point. Still it may be observed that both b and β' are nearly straight.

§ 49. The course of the retrograde condensation may be deduced from the consequent intersection of the tangent chords

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[1] Zittingsversl. Kon. Akad. Amsterdam, June, 1900. p. 171; Proc. idem. 3, 168.

[2] A drawing to scale is given in Kamerlingh Onnes's paper, Zittingsversl., etc., June, 1900, p. 213; Proc. idem. 3, 288; Comm. Leiden, No. 59*a*.

with the same line $x = \text{const}$, lying between $x = x_P$ and $x = x_R$. I give here the observations with *methyl chloride* and *carbon dioxide* of Kuenen for the mixture $x = 0.41$ at 105°, in which he first succeeded in obtaining this highly interesting phenomenon.

Total volume	Liquid volume	Pressure
117.9	0	73.3
99.6	3.9	77.2
81.2	8.2	81.8
81.0	8.6	81.8
78.6	7.6	82.4
77.3	4.3	83.1
75.3	4.7	83.3
75.4	2.8	83.5
74.3	2.5	83.8
74.0	0	83.8

A more complete review of the retrograde condensation was later given by Verschaffelt with *carbon dioxide* and *hydrogen* at $x = 0.05$ and 27.30°, the plait point temperature for the mixture being 27.10°. We call especial attention to the very clear figure given by him for the course of this phenomenon.

I know of no observations on the curves γ. From the experiments of Kuenen, however, the curve δ, passing through the projections of the various plait points, may be derived. This line is nearly parallel to the x-axis.

§ 50. For mixtures of liquids and gases, whereby at a given temperature the vapor pressure of the first component is very small in comparison with that of the second, the molecular volume of the vapor of the first component is in consequence relatively very large. The projection of the transverse plait and of the connecting lines of its coexisting phases, — bearing in mind the large difference $x' - x$, — if its double fan-shape is to remain apparent, must attain dimensions greater than those that correspond to the foregoing mixtures, and which have been necessarily omitted. Data for the curve a in this case are provided by determinations of the densities of solutions of gases.

For *water* and *sulphur dioxide* these have been carried out by

Giles and Schearer, extending to $x = 0.04$. In this case the curve *a* is convex towards the x-axis, and so contraction occurs on mixing.

At higher pressures the specific gravity of *water* and *carbon dioxide* has been determined by Blümcke (1); these experiments include mixtures from $x = 0$ to $x = 0.0265$ at 2° to 5°, and to $x = 0.022$ at 18° to 20°. The end-pressures observed here were 37 to 53½ atms, but the vapor pressures of these mixtures are probably not so high. The appearance of a second liquid layer containing more carbon dioxide is not mentioned.

For *alcohol* and *carbon dioxide* the curve *a* has been followed by Blümcke (2) over the whole breadth; it is convex towards the x-axis at 0.4°, and has moreover a minimum volume at 17° and 25°, approximately at $x = 0.8$.

Chapter C.—Mixtures of the second type. Plate II.

§ 51. The behavior of mixtures having a maximum vapor pressure, or, what is practically the same thing, a minimum boiling-point, is represented on Plate II. by Figs. 1 to 6. For these fluid pairs, the component with the lower critical pressure is usually chosen as the first substance.

1. The x,P-diagram

§ 52. Let us in the first place consider the curves that represent P as a function of x at constant temperature.

The curves *a* and *a'* represented diagrammatically in Fig. 2, and to scale in Fig. 6, correspond respectively to liquid mixtures and to the vapor mixtures coexisting therewith, in states far removed from the critical point. The following investigations refer to these:

Ether and *carbon disulphide.* Guthrie: curve *a* for 18.88°; maximum pressure 433 mm at $x = 0.20$; $P_1 = 432.1$ mm; $P_2 = 284.5$ mm.

Chloroform and *carbon disulphide.* Guthrie: curves *a* for 13.8° and 16.0°; maximum pressure respectively 255.7 and 270.4 mm. at $x = 0.97$; P_1 respectively 158.4 and 169.2 mm; P_2 respectively 251.46 and 264.8 mm.

Acetone and *carbon disulphide.* *von Zawidski: curves a and a' for 35.17°; $P_m = 655$ mm at $x = 0.668$; $P_1 = 343.8$, $P_2 = 512.3$ mm; maximum value of $x' - x = 0.292$.

Ethyl acetate and *carbon tetrachloride.* *von Zawidski: curves a and a' for 49.99°; $P_m = 318.8$ mm at $x = 0.673$; $P_1 = 280.5$, $P_2 = 306.0$ mm; $(x' - x)_{max} = 0.046$.

Ethyl acetate and *ethyl iodide.* *von Zawidski: curves a and a' for 49.99; $P_m = 363.5$ mm at $x = 0.75$; $P_2 = 353.4$; $(x' - x)_{max} = 0.088$.

Carbon tetrachloride and *ethyl iodide.* *von Zawidski: curves a and a' for 49.99° between $x = 0$ and $x = 0.498$, $x' = 0.522$; $P = 351.2$ mm; a maximum pressure may hence be expected.

Methylal and *carbon disulphide.* *von Zawidski: curves a and a' for 35.17°; $P_m = 703.3$ mm at $x = 0.475$; $P_1 = 587.7$; $P_2 = 514.5$ mm.

Ethyl acetate and *benzene.* Lehfeldt (1) determined the corresponding values of x and x' at 18°, but without measuring the vapor pressures. From the observations it is seen that the pressure is a maximum at $x = 0.79$; the greatest difference $x' - x$ is 0.018.

Alcohol and *carbon disulphide.* Bussy and Buignet: curve a for 19°; maximum pressure ± 312 mm between $x = 0.7$ and $x = 0.9$; $P_1 = 41.4^5$ mm; $P_2 = 286.2$ mm.

Benzene and *alcohol.* Lehfeldt (2): curves a and a' at 50°; $P_m = 407$ mm at $x = 0.406$; $P_1 = 270.9$ mm; $P_2 = 219.5$ mm; $(x' - x)_{max} = 0.22$.

Toluene and *alcohol.* Lehfeldt (2): curves a and a' for 50°; $P_m = 250$ mm at $x \doteq 0.741$; $P_1 = 93.0$ mm; $P_2 = 219.5$ mm; $(x' - x)_{max} = 0.46$.

Methyl alcohol and *water.* Konowalow: curves a for different temperatures, obtained from the border curves of mixtures with $x = 0.405$ to 0.845, are nearly straight. The curve a for 100° is drawn in the figure.

Tammann: addition of 0.2 percent by weight of water to methyl alcohol causes an increase of the vapor pressure at the boiling-point of 10 mm. (Comp. § 37.)

Ethyl alcohol and *water.* Dronke: curves *a* for temperatures between 10° and 81°, to be obtained from the border curves of nine mixtures, with $x = 0.242$ to 0.983.

Konowalow: curves *a* for temperatures between 21° and 80°, to be obtained from the border curves of four mixtures at $x = 0.299$ to 0.837.

The numerical values of the pressures observed in these two investigations do not wholly agree; yet the character of the curves *a* obtained is the same; i. e., steadily falling with a low pitch up to $x = 0.9$, and steeply falling thereafter.

Tammann: addition of 0.5 percent by weight of water to ethyl alcohol increases the vapor pressure by 3 mm at the boiling-point of this substance. (Comp. § 37.)

Propyl alcohol and *water.* Konowalow: curves *a* for temperatures between 19° and 88°, obtained from the border curves of six mixtures, $x = 0.296$ to 0.98; the curve for 80° is drawn in the figure. Here $P_m = 560$ mm at $x = 0.4$ to 0.45; $P_1 = 376$; $P_2 = 352.8$ mm. With rising temperature, the maximum mixture is slightly displaced towards the side of the first component.

Chancel obtained a minimum boiling-point at 87.5°, at $P = 738$ mm and $x = 0.5$.

Winkelmann observed for some temperatures the points on the curve *a'* corresponding to a given liquid mixture. The greatest distance between the lines *a* and *a'* derived from this investigation is nearly 0.3.

Benzene and *acetic acid.* *von Zawidski: curves *a* and *a'* for 49.99°. No maximum pressure is found, but with regard to the observations of Nernst (§ 56) this liquid pair belongs to the second type.

Toluene and *acetic acid.* *von Zawidski: curves *a* and *a'* for 69.94° and for 80.05°; P_m resp. 225.8 and 333.6 mm at $x = 0.40$ and 0.41; $(x' - x)_{max} =$ about 0.20.

Pyridine and *water.* *von Zawidski: curves *a* and *a'* for 80.05°; $P_m = 441.0$ mm at $x = 0.75$.

Butyric acid and *water.* Konowalow: curves *a* for temperatures between 19° and 99°, derived from the border curves of three mixtures with $x = 0.676$ to 0.934. The maximum pressure is only a few mm higher than the vapor pressure of water. So, for example at 80°, $P_m = 359.2$ mm. at $x = 0.88$; $P_1 = 27.5$; $P_2 = 352.8$. With elevation of temperature the maximum mixture is displaced toward the side of the second component.

Phenol and *water*. Van der Lee: curves a for temperatures between 72° and 87°, to be obtained from the border curves of seven mixtures with $x = 0.50$ to 0.99. Within these temperature limits, the composition of the maximum mixture $x = 0.9$ is constant. At 85° P_m is 440 and $P_2 = 433$ mm.

*Lehfeldt (3): curves a for temperatures between 75° and 90°, may be obtained from experiments with four mixtures, $x = 0.32$ to 0.68; that is to say, beyond the maximum mixture. The curves of these two observers are not at all in good agreement.

*Schreinemakers: curves a and a' for 56.3°, 75°, and 90°, in very good agreement with Lehfeldt; maximum mixtures: at 56.3° $x = x' = 0.989$; $P = 127$ mm; at 75° $x = x' = 0.985$; $P = 294$ mm; at 90° $x = x' = 0.983$; $P = 531$ mm.

§ 53. At temperatures nearer the critical point, chiefly Kuenen has carried out investigations on this type of fluid pairs. (See Fig. 2.) These include the following mixtures:

Ethane and *nitrous oxide*. Kuenen (5): curves b, b', and c, to be obtained from the border curves of five mixtures. The minimum critical temperature 25.8° occurs at the mixture $x = \pm 0.5$ (point A). The composition of the maximum mixture $x = 0.8$ alters very little with the temperature. The solid curves b and b' at 20°, c at 26°, c_0 at 29°, and the slightly curved plait point line d_T record these observations.

Ethane and *carbon dioxide*, and *ethane* and *acetylene*. Kuenen (5): curves b, b', and c, to be obtained from the border curves of four and five mixtures respectively (not included in the figure). The intersection of b and b' (point A) occurs at 17.6° and $x = \pm 0.55$, and at 19.5°, $x = \pm 0.5$ respectively. Retrograde condensation of the first kind was sometimes observed.

Ethane and *hydrochloric acid.* *Quint: from the border curves of four mixtures can be obtained curves *b*, *b'*, and *c*. The minimum critical temperature 27.2° corresponds to $x = 0.38$; the mixture $x = 0.56$ has a maximum pressure.

2. The T,P-diagram

§ 54. Fig. 3 represents the vapor pressure curves and border curves. With regard to the liquid branch at low temperatures and pressures, the following observations have been made.

Ether and *carbon disulphide.* Regnault: the four border curves observed for the mixtures $x = 0.493$ from $-16.7°$ to 9°, $x = 0.556$ and $x = 0.736$ from 4° to 39°, and $x = 0.610$ from 20.8° to 121.5° lie all between the curves f_1 and f_2 of the components. The pressures at 18.88° differ greatly from those which follow from the curve *a* determined by Guthrie at this temperature. (See § 52.) The differences amount to as much as 15 mm.

Benzene and *alcohol.* Regnault: the border curve of the mixtures $x = 0.603$ lies far above the curves f_1 and f_2 of the components. The pressure at 50° agrees exactly with the curve *a* determined by Lehfeldt at this temperature. (See § 52.)

The border curve of another mixture, the composition of which is not given, lies a little above curve f_2.

Methyl alcohol and *water*, and *ethyl alcohol* and *water.* Konowalow and Dronke: the curves *f* for the mixtures observed all lie between those of the components. (See § 52.)

Propyl alcohol and *water*, and *butyric acid* and *water.* Konowalow: the curves *f* of the substances observed lie for the most part above the curves f_1 and f_2. (See p. 484.)

Phenol and *water.* Van der Lee: the curves *f* for the five mixtures between $x = 0.82$ and 0.99 lie above the curve f_2.

§ 55. The form of the plait point curve *d* and of complete border curves *f*, in the neighborhood thereof, have been investigated chiefly by Kuenen. For the mixtures of *ethane* with *nitrous oxide*, with *carbon dioxide*, and with *acetylene*, the plait point curves *d* are reproduced in Fig. 3, and also the border curves for the fluid mixtures $x = 0.43$ and $x = 0.76$ of the first fluid pair.

The border curves are mostly very narrow; with the second fluid pair accurate observation of the points P, M, and R was always possible on account of the great purity of the substances, (freedom from air).

Ethane and *hydrochloric acid.* *Quint: the border curves of the four mixtures are all above the curves f_1 and f_2.

3. The x,T-diagram

§ 56. In Fig. 4, the relations between x and T at constant pressure are represented by the curves g and g'. At a pressure nearly equal to the barometric pressure, the following observations relating thereto were obtained:

Ether and *carbon disulphide.* *Alluard: curves g for 730 and 760 mm from $x = 0.66$ to $x = 1$; the mixture $x = 0.09$ has the same boiling-point as pure ether.

*Ryland finds $x = 0.35$ to be the constant boiling mixture.

As in other cases, the observations of Ryland are in contradiction with those of others, and moreover are very inaccurate; they are not mentioned in this compilation.

Alcohol and *carbon disulphide.* Berthelot: the mixture $x = 0.858$ distilled over unchanged; boiling-point 43° to 44°; $T_1 = 78°$, $T_2 = 48°$. The barometric pressure was not given. Further corresponding values of x and x' are: $x = 0.99$, $x' = 0\ 86$; and $x = 0.33$, $x' = 0.85$.

*Alluard: curves g for 725 and 760 mm; from $x = 0$ to $x = 0.24$.

Brown, by distillation, obtains finally a distillate $x' = 0.874$; this alcohol contains 0.8 percent of water, as may be seen by the density. This observation agrees well with the first one. In connection with the observation of Bussy and Buignet, the possibility is noticed that the maximum mixture should be displaced towards the side of the carbon disulphide on elevation of the temperature.

Ethyl acetate and *carbon disulphide.* Brown: the mixture $x = 0.72^5$, distilled over unchanged.

Carbon tetrachloride and *methyl alcohol.* Thorpe: the mixture $x = 0.581$ boils at 55.6° to 55.9°; $T_1 = 76.6°$; $T_2 = 65.2°$.

*Haywood (2): curve *g* for 765.5 mm; $T_m = 55.95°$ at $x = 0.52$.

Chloroform and *methyl alcohol.* *Haywood (1): curve *g* for 770.2 mm; $T_m = 54°$ at $x = 0.34$.

*Pettit: curve *g* for 746.2 mm; $T_m = 53.5°$ at $x = 0.30$ to 0.34.

Acetone and *methyl alcohol.* *Haywood (1): curve *g* for 764.8 mm; $T_m = 55.9°$ at $x = 0.195$.

*Pettit: curves *g* and *g'* for 760 mm; $T_m = 55.93°$ at x approximately $= 0.21$.

These curves agree very well.

Benzene and *methyl alcohol.* *Haywood (2): curve *g* for 760.7 mm; $T_m = 58.3°$ at $x = 0.54$ to 0.68.

Carbon tetrachloride and *acetone.* *Haywood (1); curve *g* for 773.0 mm; $T_m = 56.95°$ at x about 0.94.

Carbon tetrachloride and *alcohol.* *Haywood (1): curve *g* for 768.4 mm; $T_m = 65.5°$ at $x = 0.411$.

Methyl cyanide and *methyl alcohol.* *Vincent and Delachanel: curve *g*; $T_m = 63.7°$ at $x = 0.84$; $T_1 = 81.6°$.

Methyl cyanide and *ethyl alcohol.** Vincent and Delachenel: curve *g*; $T_m = 72.6°$ at $x = 0.53$.

Ethyl iodide and *methyl alcohol.* Wanklyn: from the liquid mixture $x_1 = 0.84$, the distillate $x_2 = 0.77$ was obtained. $T_1 = 72°$; $T_2 = 66°$. The less volatile constituent thus passes over more rapidly.

Chloroform and *alcohol.* Thayer (2): curve *g* for 744.2 mm; $T_m = 59.09°$ at $x = 0.17$; $T_1 = 60.93°$; $T_2 = 77.86$; (a portion of curve *g* for 732.5 mm; $T_m = 58.5°$, $T_1 = 60.5°$, is not included).

Benzene and *alcohol.* Thayer (1): the mixture $x = 0.46$ has a constant boiling-point 66.7° at $P = 737$ mm; curve *g* was determined completely at 728.5 to 737 mm. The data derived therefrom for the mixture $x = 0.603$, $T = 67.3$, at $P = 734$ mm are very different from those calculated from the curve f determined by Regnault for this composition, namely, $T = 6.59°$ at $P = 734$ mm. (See § 54.)

Compared with Lehfeldt's experiments (§ 52) the maximum mixture is thus seen to move rapidly towards the side of the second component on elevation of the temperature.

Thayer thinks this movement is improbable, and seeks the cause of this difference in Lehfeldt's experiments, inasmuch as in these the value of $x_{\text{max.}}$ was obtained by interpolation. As, however, this interpolation is between very narrow limits (and the values of x' are also always observed), and the numerical values obtained by Lehfeldt and Regnault agree, and since, moreover, this important movement is improbable, it is preferable to assume that in Thayer's investigation errors have crept in, such as, for example, impurity of the substances.

Benzene and *acetic acid.* Nernst: additions of small quantities of acetic acid to benzene cause at first a reduction of the boiling-point. The greatest alteration $T_1 - T_m = 0.155°$ at $x = 0.023°$.

Alcohol and *water.* *Alluard: curves g for 735 and 760 mm from $x = 0.79$ to $x = 1$.

*Haywood (1): curve g for 753 mm from $x = 0.3$ to $x = 1$.

Dronke's observations agree with these two.

Le Bel found at barometric pressure a minimum boiling mixture $x = 0.073$.

Isopropyl alcohol and *water.* Erlenmeyer finds the mixture $x = 0.33$ boiling at 80°; Linnemann $x = 0.4$ at 78° to 80°; $T_1 = 84°$.

Trimethyl carbinol and *water.* Butlerow: the mixture $x = 0.29$ to 0.30 boils at 80°; $T_1 = 82.5°$.

Chloral and *water.* *Christensen: the mixture $x = 0.994$ boils at 95.2°; $T_1 = 97.2°$.

Pyridine and *water.* Goldschmidt and Constam: constant boiling-point 92° to 93° at $x = 0.775$. (See § 52.)

Phenol and *water.* Van der Lee: for $P = 260$ mm, $T_{\text{min.}}$ between $x = 0.83$ and 0.91; for $P = 390$ mm between $x = 0.91$ and 0.96; $T_2 - T_{\text{min.}} = 0.4°$ to $0.5°$.

*Lehfeldt (3): for P = 760 mm, T_{min} between $x = 0.97$ and 0.98, $T_2 - T_{min.} = 0.17°$; hence with rise of temperature the minimum mixture seems to move toward the second component. (Compare *Schreinemakers, § 52.)

Water and ammonia. Raoult (1): curve *g* from $x = 0$ to $x = 0.51$. $T = 0°$ is nearly straight.

*Mallet: curve *g* from $x = 0.50$, $T = -3.9°$, to $x = 0.76$ $T = -40°$. Since $T_2 = -38°$, this combination has a minimum boiling-point.

§ 57. Curves *h* and *k* and the plait point curve d_P in the neighborhood thereof, have been investigated principally by Kuenen for the already mentioned mixtures.

For *ethane* and *nitrous oxide*, the lines *h* drawn in Fig. 4, at 45 atm, *k* at 55 atm, k_0 at 65 atm, and the critical contact point curve l_P represent the observations to scale.

With regard to the curve d_P, the following investigations, not included in the diagram, have also been carried out.

Ether and *carbon disulphide.* Galitizine: curve d_P between $x = 0.7$ and $x = 1$; the drop of this portion makes the assumption of the existence of a minimum critical temperature quite probable.

Alcohol and *water.* Strauss: line d_P, between $x = 0$ and $x = 0.72$, is approximately straight; a minimum critical temperature does not follow from the observations.

4. The x,V-diagram

§ 58. Fig. 1 gives a representation of the shape of the transverse plait. For the vapor of ordinary liquid mixtures, the curve *a'* may be approximately obtained from the observed vapor pressure curve *a'* of Fig. 10. Here, accordingly, a minimum volume (point E') may occur with the vapor phase of a maximum pressure mixture. Observations in reference to this are unknown to me. Curves *a* over the whole breadth (not included in the figure) have been determined for:

Methyl alcohol and *water*, by Ditmar and Fawsitt.

Ethyl alcohol and *water*, by Mendelejeff.

According to these observations, contraction occurs on mixture, with both these liquid pairs. Furthermore, the following volume changes of the liquid phase on mixing have been observed by Bussy and Buignet, by Guthrie, and by Vincent and Delachanel (likewise omitted from the figure).

(Contraction is indicated by +.)

	Change of volume
Ether and *carbon disulphide*	+ 0.002 in maximum (B. and B.)
" " " "	+ 0.0007 at $x = 0.43$ (B. and B.)
" " " "	− 0.001556 at $x = 0.62$ (G.)
Chloroform and *carbon disulphide*	− 0.006(max) at $x = 0.6$ (B. and B.)
" " " "	− 0.006885 at $x = 0.56$ (G.)
Alcohol and *carbon disulphide*	− 0.01(max) at $x = 0.38$ (B. and B.)
" " " "	− 0.007278 at $x = 0.48$ (G.)
Chloroform and *alcohol*	+ 0.003 at $x = 0.8$ (B. and B.)
" " "	+ 0.002488 at $x = 0.58$ (G).
Benzene and *alcohol*	− 0.000249 at $x = 0.60$ (G).
Methyl cyanide and *methyl alcohol*	+ 0.00384 at $x = 0.74$ (V. and D.)
Methyl cyanide and *ethyl alcohol*	+ 0.00251 at $x = 0.78$ (V. and D.)

§ 59. In the neighborhood of the critical state, Kuenen has determined the curves β, β', and γ' for the mixtures named. In connection with the curves reproduced in Fig. 2, the full curves β and β' at 20°, γ at 26°, γ_0 at 29°, and the plait point curve δ, and the contact point curve λ, refer to *ethane* and *nitrous oxide*. Here, too, curves β' and also a' possess a maximum; however, the vapors depart too much from the gas laws for a minimum vapor volume to be expected just at the maximum pressure mixture.

Chapter D.—Mixtures of the third type

§ 60. Inasmuch as for this type observations far below the critical point have been obtained, the diagrams are more simply discussed than those of the previous types.

1. The x,P-diagram

§ 61. Fig. 2 includes the curves a and a' with the points E on the line e_T. In this connection we have the following:

Water and *hydrochloric acid.* Roscoe and Dittmar: curve a at 0° is concave toward the x-axis, between $x = 0$ and $x = 0.3$;

point E at $x = 0.142$. Line e_T is not parallel to the P-axis; its slope increases with the temperature, as may be seen from the following values:

At 55°	$P_{min.} = 50$ mm	for $x = 0.130$
75°	200	0.124
90°	400	0.119
110°	760	0.111^6

This last value was also found by Bineau. At 18.4° Allan has determined the portion of the curve a between $x = 0.16$ and 0.22, the slopes of these agree well with the observations of Roscoe and Dittmar at 0°.

Sulphuric acid and *water*. Marignac obtained by distilling dilute as well as fuming sulphuric acid a solution of the strength $x = 0.934$. This had the constant boiling-point $T = 338°$. Roscoe's investigation confirms this entirely.

Reghault (1): the curves a for temperatures between 5° and 35° are all convex toward the x-axis. The experiments were carried out with mixtures from $x = 0.5$ to $x = 1$.[1]

Water and *formic acid*. Konowalow has derived the curves a from border curves obtained by him for three different mixtures: these all have minimum points E. Of these lines, that at 100° is drawn. From his diagram it follows that this point is situated

for 42°	at $P_{min.} = 45$ mm	and $x = 0.48$
100°	565	0.53

while according to Roscoe's (2) observations it is found

for 107.1° at $P_{min.} = 760$ mm and $x = 0.57$.

Chloroform and *acetone*. *Von Zawidski: curves a and a' for 35.17°; $P_{min.} = 248.4$ mm at $x = 0.38$.

Pyridine and *acetic acid*. *Von Zawidski: curves a and a' for 80.05°; $P_{min.} = 84.6$ mm at $x = 0.62$.

Methyl ether and *hydrochloric acid*. Friedel obtained condensation of a mixture of these gases at ordinary barometric pressure and at −3° to −1°; the liquid that evaporated at

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[1] Van der Waals has theoretically discussed these observations. Zittingsversl. Kon. Akad. Amsterdam., March, 1891, p. 421 seq.

$-2°$ had a composition $x = \pm 0.45$. Condensation also occurred at $+1°$ and 850.2 mm.

This isolated observation is not included in the diagram.

*Kuenen (8) pointed out the existence of a minimum pressure up to the critical state.

2. The T,P-diagram

§ 62. Curves f for this type have been investigated only by Konowalow and *Kuenen (8) (see § 61). They are not included in the diagram.

Kuenen (8) also made observations on parts of the plait point curve d_x.

3. The x,T-diagram

§ 63. Fig. 4 represents the following observations:

Water and *hydrochloric acid.* Roscoe and Dittmar investigated the portion of the curve g at $P = 760$ mm between $x = 0.217$, $T = 60°$, and $x = 0.290$, $T = 0°$. With these observations those of Deicke between $x = 0.2602$, $T = 23°$, and $x = 0.289{,}^5$ $T = 0°$, entirely agrees; while those of Bakhuis Roozeboom between $x = 0.294$, $T = 0°$, and $x = 0.334$, $T = -24°$, connect with these in a satisfactory manner.

Water and *hydrobromic acid.* Constant boiling mixtures are obtained by:

Roscoe (1) at 126°	and	760 mm	$x = 0.1696$
153°		1952	0.162
Bineau at 20 to 25°			0.182
126°		750	0.166
Topsöe at 125° to 125.5°,		758	0.1715

With increase of temperature and pressure, the mixture thus moves toward the side of the water, which is also seen from the following observations by Roscoe, obtained by drawing dry air through the liquid:

$T = 16°$	$x_m = 0.1923$
100°	0.1784

This mixture, like the three following, is omitted from the diagram.

Water and *hydriodic acid.* The following maximum boiling-points are found:

Roscoe (1) at	100°	and	$x = 0.164$
	127°		0.157
Topsöe at	127°		0.162
Bineau at	128°		0.154

Water and *hydrofluoric acid.*

Gore at	125°	and	$x = 0.46$
Bineau	120°		0.33

Water and *nitric acid.* Roscoe (1): constant boiling mixture $x = 0.378$ at 120.5° and 735 mm. On increase of pressure and temperature, the maximum boiling-point and minimum pressure move toward the side of the nitric acid as follows:

At 65° to 70°	$P_{\text{min.}} = 70$ mm	$x = 0.364$
?	150	0.373
120.5°	735	0.378
?	1220	0.383

Mitscherlich's observations are in agreement with these.

Sulphuric acid and *water.* Lunge observed the curve g for $P = 720$ to 730 mm, between $x = 0.91$, $T = 110°$, and $x = 0.22$, $T = 295°$. The line is for the most part nearly straight. Its slope makes a maximum boiling-point very probable.

Chloroform and *acetone.* Thayer (2): curve g for $P = 735.5$ mm. $T_{\text{max.}}$ 63.3° at $x = 0.32^5$, $T_1 = 60.4°$, $T_2 = 55.3°$.

To this group of observations the following maximum boiling-points, omitted in the diagram, also belong:

Pyridine and *formic acid* ($T_1 = 116.7°$; $T_2 = 100.6$)

Gardner:	$T_m = 148°$ to 150°	at 760 mm	and	$x = 0.72$
	66°	20		0.72
André (1):	148° to 151°	761		0.70
	74.5°	36		0.70

Pyridine and *acetic acid* ($T_2 = 118.1°$)

Gardner:	$T_m = 139°$ to 140°	at 760 mm	and	$x = 0.60$
André (1):	139° to 140°	760		0.60
	74° to 74.5°	61		0.606
*Von Zawidski: (See § 61)	80.05	84.6		0.62

Pyridine and *propionic acid* ($T_2 = 140.7°$)

Gardner:	$T_m = 148°$ to 150°	at 760 mm	and	$x = 0.75$
André (1):	150° to 151.5	760		0.67
	± 60°	15		0.57

Picoline and *formic acid* ($T_1 = 133°$ to $135°$)

Gardner: $T_m = 156°$ to $159°$ at $x = 0.70$

Picoline and *acetic acid*

Gardner: $T_m = 145°$ to $148°$ at $x = 0.60$

Trimethylamine and *formic acid* ($T_1 = 3.2°$ to $3.8°$)

André (2): $T_m = 179.5°$ at 750 mm and $x = 0.70$
$95.5°$ 16 0.70

Trimethylamine and *acetic acid*

André (2): $T_m = 154°$ at 755.5 mm and $x = 0.797$
$80°$ to $81°$ 37 0.773

Triethylamine and *acetic acid* ($T_1 = 89°$ to $89.5°$)

Gardner: $T_m = 162°$ at $x = 0.80$

4. The x,V-diagram

§ 64. Lastly, we will consider Fig. 1, which is chiefly included for the sake of the theoretical discussion.

Curves a for the liquid are determined:

For *water* and *nitric acid*, and for *water* and *sulphuric acid*, over the whole breadth by Lunge (2).

For *water* and *hydrochloric acid*, by Lunge (2), up to $x = 0.24$

For *water* and *hydrobromic acid*, by Lunge (2), up to $x = 0.17$.

For *water* and *hydroiodic acid*, by Lunge (2), up to $x = 0.16$.

The first three lines are convex toward the x-axis, the latter two are straight. They are omitted in the figure.

The curves a' for the vapor phase are not more investigated than in the case of the other types; they may be, however, to a certain extent derived from the pressure, as in cases where, for example, Friedel has observed that the vapor densities of the mixture of *methyl ether* and *hydrochloric acid* mentioned $x = \pm 0.45$ are as follows:

1.464	at	100.5°
1.480		78.5°
1.698		1.5°

while the vapor density which would be obtained without contraction is 1.442.

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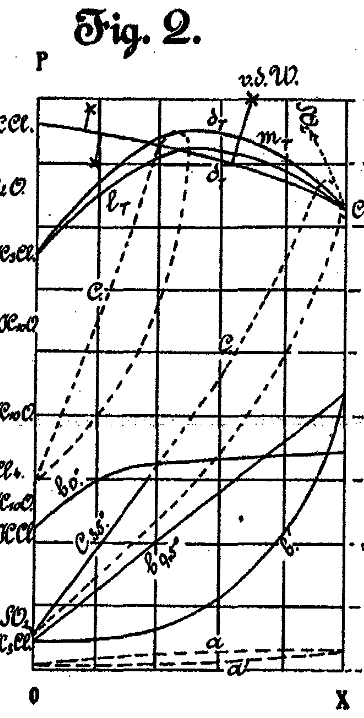
Fig. 2.



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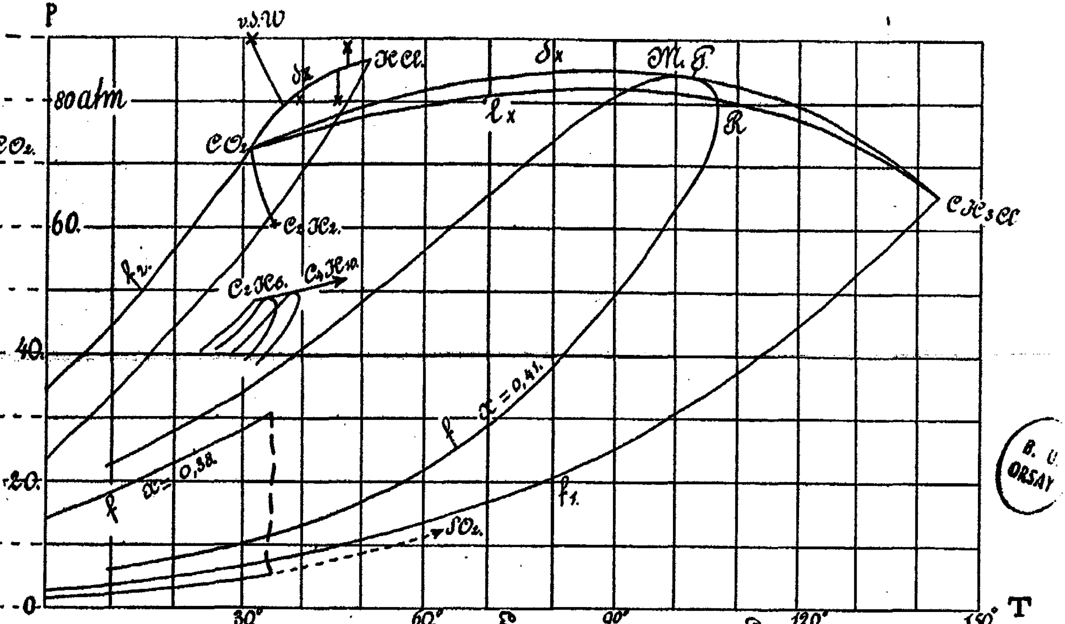

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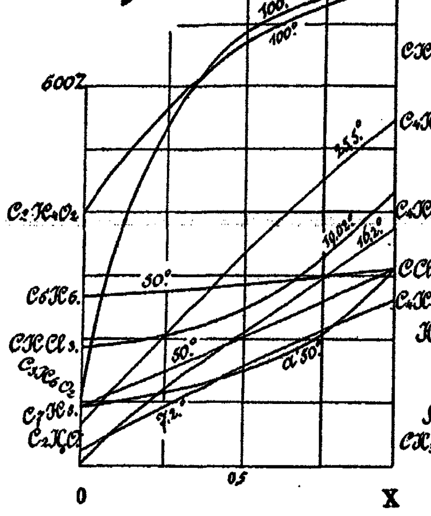

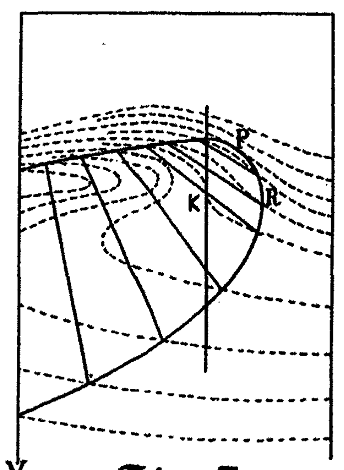

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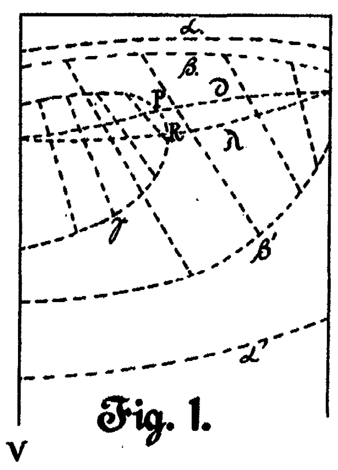

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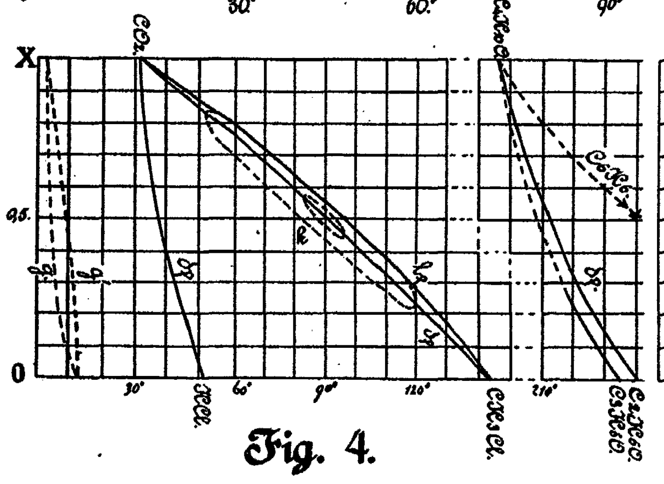

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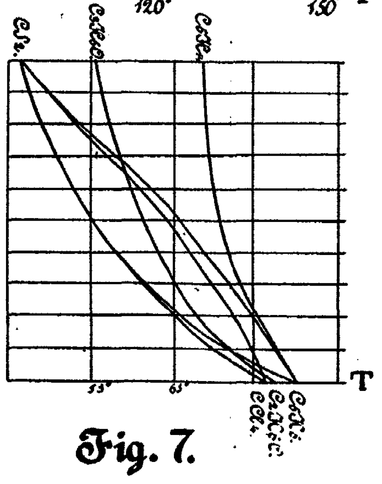
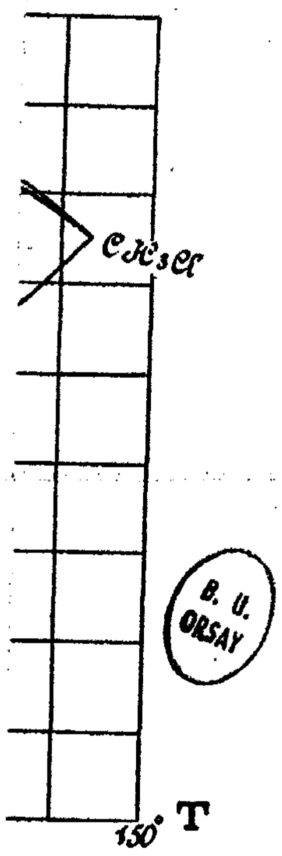
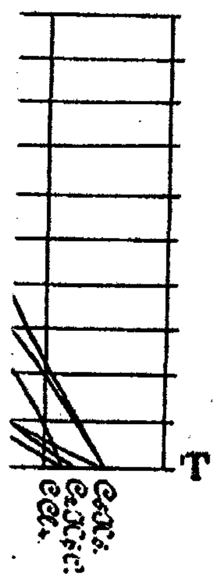


Fig. 7.

PLATE I.





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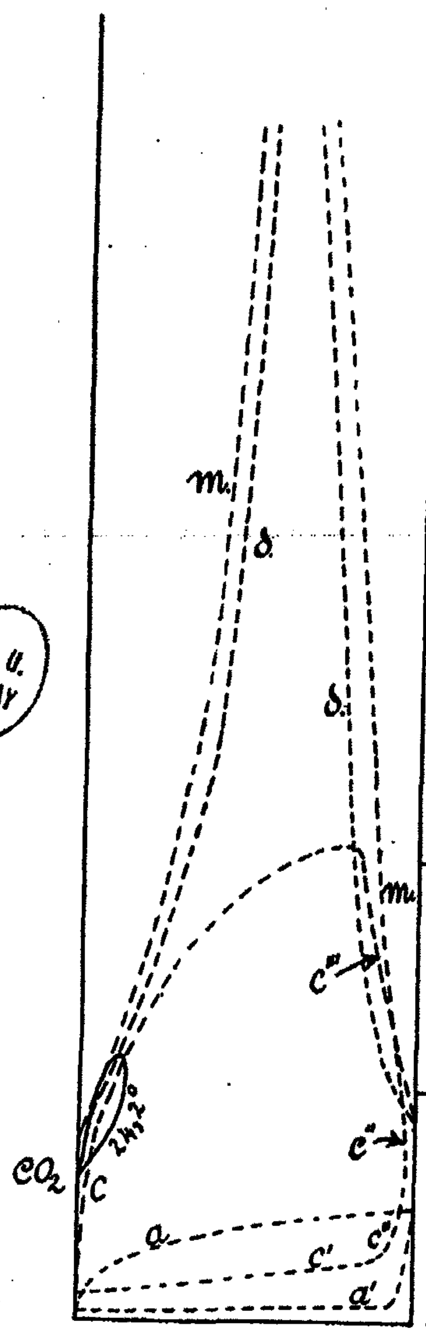

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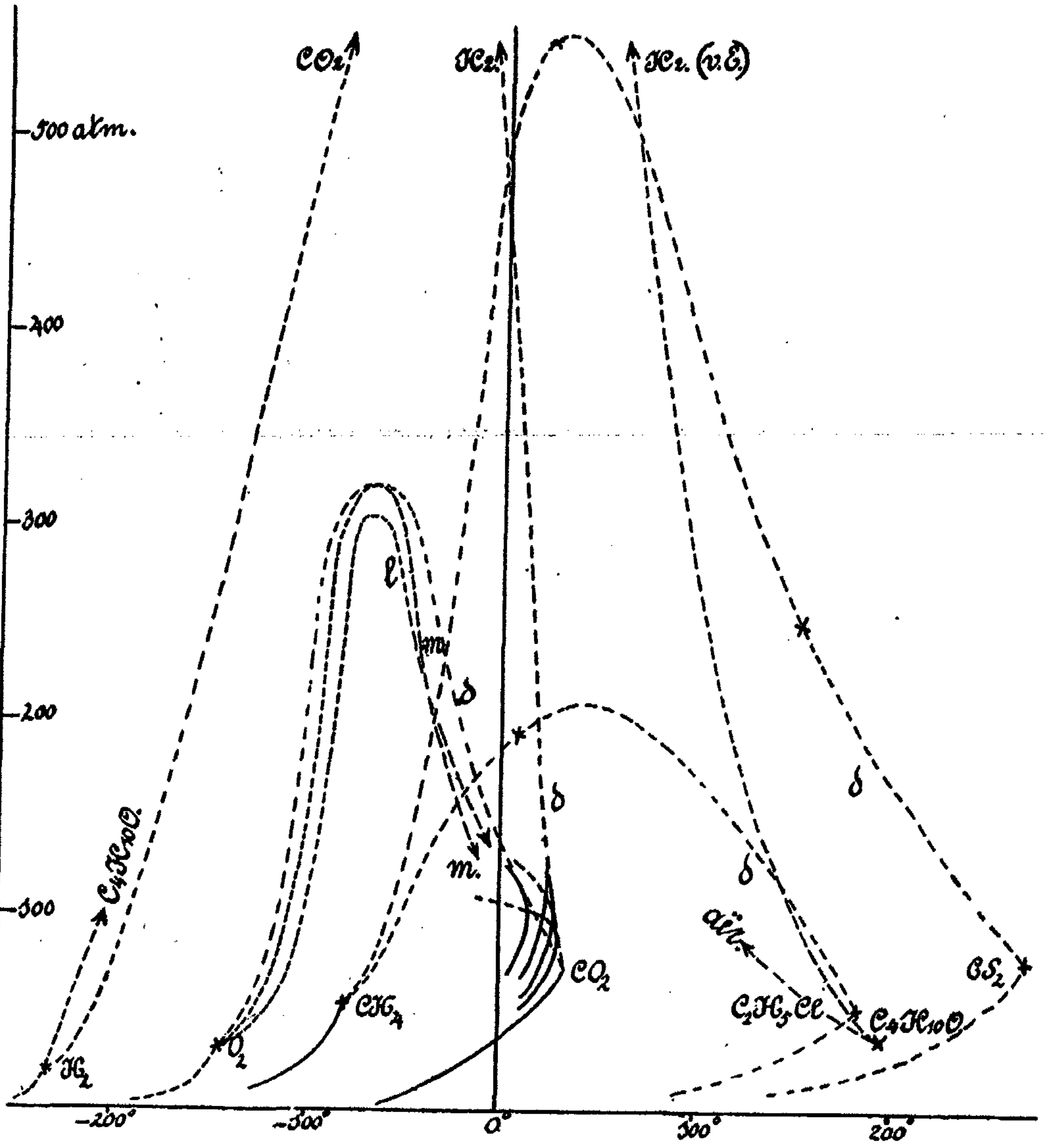
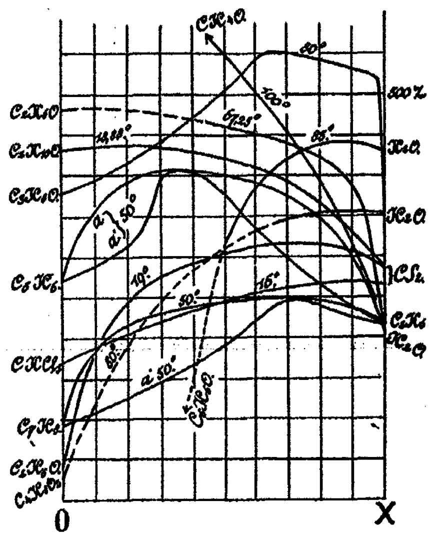


PLATE II.

Fig. 6.



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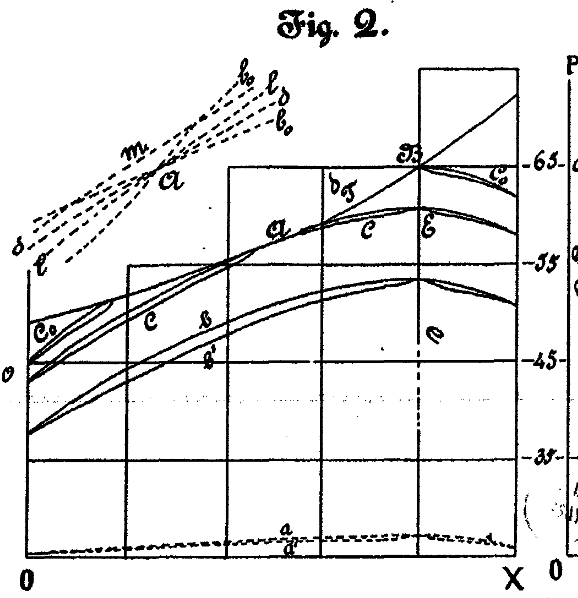

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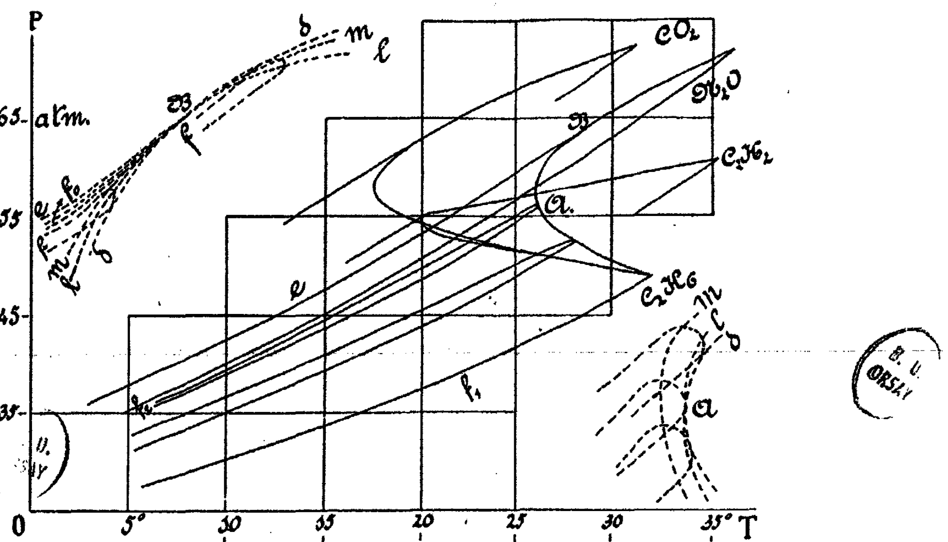

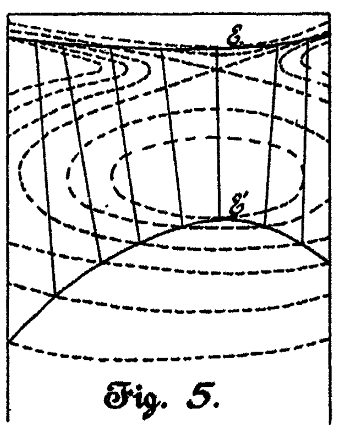

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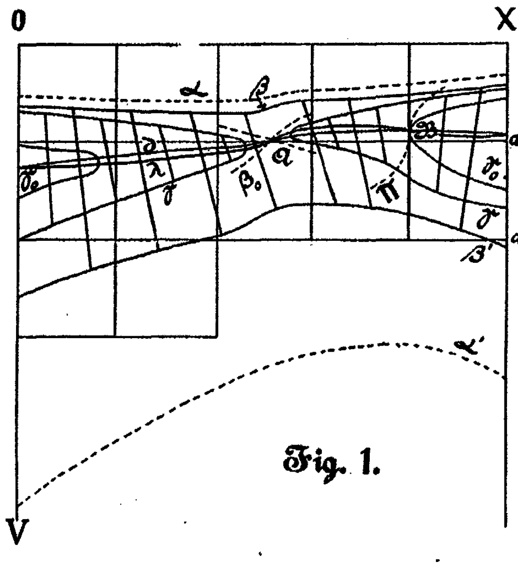

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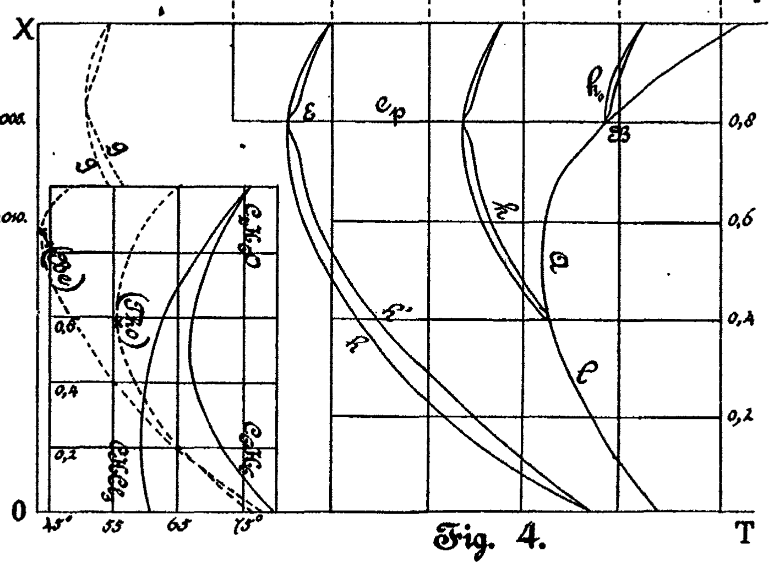
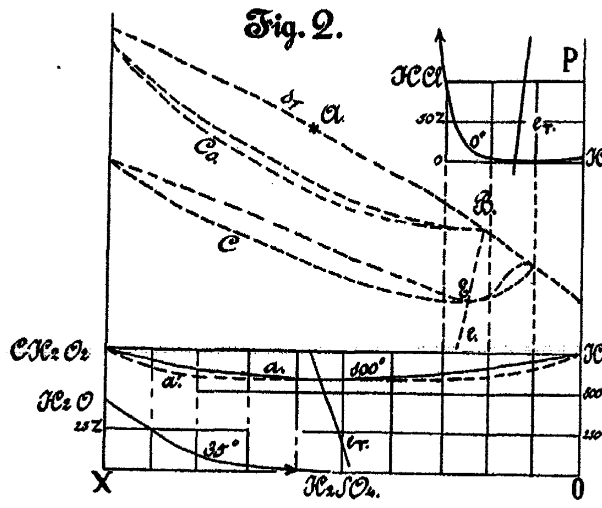


Fig. 4.

PLATE III.



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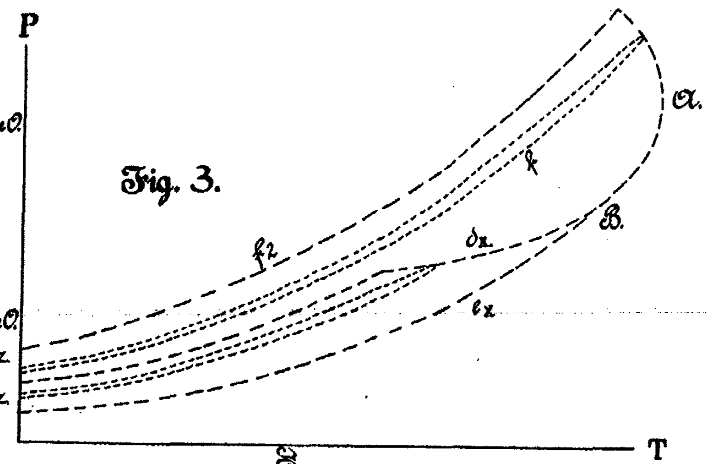

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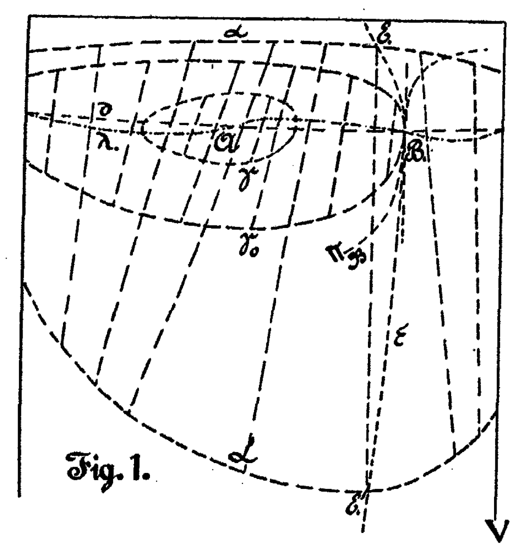

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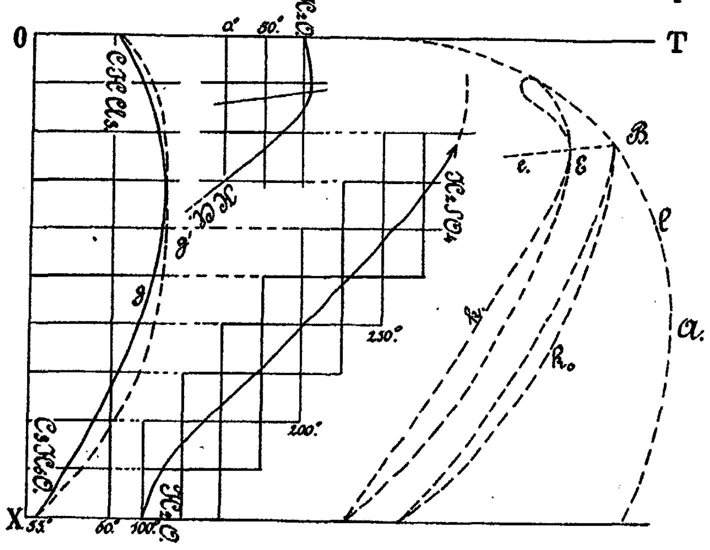

Fig. 4.

(Contribution from the Kent Chemical Laboratory of the University of Chicago.)

A NEW PROOF OF THE FORMULA $d = \frac{.02T^2}{L}$

BY FELIX LENGFELD

The ordinary student of chemistry has a rather vague conception of thermodynamics, and therefore in van 't Hoff's[1] demonstration of the relation between the lowering of the freezing-point of a solution (or the rise of the boiling-point) and certain physical constants of the solvents, he does not know why work is equal to

$$\frac{dT\,N\,L}{T\,n},$$

and hence it loses its entire meaning. The following modification of van 't Hoff's demonstration has been found of real value with such students.

Let a solution containing n gram-molecule solute in N grams solvent be put into a cylinder provided with a semi-permeable end and with a movable piston. At $T - dT$ the freezing-point of the solution let freeze out a quantity of the solvent that originally contained one gram-molecule solute, viz., $\frac{N}{n}$ grams. If L′ be the latent heat of fusion of the solvent at the temperature $T - dT$, there will be evolved $\frac{N}{n}$ L′ calories. Separate the solid from the solution and bring the whole to the temperature T, the melting-point of the solvent. To do this a calories must be added. Allow the solvent to melt. If its latent heat of fusion at the temperature T be L, it will absorb $\frac{N}{n}$ L calories. Now bring the liquid solvent into contact with

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[1] Zeit. phys. Chem. 1, 496 (1887).

the solution at the semi-permeable membrane with the pressure on the solution equal to the osmotic pressure. Raising the piston under this constant pressure the solvent passes through the diaphragm, mixing with the solution. The work done on the piston is equal to the osmotic pressure P into the volume of the solvent V. As V is the volume that contained one gram-molecule solute $PV = RT$, or if we express R in thermal units, Work $= PV = 2T$.

Bring the whole to the original temperature $T - dT$, thus coming back to the starting-point. During this last process b calories are evolved. We therefore have $\left(\frac{N}{n}L + a\right)$ calories absorbed and $\left(\frac{N}{n}L' + b\right)$ calories are evolved. The work done must be the difference between these, or as a and b are practically equal, we may consider $2T = \frac{N}{n}(L - L')$. Consider the solvent an ideal liquid that may be supercooled indefinitely, and let the specific heats of both liquid and solid be constants from absolute zero to the normal melting-point T. If one gram of the liquid phase be at absolute zero it will absorb in going to the temperature T'', h_lT'' calories if h_l be its specific heat. In like manner, one gram of the solid will absorb h_sT'' calories if h_s be its specific heat. The latent heat of fusion at the temperature T' will therefore be $(h_l - h_s)T''$, and at any temperature T it will be $(h_l - h_s)T$. Substituting for L and L′ in the expression $2T = \frac{N}{n}(L - L')$ their values $(h_l - h_s)T$ and $(h_l - h_s)(T - dT)$, we get $2T = \frac{N}{n}(h_l - h_s)dT$, and substituting for $h_l - h_s$ its value $\frac{L}{T}$, the expression becomes $2T = \frac{N}{n}dT\frac{L}{T}$ or $dT = \frac{2T^2}{L} \cdot \frac{n}{N}$ or for one gram-molecule solute in 100 grams solvent $dT = \frac{.02T^2}{L}$.

Of course we have assumed ideal conditions but they may be considered as realized for very dilute solutions and slight differences of temperature. The corresponding expression for the rise of the boiling-point may be derived in a similar manner.

A point made clear by this demonstration is that the specific heat of a liquid must be greater than that of its solid or its vapor within the same range of temperature. Otherwise the solution might have a lower boiling-point or a higher freezing-point.

(CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.)

THE INFLUENCE OF ELECTRICAL WAVES ON CHEMICAL ACTION

BY FELIX LENGFELD AND JAMES H. RANSOM

Though the influence of short ether waves on many chemical reactions has been carefully studied, nothing has been done with the longer electrical waves. A few experiments in this direction have been carried out, and though the results so far have been purely negative, the investigation will be continued, varying the length of wave and the reaction. Glass bulbs and afterwards tubes were filled with electrolytic mixtures of hydrogen and chlorine (1 to 1) and of hydrogen and oxygen (2 to 1). Some were then wrapped in cotton wool and put into wooden boxes, others were wrapped in tinfoil and put into tightly closed tin cans. They were then placed in the field of a modified Toepler-Holtz influence machine, giving rise to electrical waves of about 300 meters. After forty-five minutes bulbs protected from the waves by the metal and others not so protected were opened under salt water. No change of volume was observed and therefore the action was continued forty-eight hours. Bulbs were again opened under salt water, but there was no change of volume or absorption showing that electrical waves of 300 meters cause no reaction between hydrogen and chlorine, or hydrogen and oxygen.

ON THE DIELECTRIC CONSTANTS OF PURE SOLVENTS[1]

BY HERMAN SCHLUNDT

INTRODUCTION

In 1893, Nernst,[2] from theoretical considerations based upon the theory of electrolytic dissociation, deduced his well known rule, that other things being equal, the greater the dielectric constant of a medium, the greater is its dissociating power. In the same year J. J. Thomson[3] also pointed out this relation, saying that if we accept the view that the forces between the atoms are electrical in their origin, then the effect of surrounding the molecules of a substance by a medium possessing a very high dielectric constant like water, would be to practically dissociate them. According to Nernst, proportionality between the dielectric constant and dissociating power need not necessarily exist. The experimental facts, he says, show beyond a doubt that a marked parallelism exists between the dissociating power and the dielectric constant of a solvent. Exceptions to the rule, Nernst explains by assuming the existence of specific influences of which the association of the ions with the molecules of the solvent is probably of prime importance.

The existing experimental data, at the time the above relation between the dielectric constant and dissociating power was pointed out, accorded well with it;[4] and subsequent investiga-

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[1] Extract from the author's dissertation submitted for the Degree of Doctor of Philosophy at the University of Wisconsin. A part of this investigation appeared in Volume 5, p. 157 (1901) of this Journal. The present article completes the paper as it is printed in full as a Bulletin of the University of Wisconsin, Science Series, 1901.

[2] Gött. Nach. No. 12 (1893). Also Zeit. phys. Chem. 13, 531 (1894).

[3] Phil. Mag. 36, 320 (1893).

[4] See Nernst: "Theoretische Chemie," p. 365. (Dritte Auflage.)

tions furnished numerous additional examples in its support. But exceptions also appeared, which point to a marked specific influence of the solvent. Some of these exceptions are noted and discussed in another part of this article.

Since the formulation of the Nernst-Thomson rule, excellent new methods for determining dielectric constants have been devised by Thwing,[1] Nernst,[2] and Drude;[3] and these investigators have measured the dielectric constants of a number of substances. The pupils of Nernst, and Drude, and others have elaborated, modified, and perfected these respective methods, so that the determination of dielectric constants at ordinary temperatures is now a comparatively simple operation. During this period the electrical conductivity of non-aqueous solutions has also received considerable study, and the dissociating power of various solvents which yield conducting solutions has moreover been investigated by means of cryoscopic and boiling-point determinations. The selected examples given in the following table will serve to show that various other solvents besides water possess ionizing power in a very marked degree. Under V, in the third column, the volume in liters is given, in which one gram-molecule of substance is dissolved; and the next column indicates the corresponding molecular conductivity, while the fifth column gives the temperature at which the measurements were made.

The dielectric constants of the last four solvents given in the table have, to my knowledge, not been determined before. In a previous communication[4] on this subject, the values obtained for the dielectric constants of the aliphatic nitriles were given, and it was stated that Drude's "second" method was followed in making the measurements. The results which follow were obtained with the same apparatus. Besides the substituted ammonias, this investigation embraces a number of other or-

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[1] Zeit. phys. Chem. 14, 286 (1894). Also Phys. Review, 2, 35 (1894).

[2] Ibid: 14, 622 (1894).

[3] Ibid. 23, 267 (1897).

[4] Jour. Phys. Chem. 5, 157 (1901).

TABLE I.

Solvent	Solute	v	μ_v	t°	Observer
Water	KI	2	99.7	18	Kohlrausch[1]
		10.0	116.1		
		1000	120.3		
Methyl alcohol	LiCl	11.7	40.1	18	Völlmer[2]
		117.4	57.5		
		1174	65.3		
Formic acid	KCl	32	40.7	25	Zanninovich-Tessarin[3]
		1024	57.8		
Liquid ammonia	KBr	301.9	210.6	−38	Franklin and Kraus[4]
		1354	272.9		
		65040	340.2		
Acetone	KI	144.7	109.4	18	St. v. Lascynski[6]
		1157.6	145.8		
Liquid sulphur dioxide	$N(C_2H_5)_4I$	16	43.1	0	Walden[5]
		128	51.6		
		1024	54.8		
Benzonitrile	$AgNO_3$	9.43	5.2	25	Lincoln[7]
		151.96	16.4		
Acetonitrile	$AgNO_3$	.8	54.5	25	Dutoit and Friderich[8]
		128	118.3		
Pyridine	NH_4I	79.02	16.7	25	St. v. Lascynski and St. v. Gorski[9]
		1264.32	36.9		
Phosphorus oxychloride	$S(CH_3)_3I$	204	26.4	25	Walden[10]
		1224	38.2		
Arsenic trichloride	$S(CH_3)_3I$	250	51.4	25	Walden[10]
		1500	66.6		

ganic compounds containing nitrogen, and includes most of the inorganic solvents in which Walden[10] made electrical conductivity measurements.

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[1] Wied. Ann. 26, 161 (1885).
[2] Ibid. 52, 328 (1894).
[3] Zeit. phys. Chem. 19, 251 (1896).
[4] Amer. Chem. Jour. 23, 288 (1900).
[5] Ber. chem. Ges. Berlin, 32, 2862 (1899).
[6] Zeit. Elektrochemie, 2, 55 (1895).
[7] Jour. Phys. Chem. 3, 457 (1899).
[8] Bull Soc. Chim. Paris, [3] 19, 327 (1898).
[9] Zeit. Elektrochemie, 4, 290 (1897).
[10] Zeit. anorg. Chem. 25, 209 (1900).

Experimental Results

In addition to the nitriles previously measured, the dielectric constants of ethylene cyanide, mandelic nitrile, α- and β-naphthonitriles were measured.

Ethylene cyanide

The sample of succinic acid nitrile was Schuchardt's make. It was treated with fused calcium chloride, filtered, and was twice redistilled under diminished pressure. Its boiling-point was 168° under a pressure of 28 mm. A solid, almost colorless mass was thus obtained which melted at 55° C. Its D.C.[1] was measured in the form of cell Drude[2] used for the measurement of substances at higher temperatures. In making the measurements the cell was kept in an oil-bath, of the form figured by Coolidge,[3] attached to the apparatus. The temperature of the bath was kept at 60° C during the measurements of the liquid ethylene cyanide. The average of three determinations gave the value 61.2 for the D. C. The D. C. of the solid compound was also determined. Four determinations gave an average of 65.3 at 23° C. No sudden change was observed in the D. C. at the melting-point. The absorption of the solid ethylene cyanide was very slight, but the liquid sample did not show quite as well a defined maximum resonance, which was found to be due to its greater conductivity. In fact the qualitative measurements of its resistance show that the resistance increases very rapidly as the temperature is lowered, but no sudden change in the resistance was observed at the melting-point.

α-Naphthonitrile

Schuchardt's preparation was redistilled under diminished pressure. Its melting-point was 37° C, but the substance may easily be kept in a liquid state at 20° C provided the solid phase is not present. The following values were found for the D. C. of the liquid sample:

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[1] In the presentation of results this abbreviation is used for dielectric constant.

[2] See Fig. 7, p. 285, Zeit. phys. Chem. 23.

[3] Wied. Ann. 69, 1, 33 (1899).

D. C. = 16.0 at 70° C.
" = 17.9 at 42° C.
" = 19.2 at 22° C.

The position for maximum resonance was not well defined. My efforts to determine the D. C. of the solid sample did not yield satisfactory results. In solidifying, the mass between the plates of the condenser did not become compact and homogeneous; air spaces seemed to exist, and a well defined maximum was not observed. The value 6.3 at 21° C must therefore be regarded as only approximate.

β-Naphthonitrile

This sample was also redistilled under diminished pressure. Its boiling-point was 190° under 35 mm of pressure. Its melting-point was 64° C. It could not be supercooled. The D. C. for the liquid was found to be 16.9 at 70°, and for the solid the value 4.3 at 22° C was found.

Mandelic nitrile

The preparation from which the sample was obtained showed decided signs of decomposition, being of a dark brown color, and somewhat syrupy. It was treated with fused calcium chloride for two weeks, was then filtered and distilled under diminished pressure. The sample thus obtained was redistilled; its boiling-point was 94° under a pressure of 50 mm. A mobile, colorless liquid was thus obtained, whose specific conductivity was found to be 2.2×10^{-10} reciprocal ohms. Its D. C. was found to be 17.82 at 23°. Absorption of about the same order as that of nitrobenzene was observed. Its absorption index was also determined by the method outlined by Drude.[1] The value obtained in this way was 0.045, agreeing very well with that of nitrobenzene, which Drude places at 0.05. Drude has found that this anomalous absorption is characteristic of compounds containing hydroxyl.

The Substituted Ammonias

The amines whose dielectric constants were measured are enumerated in Table I. The samples used were Schuchardt's

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[1] Zeit. phys. Chem. 23, 292-297.

preparations with the exception of the two toluidines and the xylidine, which were of Trommsdorff's manufacture. Each sample, except methylamine, was dehydrated with fused potassium hydroxide and then distilled, and in many cases the distillate was again treated with fused potash and redistilled. The sample of methylamine was doubtless impure for, upon evaporation it left a residue, and it did not yield a well defined position for maximum resonance, while with all the other samples well defined maxima were observed. Hence the value found for the D.C. of methylamine is doubtless too high.

The third column in the following table gives the boiling-points of the samples taken for the measurements, and the fourth column indicates the corresponding barometric pressure, while the last column gives the temperature at which the dielectric constant was measured.

TABLE II.

Name	Formula	B.P.	P.	D.C.	*t*°
Methylamine	CH_3NH_2	—	—	<10.5	21
Ethylamine	$C_2H_5NH_2$	<17.5	752	6.17	21
Isopropylamine	$(CH_3)_2CHNH_2$	36	750.5	5.45	20
Butylamine(*n*)	$C_4H_9NH_2$	76–77	740.0	5.30	21
Isobutylamine	$(CH_3)_2CHCH_2NH_2$	68	745.2	4.43	21
Amylamine	$C_5H_{11}NH_2$	94–95	740.4	4.50	22
Diethylamine	$(C_2H_5)_2NH$	54.5	733.4	3.58	21
Dipropylamine	$(C_3H_7)_2NH$	108-108.5	745.5	2.90	22
Diisobutylamine	$[(CH_3)_2CHCH_2]_2NH$	134.5	735.0	2.65	22
Trimethylamine	$(CH_3)_3N$	<8	750	2.95	4
Aniline[1]	$C_6H_5NH_2$	179.4	741	7.2	18.5
Toluidine(*o*)	 $C_6H_4<\begin{smallmatrix}CH_3\\NH_2(o)\end{smallmatrix}$	194.5	738.0	5.93	20
Toluidine(*m*)	 $C_6H_4<\begin{smallmatrix}CH_3\\NH_2(m)\end{smallmatrix}$	194.2	738.2	5.95	20
Xylidine 1 : 3 : 4	 $C_6H_3\begin{smallmatrix}CH_3\ 1\\CH_3\ 3\\NH_2\ 4\end{smallmatrix}$	209.5	737.0	4.90	20
Monomethylaniline	$C_6H_5NHCH_3$	189.4	740.5	5.8	20
Dimethylaniline	$C_6H_5N(CH_3)_2$	191.5	735.0	5.07	20
Dibenzylamine	$(C_7H_7)_2NH$	200	40.0	3.55	20

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[1] The value 7.15 (at 21°) was found by Drude; and 7.22 (at 15°) by Ratz. Zeit. phys. Chem. 19, 94 (1896).

Miscellaneous Organic Compounds

a-Picoline

The sample was Schuchardt's preparation. It was treated with fused calcium chloride, and redistilled. The boiling-point of the portion taken for the measurements was 128.5°–129.5° C at 736 mm of pressure. The value found for the D. C. is 9.8 at at 20° C.

Piperidine

The sample was E. de Haën's preparation. It was redistilled and the portion distilling between 105.5°–107.0° C under a pressure of 745 mm was used for the measurements. It was an almost colorless liquid and showed no absorption. The value found for its D. C. was 5.8 at 22° C.

Carbon dichloride

The sample used was of Schuchardt's make. Its boiling-point was 118° at 726.5 mm of pressure. The value 2.46 was found for its D. C. at 21° C.

Nitromethane

Schuchardt's preparation was treated with fused calcium chloride and redistilled. Its boiling-point was 99.9° under a pressure of 738.4 mm. The dielectric constant found was 40.4 at 19° C. Thwing[1] gives the value 56.36 at 15° C.

Nitroethane

Schuchardt's preparation was dehydrated and rectified as in the case of nitromethane. Its boiling-point was 110.5° C under a pressure of 738.3 mm of pressure. The value of its D. C. was found to be 29.5 at 18° C.

Methyl nitrate

The sample of methyl nitrate used for the measurements was prepared from Kahlbaum's best methyl alcohol by treating it with nitric acid according to the method of J. Lea.[2] The

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[1] Phys. Review, 2, 35 (1894).

[2] See Beilstein. "Handbuch der Organischen Chemie." Third Edition· Vol. I., p. 324.

sample was washed with water containing a small amount of sodium carbonate, and then with distilled water. It was dehydrated with fused calcium chloride and finally distilled from a water-bath. Its boiling-point was 64.4° C at 730.2 mm of pressure. The value 23.5 was found for its D. C. at 18° C. No absorption was observed.

Ethyl nitrate

Schuchardt's preparation was washed with water containing a trace of sodium carbonate to remove traces of nitric acid and alcohol. It was then dried with fused calcium chloride and redistilled twice. The boiling-point was 86.1° under a pressure of 729.4 mm. The average of three determinations gave the value 18.3 at 18° C for its D. C. Thwing found the value 17.72 at 15°, and Drude found 19.6 for the D. C. of this compound at 17° C.

Propyl nitrate

This compound was prepared according to the method of Wallach and Schulze.[1] The propyl alcohol used for its preparation was redistilled. Its boiling-point was 95.8° under a pressure of 752 mm. The sample of propyl nitrate was dehydrated and rectified as described for methyl nitrate. Its boiling-point was 108.5° C under 738.5 mm of pressure. The value 13.9 was obtained for its D. C. at 18° C.

Isobutyl nitrate

Schuchardt's preparation was redistilled. Its boiling-point was 120.0° under 738.2 mm of pressure. One series of measurements was made which gave the value 11.7 for its D. C. at 19° C.

Isopropyl nitrite

A sample of isopropyl nitrite, probably not entirely free from nitrous acid, was measured. The value 11.5 was found for its D. C. at 19° C.

Ethyl urethane

The sample used for the measurements was kindly furnished by the School of Pharmacy of this University. Its melting-

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[1] Ber. chem. Ges. Berlin, 14, 422.

point was 48° C. The value found for the D. C. of the liquid sample at 60° was 13.6; the solid form gave the value 3.18 at 23° C.

Amylsulphydrate

The boiling-point of the sample was 116.5° C under 752 mm of pressure. The D. C. found was 4.35 at 22° C.

With the exception of the substituted ammonias, the foregoing results are summarized in the following table: The third column gives the boiling-points of the samples used for the measurements, and the fourth column indicates the corresponding barometric pressures, while the last column gives the temperatures at which the dielectric constants were measured.

TABLE III.

Name	Formula	B.P.	P.	D.C.	*t*°
Nitromethane[1]	CH_3NO_2	99.9	738.4	40.4	19
Nitroethane	$C_2H_5NO_2$	110.5	738.3	29.5	18
Methyl nitrate	CH_3NO_3	64.4	730.2	23.5	18
Ethyl nitrate[2]	$C_2H_5NO_3$	86.1	729.4	18.3	18
Propyl nitrate	$C_3H_7NO_3$	108.5	738.5	13.9	18
Isobutyl nitrate	$(CH_3)_2CHCH_2NO_3$	120.0	738.2	11.7	19
Isopropyl nitrite	$(CH_3)_2CHNO_2$	—	—	11.5?	19
Ethyl urethane	$CO(NH_2)(OC_2H_5)$	—	—	13.6	60
Ethyl urethane (solid)	——	—	—	3.18	23
α-Picoline	$C_5H_4N.CH_3(\alpha)$	128.5–129.5	736	9.8	20
Piperidine	$C_5H_{11}N$	105.5–107	745	5.8	20
Carbon dichloride	C_2Cl_4	118	726.5	2.46	21
Amylsulphydrate	$C_5H_{11}SH$	116.5	752	4.35	22
Ethylene cyanide	$C_2H_4(CN)_2$	168	28	61.2	60
“ “ (solid)	“	—	—	65.3	23
α-Naphthonitrile	$C_{10}H_7CN(\alpha)$	—	—	16.0	70
“ (liquid)	“	—	—	17.9	42
“ “	“	—	—	19.2	22
“ (solid)	“	—	—	6.3?	21
β-Naphthonitrile	$C_{10}H_7CN(\beta)$	190	35	16.9	70
“ (solid)	“	—	—	4.3	22
Mandelic nitrile	$C_6H_5CH<\begin{matrix}OH\\CN\end{matrix}$	94	50	17.82	23

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[1] Thwing gives the value 56.36 for its D. C. at 15°.

[2] Thwing found the value 17.72 at 15°, and Drude found 19.6 at 17°.

Inorganic Solvents

Phosphorus trichloride

The sample used was of Kahlbaum's manufacture. It was redistilled, boiling at 74.1° C under a pressure of 740 mm. The average of two determinations gave the value 3.36 for its D.C. at 22° C. No absorption was observed.

Arsenic trichloride

The sample which served for the measurements had been prepared in this laboratory by Dr. Lincoln. It was dried with fused calcium chloride and was redistilled. The sample used boiled from 127°-128° C under 740 mm of pressure. The value 12.35 was obtained for its D.C. at 21° C. Slight absorption, which was doubtless due to conduction, was observed.

Antimony trichloride

The sample used for the measurements conducted about as well in the fused state, at 70° C, as a fiftieth-normal sodium chloride solution at 25° C. The position for maximum resonance was still well enough defined without increasing the intensity of the oscillations in the secondary circuit, but the absorption was more marked than with arsenic trichloride. Hence it seemed advisable to determine the D.C. by the method outlined by Drude[1] for substances which show absorption. The value thus obtained was 33.2 at 75° C. For the solid compound the value 5.4 was found at 18° C.

Antimony pentachloride

The sample used was E. de Haën's preparation. It was found securely stoppered, and hence was not rectified. The value 3.78 was obtained for its D.C. at 21.5° C.

Stannic chloride

Kahlbaum's preparation was redistilled. Its boiling-point was 117.5° C under 750 mm of pressure. The value found for its D.C. is 3.2 at 22° C.

Sulphur monochloride

The sample used for the measurements had been prepared

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[1] See Drude. Zeit. phys. Chem. 23, 294-297.

in this laboratory by Mr. Harry Eggers. It was redistilled and found to boil at 136.2° under 738 mm of pressure. The value 4.8 was found for its D. C. at 22° C.

Sulphur trioxide

A sample of Kahlbaum's sulphur trioxide was measured in both the solid and the liquid states. The value 3.56 was obtained for the D. C. of the liquid sample at 21°, and 3.64 for the solid at 19° C.

Phosphorus oxychloride

The sample used for the measurements was prepared according to the method described by Gerhardt.[1] About 150 g of phosphorus pentachloride was mixed with one-half its weight of dry oxalic acid in a retort and heated gently. The distillate thus obtained was redistilled and found to boil at 105.1° under a pressure of 739.2 mm. The value obtained for its D. C. was 13.9 at 22° C.

Sulphuryl chloride (SO_2Cl_2)

This compound was prepared by the method of Schulze.[2] A quantity of camphor was liquefied by passing dry sulphur dioxide into the containing vessel. Dry chlorine gas was then passed into the liquid and the current of sulphur dioxide was also continued. In the presence of the camphor, chlorine and sulphur dioxide unite to form sulphuryl chloride. After several distillations a product boiling at 68.4° under 740.2 mm of pressure was obtained. The value 9.15 was found for its D. C. at 22° C.

Thionyl chloride ($SOCl_2$)

The sample used for the measurements was prepared in the usual way, namely, by the reaction of dry PCl_5 with dry SO_2. [$PCl_5 + SO_2 = POCl_3 + SOCl_2$]. About 150 g of PCl_5 were placed in a retort connected with a reflux condenser and a stream of SO_2 was conducted in till the PCl_5 had become liquefied; another portion of PCl_5 was then added, and the stream of

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[1] Ann. Chim. Phys. [3], 44, 102.

[2] Jour. prakt. Chem. 23, 351.

SO_2 was continued. The liquid thus obtained was heated for some time, with the return condenser still attached, to free it from SO_2; and finally, by repeated fractional distillation a sample of $SOCl_2$ was obtained, which had a constant boiling-point of 76.8° under a pressure of 751.3 mm. The value found for its D. C. is 9.05 at 22° C. Slight absorption was observed.

Liquid sulphur dioxide

A sample of liquid sulphur dioxide was measured in a sealed cell. The value found for its D. C. at 22° is 12.35. Linde,[1] by Nernst's method, found the value 14.8 at 23°, while Coolidge[2] found the value 13.75 at 14.5°. I made but one determination.

Bromine

The sample of bromine which served for the measurements was prepared by Miss Winifred Titus from potassium bromide, potassium bromate, and sulphuric acid according to the method of J. S. Stas.[3] The value 3.18 was obtained for its D. C. at 23° C. The measurements were made soon after the bromine had been introduced into the cell so as to minimize the action of the bromine on the platinum plates.

Iodine

Pure, resublimed iodine obtained from the chemical works of de Haën at List, near Hannover, was once more sublimed by Prof. Kahlenberg. An attempt was made to determine its D. C. in the solid and the liquid states in a sealed cell. With the solid sample the position for maximum resonance was still fairly well defined, but after removing the iodine from the cell it was found that the plates of the condenser were covered with a black coating, which doubtless introduced an error. Hence the value 10.3, which was found for its D. C. at 23°, must be regarded as only approximate. With the liquid sample no distinct maximum resonance was obtained.

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[1] Wied. Ann. 56, 546 (1895).

[2] Ibid. 69, 130 (1899).

[3] Untrs. über Proport. u. Atomg. Leipzig, 1867, p. 220. See also Fehling's Handwörterbuch d. Chemie, I., p. 235.

Cyanogen (liquid)

In view of the high dielectric constant obtained for hydrocyanic acid, it seemed of special interest to determine the D. C. of liquid cyanogen. Prof. Kahlenberg kindly offered to undertake the preparation of this compound with me. We evolved the cyanogen by treating a strong solution of copper sulphate with a concentrated solution of potassium cyanide. The gas was dried by passing it through two large U-tubes filled with fused calcium chloride. It was condensed by means of solid carbonic acid. The D. C. was measured in a sealed cell at 23° C. We found the value 2.52, the position for maximum resonance being well defined.

The foregoing values obtained for the dielectric constants of the inorganic solvents enumerated are summarized in the following table:

TABLE IV.

Name	Formula	B.P.	P.	D. C.	$t°$
Phosphorus trichloride	PCl_3	74.1	740	3.36	22
Arsenic "	$AsCl_3$	127–128	740	12.35	21
Antimony "	$SbCl_3$	—	—	33.2	75
" " (solid)	"	—	—	5.4	18
Antimony pentachloride	$SbCl_5$	—	—	3.78	21.5
Stannic chloride	$SnCl_4$	117.5	750	3.2	22
Sulphur monochloride	S_2Cl_2	136.2	738	4.8	22
Sulphur dioxide[1]	SO_2	—	—	12.35	22
Sulphur trioxide	SO_3	—	—	3.56	21
" " (solid)	"	—	—	3.64	19
Sulphuryl chloride	SO_2Cl_2	68.4	740.2	9.15	22
Thionyl "	$SOCl_2$	76.8	751.3	9.05	22
Phosphorus oxychloride	$POCl_3$	105.1	739.2	13.9	22
Cyanogen	$(CN)_2$	—	—	2.52	23
Bromine	Br	—	—	3.18	23
Iodine (solid)	I	—	—	10.3?	23

Discussion of Results

The results given in the foregoing tables show that in an

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[1] Linde gives the value 14.8 at 23° for the D. C. of liquid SO_2. Coolidge gives the value 13.75 at 14.5° for the D. C. of the liquid SO_2.

homologous series of compounds the dielectric constants decrease with increase of molecular weight. The compounds investigated offer no exceptions to this rule. The primary amines have higher values for their dielectric constants than the corresponding secondary amines; and the values for the secondary amines are higher than those for the tertiary, as is shown by the following examples:

Ethylamine,	D. C. = 6.17
Diethylamine,	D. C. = 3.58
Trimethylamine,	D. C. = 2.95

A further inspection of the values of the dielectric constants of the several homologous series of liquid compounds investigated by other observers shows that a decrease in the value of the dielectric constant with increase of moleculor weight is the general rule. Tereschin[1] first pointed out this fact in connection with the values he obtained for the dielectric constants of a number of homologous esters of the aliphatic acids and of benzoic acid. The values obtained by Tomaszewski[2] for the dielectric constants of the homologues of benzene, however show that their dielectric constants increase with increase of molecular weight. The dielectric constants of the homologues of benzene and a number of aliphatic hydrocarbons have been determined by Landolt and Jahn[3], by Nernst,[4] and by others. Some of these results are given in the following table. The second column indicates the values of the dielectric constants obtained by Tomaszewski, the third column the values obtained by Landolt and Jahn; while the last column gives the values obtained by Nernst. From the results of Landolt and Jahn and those of Nernst, it appears that the dielectric constants at first increase with increase of molecular weight, and subsequently they decrease as the molecular weight increases. Tomaszewski's values show an increase with increase of molecular weight throughout. Re-

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[1] Wied. Ann. 36, 801 (1889).
[2] Ibid. 33, 41 (1888).
[3] Zeit. phys. Chem. 10, 289 (1892).
[4] Ibid. 14, 622 (1894).

gardless of which series of values for the dielectric constants is correct, the results show that these hydrocarbons do not follow the rule observed in connection with most other homologous series of compounds, namely, that an increase in molecular weight is accompanied by a decrease in the value of the dielectric constant.

TABLE V.

Substance	D. C. (Tomaszewski)	D. C. (L. and J.)	D. C. (Nernst)
Benzene	2.218	2.222	2.255
Toluene	2.303	2.387	2.355
Xylene (ortho)	——	2.583	2.567
" (meta)	——	2.35	2.372
" (para)	2.383	2.245	2.251
Mesitylene	——	2.30	——
Pseudo cymene	——	2.417	2.415
Cymene	2.442	2.231	2.249
Benzene	2.218	2.222	2.255
Toluene	2.303	2.387	2.355
Ethyl benzene	——	2.414	2.424
Propyl benzene	——	2.351	2.380
Isopropyl benzene	——	2.376	2.368
Isobutyl benzene	——	2.341	2.347
Hexane	——	1.854	1.88
Octane	——	1.938	1.949
Decane	——	1.964	——

The high values obtained for the dielectric constants of the aliphatic nitriles is doubtless due to the presence of the cyanogen group. The marked effect of the presence of this group in a compound upon the value of its dielectric constant is further illustrated by comparing the dielectric constants of ethyl acetate ($CH_3CO_2C_2H_5$), and ethyl cyanacetate ($CH_2CNCO_2C_2H_5$), for which Drude[1] found the values 5.85 and 26.7 respectively. The values 26.5 and 65.3 here found for ethyl cyanide (C_2H_5CN), and ethylene cyanide ($C_2H_4(CN)_2$), respectively also exemplify this effect in a striking manner. Cyanogen itself, however, has a

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[1] Zeit. phys. Chem. 23, 308, 310 (1897).

very low dielectric constant, the value being intermediate between the values of chlorine and bromine. The dielectric constant of liquid chlorine was determined by Linde,[1] who found that value 1.93 at 14° C, and by Coolidge,[2] who obtained the value 1.87 at 14.3°. The values obtained for liquid cyanogen (Table V.) and bromine are 2.52 and 3.18 respectively at 23° C.

For the purpose of this discussion the inorganic solvents whose dielectric constants were measured are divided into two groups. One group contains the solvents whose dielectric constants range from three to five, while the other group contains the solvents whose dielectric constants range from nine to thirty-three.

D. C. 3-5	D. C. 9-33
Sulphur monochloride	Arsenic trichloride
Phosphorus trichloride	Antimony trichloride
Sulphur trioxide	Phosphorus oxychloride
Antimony pentachloride	Sulphur dioxide
Stannic chloride	Sulphuryl chloride
Bromine	Thionyl chloride

The ionizing power of these solvents has been investigated by Kahlenberg and Lincoln,[3] and more fully by Walden.[4] The electrical conductivity measurements of Walden show that the solvents with low dielectric constants yield solutions with tetraethylammonium iodide, which do not conduct well enough to make quantitative measurements profitable, while the other solvents with relatively higher dielectric constants yield solutions with the same salt and with other salts that conduct fairly well. (See Table I.) Here then we have a good illustration of the Nernst-Thomson rule, that the greater the dielectric constant of a solvent the greater is its dissociating power. The following table gives the molecular conductivities at nearly cor-

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[1] Wied. Ann. 56, 546 (1895).

[2] Ibid. 69, 123 (1899).

[3] Jour. Phys. Chem. 3, 12 (1899).

[4] Ber. chem. Ges. Berlin, 32, 2862 (1899). Zeit. anorg. Chem. 25, 209 (1900).

responding dilutions of tetraethylammonium iodide $[N(C_2H_5)_4I]$, dissolved in the solvents noted. These results are taken from the work of Walden, to which reference has already been made. The molecular conductivities in liquid sulphur dioxide were made at zero degrees; in the other solvents the conductivities were made at 25° C. The last column indicates the dielectric constants of the solvents.

TABLE VI.

Solvent	V.	μ_v	D. C.
$POCl_3$	500	33.45	13.9
$AsCl_3$	480	54.26	12.35
SO_2Cl_2	500	19.59	9.15
$SOCl_2$	514	25.50	9.05
SO_2	181[1]	126.9	13.5

In connection with the results presented in this table, it may be noted that there is no such parallelism between dielectric constant and molecular conductivity as one would expect from the Nernst-Thomson rule.

The high dielectric constant[2] found for hydrocyanic acid [D. C. = 95], is of special interest from a theoretical point of view, since by the Nernst-Thomson rule, this compound should possess extraordinary dissociating power. The qualitative tests which Prof. Kahlenberg and I have made, however, indicate that hydrocyanic acid does not possess dissociating power in a marked degree. A number of salts which yield excellent conducting solutions when dissolved in water show comparatively feeble conduction when dissolved in hydrocyanic acid. Here then is a striking exception to the Nernst-Thomson rule. The quantitative measurements of the electrical conductivity of salts dissolved in hydrocyanic acid are now in progress in this laboratory and their publication will doubtless be awaited with considerable interest.

The high dielectric constants of the nitriles and alcohols

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[1] This is the highest dilution which Walden examined.

[2] This Journal, 5, 157 (1901).

show a marked contrast to the low dielectric constants of the substituted ammonias, which are of about the same order as the dielectric constant of chloroform [D. C. = 5.0], and ether [D. C = 4.4]. Now the ionizing power of chloroform and ether is exceedingly small, which fact is in perfect accord with the Nernst-Thomson rule. But Professor Kahlenberg[1] finds that the primary amines, which have values for their dielectric constants of about the same order as those of chloroform and ether, still yield solutions that conduct fairly well. Here then we have a number of exceptions to the Nernst-Thomson rule opposite in kind to the case of solutions in hydrocyanic acid; namely, solvents with relatively low dielectric constants that still possess moderate ionizing power.

In my former communication several other exceptions[2] to the Nernst-Thomson rule were pointed out. But in the cases there mentioned, the exceptions might be explained on the basis of the theory of electrolytic dissociation. Since the molecular conductivity depends upon the speed of the ions as well as the number of ions, i. e., the degree of dissociation, it might be argued that the magnitude of the conductivity at corresponding dilutions, giving as it does the combined effect of these two factors, is therefore not a safe criterion for determining the dissociating power of a solvent, although comparisons of this kind are frequently made in support of the rule. For example, in the case of the molecular conductivities of silver nitrate in pyridine and butyronitrile, which are given in the following table:

Solvent	V.	μ_v at 25°	D. C.
Butyronitrile[3]	75.6	25.4	20.3
	150.4	32.1	
Pyridine[4]	60.9	30.17	12.4
	140.7	36.21	

If it be assumed that the speed of the ions in pyridine is

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[1] Jour. Phys. Chem., June, 1901.

[2] l. c. p. 168.

[3] Dutoit and Friderich. Bull. Soc. Chim. [3] 19, 331.

[4] Lincoln. This Journal, 3, 457 (1899).

materially greater than in butyronitrile, then the molecular conductivity in pyridine may be greater than in butyronitrile, even though the number of dissociated molecules be somewhat less, as is required if we assume the Nernst-Thomson rule to hold. In the case cited the degree of dissociation could not be computed from the electrical conductivity measurements, as no maximum value for the molecular conductivity was obtained. And since Werner[1] found normal molecular weights for silver nitrate dissolved in pyridine by boiling-point determinations, this means of calculating the degree of dissociation could of course not be applied.[2] Hence on the basis of the experimental evidence which can be applied to the example cited, it must be considered an exception to the Nernst-Thomson rule, as must also the other exception[3] previously noted.

In this connection it may be well to note a few other exceptions to the Nernst-Thomson rule. The cryoscopic and electrical conductivity measurements by Zanninovich-Tessarin[4] show that potassium chloride dissolved in formic acid is highly dissociated, as one would expect from the high dielectric constant of the latter [D. C. = 62]. But solutions of hydrochloric acid in this solvent show but slight dissociation. Nernst[5] in referring to this case assumes that some specific influence of the solvent comes into play, probably the association of the ions with the molecules of the solvent.

Another exception is noted by Franklin and Kraus[6] in their researches on the electrical conductivity of liquid ammonia solutions. Mercuric cyanide according to Ostwald[7] is not at all dissociated in water, but Franklin and Kraus find that in ammonia it forms a solution which possesses a distinct conductivity. Again the phenols yield good conducting solutions

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[1] Zeit. anorg. Chem. 15, 1 (1897).

[2] Compare Kahlenberg, Jour. Phys. Chem. 3, 397, 399, on this point.

[3] l. c. p. 168.

[4] Zeit. phys. Chem. 19, 251 (1896).

[5] "Theoretische Chemie," p. 365 (Dritte Auflage).

[6] Amer. Chem. Jour. 23, 297 (1900).

[7] Grundlinien der anorg. Chem. p. 667.

in ammonia, while in water they form solutions which have relatively low conductivity. The following table illustrates this point. It gives the molecular conductivities of orthonitrophenol in water at 18° C and the liquid ammonia at — 38° C.

TABLE VII.

Water[1]		Liquid ammonia[2]	
V.	μ	V.	μ
250	4.09	366.2	82.76
500	5.14	2299.0	148.3
1000	7.24	10380.0	203.9
2000	10.30	63860.0	240.1

$\mu_\infty = 355$

Chloral and ethyl acetate, according to Drude,[3] have the values 6.67 and 5.85 respectively for their dielectric constants. The former, according to Kahlenberg and Lincoln,[4] yields solutions with ferric chloride which show no appreciable conduction, while the latter yields solutions with it, which show a distinct conductivity. From the work of the same investigators we see that ferric chloride does not yield conducting solutions with ethylene chloride [D. C. = 11.3],[5] but it yields solutions of very distinct conductivity, with several other solvents having dielectric constants of about the same order, or even less. Here then we have a number of additional exceptions to the Nernst-Thomson rule.

The exceptions to the rule noted above in connection with liquid ammonia solutions, however, do not indicate the general behavior of ammonia solutions of the common salts. While it is true that ammonia solutions for the most part show greater molecular conductivity than aqueous solutions of the same concentration, yet the degree of dissociation is, as a rule less than that of the corresponding aqueous solutions. This point is well

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[1] Bader. Zeit. phys. Chem. 6, 296 (1890).

[2] Amer. Chem. Jour. 23, 295 (1900).

[3] l. c. p. 309.

[4] Jour. Phys. Chem. 3, 12 (1899).

[5] Jahn and Möller. Zeit. phys. Chem. 13, 385 (1894).

illustrated by the following table taken from the work of Franklin and Kraus.[1] It shows the dilution at which dissociation reaches 90 percent in the two solvents.

TABLE VIII.

Solute	Water at 18° C.	Ammonia at — 38° C.
KI	20.0	2000
KBr	20.0	4000
KNO_3	25.0	5000
NaBr	32.0	2500
$NaNO_3$	33.0	4000
NH_4Cl	25.0	5000
$AgNO_3$	40.0	1500

Carrara's scheme for comparing the dissociating power by calculating the dilution for the same solute in which a definite degree of dissociation is obtained by electrical conductivity measurements, seems an excellent one to apply in this connection to solvents which yield good conducting solutions. In the following table the volumes of solutions in the solvents enumerated correspond to a degree of dissociation equal to 76 percent according to Carrara,[2] the solute being triethylsulphine iodide, $(C_2H_5)_3SI$. Under V. the volume in liters is given, in which one gram-molecule of substance is dissolved. The dielectric constants in the second column are those found by Drude, while those in the third column are taken from the results of Nernst, Tereschin, and Thwing. According to the Nernst-Thomson rule, the volumes should increase as the D. C. decreases.

TABLE IX.

Solvent	D. C.	D. C.	Volume
Water	81.0	80	8
Methyl alcohol	32.5	32.6	39.6
Ethyl "	21.7	25.8	504.0
Propyl "	12.3	22.8	1015.0
Allyl "	20.6	21.6	89.0
Acetone	20.7	21.8	498.0

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[1] Amer. Chem. Jour. 23, 297 (1900).

[2] Zeit. Elektrochemie, 4, 475 (1897-98).

An inspection of the tables shows that with one exception there is a general parallelism between dissociating power and dielectric constant, but the example of allyl alcohol is certainly a striking exception.

Table X. gives the approximate volume of various solvents in liters in which a gram-molecule of potassium iodide is dissociated to the extent of 75 percent.

TABLE X.

Solvent	D. C.	Volume
Water	80	0.4
Methyl alcohol	32.5	29
Liquid ammonia	22.0	400
Acetone	20.5	128
Pyridine	12.4	1100

In this case we have further exceptions in liquid ammonia and acetone.

When the exceptions noted are considered collectively it becomes evident that the Nernst-Thomson rule must relinquish a good share of the prestige it has hitherto enjoyed. While it is true that in these pages a number of new examples supporting the rule have been given, yet the exceptions noted are of a kind not to be underrated. The rule as it now stands is no more general than the hypothesis of Brühl which attempts to account for the dissociating power of solvents by assuming spare valences to exist, or the parallelism that Dutoit and Aston claim between dissociating power and polymerization of the molecules of the solvent. These theories have been shown to be inadequate by Lincoln,[1] Euler,[2] and Kahlenberg.[3] These investigators cite striking exceptions to these theories and therefore hold them untenable. Hence, until we have some experimental evidence in place of the speculative "specific influences" which are said to exist, and to account for exceptions to the Nernst-Thomson rule, the latter must be considered inadequate in accounting for the dis-

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[1] Jour. Phys. Chem. 3, 457 (1899).

[2] Zeit. phys. Chem. 28, 619 (1899).

[3] Jour. Phys. Chem. June (1901).

sociating power of solvents by virtue of their high specific inductive capacity.

Relation between the dielectric constant and the latent heat of evaporation. Since Louguinine[1] and Kahlenberg[2] have recently determined the latent heats of evaporation of a number of nitriles, it seemed of interest to see how closely Obach's law, that the ratio between the dielectric constant and the latent heat of evaporation is approximately a constant for an homologous series, holds for the nitriles. The following table gives the latent heats of vaporization, the dielectric constants, and in the column headed L. H./D. C., the ratios of the heat of evaporation to the dielectric constant.

TABLE XI

Substance	L. H.	D. C.	L. H./D. C.
Acetonitrile	173.6	36.4	4.77
Propionitrile	134.4	26.5	5.07
Butyronitrile	115.25	20.3	5.48
Valeronitrile	95.96	17.4	5.51
Capronitrile	88.09	15.5	5.68

The ratios can hardly be said to be constant, although the values obtained for the nitriles show as close an agreement as the values Obach had in hand when he indicated this relation between dielectric constant and heat of vaporization, as will appear from the following table, which has been selected for comparison.[3]

TABLE XII.

Substance	L. H.	D. C.	Ratio
Methyl formate	105.8	9.9	10.7
Ethyl "	91.9	9.1	10.1
Propyl "	83.7	9.0	9.3
Isobutyl "	75.7	8.4	9.0
Amyl " (iso)	71.0	7.7	9.2

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[1] Comptes rendus, 132, 88 (1901).
[2] Jour. Phys. Chem. 5, 215 (1901).
[3] Phil. Mag. 32, 117 (1891).

Conclusion

The principal points in the foregoing presentation may be summarized in the following general statements:

1. The values of the dielectric constants for the homologous series of compounds examined decrease with increase of molecular weight.
2. The introduction of the cyanogen group in a compound causes a marked increase in the value of the dielectric constant. In this respect the cyanogen radical produces a greater effect than all other radicals which have hitherto been systematically studied.
3. The cyanogen (CN), amido (NH_2), or nitric acid (NO_3) radicals when present in compounds do not cause anomalous absorption as Drude found for the hydroxyl (OH) group.
4. A number of new examples have been given which follow the Nernst-Thomson rule.
5. Some striking exceptions to the Nernst-Thomson rule have been pointed out, from which it has been argued that the rule is inadequate. The exceptions indicate that the nature of the solvent, as well as the dissolved substance, are of prime importance in determining whether a solution will conduct electricity.
6. Obach's law holds only approximately for the nitriles.

This investigation was made in the Laboratory of Physical Chemistry of the University of Wisconsin. It was undertaken at the suggestion of Professor Kahlenberg and carried on under his supervision. I am indebted to him for the placing at my disposal many of the solvents used for these measurements, and I am under many obligations to him for his helpful suggestions and for the active interest he has always shown in my work; and I am glad to have this opportunity of acknowledging it.

Laboratory of Physical Chemistry,
University of Wisconsin,
Madison, Wis.,
June 28, 1901.

NEW BOOKS

Atoms and Energies. *By D. A. Murray. 13 × 19 cm; 202 pp. New York: A. S. Barnes and Co., 1901.*—The author assumes that atoms are all identical in substance and differ only in size and shape; that there are only two energies, one attracting and the other repelling. Granted this, he can account for all diversity of chemical affinity, cohesion, adhesion, three states of matter, immediate transition from liquid to gas, latent heat, expansion of water by freezing, etc., etc. It then becomes obvious that energy is a distinct entity and not a mode of motion.

This is an ambitious programme, and it must be admitted that the author struggles bravely through it. He makes it clear that the shapes of the atoms may be the all-important factors in science; but he cannot prove that they must be. If we assume certain shapes for water, we can see that water must expand on freezing, or even just before it freezes. If we assume other shapes for benzene, we see that it must contract on freezing. It is all very simple and may all be right, but it does not enable us to predict anything.

The author himself does not attempt to tell us what the shapes of any particular atoms are, and consequently we have no way of making certain that we do not have to assume one shape to account for one property and another shape to account for another property. The reviewer cannot tell whether the explanation on p. 141 proves that a pure liquid has a definite vapor-pressure at a definite temperature, or that it cannot have. Evaporation is an ambiguous word under the circumstances. Even if the explanation as written does not account for the facts, there is no doubt but that another explanation could be devised which would describe them. The case is very similar to the use of thermodynamics in chemistry. We deduce conclusions which involve the law of conservation of energy and which are equally immutable. After a while we can no longer ignore the facts and we at once deduce a new law of the Medes and Persians. Then we bow down and worship, and cry, "Great is the thermodynamics of the chemists."

The only real test of a hypothesis is what can be done with it and the author has not yet justified his thesis. Consequently his book is an interesting peculation, but not a bit of scientific work. *Wilder D. Bancroft*

Chimie des Matières colorantes organiques. *Par R. Nietzki. Avec préfaces de C. Friedel et E. Nœlling. Traduite sur la III^e édition allemande, et mise au courant des dernier progrès d'apres la IV^e édition allemande, par Charles Vaucher, Camille Favre, et Alfred Guyot. Paris: Georges Carré et C. Naud, 1901.*—This translation is based on the German edition of 1897, but supplemented so as to correspond to the last German edition. The general nature of the book is so well known that it is only necessary to call attention to the appearance of the translation, to congratulate the translators on the index, and the publishers on the general appearance of the book.

Wilder D. Bancroft

Select Methods on Food Analysis. *By Henry Leffmann and William Beam. 15 × 21 cm; pp. 383. Philadelphia: P. Blakiston's Son and Company. Price: cloth, $2.50.* — This book is intended to be a concise summary of analytic methods adapted to the needs of both practical analysts and advanced students in applied chemistry. In the first section the author describes the physical and chemical methods employed by analysts. The second section describes methods which are of general value in the detection of poisonous metals, colors, and preservatives. This is followed by chapters on the analysis of starches and sugars, fats and oils, milk and milk products, condiments and spices, beverages and flesh foods. The methods employed are summarized in a very clear, fair, and unbiased manner.

The ever increasing value of a knowledge of the physical constants and of methods of separation of mixtures in order to obtain these constants, and the recognition of the limits of analytical methods suggest to the physical chemist the necessity of the food analyst being a man with a broad training; nevertheless, books such as the above, which describe nothing but methods, will always be useful and essential.

H. R. Carveth

Analyse chimique et Purification des Eaux potables. *By P. Guichard. (Encyclopédie scientifique des Aide-Mémoire). 11 × 18 cm; pp. 195. Paris: Gauthier-Villars. Price: paper, 2.5; boards, 3 francs.* — The author is apparently an ardent prohibitionist and he has written this book because he feels that it is useless to start a campaign against alcohol so long as one cannot supply reasonably pure drinking water. The subdivisions are: general study of water; analysis; purification; city supplies. The general conclusions are that water for cities should be brought from a distance, should be filtered through sand by the city officials, and should receive further special treatment in private houses. The author further recommends the prompt and efficient purification of sewage, and the use of automobiles in the streets.

Wilder D. Bancroft

REVIEWS

The object of this department of the Journal is to issue, as promptly as possible, critical digests of all Journal articles that bear upon any phase of Physical Chemistry.

General

Ammonium bromide and the atomic weight of nitrogen. *A. Scott. Jour. Chem. Soc.* 79, *147* (*1901*). — Stas found for the equivalents of ammonium bromide and ammonium chloride the values 98.032 and 53.532, while the author finds 97.995 and 53.516 respectively. There seems to be some reason for suspecting the presence of impurity in Stas's ammonium salts. *W. D. B.*

On krypton. *A. Ladenburg and C. Krügel. Sitzungsber. Akad. Wiss. Berlin,* 1900, *727.* — The authors calculate that the amount of krypton in the atmosphere cannot exceed 0.00002 percent. From vapor-density determinations they deduce a molecular weight of 59.01. *W. D. B.*

Seventh annual report of the committee on atomic weights. *F. W. Clarke. Jour. Amer. Chem. Soc.* 22, *70* (*1900*). — The new values for the year 1899 are boron 11.016, nitrogen 14.031, calcium 40.126, nickel 58.709, cobalt 58.995, molybdenum 96.069, tungsten 184.0, cerium 138.81, palladium 107.014. *W. D. B.*

Are further experiments needed for determining the atomic weight of oxygen? *E. W. Morley. Jour. Amer. Chem. Soc.* 22, *51* (*1900*). — The author recommends that the complete synthesis of water should be repeated, that the density of hydrogen should be determined more accurately, and that a complete synthesis of hydrochloric acid be attempted. *W. D. B.*

Note on a method of standardizing weights. *T. W. Richards. Jour. Amer. Chem. Soc.* 22, *144; Zeit. phys. Chem.* 33, *605* (*1900*). — A description of the method of standardizing weights in use at Harvard. *W. D. B.*

One-Component Systems

A method for the determination of the melting-point. *M. Kuhara and M. Chikashigé. Amer. Chem. Jour.* 23, *230* (*1900*). — The powdered substance is pressed between microscope slides and suspended in an air-bath. In this way a melting-point of 57.2° was obtained for chloral hydrate and 203° for phthalic acid. *W. D. B.*

On the effect of very low temperatures on the color of compounds of bromine and iodine. *J. H. Kastle. Amer. Chem. Jour.* 23, *500* (*1900*). — Lead iodide, phosphorus pentabromide, phosphorus heptabromide, mercuric bromiodide, iodoform, benzene dibromsulphonamide, tribromphenol bromide, and mercuric iodide become lighter in color when cooled to — 190°. A number of other substances show a similar behavior, including an alkaline alcoholic solution of phenolphthaleine. Though red mercuric iodide becomes yellow at — 190°, this is not due to an allotropic modification, for the yellow form becomes almost white at the same temperature. *W. D. B.*

Two-Component Systems

An apparatus for determining molecular weights by the boiling-point method. *H. N. McCoy. Amer. Chem. Jour. 23, 353 (1900).*—A modification of the Sakurai-Landsberger method, in which the solute is placed in an inner tube and the solvent in an outer tube, the vapor of the solvent thus acting as jacket before passing into the inner tube. The whole apparatus is very compact, works rapidly, and calls for very little solvent. In using it, a correction must, however, be made for varying hydrostatic pressure, or else errors of 100 percent may easily be made in the apparent molecular weight. *W. D. B.*

On a minimum in the molecular lowering of the freezing-point of water, produced by certain acids and salts. *V. J. Chambers and J. C. W. Frazer. Amer. Chem. Jour. 23, 512 (1900).*—A minimum molecular lowering of the freezing-point has been observed with phosphoric acid, hydrochloric acid, sodium acetate, zinc chloride, strontium iodide, cadmium iodide, and copper sulphate. *W. D. B.*

On the supposed allotropism of phosphorus pentabromide. *J. H. Kastle and L. O. Beatty. Amer. Chem. Jour. 23, 505 (1900).*—The experiments of the authors show very definitely that the so-called red monification of phosphorus pentabromide is really a higher bromide, possibly phosphorus heptabromide. *W. D. B.*

Poly-Component Systems

Investigations on the formation of oceanic salt deposits, with special reference to those at Stassfurt, XII. *J. H. van 't Hoff and H. M. Dawson. Sitzungsber. Akad. Wiss. Berlin, 1899, 340.* **XIII.** *J. H. van 't Hoff and W. Meyerhoffer. Ibid. 372.* **XIV.** *J. H. van 't Hoff and H. M. Dawson. Ibid. 557.* **XV.** *J. H. van 't Hoff and D. Chiaraviglio. Ibid. 810.* **XVI.** *J. H. van 't Hoff and N. Kassatkin. Ibid. 951.* **XVII.** *H. A. Wilson. Ibid. 954.* **XVIII.** *J. H. van 't Hoff and E. F. Armstrong, 1900, 559.* **XIX.** *J. H. van't Hoff and H. von Euler-Chelpin. Ibid. 1018.* **XX.** *J. H. van 't Hoff and H. A. Wilson. Ibid. 1142.*—The first eleven papers of this series have already been noticed (3, 508). The twelfth deals with $MgSO_4 2H_2O$ and $MgSO_4 5/4H_2O$. In the presence of saturated magnesium chloride solution $MgSO_4 4H_2O$ changes at about 20° into the hitherto unknown compound $MgSO_4 5/4H_2O$. If the temperature be first carried to about 45° there is formed the instable $MgSO_4 2H_2O$, which then changes into the five-fourths hydrate. The thirteenth paper contains a discussion of the successive crystallizations when sea water is evaporated at 25°. The order of crystallization is NaCl, NaCl + $MgSO_4 7H_2O$, NaCl + $MgSO_4 6H_2O$, NaCl + $MgSO_4 6H_2O$ + KCl, NaCl + $MgSO_4 5H_2O$ + KCl, NaCl + $MgSO_4 4H_2O$ + $K_2MgCl_4 6H_2O$, NaCl + $MgSO_4 4H_2O$ + $K_2MgCl_4 6H_2O$ + $MgCl_2$-

$6H_2O$. There is, theoretically, another stage, but the authors do not state which compound disappears first when $MgSO_45H_2O$ and KCl are replaced by $MgSO_44H_2O$ and $K_2MgCl_46H_2O$. It is not known whether the presence of NaCl in excess does or does not prevent the formation of $MgSO_45/4H_2O$. In the fourteenth paper the authors take up the question whether compounds found in the Stassfurt beds and not stable in presence of solution at 25° were formed under pressure or at higher temperature. They show that the possible range of pressures is about 180 atm, and that this would make a difference of only 3° in the possible limits for tachhydrite, $CaMg_2Cl_612H_2O$. It is therefore probable that the effect of pressure is entirely insufficient to account for the presence of some salts. The formation of glauberite, $CaNa_2(SO_4)_2$ at 25° is the subject of the fifteenth paper. Gypsum changes into glauberite at 25° when the solution is saturated both with respect to NaCl and $Na_2SO_410H_2O$. When the last salt is not present as solid phase, gypsum and glauberite may coexist as solid phases. The composition of sea water is such that the calcium salts precipitate as gypsum at 25° and not as glauberite.

In the sixteenth paper the salt $K_2Mg_4(SO_4)_55H_2O$ is described, while in the seventeenth it is pointed out that when a solution is saturated with respect to NaCl and KCl, the addition of magnesium chloride or sulphate precipitates two of potassium chloride for every five of magnesium chloride in solution. In the eighteenth paper it is shown that the dissociation pressure of gypsum, $CaSO_42H_2O$, is one atmosphere at 101.5°. At 107° and under a pressure of 970 mm we can have $CaSO_42H_2O$ and $CaSO_4\frac{1}{2}H_2O$ in equilibrium with solution and vapor. In presence of a solution saturated with respect to sodium chloride, gypsum changes into the salt with one-half of water at about 76°. The nineteenth paper contains vapor-pressure measurements and a brief discussion of the significance of these with respect to crystallization experiments. The twentieth paper deals with the formation of syngenite, $K_2Ca(SO_4)_2H_2O$. In presence of saturated potassium sulphate solution, gypsum goes over into syngenite at 25°. The authors then studied the stability of syngenite in solutions containing the chlorides and sulphates of sodium and potassium, and, after that, introduced the further complication of the presence of magnesium salts.

W. D. B.

Experiments on the formation of marine anhydrite. *H. Vater. Sitzungsber. Akad. Wiss. Berlin,* 1900, *269*. — The experiments showed that anhydrite cannot be formed by evaporation of sea water at ordinary temperatures, while it takes place readily from a warm solution. *W. D. B.*

Synthesis of polyhalite. *E. E. Basch. Sitzungsber. Akad. Wiss. Berlin,* 1900, *1084*. — The author gives the concentrations of solutions from which polyhalite, $K_2MgCa_2(SO_4)_42H_2O$, will crystallize. *W. D. B.*

The basic nitrates of bismuth. *F. A. Allan. Amer. Chem. Jour.* 25, *307* (*1901*). — A phase rule study of the system, bismuth, nitrate, nitric acid and water. The numerous basic nitrates of the books reduced to $BiONO_3H_2O$, $Bi_{12}O_{13}(NO_3)_{10}9H_2O$ and $Bi_4O_5(NO_3)_2H_2O$, the last of the three appearing at 50°, but not at 21°. *W. D. B.*

Stereoisomers and racemic compounds. *H. C. Cooper. Amer. Chem. Jour.* 23, *255* (*1900*). —No difference could be detected between the solubilities of the two sodium hydrotartrates in aqueous dextrose solution. *W. D. B.*

The conductivities of some double salts as compared with the conductivities of mixtures of their constituents. *C. F. Lindsay. Amer. Chem. Jour.* 25, *62* (*1901*). —The molecular conductivities of solutions made by dissolving the double chloride of potassium and cadmium, the double sulphate of potassium and nickel, the double sulphate of ammonium and magnesium, are slightly less than those of the same solutions made by dissolving the mixed salts. This is interesting if true. If, as the author implies, the differences are permanent, it is safe to assume experimental error as the cause of the phenomenon.

W. D. B.

Contribution to the study of aqueous solutions of double salts, IV. *H. C. Jones and B. P. Caldwell. Amer. Chem. Jour.* 25, *349* (*1901*). — Conductivity and freezing-point measurements with double iodides, cyanides, nitrates, and sulphates. The general result is that undissociated double salt exists even in dilute solutions. The authors have repeated the experiments of Lindsay (preceding review), but their measurements do nothing to remove the doubt that hangs over the conclusions. *W. D. B.*

The precipitation of the sulphides of nickel and cobalt in an alkaline tartrate solution, together with an investigation into the nature of certain tartrates of these metals. *O. F. Tower. Jour. Amer. Chem. Soc.* 22, *501* (*1900*). — A solution of potassium nickel tartrate contains practically all of the nickel as part of the complex anion. The sulphides of nickel and cobalt, when formed in a tartrate solution, are present in the colloidal form. *W. D. B.*

Notes on lecture experiments to illustrate equilibrium and dissociation. *J. Stieglitz. Amer. Chem. Jour.* 23, *404* (*1900*). — The experiments described involve the color changes with phosphorus pentabromide and tribromide, with phosphorus trichlordibromide and trichloride, with ammonia and phenolphthaleine on addition of ammonium chloride. *W. D. B.*

Lecture experiments. Reversible chemical reactions. *W. L. Miller and F. B. Kenrick. Jour. Amer. Chem. Soc.* 22, *291* (*1900*). —The experiments are: ammonium thiocyanate and ferric chloride; bismuth chloride and water; ammonia with salts of copper and of silver; formation and dissociation of water; sulphuric acid and sodium chloride; antimony chloride and hydrogen sulphide.

W. D. B.

Estimation of alkali carbonates in the presence of bicarbonates. *F. K. Cameron. Amer. Chem. Jour.* 23, *471* (*1900*). — When sodium carbonate is treated with acid potassium sulphate, sodium bicarbonate is formed, and the end-point can be recognized with phenolphthaleine. The reaction does not take place instantaneously and the bicarbonate decomposes slowly; but both these sources of error can be eliminated. After titration, potassium chromate may be added and the chlorides determined with silver nitrate. The author therefore concludes that the anion in sodium bicarbonate is HCO_3^-.

W. D. B.

Velocities

The hydrolysis of acid amides. *E. Reid. Amer. Chem. Jour.* 24, *397* (*1900*). — A mass of data is tabulated showing the rates at which different amides are hydrolyzed in presence of hydrochloric acid or of barium hydroxide.
W. D. B.

Concerning lipase, the fat-splitting enzyme, and the reversibility of its action. *J. H. Kastle and A. S. Loevenhart. Amer. Chem. Jour.* 24, *491* (*1900*). — The presence of lipase accelerates the reaction between ethyl butyrate and water, also the reverse reaction between ethyl alcohol and butyric acid. The acceleration is roughly proportional to the concentration of the enzyme, but seems to be more or less independent of the concentration of the ester.
W. D. B.

On the effect of oxidizing agents on the reduction of mercuric chloride by oxalic acid. *J. H. Kastle and W. A. Beatty. Amer. Chem. Jour.* 24, *182* (*1900*). — One ten-thousandth of a milligram of $KMnO_4$ dissolved in 15 cc of solution has a measurable accelerating effect on the reaction between mercuric chloride and ammonium oxalate. Other oxidizing agents have a similar effect.
W. D. B.

Electromotive Forces

The solution tension of zinc in ethyl alcohol. *H. C. Jones and R. W. Smith. Amer. Chem. Jour.* 23, *396* (*1900*).—From Kahlenberg's measurements on concentration cells and Jones's boiling-point determinations of the dissociation of zinc chloride in ethyl alcohol, the authors calculate that the solution pressure of zinc in water is 10^8 times that in ethyl alcohol. *W. D. B.*

On the thermoelectricity of some metals. *L. Holborn and A. Day. Sitzungsber. Akad. Wiss. Berlin*, 1899, *691*. — The authors have studied the thermoelectric behavior between — 185° and + 1300°, of gold, silver, rhodium, iridium, palladium, a platinum-ruthenium alloy, and two platinum-palladium alloys. All were measured against a standard platinum wire. The Avenarius formula

$$e = -a + bt + ct^2,$$

holds over a very wide range of temperatures for everything except palladium and the palladium alloys. In the other cases, the authors are inclined to attribute the final inadequacy of the formula to the appearance of an allotropic modification. *W. D. B.*

On the stationary temperature in an electrically heated conductor. *F. Kohlrausch. Sitzungsber. Akad. Wiss. Berlin*, 1899, *711*. — Reviewed (4,634) from Drude's Ann. 1, 132 (1900).

Heat conductivity, electrical conductivity, specific heat and thermoelectric force. *W. Jaeger and H. Diesselhorst. Sitzungsber. Akad. Wiss. Berlin*, 1899, *719*. — An experimental application of Kohlrausch's method (preceding review). *W. D. B.*

A new bridge arrangement for the determination of electromotive force by

aid of the Lippmann electrometer. *J. L. R. Morgan. Jour. Amer. Chem. Soc.* 22, *202* (*1900*). —The author uses a bridge wire and thirteen coils exactly equal to the bridge wire and so arranged that the bridge wire may be placed at the end or between any two of the coils. *W. D. B.*

Electrolysis and Electrolytic Dissociation

The electrolytic oxidation of toluene. *A. Merzbacher and E. F. Smith. Jour. Amer. Chem. Soc.* 22, *723* (*1900*). — With concentrated sulphuric acid, alcohol and toluene at the anode, some oxidation to benzoic acid took place. Most of the benzoic acid was converted into ethyl benzoate by the alcohol. It would seem wiser in a case of this sort, to begin with solutions corresponding to those in the direct chemical oxidation and to replace the sulphuric acid by potassium bichromate. *W. D. B.*

Potassium perselenate. *L. M. Dennis and O. W. Brown. Jour. Amer. Chem. Soc.* 23, *358* (*1901*). — A saturated solution of potassium selenate was electrolyzed at 4° with a current density of about 0.2 amp/cm². The experiments are only preliminary and pure potassium perselenate was not obtained. *W. D. B.*

Permanganic acid by electrolysis. *H. N. Morse and J. C. Olsen. Amer. Chem. Jour.* 23, *431* (*1900*). —The authors have prepared solutions of pure permanganic acid by electrolyzing potassium permanganate, using a porous cup. The current yield is about ninety-one percent. Advantage is taken of electrical endosmose to concentrate the acid. Conductivity measurements confirmed the results of Lovén. *W. D. B.*

The electrolytic deposition of brass. *J. L. R. Morgan. Jour. Amer. Chem. Soc.* 22, *93* (*1900*). —The author deduces the conditions for the electrolytic deposition of brass on the assumption that the brass is a two-phase system. The deduction is interesting, but probably does not apply to this particular case. Among other things, the author tacitly postulates primary precipitation of zinc from a cyanide solution, which does not take place as a matter of fact. *W. D. B.*

The electrical conductivity of liquid ammonia solutions. *E. C. Franklin and C. A. Kraus. Amer. Chem. Jour.* 23, *277* (*1900*).—The results are summed up by the authors as follows:

1. The problem of obtaining pure liquid ammonia has been successfully solved, and a form of apparatus has been constructed which is well adapted to the study of the conductivity of liquids of low boiling-points.

2. With few exceptions, salts are dissociated to a less degree in ammonia than in water.

3. The limit of molecular conductivity of binary salts in ammonia at — 35° ranges from about 290 to 340 Kohlrausch units, which is much above the conductivity of the same salts in solution in water at 18°.

4. Ostwald's law of dilution holds approximately for binary salts. Other solutes have not been tested.

5. Silver iodide is dissociated in ammonia solution, although not to so great an extent as other binary salts.

6. Mercuric chloride reacts with ammonia to form the compound $HgCl_2 12NH_3$, which loses 10 molecules of ammonia on being warmed up at atmospheric pressure. The compound $HgCl_2 2NH_3$ is identical with mercuridiammonium chloride.

7. Mercuric cyanide and silver cyanide conduct in ammonia, but the conductivity in neither case changes much with the dilution. The molecular conductivity of the former falls slightly, the latter rises somewhat.

8. The one ternary salt measured has a high molecular conductivity, and, as in water solution, it approaches its maximum more slowly than do the binary salts.

9. Many of the nitro compounds are good conductors in ammonia solution. Some of them approach the binary salts in their power to carry the current.

10. The acid and basic amides generally dissolve in ammonia to form good conducting solutions. The conducting power of the acid amides range from a fraction of a unit to that of the binary salts.

11. The acid and basic amides may be considered as acids and bases derived from ammonia in the same manner as the oxygen acids and bases are derived from water.

12. As found by Cady, ammonia solutions of the alkali metals conduct electricity without polarization at the electrodes. The conductivity changes but slightly, if at all, with the concentration. These solutions exhibit positive temperature coefficients. *W. D. B.*

The conductivity temperature coefficient of some liquid ammonia solutions. *E. C. Franklin and C. A. Kraus. Amer. Chem. Jour. 24, 83 (1900).* — The molecular conductivity of a number of solutions of liquid ammonia passes through a maximum with rising temperature. A solution of sulphur in ammonia conducts electricity even above the critical temperature of the solution. Solutions of sodium in ammonia conduct less well the higher the temperature; but the observations are complicated by the slow action of sodium on the ammonia. Solutions of metallic iodides and bromides in methyl amine conduct fairly well. *W. D. B.*

The electrical conductivity of aqueous solutions of alkali chlorides and nitrates. *F. Kohlrausch and M. E. Maltby. Sitzungsber. Akad. Wiss. Berlin,* 1899, *665.* — The authors have redetermined the molecular conductivities of the chlorides and nitrates of potassium, sodium, and lithium from normal down to *n*/10000 solutions. Great pains were taken to make the electrical and temperature measurements as accurate as possible, and to be certain of the purity of the substances used. These are unquestionably the most accurate measurements that have yet been made with these salts. *W. D. B.*

Some α-alkyl substitution products of glutaric, adipic, and pimelic acids. *J. W. Mellor. Jour. Chem. Soc. 79, 126 (1901).* — The author has made, and determined the dissociation constants of, a number of substitution products of glutaric and adipic acids. *W. D. B.*

The wide occurrence of indicators in nature. *G. S. Fraps. Amer. Chem. Jour.* 24, *271 (1900).* — Attention is called to the fact that the coloring matters of many plants change on addition of alkali or acid. A partial list is given of these changes. *W. D. B.*

A new electrolytic cell for rectifying alternating currents. *W. L. Hildburgh. Jour. Amer. Chem. Soc.* **22**, *301* (*1900*). — The cell consists of sulphuric acid with platinum electrodes, one being smooth platinum wire and the other platinized platinum in hydrogen. *W. D. B.*

A method for the determination of electrical conductivity with direct current instruments. *J. L. R. Morgan and W. L. Hildburgh. Jour. Amer. Chem. Soc.* **22**, *304* (*1900*). — Two resistance boxes are used, the galvanometer and the hydrogen cell rectifier (preceding review) being placed in shunt with one of them. *W. D. B.*

Dielectricity and Optics

On the phosphorescence of inorganic chemical compounds. *E. Goldstein. Sitzungsber. Akad. Wiss. Berlin*, 1900, *818*. — The author finds that most substances emit two distinct kinds of light, one just where the cathode rays fall, and another which is phosphorescent. This second is the one that is usually recorded, but is now believed to be due to impurities. The real light from the sulphates, phosphates, carbonates, borates, silicates, chlorides, bromides, fluorides, oxides, or hydroxides, of lithium, sodium, potassium, rubidium, caesium, calcium, strontium, barium, aluminum, zirconium, magnesium, beryllium, zinc, and cadmium is blue to violet. These substances, with the possible exception of cadmium, all give colorless oxides. If we add to any salts of this group merest traces of the salts of copper, chromium, manganese, uranium, nickel, cobalt, lead, cerium, lanthanum, yttrium, erbium, praseodymium, or neodymium, the secondary colors at once appear, and this gives an analytical test of almost incredible delicacy. The author also describes a glow observed with moist substances under moderate pressures. *W. D. B.*

Action of light on nitrogen iodide. *F. D. Chattaway and K. J. P. Orton. Amer. Chem. Jour.* **24**, *159* (*1900*). — Light decomposes nitrogen iodide according to the equation

$$N_2H_3I_3 = N_2 + 3HI.$$

In presence of water there is also hydrolysis. Red light decomposes the substance most rapidly, and the action becomes less as the wave-length of the light diminishes. There is, however, a secondary maximum in the blue. *W. D. B.*

A simplified method for the spectrographic analysis of minerals. *W. N. Hartley and H. Ramage. Jour. Chem. Soc.* **79**, *61* (*1901.*) — The authors wrap the substance to be analyzed in an ashless filter-paper, ignite in an oxyhydrogen flame, and photograph the spectrum. *W. D. B.*

Uranium radiation. *H. Becquerel. Comptes rendus*, 130, *1583* (*1900*). — It is shown that the uranium radiations are deflected by a magnetic field. Experiments on fractional precipitation lead to the conclusion that ordinary uranium contains some very active substance, possibly actinium; but that the activity is not due to this alone, uranium itself being probably active.

W. D. B.

EQUILIBRIUM BETWEEN CARBONATES AND BICARBONATES IN AQUEOUS SOLUTION[1]

BY FRANK K. CAMERON AND LYMAN J. BRIGGS

If an aqueous solution of sodium carbonate be allowed to come to equilibrium in contact with the air, there is always formed a greater or less amount of the hydrogen carbonate, more generally known as bicarbonate.

The system is then quite complex; for, in addition to the normal carbonate and the hydrogen carbonate, there is present also sodium hydroxide from the hydrolysis of these salts, dissolved carbon dioxide, possibly carbonic acid, and the various electrolytic dissociation products. If the sodium hydrogen carbonate be considered alone, the concentration of the solution with respect to this salt will be dependent upon several factors.

(1) It is obviously dependent on the amount of normal sodium carbonate present, for it is one of the products resulting from the hydrolysis of that substance, as is indicated by the scheme

$$Na_2CO_3 + HOH \rightleftarrows NaOH + NaHCO_3.$$

(2) It will depend obviously upon the temperature, for the amount of hydrolysis of the normal carbonate is dependent upon the temperature. Further, the amount of carbon dioxide and, in consequence, the carbonic acid in the solution is a function of the temperature.

(3) It will depend upon the partial pressure of carbon dioxide in the vapor phase in contact with the solution; that is to say, upon the amount of carbon dioxide per unit volume in the atmosphere above the solution. Upon this partial pressure in the vapor phase will depend the amount of the carbon dioxide

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[1] Contribution from the Bureau of Soils, U. S. Department of Agriculture. Published by permission of the Secretary.

dissolved in the solution, and obviously the amount of the normal carbonate which will be converted by it to the hydrogen carbonate. Further, sodium hydrogen carbonate, being a salt composed of a strong base in combination with a weak acid, would be hydrolyzed unless the hydrolysis be forced back by an excess of the weak acid in solution. Walker and Cormack[1] have shown that the ions resulting from the solution of carbon dioxide in water are mainly $\overset{+}{H}$ and $H\overset{-}{C}O_3$, and to a very much less extent the ion $\overset{=}{C}O_3$. More recently Bodländer[2] has shown that the dissociation, with formation of $H\overset{-}{C}O_3$ ions is about twenty thousand times as great as with the formation of $\overset{=}{C}O_3$ ions.

Supposing the temperature to remain constant, and omitting the formal statement of the details, these facts might be schematically arranged thus:

$$NaHCO_3 \begin{cases} \longleftrightarrow Na_2CO_3 \\ \longleftrightarrow H.HCO_3 \longleftrightarrow CO_2 \text{ (vapor phase)} \end{cases},$$

where the double-headed arrow is taken to mean "is dependent upon." This schematic arrangement indicates that if some effective means were devised by which the carbon dioxide could be removed from the vapor phase as fast as it was formed, it would be possible to gradually remove all carbonic acid from the system and ultimately a solution of sodium hydroxide alone would remain. The experimental difficulties in the way of accomplishing this would undoubtedly be great and, as the matter does not appear to be of any practical importance, no attempt has been made to realize it.

This investigation was undertaken primarily to obtain light upon the conditions which prevail in certain natural environments, where the amount of carbon dioxide in the gas phase may be, and often is, relatively large. But it has seemed wisest in this preliminary study, to investigate the equilibrium of the

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[1] Jour. Chem. Soc. 47, 5 (1900).

[2] Zeit. phys. Chem. 35, 25 (1900).

system in contact with ordinary air. It is thus possible to have a vapor phase in which the partial pressure of carbon dioxide is very constant; furthermore, the results show the maximum percentage of the base which can be combined as normal carbonate for any given concentration under natural conditions.

The investigation has been made readily feasible by a method, recently devised in this laboratory, for the estimation of carbonates (with the hydrolyzed sodium hydroxide) and bicarbonates when both are in the solution simultaneously.[1] The method is based primarily upon the fact that carbonic acid is a stronger acid than phenolphthalein, and that the hydrolysis of the carbonate proceeds at a moderately rapid rate. It is therefore possible to continue titration with hydrogen potassium sulphate solution until there is no normal carbonate remaining in the solution. By then adding methyl orange, an acid indicator stronger than carbonic acid, the titration can be continued and the total amount of the base constituent present thus determined. From these data it is a simple matter, as has been pointed out elsewhere, to compute the amount of normal carbonate and hydrogen carbonate present.

It will be convenient to consider the system we are studying as made up of the normal carbonate and the hydrogen carbonate with this method of estimating them as the criterion between them. The normal carbonate, together with the hydrolyzed hydrate, will be considered under the head of normal carbonate—in contradistinction to the hydrogen carbonate which is present before the titration of the solution is commenced.

Experiments with sodium salts

Solutions of sodium carbonate of various concentrations were prepared, about 200 cc of each solution being brought into a small flask. The flasks were connected in series by a system of stoppers and tubing and were immersed in a bath, the temperature of which could be closely regulated by a thermostat. Air which had previously been passed through a wash flask,

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[1] Amer. Chem. Jour. 23, 471 (1900).

containing water slightly acidulated with sulphuric acid, was then drawn continuously by means of an aspirator through the series of flasks for lengths of time varying from four days to several weeks, depending upon what was shown by experience to be necessary to bring about a state of complete equilibrium. The solutions were then removed from the bath one by one, an aliquot portion carefully measured off by running it from a burette, and the titrations made as promptly as possible with N/10 $HKSO_4$ solution.[1]

In the accompanying tables (I., II., III., and IV.), the first column gives the number of gram atoms of sodium per liter; the second column, the number of cubic centimeters of solution taken for the titration; the third and fourth columns, the number of cubic centimeters of acid solution required in the titrations; the fifth column, the percentage of the base combined as normal carbonate and its hydrolyzed product — the hydrate; the sixth column, the percentage of the base combined as the hydrogen carbonate.

TABLE I.

System: Na_2CO_3, $NaHCO_3$, and CO_2

Temperature 25° C

Concentration. Gram atoms Na	Amount solution titrated cc.	Amount $HKSO_4$ required		Amount sodium combined	
		With ph. phth. cc.	With meth. or. cc.	As Na_2CO_3 Percent	As $NaHCO_3$ Percent
0.0044	50	0.10	2.3	8.7	91.3
	50	0.10	2.3		
0.0143	20	0.30	3.0	20.0	80.0
	20	0.30	3.0		
0.0562	10	1.10	5.9	37.3	62.7
	10	1.10+	5.9		
0.2248	10	7.0	23.6	59.3	40.7
	10	7.0	23.6		
0.8847	2	6.15	18.65	64.0	36.0
	2	5.90	18.50		
	3	9.00	27.90		

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[1] A solution containing 13.516 grams $HKSO_4$ per liter. The assumption is specifically made that the substance is a monovalent acid.

TABLE II.

System: Na_2CO_3, $NaHCO_3$, and CO_2

Temperature 37° C

Concentration. Gram atoms Na	Amount solution titrated cc.	Amount $HKSO_4$ required		Amount sodium combined	
		With ph. phth. cc.	With meth. or. cc.	As Na_2CO_3 Percent	As $NaHCO_3$ Percent
0.0019	50	0.05	0.95	10.5	89.5
	50	0.05	0.95		
0.0071	20	0.15	1.45	21.1	78.9
	20	0.15	1.40		
0.0276	10	0.55	2.75	41.3	58.7
	10	0.60	2.78		
0.1030	10	3.35	10.30	64.5	35.5
	10	3.30	10.30		
0.421	2	3.50	8.45	81.9	18.1
	2	3.40	8.40		
0.815	2	7.0	16.4	86.5	13.5
	2	7.1	16.2		
1.795	2+	15.1	36.1	83.4	16.6
	2	14.85	35.65		

TABLE III.

System: Na_2CO_3, $NaHCO_3$, and CO_2

Temperature 50° C

Concentration. Gram atoms Na	Amount solution titrated cc.	Amount $HKSO_4$ required		Amount sodium combined	
		With ph. phth. cc.	With meth. or. cc.	As Na_2CO_3 Percent	As $NaHCO_3$ Percent
0.0017	50	0.1	0.9	22.2	77.8
	25	0.05	0.45		
0.0071	20	0.25	1.50	32.9	67.1
	20	0.25	1.55		
0.0266	10	0.7	2.80	50.7	49.3
	20	1.45	5.65		
0.1014	10	3.7	10.6	70.0	30.0
	10	3.75	10.7		
0.4066	10	17.1	42.3	81.0	19.0
	2	3.5	8.6		
0.8068	2	7.2	16.5	86.8	13.2
	2	7.0	16.15		
1.7486	2.1	15.9	36.5	87.1	12.9
	2	15.2	35.0		

TABLE IV.

System : Na_2CO_3, $NaHCO_3$, and CO_2

Temperature 75° C

Concentration. Gram atoms Na	Amount solution titrated cc.	Amount $HKSO_4$ required		Amount sodium combined	
		With ph. phth. cc.	With meth. or. cc.	As Na_2CO_3 Percent	As $NaHCO_3$ Percent
0.003	50	0.2—	1.4	25.7	74.3
	25	0.1	0.7		
	25	0.08	0.7		
0.019	20	0.3	1.75	34.8	65.2
	20	0.3	1.70		
0.036	10	0.9	3.3	55.7	44.3
	10	0.95	3.35		
0.270	5	4.9	12.5	79.5	20.5
	5	5.0	12.4		
0.702	1	2.7	6.45	85.0	15.0
	1	2.75	6.5		
6.56	1	25.8	60.0	84.8	15.2
	1	25.5	61.0		

The results given in these tables are graphically presented in Fig. 1.

It will be observed that the curves are all of the same

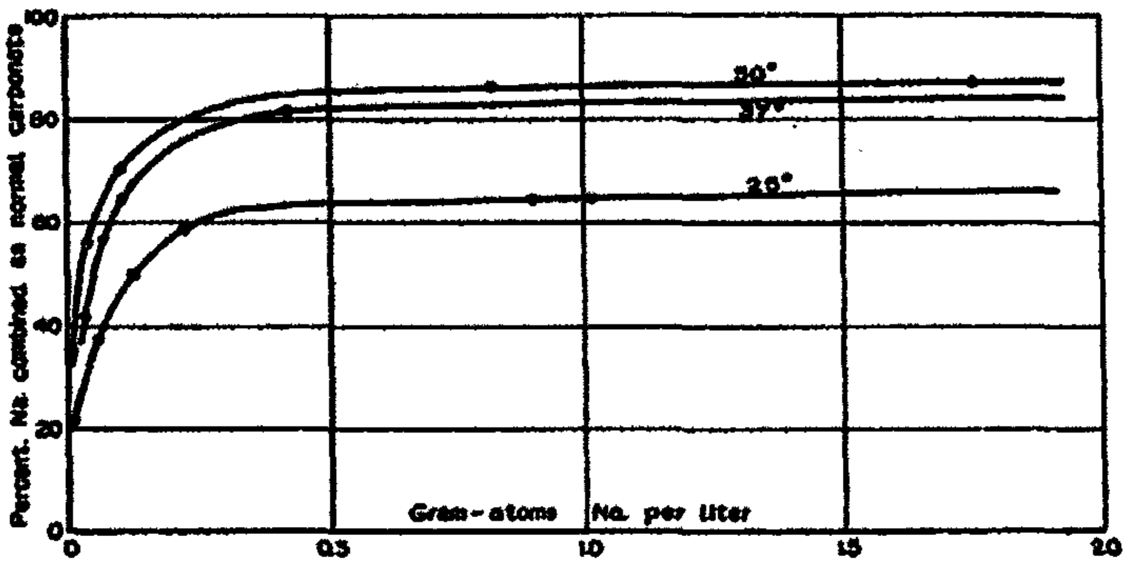

Fig. 1

general nature, that is, with increasing concentration the proportion of normal carbonate rapidly increases at first, but soon comes almost to a maximum, and from that point on there is a very small increase in the proportion of normal carbonate with an increase in the total concentration. The higher the temperature the more nearly does the flat part of the curve lie parallel to the axis of abscissas, until at 100° C practically the whole length of the curve is parallel to it. The curve plotted from the data obtained at 75° C lies so close to that for 50° C, that it is not practicable to distinguish it from the latter on a chart of the scale represented in the figure.

For any given concentration the proportion of normal carbonate increases with the temperature, until at 100° C for almost all concentrations the percentage of normal carbonate is practically 100; for 25° C about 50 percent of the sodium is in the form of normal carbonate when the total concentration is 0.12 to 0.13 gram-atoms of sodium per liter; with a concentration of 0.4 gram-atoms of sodium per liter about 63 percent of the sodium is in the form of the normal carbonate; and there is a gradual increase from this point on, until at a concentration of 0.89 gram-atoms of sodium per liter about 64 percent of the sodium is in the form of normal carbonate, and at a concentration of 8.0 gram-atoms of sodium about 86 to 87 percent of the sodium is in the form of the normal carbonate. Similar data can readily be obtained for the other temperatures by interpolation on the charted curves.

A curious fact brought out by an inspection of the chart is, that at all temperatures there is a rapid increase in the percentage of normal carbonate up to a concentration of about 0.4 gram-atoms of sodium per liter, and from this point on the percentage of normal carbonate increases very slowly; that is to say, a change from a rapid to a slow increase in the percentage of normal carbonate with increasing concentration comes at about the same concentration, irrespective of the temperature, at least below 75° C. What special significance, if any, this may have, is not apparent at present.

By referring to Table IV. it will be observed that in the solution containing 6.56 gram-atoms of sodium per liter there appeared to be actually a lesser percentage of the normal carbonates than in the solution containing 0.7 gram-atoms of sodium per liter. At first it was supposed that this indicated a faulty determination of the carbonates, and that the true interpretation of the result was that beyond a concentration of 0.7 gram-atom of sodium per liter the curve for 75° C was practically horizontal to the axis of abscissas. It appeared later, however, that in all probability, and at all temperatures, there is a maximum point on the curve beyond which there is an actual falling off in the percentage of normal carbonate with increased concentration of the solution. It is not possible to offer an explanation for this phenomenon at present, but it is intended to give the subject further attention at some future time.

It was hoped that possibly an approximation to the amount of hydrolization of sodium carbonate in solutions of varying concentration might be made from our results, by considering the amount of the hydrogen carbonate formed from the dissolved carbon dioxide as small and constant in amount on account of the small and constant partial pressure of this latter substance in the vapor-phase. The nature of the curves at the lower concentrations, however, show conclusively that no such assumption can be made, and that the influence of the dissolved carbon dioxide cannot be disregarded. If the hydrolysis of the sodium carbonate be supposed to take place according to the scheme

$$Na_2CO_3 + HOH \rightleftarrows NaOH + NaHCO_3$$

then there must necessarily be as many reacting weights of sodium hydroxide in the solution as there are reacting weights of sodium hydrogen carbonate. But the curves vary continuously and without breaks, until at infinite dilution there is 100 percent of the sodium in the form of hydrogen carbonate present and no sodium in the form of hydrate or normal carbonates. It is therefore apparent that the influence of the dissolved carbon dioxide, even though it be quite small in amount, can not be neglected, and the attempt to get a measure of the hydrolysis from the data here presented is vain. It may afford an explanation in part of why Walker and Cormack[1] found such a large proportion of HCO_3 ions as compared with CO_3 ions in their dilute solutions, and is probably the reason why they did not observe any hydrolysis of sodium hydrogen carbonate in dilute solutions.

The data contained in Table I. have been recalculated and are presented in Table V. in another form. The first column gives the concentration in grams per liter with respect to the sum of the weights of normal carbonate and bicarbonate present; the second and third columns give the weight per liter and the percentage of normal carbonate present; the fourth and fifth columns, the corresponding data for the bicarbonate or hydrogen carbonate.

TABLE V.

System: Na_2CO_3 and $NaHCO_3$ at 25° C

Total salts dissolved. Grams	Na_2CO_3		$NaHCO_3$	
	Weight. Grams	Percent	Weight. Grams	Percent
0.3555	0.0203	5.71	0.3352	94.29
1.1053	0.1505	13.62	0.9548	86.38
4.0443	1.1041	27.30	2.9402	72.70
14.6558	7.0212	47.91	7.6346	52.09
56.3982	29.8223	52.88	26.5759	47.12

An inspection of a curve, illustrating these data, shows that at 25° C there are equal weights of sodium carbonate and sodium hydrogen carbonate in a solution in which the total weight of both salts is approximately 21.6 grams per liter, or 10.8 grams per liter of each. Even with a concentration with respect to both salts of 60 grams to the liter the amount of normal carbonate rises only to about 53.5 percent of the total weight of the two salts present.

Experiments with potassium salts

In Table VI. are given the results obtained from a series of experiments upon the equilibrium between the normal carbon-

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[1] loc. cit.

ate and hydrogen carbonate of potassium at 25° C. The increase in the percentage of normal carbonate with increasing concentration of potassium is not quite so rapid as in the case of the sodium salts for the lower concentrations, but is more rapid for higher concentrations than is the case with the sodium salts. The examination was extended to solutions of a higher concentration in this case to settle definitely the question of the existence of a maximum point in the curve. It unquestionably exists somewhere in the neigborhood of a concentration of two reacting weights of potassium per liter; beyond this point there appears to be a very gradual diminution of the percentage of normal carbonate.

TABLE VI.

System: K_2CO_3, $KHCO_3$, and CO_2

Temperature 25° C

Concentration. Gram-atoms K	Amount solution titrated cc.	Amount $HKSO_4$ required		Distribution of potassium	
		With ph. phth. cc.	With meth. or. cc.	As K_2CO_3 Percent	As $KHCO_3$ Percent
0.393	5	7.6	19.6	77.5	22.5
	5	7.65	19.75		
0.553	2	4.75	11.0	83.9	16.1
	5	11.25	27.8		
1.025	2	8.9	20.5	86.8	13.2
	2	9.1	20.8		
	2	8.8	20.2		
1.865	2	17.1	37.1	91.4	8.6
	2	17.0	37.5		
2.820	2	25.2	56.4	89.0	11.0
	2	25.1	56.3		
3.710	2	33.15	74.2	88.6	11.4
	2	32.9	74.6		
4.310	1	19.3	43.0	89.6	10.4
	1	19.3	43.2		
5.695	1	25.25	56.9	88.7	11.3
	1	25.3	57.0		

The last two determinations given in the table do not appear quite consistent with the others. They were made subsequently to the others, smaller quantities of the solution being taken for the titrations, and no special care being exercised to obtain great accuracy, as they were made solely for the purpose of establishing the fact that a maximum point really existed in the curve (Fig. 2). In a general way the phenomena presented by the potassium salts were so closely analogous to those presented by the sodium salts that it was not deemed advisable, from press of time, to extend the investigation of the former to higher temperatures at present.

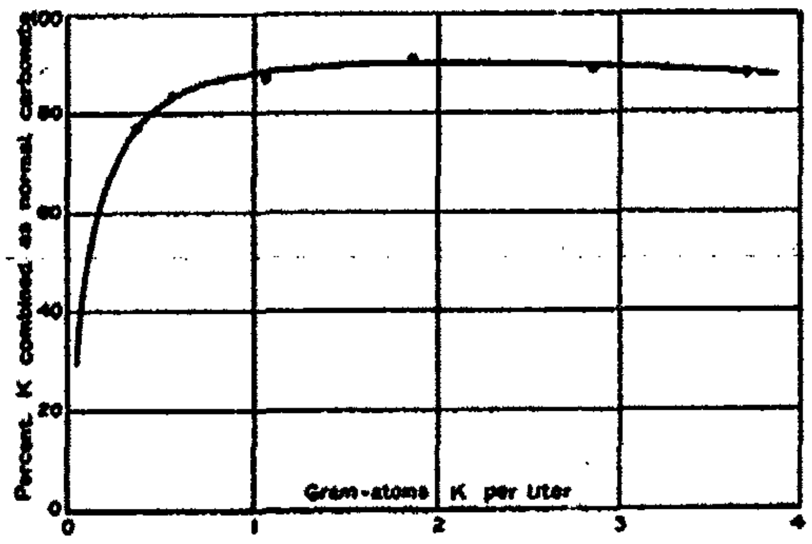

Fig. 2

The calcium salts

The solubility of calcium carbonate in pure water at 16° C is according to Schlœsing, about 0.0131 gram per liter. In such a solution Bodländer[2] has shown that in all probability about 80 percent of the salt is hydrolyzed and dissociation is so complete that practically all the calcium in the solution is in the form of ions. With the addition of carbon dioxide to the vapor phase, however, the solubility of the calcium carbonate is much increased, owing to the formation of the more soluble calcium hydrogen carbonate. According to Schlœsing,[3] at a partial pressure for the carbon dioxide in the gas phase of 0.9841 atmosphere, and at a temperature of 16° C, the solubility is increased

[1] Comptes rendus, 74, 1552 (1872).

[2] Zeit. phys. Chem. 35, 28 (1900).

[3] Comptes rendus, 75, 70 (1872).

so that there is the equivalent of 1.086 grams per liter of calcium carbonate in the solution. Treadwell and Reuter[1] found that at 15° C and under a partial pressure of the carbon dioxide in the gas phase equal to an atmosphere, the material dissolved was equivalent to 1.156 grams of calcium carbonate per liter. Under such conditions there could be no hydrolysis of the salts, and in the case of Treadwell and Reuter's experiment all the dissolved material must have been in the form of the hydrogen carbonate. The solubility of the calcium is certainly increased nearly ninety times.

In the case of natural solutions the partial pressure of the carbon dioxide is probably somewhere between the limits 0.0 and one atmosphere, and the solubility of calcium carbonate will be somewhere between the extremes noted above. An approximation to its solubility in solutions in contact with the air can be obtained from Schlœsing's figures. This authority found that at 16° C, and a pressure for the carbon dioxide equal to 0.000504 atmosphere, the solubility was 0.0746 gram per liter — calculating the salt as normal carbonate — or in effect the solubility is nearly six times what it would be in pure water.

But another aspect of the question must be borne in mind in this connection. Treadwell and Reuter have definitely shown that calcium hydrogen carbonate in aqueous solution is a rather stable compound, at least at 15° C, and that it does not always decompose at once with the partial inversion to the normal carbonate as the partial pressure of the carbon dioxide in the vapor phase is lowered. They found that after reducing the partial pressure of the carbon dioxide in the gas phase to zero, there remained no free carbon dioxide in the solution, but that the solution still contained an amount of calcium, entirely in the form of hydrogen carbonate, equal to 0.3850 gram per liter of this salt. This would be equivalent to 0.2380 gram per liter of the normal carbonate, or 18.16 times the amount found soluble in pure water by Schlœsing. Therefore the origin and past history of a solution is of the utmost importance in considering its con-

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[1] Zeit. anorg. Chem. 17, 178 (1898).

centration with respect to calcium carbonate or hydrogen carbonate. For example, a solution which has been formed in a soil in which there is a large amount of carbon dioxide, and which subsequently comes to equilibrium with the air, may well be very different in concentration from a solution which was formed directly in contact with the air. It is probable, however, that with agitation of the solution, such as would occur in a turbulent stream, for example, the stability of the calcium hydrogen carbonate would be considerably lessened, and that it would partially decompose, the concentration being reduced to the point which would result from the solution of calcium carbonate by water in contact with air.

The experiment has been made in this laboratory of preparing two solutions of calcium carbonate — one made by dissolving the calcium carbonate in distilled water from which the dissolved carbon dioxide has been expelled by boiling, the other by dissolving the salt in distilled water containing somewhat more carbon dioxide than would be dissolved from the air. A few drops of alcoholic solution of phenolphthalein were added to each. The first showed an intense red color, but the second showed no color, indicating that there was practically no hydrolyzed base in the solution. A current of air was passed through both solutions continuously for three days. Aliquot portions of both solutions gave practically identical results for calcium determinations. After the passage of the air through the solutions had been stopped they both showed a faint trace of pink color on the addition of phenolphthalein. The amount of material in solution was so small that it did not seem worth while to attempt very accurate measurements, but the mean of two closely agreeing series of titrations indicated that at 30° C in equilibrium with the air not more than 3 percent of the calcium present could be combined as normal carbonate. At lower temperatures and lesser concentrations the percentage of normal carbonate must be even less. It did not seem advisable, therefore, to attempt any further study of the distribution of the base calcium between the normal carbonic acid and the hydrogen carbonic acid in solutions of these salts in equilibrium with atmospheric air, or in equilibrium with a gas phase containing a larger proportion of carbon dioxide than ordinary air.

The facts just presented are of very great importance in the study of natural waters, for it is evident that with solutions such as we have been discussing, one is dealing almost entirely with calcium hydrogen carbonate; and in the reactions with other electrolytes which may come into the solution, it is the hydrogen carbonate which must be considered.

Another interesting point is that although a solution may be holding as much of this salt as is possible under existing conditions, it cannot be considered as saturated with respect to it, for it may be able to take up more of the salt by increasing the partial pressure of the carbon dioxide in the gas phase. It would be interesting to know what the absolute solubility of calcium hydrogen carbonate is for some temperatures. It is probable that it is considerable in amount, and it is not so surprising that deep-seated waters are able to carry such relatively large quantities of this salt. The much increased solvent action of waters carrying much dissolved carbon dioxide upon calcium-bearing rocks is readily intelligible in the light of these facts.

Magnesium salts

The solubility of magnesium carbonate in pure water at 12° C is given by Engel[1] as 0.970 gram per liter. Treadwell and Reuter[2] found the solubility at 15° C, in contact with a vapor phase in which the partial pressure of the carbon dioxide has been reduced to zero, to be about 0.627 gram per liter. These investigators found that under a partial pressure for the carbon dioxide equal to one atmosphere there was in solution 12.105 grams per liter of the magnesium hydrogen carbonate—equivalent to 6.977 grams per liter of the normal carbonate. Unlike the corresponding calcium salt, they found the magnesium hydrogen carbonate to be very unstable, and that all the magnesium could remain in the form of this salt only when there

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[1] Comptes rendus, 100, 144 (1885); Ann. Chim. Phys. (6) 13, 349 (1888).

[2] Zeit. anorg. Chem. 17, 199 (1898).

was a considerable excess of carbon dioxide dissolved in the solution.

Every investigator who has attempted to study magnesium carbonate in solution has experienced very great experimental difficulties. There is good reason to believe, as Bodländer[1] has pointed out, that these difficulties are due to the formation of complex molecular species $n\mathrm{Mg(OH)_2}m\mathrm{MgCO_3}$ with complex ions, resulting in the presence of considerable quantities of hydroxyl ions ($\overset{+}{\mathrm{O}}\mathrm{H}$) in the solution. This is tantamount to saying that there is considerable hydrolyzed normal carbonate in the solution — a fact which is apparent when one adds phenolphthalein to a solution of magnesium carbonate.

In saturated solutions of magnesium carbonate the formation of these complex compounds is of undoubted importance, and their study, as has been said above, is exceedingly difficult. In all probability they are mainly responsible for the discrepancies in the observations of various investigators of this subject. But in solutions of lesser concentration, and especially when there is some excess of dissolved carbon dioxide, they do not assume any practical importance even if they have an actual existence under such circumstances.[2] To all intents and purposes the solution may be considered as containing only the solutes normal magnesium carbonate (with the hydrolyzed free base) and magnesium hydrogen carbonate. It appears worth while, therefore, to get some idea as to the distribution of the base between the two acids by the method described in connection with the work on the sodium salts. The results are given in Table VII., which is self explanatory.

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[1] Zeit. phys. Chem. 35, 31 (1900).

[2] See Bodländer. loc. cit.

TABLE VII.

System : $MgCO_3$, $Mg(HCO_3)_2$, and CO_2

Temperature 30° C

Total Mg (grams per liter)	Mg as $MgCO_3$ (grams per liter)	Mg as $Mg(HCO_3)_2$ (grams per liter)
0.02410	0.01205	0.01205
0.13135	0.06820	0.06314
0.16087	0.08676	0.07411

Total Mg (gram-atoms per liter)	Mg as $MgCO_3$ Percent	Mg as $Mg(HCO_3)_2$ Percent
0.00100	50.00	50.00
0.00545	51.92	48.08
0.00667	53.93	46.07

Total salts in solution. (grams per liter)	Normal carbonate		Hydrogen carbonate	
	Grams per liter	Percent	Grams per liter	Percent
0.1144	0.0418	36.5	0.0726	63.5
0.6174	0.2368	38.2	0.3806	61.7
0.7479	0.3012	40.3	0.4467	59.7

Assuming that at infinite dilution all the magnesium will be in the form of hydrogen carbonate, it is evident that the curve for the more dilute solutions is much steeper than the curve for the corresponding concentrations with respect to the sodium salts. But the general nature of the curve will be the same, the upper part being very flat. It would appear probable, therefore, that in all solutions of the magnesium salts with which one has to deal practically, and which are in equilibrium with the air, but not in contact with the magnesium carbonate in the solid phase, about 50 percent (in round numbers) of the magnesium is in the form of the normal carbonate. Solutions of the magnesium salts are therefore in strong contrast to solutions of the calcium salts when practically all the base is combined in the form of the hydrogen carbonate.

But in contact with the magnesium carbonate in the solid phase quite different conditions may obtain when there is also an excess of carbon dioxide in the solution. Some carefully prepared magnesium carbonate was suspended in distilled water and a current of air, which had previously been washed in a dilute solution of sulphuric acid, was passed through continuously for twenty-nine days. The solution then contained 0.1530 gram of magnesium per liter, of which 0.0446 gram of magnesium per liter, or 29.1 percent of the total, were in the form of the normal carbonate. The current of air was then passed through the solution for seventeen days longer. The solution then contained 0.1837 gram per liter of magnesium, of which 0.0542 gram, or 29.5 percent, was in the form of normal carbonate. The flask containing the solution and suspended solid magnesium carbonate was then put aside for fifty-four days longer. The solution was then found to contain 0.1808 gram of magnesium per liter, of which 0.0615, or 33.9 percent, were combined as normal carbonate.

The total amount of magnesium in the solution, as shown by the last determination, is equivalent to 0.6276 gram normal carbonate per liter, which agrees with the figure (0.627) obtained by Treadwell and Reuter,[1] although the mean temperature of the solution in the experiments here described was about 22° C instead of 15° C, the temperature at which the investigators quoted worked. Moreover the solution of Treadwell and Reuter was supposed to contain no free carbon dioxide or carbonic acid.

From the data which have been presented above, it would appear that in a solution near the saturation point and in equilibrium with atmospheric air upwards of 50 percent of the magnesium would be in the form of the normal carbonate. When the solution was brought in contact with the salt in the solid phase and allowed to remain in equilibrium with atmospheric air more of the substance would go into solution (as the hydrogen carbonate) until the proportion of the base combined as normal carbonate would fall to about 34 percent or lower.

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[1] Zeit. anorg. Chem. 17, 199 (1898).

There is evidently a marked difference in this respect, as well as in total solubility, between the carbonates of calcium and magnesium. It should be borne in mind that natural waters frequently carry much more dissolved carbon dioxide or carbonic acid than solutions in equilibrium with atmospheric air; and in such solutions the relative percentage of the magnesium in the form of normal carbonate may well be much less than what has just been considered in the foregoing paragraphs.

Another point to which it seems worth while to call attention here, and which is well illustrated by the experiments described above, is the comparatively long periods of time required to bring a solution to equilibrium with a solute in the solid phase, when the solute is sparingly soluble. Attention has been called to this in connection with some other investigations made in this laboratory, and it must be insisted that this is an important matter in considering such phenomena, although a factor most difficult to control and for which to make proper allowance.

Summary

From the facts presented in this paper the following conclusions are drawn:

1. When in equilibrium with air every aqueous solution of sodium normal carbonate contains necessarily some sodium hydrogen carbonate. And, conversely, every solution of sodium hydrogen carbonate contains necessarily some normal sodium carbonate. At equilibrium there is a definite distribution of the base between the two acids.

2. The equilibrium is conditioned by the concentration, the temperature, and the partial pressure of the carbon dioxide in the vapor phase.

3. At any given concentration the proportion of normal carbonate increases with the rise of temperature. Conversely at any given temperature the proportion of normal carbonate increases with the total concentration, except at very great concentrations.

4. The phenomena presented by the solutions of the carbonate and hydrogen carbonate of potassium are strictly analo-

gous to those presented by the sodium salts, differing only in the quantitative relations.

5. Above some concentrations, relatively large, there is a gradual diminution of the percentage of normal carbonate; that is, there is an actual maximum point to the curve. The significance of this maximum point is not understood at present.

6. It seems improbable that more than 3 percent of the calcium is ever combined as the normal salt in solutions of the carbonates of this base when in contact with a vapor phase containing as much or more carbon dioxide than atmospheric air. Practically one has to consider only solutions of the hydrogen carbonate.

7. Solutions of the carbonates of magnesium are in marked contrast to those of the calcium salts. When the partial pressure of the carbon dioxide in the gas phase is not less than in atmospheric air, upward of 50 percent of the base may be combined as normal carbonate, if the solution is not in contact with the salt in the solid phase; the percentage falls below 35 percent when in contact with the solid normal carbonate. Both normal carbonate and hydrogen carbonate are to be considered in dealing with solutions of the magnesium salts.

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SOLUBILITY OF GYPSUM IN AQUEOUS SOLUTIONS OF SODIUM CHLORIDE[1]

BY FRANK K. CAMERON

The effect of one electrolyte in determining the solubility of another in water solutions has received considerable attention from investigators within the past few years. This work has been directed mainly to a verification of theories deduced from applications of the mass law to electrolytic dissociation, and quite satisfactory results have been obtained for very dilute solutions.

Excepting the early and now classical researches of Kopp,[2] Karsten,[3] Rüdorff,[4] and Engel,[5] but little satisfactory work is to be found described in the literature on this subject when concentrations of any magnitude were involved or when the work was carried on through any great range of concentration. Moreover, the cases thus studied have been carefully selected so as to take advantage of some peculiar characteristic of one or more of the components in the system under consideration and thus simplify the theoretical formulation of the factors involved. Such cases as one meets most frequently in every-day practice — two strong electrolytes in water, for example — have received but scant attention. The reason for this is that such cases *a priori* could not be expected to give satisfactory results, so far as the theories under examination were concerned, it being a well-established fact that for such electrolytes the dissociation does not take place in accordance with the *mass law*, as we now formulate it. For many technical problems, studies in geology, and similar investigations this mutual influence of salts or electrolytes in solution is of very great importance. Qualitatively we already

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[1] Contribution from the Bureau of Soils, U. S. Department of Agriculture. Published by permission of the Secretary of Agriculture.

[2] Liebig's Annalen, 34, 260 (1840).

[3] Abhandl. der Berlin Akad. (1841).

[4] Pogg. Ann. 148, 456, 555 (1873). Wied. Ann. 25, 626 (1885).

[5] Comptes rendus, 102, 113 (1886).

know something in this connection, but quantitative data have been almost entirely wanting up to the present.[1]

In such studies we have to do with solutions often far from dilute, and we have no consistent theory to guide us; furthermore, the particular salts involved in these problems have but seldom commended themselves to investigators.

It is not often that we have to deal with but one pair of electrolytes and their metathetical products in the study of such problems, but in the absence of satisfactory available data it was deemed wise to take a case of this kind for a preliminary study. Accordingly, from time to time, as attention to other work of the laboratory permitted, the solubility curves for several pairs of electrolytes have been followed quantitatively. Some results are here recorded for the system: Water, calcium sulphate, sodium chloride, and their reaction products.

Solutions of sodium chloride of various concentrations were prepared. The sodium chloride used was chemically pure material obtained from Eimer and Amend and tested by analyzing for chlorine with very satisfactory results. Into these sodium chloride solutions an excess of calcium sulphate in the form of gypsum ($CaSO_4.2H_2O$), finely divided, was introduced, and the solutions then allowed to stand, with frequent shakings, from one to fourteen days, according to the temperature at which the work was being done, in order that equilibrium might be reached. The gypsum used in the experiments described in this paper was from two sources. One sample was a very finely powdered gypsum obtained from Hot Springs, Fall River County, S. Dak., an analysis of which gave very satisfac-

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[1] For a review of the earlier work see W. W. J. Nicol (Phil. Mag. 31, 369 (1891)) and J. E. Trevor (Phil. Mag. 32, 75 (1891)). More recent investigations of interest in this connection are the "Solubility of Calcium Bicarbonate in Sodium Chloride Solutions," Treadwell and Reuter (Zeit. anorg. Chem. 17, 192 (1898)); "Solubility of Gypsum in Solutions of Hydrochloric Acid and Calcium Chloride," Lunge (Jour. Soc. Chem. Ind. 4, 31 (1885)); "Solubility of Gypsum in Solutions of Ammonium Chloride, Magnesium Chloride, and Calcium Chloride," Tilden and Shenstone (Proc. Roy. Soc. 38, 335 (1885)); "Solubility of Calcium Sulphate in Several Acids," Ostwald and Banthisch (Jour. prakt. Chem. [2] 29, 52 (1884)).

tory results for the formula $CaSO_4.2H_2O$. The material was powdered so finely that it displayed a decided tendency to "cake," and when used the solutions had to be shaken frequently. This "caking" did not resemble the setting of plaster of Paris, but the substance behaved more like a plastic clay. The other gypsum sample was obtained by pulverizing in an agate mortar some very fine crystals of gypsum kindly furnished by Mr. Wirt Tassin, of the United States National Museum. It may be said at once that curves were plotted from data obtained with both these materials and with calcium sulphate obtained by precipitation from mixing solutions of calcium chloride and sodium sulphate, all of which agreed most satisfactorily. The material first described possessed one advantage in that its very finely divided condition enabled it to go into solution more rapidly and greatly shortened the time required to obtain final equilibrium in the system.

Preliminary experiments indicated the advisability of using rather large volumes of solution. About 300 cc was found to be a very convenient amount. In the experiments at higher temperatures the portions of solutions required for analysis were drawn off with a pipette as quickly as possible, care being taken to avoid drawing off any solid gypsum. In some cases considerable difficulty was experienced in this respect, but it is not believed that any of the results here presented are open to criticism on this account. When working at the lower temperatures, a 100 cc portion was filtered through a "Schleicher und Schüll" folded filter, discarding the first runnings. This 100 cc portion was then diluted to 500 cc, and aliquot parts taken for the analytical determinations. The chlorine was determined by titrating with a carefully standardized silver nitrate ($N/10AgNO_3$) solution, using potassium chromate as indicator. The sulphates were estimated gravimetically as barium sulphate, in the usual manner. In some cases the calcium was also determined, but as nothing especial was thus gained, this last procedure did not seem to be advisable.

For a constant temperature bath a large washtub filled with water was used. With such a large volume of water the temperature changed quite slowly, and by passing in a stream of water or steam, as the case might be, no serious difficulty was experienced in keeping a temperature constant within a degree or a degree and a half Celsius. To attempt greater accuracy in this direction was not justifiable in view of the results obtained, and the advantage derived in being able to work with large volumes of solution in a bath of this size far outweighed any disadvantage arising from a variation in the temperature of the magnitude described.

Determinations made at 15° C

The first series of determinations obtained were made at 15° C. They are given in Table I., in which the first column contains the amounts of sodium chloride in the solution, assuming all the sodium and chlorine to be thus combined, and the second column containing the corresponding amounts of calcium sulphate found to be soluble. A much more complete set of determinations was then made at 23°.

TABLE I.

$NaCl$ and $CaSO_4$ in water at 15° C

Grams $NaCl$ per liter	Grams $CaSO_4$ per liter
0.6	2.3
1.1	2.5
5.1	3.1
10.6	3.7
31.1	4.8
51.4	5.6
139.9	7.4

Determinations made at 23° C

The data given in Table II. are the results of experiments made with more than ordinary care. The calcium sulphate used was prepared by pulverizing selected gypsum crystals. Other series made at this temperature with calcium sulphate from various sources showed most satisfactory agreements, and it is not deemed worth while to present them here. The results given in this table are presented graphically in Fig. 1. The ordinates represent reacting weights gypsum per liter of solution, and the abscissas the corresponding reacting weights of sodium chloride. For convenience in reference, the corresponding values in grams per liter and for anhydrous calcium sulphate are also given in the table.

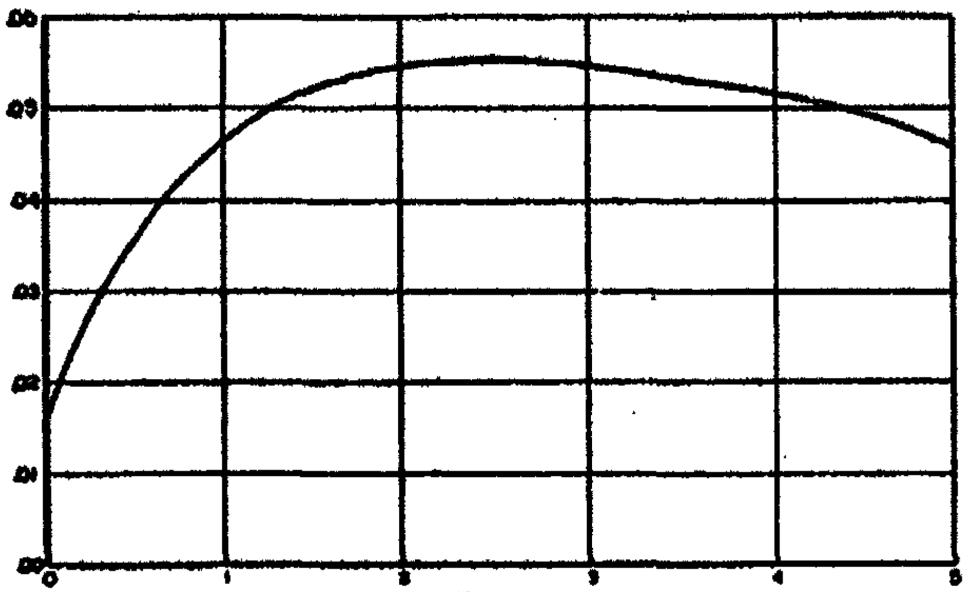

Fig. 1.

TABLE II.

NaCl and $CaSO_4$ in water at 23° C

Grams NaCl per liter	Reacting weights NaCl per liter	Grams $CaSO_4$ per liter	Reacting weights $CaSO_4$ per liter	Grams gypsum per liter
0.99	0.0171	2.37	0.0176	2.99
4.95	0.0852	3.02	0.0223	3.82
10.40	0.1790	3.54	0.0262	4.48
30.19	0.5200	4.97	0.0368	6.31
49.17	0.8471	5.94	0.0439	7.51
75.58	1.3018	6.74	0.0499	8.53
129.50	2.2314	7.50	0.0555	9.42
197.20	3.3968	7.25	0.0536	9.17
229.70	3.9568	7.03	0.0520	8.88
306.40	5.2785	5.68	0.0420	7.19
315.55[1]	5.4348	5.37	0.0397	6.79

By referring to Fig. 1 it will be observed that the solubility of the calcium sulphate or gypsum reaches a maximum in solu-

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[1] The solution in this case was in contact with both gypsum and sodium chloride in the solid phase.

tions containing about 135–140 grams of sodium chloride per liter, upward of 7.5 grams calcium sulphate — equivalent to 9.3 grams gypsum — being dissolved at this concentration, against approximately 2 grams calcium sulphate, equivalent to 2.7 grams gypsum soluble in pure water.

In view of the generally accepted ideas on the mutual effect of electrolytes in solution, the existence of this maximum solubility point was entirely unexpected and surprising.[1] The data given are calculated with reference to a constant volume of solution. It seemed possible that the relatively large amounts of salts present in the more concentrated solutions had replaced so much of the volume of the solvent in this constant volume of solution that the existence of this maximum solubility was only apparent and not real. Experiments to test this point will be described presently.

It was deemed advisable to determine experimentally whether or not the composition of the solid phase, containing both sodium chloride and gypsum, would affect the composition of the solution in contact with it. Therefore two mixtures containing, respectively, 45 grams of sodium chloride with 1 gram of gypsum and 45 grams of sodium chloride with 10 grams of gypsum, were each brought into contact with 100 cc of distilled water. The mixtures were shaken continuously for four days, then placed in the constant temperature bath and allowed to settle. An analysis of the supernatant solutions gave identical results for both cases. As there was no reason *a priori* to expect a different result with this pair of electrolytes no further experiments on this point were deemed necessary.

Determinations made at higher temperatures

In Table III. the data obtained at higher temperatures are given. The results are not presented in graphic form because the curves would lie so close together, when plotted on any convenient scale, as to fail to bring out more clearly than the tables do any points especially worth noting.

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[1] It had been observed, however, by Tilden and Shenstone, Proc. Roy. Soc. 38, 335 (1885).

TABLE III.

NaCl and $CaSO_4$ in water at various temperatures

30° C		52° C		70° C		82° C	
Grams NaCl per liter	Grams $CaSO_4$ per liter	Grams NaCl per liter	Grams $CaSO_3$ per liter	Grams NaCl per liter	Grams $CaSO_4$ per liter	Grams NaCl per liter	Grams $CaSO_4$ per liter
0.5	2.5	0.5	2.3	0.5	2.2	0.0	2.07
10.3	3.6	1.1	2.4	10.0	3.4	1.0	2.18
30.3	5.0	5.0	2.9	29.6	4.9	5.0	2.65
47.3	6.1	10.1	3.5	48.8	5.8	10.1	3.30
73.4	6.9	29.6	5.0	132.7	7.4	29.5	4.68
126.9	7.3	48.3	5.8	195.0	7.6	48.8	5.54
192.4	7.7	75.7	6.6	—	—	74.9	6.23
—	—	131.6	7.1	—	—	128.7	7.00
—	—	195.9	7.4	—	—	195.1	7.51

By referring to the tables it will be observed that the curve for 30° C would lie above that for 23° for the most part, but the curves for 50° and the higher temperatures, respectively, would fall lower and lower on the chart. At first sight this might be attributed to the fact that gypsum shows a maximum solubility in pure water at about 37.5° C, as may be seen by referring to Marignac's results.[1] But that this fact alone is not sufficient to account for the results noted seems probable when it is observed that the solubility of the gypsum in the sodium chloride solutions, even at 80°, may be increased to nearly 3.5 times its solubility in pure water, whereas the solubility of the calcium sulphate in pure water is 37.5°, the maximum point, is about 1.119 times its solubility at 0°, and about 1.243 times its solubility at 99°, as calculated from Marignac's data. That a causal relation exists between the facts observed is to be expected, but what it may be is not obvious at present.

As far as was observed, the curves determined at temperatures above 30° C were asymptotic, and did not show the existence of "maximum" points. That such points may exist is of course possible, but if so they must lie near the points indicating

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[1] Ann. Chim. Phys. (5) 1, 274 (1874).

the extreme solubility of sodium chloride in the system. The labor involved in attempting to locate them did not appear to be justified at the time the curves were determined, and the purposes for which this investigation was undertaken has not since indicated the desirability of a more exhaustive examination for them.

Determinations made at 26° C

In this series the determinations were made on solutions of the volume of a small pycnometer or specific gravity bottle, and in each case the actual weight of the solutions was determined. Having determined the weights of the salts present, the weights of water actually present as solvent were then calculated by subtracting the weights of the salts present from the total weights of the solution.

The volume of the pycnometer at 26° was carefully determined by boiling it for some time in distilled water, cooling to 26°, weighing it filled, carefully drying, and weighing it empty. The data obtained follows:

	Grams.
Weight of pycnometer filled	135.5364
Weight of pycnometer empty	35.7956
Weight of water	99.7408

The density of water at 26° being taken as 0.99687,[1] the volume of the pycnometer was 100.05 cc; therefore no attempt was made to correct the data obtained to the basis of 100 cc, the variations being very probably within the limits of error of the methods used.

Table IV. contains data obtained from experiments made at 26° C. A comparison of the data in Table IV. with that in Table II. shows a very satisfactory agreement between the two series of determinations made at 23° and 26°, respectively.

Nature of the curve referred to a constant weight of solvent

From the results given in Table IV. were calculated those given in Table V.; that is to say, the amounts of calcium sul-

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[1] Smithsonian Physical Tables, Gray, p. 94 (1896).

phate in a solution saturated with respect to it and the corresponding amounts of sodium chloride when the solution contains exactly 100 grams of water and irrespective of whatever volume the solution might have.

TABLE IV.

NaCl and $CaSO_4$ in water at 26° C

Grams solution per 100 cc.	Grams water per 100 cc.	Grams NaCl per 100 cc.	Grams $CaSO_4$ per 100 cc.
99.9848	99.7727	0.0000	0.2121
106.4441	96.6631	9.1154	0.6656
109.8113	94.6945	14.3989	0.7179
110.1215	94.5708	14.8343	0.7164
111.9622	93.6001	17.6502	0.7119
114.8826	91.3276	22.8756	0.6794
117.0720	90.0049	26.4173	0.6498
120.3439	87.7233	32.0491	0.5715

TABLE V.

Total NaCl and $CaSO_4$ in water at 26° C

NaCl per 100 grams water	$CaSO_4$ per 100 grams water
0.0000	0.2126
9.4307	0.6886
15.2056	0.7581
15.6859	0.7575
18.8570	0.7605
25.0478	0.7439
29.3509	0.7219
36.5343	0.6515

From this table it will be seen that a well-marked maximum solubility point does exist. This point corresponds in round numbers to 0.76 gram of calcium sulphate and 15.3 grams of sodium chloride in 100 grams of water. The sixth determination shows an apparent discrepancy, but this is probably due to an inaccurate weighing of the solution, since the data of Table IV. agree so well with the very carefully established data in Table II.

Tilden and Shenstone[1] obtained similar results for this pair of electrolytes working at 20° C. The curve obtained by them follows very closely a curve illustrating the data given here, but lies somewhat above. Nevertheless, it is believed that the results given here are the more reliable, as they have been repeated several times and with great care. The maximum point on Tilden and Shenstone's curve would be displaced somewhat further to the right than the curve for the results here given. It seems possible that the discrepancies between the two curves at highest concentration might disappear if they could be compared on exactly the same basis; but the statement of the results of the authors quoted is somewhat vague on this point, and it is not quite certain on what basis their results were computed.

Solubility changes for gypsum with varying temperature

Above 37° to 38° the solubility of gypsum in pure water decreases with rising temperature, and, as will be seen from Marignac's[2] results, at a point a little above 80° the solubility becomes less than at any lower temperature.

From the data presented above it would appear that the solubility of gypsum follows the same general law when sodium chloride is present, up to a concentration for this latter salt of about 135–140 grams per liter of solution. The figures of Tilden and Shentone[3] for the solubility of gypsum in a 25 percent solution of ammonia chloride indicate that while a maximum solubility point is reached with rising temperature it lies at or above 60° C. It seems very desirable, however, that their results for this particular case should be repeated before much weight be given them. On the other hand, they showed that when the gypsum was dissolved in solutions of calcium chloride, in which case the two substances furnish a common ion, that the solubility steadily increased without the appearance of any maximum solubility point, at least as far as 94° C.

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[1] Proc. Roy. Soc. 38, 335 (1885).

[2] See also Goldammer (Chem. Centralb., p. 708 (1888)), whose results indicate a maximum solubility for gypsum in water at about 37.5° C, while Poggiale (Ann. Chim. Phys. (3) 8, 469 (1843)) found it to be at 35° C.

[3] l. c.

Change in density of the solvent

In the course of experiments for the solubility curve at 26° C the fact was brought out that calcium sulphate dissolved in water caused a contraction of the solvent, as will be seen from the following figures:

	Grams.
Weight of pycnometer filled with water at 26° C	135.5167
Weight of pycnometer empty	35.7965
Weight of water	99.7202
Weight of pycnometer filled with solution of calcium sulphate saturated at 26°	135.7813
	35.7965
Weight of solution	99.9848
Weight of calcium sulphate	0.2121
Weight of water as solvent	99.7727
Weight of water alone	99.7202
	0.0525

In other words, although a portion of the volume of the water was displaced by the calcium sulphate in solution, the water as solvent weighed 0.0525 gram more. Therefore, there must have been an actual condensation of the solvent. The fact that such a condensation does take place as a rule when salts are dissolved in water has been known for some time, and Nernst[1] has suggested that this fact may possibly be connected with the phenomona of electrolytic dissociation, but as yet the nature of this connection has not been ascertained. The experiment was repeated with results agreeing fairly well with those given, but as the temperature was not noted, it is not considered worth while to present them here. The water used in the experiments just described was not boiled. But if we take the results given on page 563 we have the following data for 26° C:

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[1] Theoretical Chemistry (translated by Palmer), p. 332 (1895).

	Grams.
Weight of pycnometer with water	135.5364
Weight of pycnometer empty	35.7956
Weight of water (boiled)	99.7408
Weight of water as solvent	99.7727
	0.0319

From these figures it would appear that the condensation was somewhat less than the first figures indicated, and that it would be worth while to redetermine the condensation by boiling both the pure water and the solution. This was done, but owing to a misunderstanding the determinations were made at 31° C instead of 26° C. The weight of calcium sulphate taken was not determined directly, but was obtained by interpolation on the curve plotted from Marignac's results.

	Grams.
Weight of pycnometer filled with water	135.4241
Weight of pycnometer empty	35.7965
Weight of water (boiled)	99.6276
Weight of pycnometer filled with solution	135.7344
Weight of pycnometer empty	35.7965
Weight of solution (boiled)	99.9379
Weight of calcium sulphate	0.2130
Weight of water as solvent	99.7249
Weight of water (boiled)	99.6276
	0.0973

From the figures just presented the density of the calcium sulphate solution will be 1.0031 at 31° when compared with water at the same temperature. Making the assumption that the air dissolved in both solution and in water alone was the same, the density at 26° would be 1.0026. It is given as 1.0022 at 15° by Stolba[1] It would be interesting to compare these values by the methods of Valson[2] and Bender.[3] But a saturated

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[1] Jour. prakt. Chem. 97, 503 (1866).

[2] Comptes rendus, 73, 441 (1871); 77, 806 (1873).

[3] Wied. Ann. 20, 560 (1883).

solution of calcium sulphate is only about a hundred and fiftieth normal (N/150), and in consequence we have not been able to find any data already determined and suited to this purpose.

Composition of the hydrate of calcium sulphate in contact with solutions

It has frequently been necessary in the work of the laboratory to heat solutions containing calcium and sulphuric acid salts to temperatures higher than 80°, and the frequent precipitation of calcium sulphate under these circumstances had raised the suspicion that possibly some other hydrate of calcium sulphate than the dihydrate was formed at this temperature.

The suspicion was strengthened by the frequently observed fact that when solutions containing calcium sulphate and other salts were evaporated to dryness the residue apparently would not redissolve in the amount of water originally present. A microscopic investigation of this apparently insoluble residue left but little doubt that it was composed entirely of small gypsum crystals. These might of course have resulted from another hydrate on standing at a temperature at which the dihydrate was the stable form; but this would have assumed a high speed of transformation, as in some cases the microscopic examination was made as soon as possible after removing the material from the steam bath.

Hoppe-Seyler observed that gypsum lost water when heated to 120°–130° in contact with saturated solutions of sodium chloride or calcium chloride. Rose[1] observed the same phenomenon when the gypsum was heated in contact with a solution of sodium sulphate, although he doubted if it took place with a solution of sodium chloride.

Three 100 cc measurings flasks were filled with solutions containing considerable amounts of sodium chloride, and saturated with respect to gypsum. The contents of the flasks were evaporated to dryness in platinum dishes on the steam bath; the residues were then washed back into the 100 cc measuring

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[1] Pogg. Ann. 93, 606 (1854).

flasks, which were filled to mark, stoppered, and set aside. From time to time these flasks were vigorously shaken. In one case the solution had been frequently stirred while evaporating on the water-bath, and the gypsum crystals which separated were very small. In this case about eight days were required for re-solution to be complete; in the two other cases about sixteen and twenty-two days, respectively, were required, but in all three cases the re-solution was complete in the course of time. It thus appeared that the formation of a different hydrate above 80° was a gratuitous assumption; the more probable explanation of the facts observed is that the rate of solution of gypsum crystals is very slow, even when large amounts of sodium chloride are present.[1]

Since the experiments just described were made, a paper by van 't Hoff and Armstrong[2] has been published, from which it appears that the transition point for the two solid hydrates, $CaSO_4.2H_2O$ and $CaSO_4.\frac{1}{2}H_2O$, is 101.45° when in contact with a solution of sodium chloride of considerable concentration. With certain other substances however, this transition temperature is much lower. For example, these investigators found it convenient to prepare the hydrate, $CaSO_4.\frac{1}{2}H_2O$, by keeping gypsum, $CaSO_4.2H_2O$, in contact with concentrated nitric acid at 40° for some time. It might be supposed that this transition takes place at this lower temperature on account of the strong affinity of the nitric acid for water. The results of Vater,[3] rather tend to confirm this view. He found that from saturated solutions of sodium chloride at all ordinary temperatures calcium sulphate separated in the form of gypsum, $CaSO_4.2H_2O$. This

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[1] Since this work was done, Ostwald (Zeit. phys. Chem. 34, 495 (1900)) has suggested that a substance may have different solubilities, depending upon the size of the particles of the solid in contact with its solution, and Hulett (Zeit. phys. Chem. 37, 385 (1901)) has verified the fact for gypsum. It is believed, however, that it has been amply demonstrated that in these gypsum solutions final equilibrium conditions will be the same, and it is the rate of solution which has been the main disturbing factor hitherto in their study.

[2] Sitzungsber. Akad. Wiss. Berlin, 28, 559-576 (1900).

[3] Sitzungsber. Akad. Wiss. Berlin, 28, 269-294 (1900). See also Zunino. Gazz. chim. Ital. 30, I., 333 (1900).

hydrate also separated from solutions containing as much as 3 percent of magnesium chloride; but from saturated solutions of magnesium chloride gypsum, $CaSO_4.2H_2O$, separated below 40°, and the hydrate, $CaSO_4.\frac{1}{2}H_2O$, above 40°. Magnesium chloride has a strong tendency to crystallize under such conditions as the hexahydrate; that is to say, shows a strong affinity for water. From these facts it would seem that gypsum is not a stable hydrate above 40° in the presence of other substances which are strongly deliquescent, but that in the presence of a neutral substance like sodium chloride, which does not form a hydrate either in the solid or liquid phase, it is stable up to a temperature of 101.45° C.

It will be recalled that the maximum solubility of calcium sulphate in water is at about 40° C (more exactly 37.5°), and the idea suggests itself that perhaps this is the true transition point; the supposed solubility curve for gypsum from 0° to 100° being in reality two solubility curves—one for the dihydrate and the other for the hemihydrate—intersecting at 37.5°, both being so flat they run into each other as though but one curve. But this view is negatived by the fact that the transition does not take place in contact with sodium chloride solution until a temperature of 101.45°; and, as will presently be shown, it does not apparently take place at all in a perfectly indifferent medium at any temperature below that sufficient to drive out all the water from the substance. Further, the transition of gypsum to the hemihydrate when in contact with pure water above 40° has not yet been observed.

The statements of van 't Hoff and Armstrong and of Vater were confirmed by experiments in which some cleavage pieces of a very fine gypsum crystal were put into the various solutions at the temperatures stated. When transformation to the hemihydrate, $CaSO_4.\frac{1}{2}H_2O$, took place, the surface of the gypsum soon became very white and opaque and the surface roughened, but after standing some time, if dropped into water, the opacity disappeared and the substance gradually became perfectly clear and transparent again. This transformation from one hydrate to another could be very beautifully and readily followed when the cleavage piece was in contact with sodium chloride solutions, for the changes were then fairly rapid. It seemed worth while to see if the transition temperature would be the same when the hydrate was in contact with other presumably neutral substances. Therefore a clear transparent cleavage piece of gypsum crystal was dropped into a test-tube containing melted paraffin and the temperature gradually raised by immersing in a water-bath to which sodium chloride was added from time to time to raise the boiling temperature. No transition to the hemihydrate appeared when the temperature reached 101.50° C. The temperature was then raised to 104° and kept constant for about six hours. No formation of the hemihydrate could be observed, and the temperature was then gradually raised to 115° without any change in the gypsum being apparent. The test-tube containing the paraffin and gypsum was then withdrawn from the bath and quickly heated to about 145° C over a Bunsen lamp. At this temperature the crystal rapidly lost water, crumbled to pieces, and the residue appeared to be the anhydrous salt, $CaSO_4$, although a more thorough analytical examination would be desirable before making this statement positively. From these facts it is apparent that the equilibrium between the hydrates of calcium sulphate needs further study. But the work was stopped at this point, as further investigation in this direction was scarcely pertinent to the subject of this paper.

Solubility of gypsum in pure water

The solubility of calcium sulphate in pure water has been frequently determined, but the published results are very conflicting. To account for the discrepancies most astonishing statements as to the supersaturation and under saturation, etc., are recorded. The real cause of the difficulty seems to have been the very slow rate of solution, the time necessary for the obtaining of final equilibrium between the solid solute and solution being relatively very long. For the sake of a comparison, some of the principal determinations at temperatures near that at which we worked are presented in Table VI.

TABLE VI.

Solubility of gypsum in pure water

Authorities	Temperature	Parts water required to dissolve 1 part calcium sulphate	Parts water required to dissolve 1 part gypsum
Marignac[1]	24°	479	378
	18	488	386
Poggiale[2]	20	415	—
Church[3]	21.2	—	419
Cozza[4]	22	538	426
Droeze[5]	20	—	371
	25	—	365
Goldammer[6]	22.5	480	—
Kohlrausch and Rose[7] [8]	18	483	383
From data of this paper	26	469	372

The first column gives the authority, with reference; the second column, the temperature at which the solubility was determined; the third column, the parts of water required to dissolve one part of calcium sulphate, calculated on the basis of the anhydrous salt; and the fourth column, the corresponding calculation on the basis of the dihydrate.

Droeze seems to have given much attention to this solubility determination and, besides making experimental investigations himself, has given a critical review of the work of his predecessors in this direction. He objects to Poggiale's figures, that they were probably obtained by working with a supersaturated solution. That this could have been possible seems absurd, and

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[1] Ann. Chim. Phys. (5) 1, 274 (1874).

[2] Ibid. (3) 8, 469 (1843).

[3] Jsb. Chem. p. 192 (1867).

[4] Gazz. Chim. Ital. p. 135 (1873).

[5] Ber. chem. Ges. Berlin, 10, 330 (1877).

[6] Chem. Centrbl., p. 708 (1888).

[7] Zeit. phys. Chem. 12, 241 (1893).

[8] Calculated from the published data. Under the circumstances the agreement with Marignac's results is remarkable.

it is much more probable that Poggiale did some very bad analytical work, for his results are phenomenally high. Again, Droeze objects to Church's results, that they were obtained from unsaturated solutions. The reasons for this conclusion are vague, but we are inclined to hold the conclusion itself to be correct, for Droeze's results agree fairly well with those of Marignac, Goldammer, and Kohlrausch and Rose, while the figures of Poggiale, Church, and Cozza show wide variations.

The solubility, as determined from the data presented in this paper, is somewhat greater than is indicated by the figures of the majority of the investigators cited, but not quite as great as found by Droeze. No special care was observed in obtaining this determination, for at the time the experiment was made it was regarded only as an incident in the gathering of data for the solubility curve and not as a point under special investigation. Nevertheless, it is believed that the value as given here is approximately correct, for it is not easy to see in what respect the details of the experimental determination could be bettered. There can be little or no doubt that final equilibrium between the solid salt and the solution had been reached. The analytical operations involved were carefully performed and the calculations were based on the actual weights of the solvent, as well as the solute found to be present.

Theoretical Discussion

The effect of one electrolyte upon another in aqueous solution can be accounted for by the electrolytic dissociation theory, at least qualitatively. Attempts have not been wanting to formulate a quantitative expression for the phenomena observed. Nernst[1] and Noyes,[2] with his pupils, in particular have attacked the problem with marked success by applying the *mass law* of Guldberg and Waage to the particular types of equilibria

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[1] Zeit. phys. Chem. 4, 372 (1889); Theoretical Chemistry (Palmer), p. 406.

[2] Zeit. phys. Chem. 6, 241 (1890); 9, 603 (1892); 16, 125 (1894); 26, 152 (1898); 27, 267 (1898); Jour. Am. Chem. Soc. 19, 930 (1898): 20, 194, 742, 751 (1898); 21, 217, 511 (1899).

between electrolytes and their resulting ions which may be presented.

For the case where a pair of binary electrolytes reacts with the formation of another pair of binary electrolytes and four ions the theory involves the solutions of nine simultaneous equations containing nine variables. For particular cases eight of these variables are determined by various means, and in consequence there is obtained one equation in one unknown quantity, but it is of a high order and involves a very large number of terms. In all the cases so far studied they were so selected that certain restrictions were imposed, arising from the nature of the particular cases themselves, which greatly facilitated their study. Certain special assumptions could be made by which the algebraic expression of the relation between the quantities involved would be very much simplified.

In the case which is the subject of this paper no such assumptions appear justified. In the first place, the concentrations involved are far from what may fairly be considered dilute. All the substances involved in the metathesis

$$CaSO_4 + NaCl \rightleftarrows CaCl_2 + Na_2SO_4$$

are *strong* electrolytes to which the Ostwald dilution law does not apply — that is to say, to which the mass law is *not* applicable as a statement of the equilibria between the quantities of dissociated ions and undissociated salt through any range of concentrations. The ionization constants, which appear in the equations to which reference has just been made, can not be obtained, therefore, in any way which we can at present see. In the case of the calcium chloride and the sodium sulphate supposed to be in the solution there did not appear to be any practicable way to decide in how far the dissociation would take place as for a di-ionic electrolyte, or how far as for a tri-ionic electrolyte, with a consequent modification of the theoretical statements. These considerations have finally caused the abandonment of any attempt to make a comparison between theoretically computed results and those actually found, and, in the present state of our knowledge, the results can be presented only as empirical determinations in the trust that in time they may find use in helping to develop a more comprehensive and satisfactory theory for solutions.

There does not appear to be any rational explanation for the appearance of the maximum point on the solubility curve. One would naturally expect the solubility of the gypsum to continually increase as the concentration with respect to sodium chloride increases. Noyes[1] has brought forward some evidence to show that as the concentration increases with respect to chlorides of the alkali earth metals, there is a formation of complex ions, for example, $\overline{\mathrm{Ca}}\mathrm{Cl}_3$ or $\overline{\mathrm{Ca}}\mathrm{Cl}_4$. The evidence he obtained was rather against the assumption that the sulphates of the alkali metals would dissociate in any but a normal way, as triionic electrolytes; but he worked with quite dilute solutions (up to a tenth molar), and it does not follow that complex ions would not be found in solutions of the concentrations considered in this paper. It is difficult to see how the formation of such complex ions could affect the gypsum in contact with the solution, otherwise than to increase its solubility; and the fact that the solubility actually decreases beyond the maximum point is, as far as it goes, rather to be considered as evidence against the formation of the complex ions. The same thing might be said as to the suggestion that all electrolytes are considerably hydrolyzed at high concentrations.

It seems more probable that the phenomenon is connected with the condensation of the solvent and the effect of such condensation upon the solution tensions of the various electrolytes, and it is earnestly to be desired that some one with time and opportunities undertake an investigation of this subject.

For assistance in carrying out the experimental and analytical details of the work described in this paper, the author wishes to record his sincere acknowledgments to Messrs. Frank D. Gardner and Atherton Seidell.

Summary

Some of the points brought out in the foregoing pages to which attention is especially directed, may be stated as follows:

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[1] Phys. Rev., 12, 15 (1901); Jour. Am. Chem. Soc. 23, 37 (1901); Zeit. phys. Chem. 36, 61 (1901).

(1) Below 37.5° C the solubility curves for gypsum in aqueous solutions of sodium chloride show a maximum point. Above this temperature the existence of maximum points is doubtful.

(2) At 23° C this maximum solubility takes place in a solution containing from 135 to 140 grams sodium chloride per liter.

(3) The solubility of gypsum at 23° in a solution containing 135 grams of sodium chloride per liter is about 9.3 grams per liter. This is equivalent to about 7.5 grams of anhydrous calcium sulphate per liter.

(4) The solubility of gypsum in solutions containing less than 140 grams of sodium chloride per liter is very little affected by change of temperature.

(5) Maximum points in the solubility curve still persist, even if the solubilities be calculated on the basis of the weight of solvent present rather than the volume of the solution.

(6) A condensation of the water as solvent takes place when gypsum and sodium chloride are brought into solution.

(7) The rate of solution of gypsum is very slow, and at ordinary temperatures the time required for equilibrium to be brought about is often great. This fact accounts for the apparent insolubility of gypsum crystals in that volume of solution from which they may have been originally obtained.

(8) The transition temperature at which the dihydrate and hemihydrate of calcium sulphate are in equilibrium appears to be dependent upon the nature of the substance or substances in the solution with which they are in contact.

(9) At 26° the solubility of gypsum is about 1 part in 372 parts of pure water.

(10) The specific gravity of a saturated solution of gypsum in pure water is 1.0026 at 26° C, and 1.0031 at 31°.

(11) The application of the mass law, as formulated by Guldberg and Waage, to the phenomena of electrolytic dissociation fails to account for the observations here recorded.

(12) The existence of a maximum point on the solubility curve is not satisfactorily accounted for by the hypothesis of the existence of complex ions in the solution. It is probably connected with the condensation of the solvent in aqueous solutions of electrolytes.

THE MATHEMATICAL EXPRESSION OF THE PERIODIC LAW

BY S. H. HARRIS

By a close comparison between a table of the atomic weights in numerical order and F. P. Venable's table of the elements, we arrive at some interesting relations. The table of elements was taken from Paul C. Freer's work on Inorganic Chemistry and Venable's table is inserted, containing the calculated atomic weights of several unknown elements as derived by formulae obtained by the author from a study of the table. The atomic weights are themselves only approximately determined at present and we could not reasonably expect to find a law which is exactly fulfilled in all cases.

We can, however, find a law that will hold good approximately, and use it to calculate atomic weights of unknown elements with a fair degree of exactness.

The series Li, Be, B, C, N, O, F are called bridge elements and the series Na, Mg, Al, Si, P, S, Cl are called typical elements.

Let us for a moment consider the typical and bridge elements alone thus:

$$\begin{tikzcd}
\mathrm{Li} \arrow[r, dash] \arrow[d, dash] & \mathrm{Be} \arrow[r, dash] \arrow[d, dash] & \mathrm{B} \arrow[r, dash] \arrow[d, dash] & \mathrm{C} \arrow[r, dash] \arrow[d, dash] & \mathrm{N} \arrow[r, dash] \arrow[d, dash] & \mathrm{O} \arrow[r, dash] \arrow[d, dash] & \mathrm{F} \arrow[d, dash] \\
\mathrm{Na} \arrow[r, dash] & \mathrm{Mg} \arrow[r, dash] & \mathrm{Al} \arrow[r, dash] & \mathrm{Si} \arrow[r, dash] & \mathrm{P} \arrow[r, dash] & \mathrm{S} \arrow[r, dash] & \mathrm{Cl}.
\end{tikzcd}$$

From this we observe this relation

$$\log \mathrm{Li} : \log \mathrm{Be} = (\mathrm{Na})^2 : (\mathrm{Mg})^2 .$$

Working this out, using logarithms to base 10, we obtain in verification $499.76 = 506.99$. We do not obtain exact equality as any inherent error in atomic weights when squared is considerably increased.

Venable's Table with Calculated Atomic Weights of Several Unknown Elements

						MH_4		MH_3		MH_2		MH				
M^2O		MO		M^2O_3		MO_2		M_2O_5		MO_3		M_2O_7				
Li		Be		B		C		N		O		F				
Na		Mg		Al		Si		P		S		Cl				
K	Cu	Ca	Zn	Sc	Ga	Ti	Ger	V	As	Cr	Se	Mn	Br	Fe	Co	Ni
Rb	Ag	Sr	Cd	Yt	In	Zr	Sn	Nb	Sb	Mo	Te	(98 87)	I	Ru	Rh	Pd
Cs	Au	Ba	Hg	La	Tl	Ce	Pb	Ta	Bi	W	(212.58)	(189.51)	(218.94)	Os	Ir	Pt
(204.6)	( )	(208.23)	( )	(221.45)	( )	Th	( )	(235.32)	( )	Ur	( )	(246.71)	( )			

2. $\log \mathrm{Be} : \log \mathrm{B} = \mathrm{Mg} : \mathrm{Al}$
verification $25.76 = 25.3$

3. $\log \mathrm{B} : \log \mathrm{C} = \sqrt{\mathrm{Al}} : \sqrt{\mathrm{Si}}$
$5.55 = 5.60$

4. $\log \mathrm{C} : \log \mathrm{N} = \sqrt{\mathrm{Si}} : \sqrt{\mathrm{P}}$
$6.00 = 6.11$

5. $\log \mathrm{N} : \log \mathrm{O} = \mathrm{P} : \mathrm{S}$
$36.68 = 37.32$

6. $\log \mathrm{O} : \log \mathrm{F} = \mathrm{S}^2 : \mathrm{Cl}^2$
$1517.49 = 1309.44$

wide discrepancy. Error greatly multiplied in squaring, because numbers are large.

On collecting these proportions in a table we obtain the following very remarkable series:

$$\begin{cases} 1.\ \log \mathrm{Li} : \log \mathrm{Be} = \mathrm{Na}^2 : \mathrm{Mg}^2 \\ 2.\ \log \mathrm{Be} : \log \mathrm{B} = \mathrm{Mg} : \mathrm{Al} \\ 3.\ \log \mathrm{B} : \log \mathrm{C} = \sqrt{\mathrm{Al}} : \sqrt{\mathrm{Si}} \\ 4.\ \log \mathrm{C} : \log \mathrm{N} = \sqrt{\mathrm{Si}} : \sqrt{\mathrm{P}} \\ 5.\ \log \mathrm{N} : \log \mathrm{O} = \mathrm{P} : \mathrm{S} \\ 6.\ \log \mathrm{O} : \log \mathrm{F} = \mathrm{S}^2 : \mathrm{Cl}^2 \end{cases}$$

From this table we see an approximate relationship between the bridge elements and the typical elements.

Approximate law

The ratios of the logarithms of the atomic weights of bridge elements and typical elements, which stand next to them in the table, decrease in a certain geometrical progression as we pass from the left or positive side of the table toward the central carbon atom and increases as we pass from the carbon atom toward the right or negative end of the table.

Relations between every other or alternate bridge element

Consider the first two ratios in the previous table. From them we obtain the following:

$$(1)\quad \log \mathrm{Be} = \frac{\mathrm{Mg}^2 \cdot \log \mathrm{Li}}{\mathrm{Na}^2} \qquad (2)\quad \log \mathrm{Be} = \frac{\mathrm{Mg} \cdot \log \mathrm{B}}{\mathrm{Al}}$$

$$\text{or}\quad \frac{\mathrm{Mg}^2\cdot\log\mathrm{Li}}{\mathrm{Na}^2}=\frac{\mathrm{Mg}\cdot\log\mathrm{B}}{\mathrm{Al}}.$$

Dividing both sides by Mg^2 and manipulating we obtain

$$\frac{\log\mathrm{Li}}{\log\mathrm{B}}=\frac{\mathrm{Na}^2}{\mathrm{Mg}\cdot\mathrm{Al}}.$$

In a similar manner we may combine all these six ratios and obtain five new ones tabulated as follows:

$$\left\{\begin{array}{l}
1.\ \log\mathrm{Li}:\log\mathrm{B}=\mathrm{Na}^2:\mathrm{Mg}\cdot\mathrm{Al}\\
2.\ \log\mathrm{Be}:\log\mathrm{C}=\sqrt{\mathrm{Al}}\cdot\mathrm{Mg}:\mathrm{Al}\cdot\sqrt{\mathrm{Si}}\\
3.\ \log\mathrm{B}:\log\mathrm{N}=\sqrt{\mathrm{Al}}:\sqrt{\mathrm{P}}\\
4.\ \log\mathrm{C}:\log\mathrm{O}=\mathrm{P}\sqrt{\mathrm{Si}}:\sqrt{\mathrm{P}}\cdot\mathrm{S}\\
5.\ \log\mathrm{N}:\log\mathrm{F}=\mathrm{P}\cdot\mathrm{S}:\mathrm{Cl}^2
\end{array}\right.$$

Here the logarithmic ratio decreases as we pass towards center and increases in same way as we go to negative end.

Typical elements and periods

The following ratios have been observed between the typical elements and periods which underlie them:

Summary	Verifications
$\log\mathrm{Na}:\log\mathrm{Mg}=\mathrm{K}:\mathrm{Ca}$	54.46 = 54.19
$\log\mathrm{Mg}:\log\mathrm{Al}=\sqrt{\mathrm{Ca}}:\sqrt{\mathrm{Sc}}$	9.18 = 9.05
$\log\mathrm{Al}:\log\mathrm{Si}=\sqrt[3]{\mathrm{Sc}}:\sqrt[3]{\mathrm{Ti}}$	5.19 = 5.13
$\log\mathrm{Si}:\log\mathrm{P}=\sqrt[3]{\mathrm{Ge}}:\sqrt[3]{\mathrm{As}}$	6.12 = 6.21
$\log\mathrm{P}:\log\mathrm{S}=\sqrt{\mathrm{As}}:\sqrt{\mathrm{Se}}$	13.24 = 13.04
$\log\mathrm{S}:\log\mathrm{Cl}=\mathrm{Se}:\mathrm{Br}$	120.34 = 122.46

Typical elements and second group

Summary	Verifications
$\log\mathrm{Na}:\log\mathrm{Mg}=\mathrm{Rb}:\mathrm{Sr}$	119.28 = 118.46
$\log\mathrm{Mg}:\log\mathrm{Al}=\sqrt{\mathrm{Sr}}:\sqrt{\mathrm{Yt}}$	13.08 = 13.39
$\log\mathrm{Al}:\log\mathrm{Si}=\sqrt[3]{\mathrm{Yt}}:\sqrt[3]{\mathrm{Zr}}$	6.43 = 6.49
$\log\mathrm{Si}:\log\mathrm{P}=\sqrt[3]{\mathrm{Sn}}:\sqrt[3]{\mathrm{Sb}}$	7.18 = 7.33
$\log\mathrm{P}:\log\mathrm{S}=\sqrt{\mathrm{Sb}}:\sqrt{\mathrm{Te}}$	16.67 = 16.48
$\log\mathrm{S}:\log\mathrm{Cl}=\mathrm{Te}:\mathrm{I}$	190.92 = 193.77

Comparing these proportions to those already given, we obtain:

$$\left\{\begin{array}{l}
\mathrm{K} : \mathrm{Ca} = \mathrm{Rb} : \mathrm{Sr} \\
\mathrm{Ca} : \mathrm{Sc} = \mathrm{Sr} : \mathrm{Yt} \\
\mathrm{Sc} : \mathrm{Ti} = \mathrm{Yt} : \mathrm{Zr} \\
\mathrm{Ge} : \mathrm{As} = \mathrm{Sn} : \mathrm{Sb} \\
\mathrm{As} : \mathrm{Se} = \mathrm{Sb} : \mathrm{Te} \\
\mathrm{Se} : \mathrm{Br} = \mathrm{Te} : \mathrm{I}
\end{array}\right.$$

Summary	Verifications
1. $\log \mathrm{Na} : \log \mathrm{Mg} = \mathrm{Cs} : \mathrm{Ba}$	$187.14 = 184.14$
2. $\log \mathrm{Mg} : \log \mathrm{Al} = \sqrt{\mathrm{Ba}} : \sqrt{\mathrm{La}}$	$16.29 = 16.77$
3. $\log \mathrm{Al} : \log \mathrm{Si} = \sqrt[3]{\mathrm{La}} : \sqrt[3]{\mathrm{Ce}}$	$7.44 = 7.51$
4. $\log \mathrm{Si} : \log \mathrm{P} = \sqrt[3]{\mathrm{Pb}} : \sqrt[3]{\mathrm{Bi}}$	$8.62 = 8.61$
5. $\log \mathrm{P} : \log \mathrm{S} = \sqrt{\mathrm{Bi}} : \sqrt{x}$	$x = 212.58$
6. $\log \mathrm{S} : \log \mathrm{Cl} = x : y$	$y = 218.94$

Calculating atomic weights of unknown elements

By an examination of Venable's table we see that the element lying just below Te in sixth group is unknown. To calculate its atomic weight

$$\begin{aligned}
\log \mathrm{P} : \log \mathrm{S} &= \sqrt{\mathrm{Bi}} : \sqrt{x} \\
x &= 212.58 \\
&= \text{calculated atomic weight}
\end{aligned}$$

To calculate the element following iodine in seventh group

$$\begin{aligned}
\log \mathrm{S} : \log \mathrm{Cl} &= x : y \\
\text{but } x &= 212.58 \\
y &= 218.94
\end{aligned}$$

These two unknown elements fill the gap between Bi = 208.9 and Th = 232.6.

By comparing the last two sets of ratios, we obtain

$$\begin{array}{l}
\mathrm{Cs} : \mathrm{Ba} = \mathrm{Rb} : \mathrm{Sr} \\
\mathrm{Ba} : \mathrm{La} = \mathrm{Sr} : \mathrm{Yt} \\
\mathrm{La} : \mathrm{Ce} = \mathrm{Yt} : \mathrm{Zr} \\
\mathrm{Pb} : \mathrm{Bi} = \mathrm{Sn} : \mathrm{Sb} \\
\mathrm{Bi} : x = \mathrm{Sb} : \mathrm{Te} \\
x : y = \mathrm{Te} : \mathrm{I}
\end{array}$$

To obtain the atomic weight of the unknown element following La in third group, we have

$$\log \mathrm{Al} : \log \mathrm{Si} = \sqrt[3]{x} : \sqrt[3]{\mathrm{Th}}$$

$$\text{solving, } x = 221.45$$

For the unknown following Ba in second group

$$\log \mathrm{Mg} : \log \mathrm{Al} = \sqrt{x} : \sqrt{221.45}$$

$$x = 208.23$$

Element following Cs in first group

$$\log \mathrm{Na} : \log \mathrm{Mg} = x : 208.23$$

$$x = 204.64$$

Summary	Verifications
1. $\log \mathrm{Na} : \log \mathrm{Mg} = \mathrm{Cu} : \mathrm{Zn}$	$88.92 = 88.12$
2. $\log \mathrm{Mg} : \log \mathrm{Al} = \sqrt{\mathrm{Zn}} : \sqrt{\mathrm{Ga}}$	$11.52 = 11.56$
3. $\log \mathrm{Al} : \log \mathrm{Si} = \sqrt[3]{\mathrm{Ga}} : \sqrt[3]{\mathrm{Ger}}$	$5.96 = 5.96$
4. $\log \mathrm{Si} : \log \mathrm{P} = \sqrt[3]{\mathrm{Ti}} : \sqrt[3]{\mathrm{V}}$	$5.40 = 5.41$
5. $\log \mathrm{P} : \log \mathrm{S} = \sqrt{\mathrm{V}} : \sqrt{\mathrm{Cr}}$	$10.75 = 10.79$
6. $\log \mathrm{S} : \log \mathrm{Cl} = \mathrm{Cr} : \mathrm{Mn}$	$82.78 = 80.77$

Deduced ratios

$\mathrm{Cu} : \mathrm{Zn} = \mathrm{Cs} : \mathrm{Ba}$

$\mathrm{Zn} : \mathrm{Ga} = \mathrm{Ba} : \mathrm{La}$

$\mathrm{Ga} : \mathrm{Ger} = \mathrm{La} : \mathrm{Ce}$

$\mathrm{Ti} : \mathrm{Va} = \mathrm{Pb} : \mathrm{Bi}$

$\mathrm{V} : \mathrm{Cr} = \mathrm{Bi} : x$

$\mathrm{Cr} : \mathrm{Mn} = x : y$

Summary	Verifications
1. $\log \mathrm{Na} : \log \mathrm{Mg} = \mathrm{Ag} : \mathrm{Cd}$	$152.51 = 149.53$
2. $\log \mathrm{Mg} : \log \mathrm{Al} = \sqrt{\mathrm{Cd}} : \sqrt{\mathrm{In}}$	$14.77 = 15.14$
3. $\log \mathrm{Al} : \log \mathrm{Si} = \sqrt[3]{\mathrm{In}} : \sqrt[3]{\mathrm{Sn}}$	$7.04 = 7.04$
4. $\log \mathrm{Si} : \log \mathrm{P} = \sqrt[3]{\mathrm{Zr}} : \sqrt[3]{\mathrm{Nb}}$	$6.60 = 6.69$
5. $\log \mathrm{P} : \log \mathrm{S} = \sqrt{\mathrm{Nb}} : \sqrt{\mathrm{Mo}}$	$14.61 = 14.59$
6. $\log \mathrm{S} : \log \mathrm{Cl} = \mathrm{Mo} : x$	$x = 98.87$

This x follows Mn in seventh group.

Deduced ratios:

$$\begin{array}{llll}
\mathrm{Ag} & : \mathrm{Cd} = & \mathrm{Cu} & : \mathrm{Zn} \\
\mathrm{Cd} & : \mathrm{In} = & \mathrm{Zn} & : \mathrm{Ga} \\
\mathrm{In} & : \mathrm{Sn} = & \mathrm{Ga} & : \mathrm{Ger} \\
\mathrm{Zr} & : \mathrm{Nb} = & \mathrm{Ti} & : \mathrm{Va} \\
\mathrm{Nb} & : \mathrm{Mo} = & \mathrm{V} & : \mathrm{Cr} \\
\mathrm{Mo} & : x = & \mathrm{Cr} & : \mathrm{Mn}
\end{array}$$

Summary	Verifications
1. $\log \mathrm{Na} : \log \mathrm{Mg} = \mathrm{Au} : \mathrm{Ag}$	$272.35 = 273.3$
2. $\log \mathrm{Mg} : \log \mathrm{Al} = \sqrt{\mathrm{Hg}} : \sqrt{\mathrm{Tl}}$	$19.80 = 20.23$
3. $\log \mathrm{Al} : \log \mathrm{Si} = \sqrt[3]{\mathrm{Tl}} : \sqrt[3]{\mathrm{Pb}}$	$8.48 = 8.56$
4. $\log \mathrm{Si} : \log \mathrm{P} = \sqrt[3]{\mathrm{Ce}} : \sqrt[3]{\mathrm{Ta}}$	— —
5. $\log \mathrm{P} : \log \mathrm{S} = \sqrt{\mathrm{Ta}} : \sqrt{\mathrm{W}}$	$20.22 = 20.33$
6. $\log \mathrm{S} : \log \mathrm{Cl} = \mathrm{W} : x$	$x = 189.51$

$x =$ at. wt. second element below Mn in seventh group. At. wts. Ce and Ta are faulty. Rule fails to work.

Deduced relations:

$$\begin{array}{llll}
\mathrm{Au} & : \mathrm{Ag} = & \mathrm{Ag} & : \mathrm{Cd} \\
\mathrm{Hg} & : \mathrm{Tl} = & \mathrm{Cd} & : \mathrm{In} \\
\mathrm{Tl} & : \mathrm{Pb} = & \mathrm{In} & : \mathrm{Sn} \\
 & : \quad = & \mathrm{Zr} & : \mathrm{Nb} \\
\mathrm{Ta} & : \mathrm{W} = & \mathrm{Nb} & : \mathrm{Mo} \\
\mathrm{W} & : x = & \mathrm{Mo} & : x
\end{array}$$

Other unknown elements

$$\log \mathrm{S} : \log \mathrm{Cl} = \mathrm{Ur} : x$$
$$x = 246.71$$

This is the third unknown element lying below Mn in seventh group.

$$\log \mathrm{P} : \log \mathrm{S} = \sqrt{x} : \sqrt{\mathrm{Ur}}$$
$$x = 235.32$$

By combining and manipulating different sets of ratios in the foregoing pages, we obtain the following series:

Summary	Verificatiosn
Ti = $\sqrt{Mn \cdot Ca}$	48. = 47.
Sc = $\sqrt{K \cdot Cr}$	44. = 45.1
Zr = $\sqrt{Rb \cdot Mo}$	90.6 = 90.6
Gad = $\sqrt{Cs. W}$	156. = 156.4
Al = $\sqrt{Na \cdot S}$	27. = 27.3
Mo = $\sqrt{Ru \cdot Zr}$	90.6 = 90.6
Cs = $\sqrt{La \cdot I}$	132.9 = 132.6
Fl = $\sqrt{Al \cdot N} = \sqrt{Na \cdot O}$	19.1 = 19.2
C = $\sqrt{Be \cdot O}$	12. = 12.
Si = $\sqrt{Cl \cdot Na}$	28.4 = 28.4
Cl = $\sqrt{S \cdot Ca} = \sqrt{Si \cdot Sc}$	35.5 = 35.4
Se = $\sqrt{Ger \cdot Sr}$	79. = 79.
O = $\sqrt{Na \cdot B} = \sqrt{x \cdot C}$	16. = 15.92
Cu = $\sqrt{Ni \cdot Ga}$	63.64 = 63.6
Mn = $\sqrt{Ni \cdot Va}$	55. = 55.
Zn = $\sqrt{Ge \cdot Ni}$	65.1 = 65.3
Ge = $\sqrt{Br \cdot Zn}$	72.25 = 72.3
Pd = $\sqrt{Ru \cdot Cd}$	106.6 = 106.6
S = $\sqrt{Al \cdot K}$	32.06 = 32.4
P = $\sqrt{Al \cdot Cl}$	30.9 = 31.
Na = $\sqrt{Fl \cdot Si}$	23.2 = 23.05
Mg = $\sqrt{Fl \cdot P}$	24.3 = 24.3
N = $\sqrt{Fl \cdot B}$	14.1 = 14.
Sr = $\sqrt{Mo \cdot Br}$	87.6 = 87.6
Rb = $\sqrt{Br \cdot Zr}$	85.11 = 85.5
Va = $\sqrt{Ti \cdot Mn}$	51.3 = 51.4
I = $\sqrt{Cs \cdot Sn}$	126.6 = 126.85
Ba = $\sqrt{Cs \cdot Ce}$	137. = 137.43
Tl = $\sqrt{Hg \cdot Bi}$	204.4 = 204.18
Hg = $\sqrt{Pt \cdot Tl}$	199.6 = 200.
Pb = $\sqrt{Tl \cdot Bi}$	206.52 = 206.95
Au = $\sqrt{Pt \cdot Hg}$	197.4 = 197.3
Pt = $\sqrt{Ir \cdot Au}$	195.1 = 195.

Summary	Verifications
Ir = $\sqrt{Os \cdot Pt}$	$193. = 193.1$
Ta = $\sqrt{Yt \cdot Ir}$	$182.7 = 182.6$
Os = $\sqrt{W \cdot Au}$	$190.7 = 190.8$
W = $\sqrt{Yt \cdot Pt}$	$183.7 = 184.$
Tb = $\sqrt{Sa \cdot Tm}$	$160. = 160.$
Erb = $\sqrt{Sa \cdot Ta}$	$166.4 = 166.3$
Tm = $\sqrt{Tb \cdot Ta}$	$170.9 = 170.7$
Sa = $\sqrt{Pr \cdot Gad}$	$149.99 = 150.$
Pr = $\sqrt{La \cdot Sa}$	$143.9 = 143.5$
Neo = $\sqrt{Ba \cdot Pr}$	$140.43 = 140.5$
La = $\sqrt{Cs \cdot Pr}$	$138.1 = 138.2$
Sn = $\sqrt{In \cdot Te}$	$119.2 = 119.$
Sb = $\sqrt{In \cdot I}$	$120.09 = 120.00$
Te = $\sqrt{In \cdot Ba}$	$125 = 125.$
In = $\sqrt{Ag \cdot Sn}$	$113.4 = 113.7$
Yt = $\sqrt{Rb \cdot Cb}$	$89.6 = 89.1$
Ru = $\sqrt{Mo \cdot Ag}$	$101.7 = 101.6$
Rh = $\sqrt{Zr \cdot Pd}$	$103.2 = 103.$
Ag = $\sqrt{Rh \cdot In}$	$108.2 = 107.92$
Cd = $\sqrt{Pd \cdot Sn}$	$112.6 = 112.$
Cb = $\sqrt{Sr \cdot Ru}$	$94.3 = 94.$
Bi = $\sqrt{x \cdot Th}$	$x = 208.98$
Ca = $\sqrt{P \cdot Va}$	$39.92 = 40.$

By assuming that every element is a mean proportional between an element preceding it and one following it, at say two elements before and three after, or three before and two after, or one before and two after, or six before and seven after, which order of succession we may trace by comparing the above given radicals with the table of atomic weights in numerical succession, we may calculate atomic weights of unknown elements.

$$x = \sqrt{As \cdot Sr} = 81.05.$$

This is the atomic weight of the unknown element lying between Br and Rb.

$$x = \sqrt{\mathrm{Mg} \cdot \mathrm{Fl}} = 21.5.$$

This is the calculated atomic weight of the element lying between Fl and Na, probably argon.

$$x = \sqrt{\mathrm{Br} \cdot \mathrm{Yt}} = 84.4.$$

Second unknown lying between Br and Rb.

$$x = \sqrt{\mathrm{Ca} \cdot \mathrm{V}} = 45.4.$$

This is the element lying between Sc and Ti.

$$x = \sqrt{\mathrm{K} \cdot \mathrm{Ti}} = 43.32.$$

Unknown element lying between Ca and Sc

$$x = \sqrt{\mathrm{Cb} \cdot \mathrm{Rh}} = 98.4.$$

Unknown element following Mo.

The ratios and equations are all verified by the figures, and while not always exact, are sufficiently near the truth to show important facts.

THE OPTICAL ROTATORY POWER OF CANE SUGAR WHEN DISSOLVED IN PYRIDINE

BY GUY MAURICE WILCOX

Since Biot first measured the specific rotation of cane sugar in 1835, many observers have repeated his experiments, and the effects of concentration and temperature, upon the specific rotation have been carefully determined, the former by Tollens,[1] Schmitz, and others; the latter by Andrews, Schönrock, and recently by Pellat.[2] Naturally, water was the solvent first used; and no others seem to have been employed, probably on account of the difficulty in finding other liquids in which sugar is soluble.

Tollens[3] gives 68.63 as the specific rotation of 10 parts of sugar dissolved in a mixture of 67 parts methyl alcohol and 23 parts water. He also found the specific rotations in ethyl alcohol, and in acetone, mixed with water in the same proportions to be 66.83 and 67.40 respectively. With the exception of these results, there are apparently no data published concerning the optical rotatory power of sugar in solvents other than water.

The effect of various solvents upon the rotation of other optically active substances has been investigated by Freundler,[4] Landolt, and Pribram; also, recently, by Patterson,[5] and by Purdie and Barbour.[6] Various theories have been advanced to explain the variations of the specific rotation with concentration, temperature, and nature of the solvent used. Among these may

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[1] Complete references are given in Landolt, "Das optische Drehungsvermögen organischer Substanzen," Zweite Auflage, pp. 171–173, 530, 531.

[2] Ann. Chim. Phys. (7) 23, 289 (1901).

[3] Ber. chem. Ges. Berlin, 13, 2303 (1880).

[4] References are given in Landolt. l. c. pp. 182, 183.

[5] Jour. Chem. Soc. 79, 167, 477 (1901).

[6] Ibid., 79, 971 (1901).

be mentioned the assumption of polymerization of the active molecules in solution, the dissociation theory, chemical action between solvent and dissolved substance, and the recent theory supported by Patterson that variations in specific rotation are dependent upon changes of internal pressure in the solution. It is evident that a vast amount of work must still be done before sufficient data can be accumulated upon which to base satisfactory conclusions in regard to these theories. It is not the intention to discuss the theories here; but the results of the following investigation are submitted in the hope that they may prove useful in the ultimate solution of the apparently complicated problem of the effect of the properties of the solvent on the specific rotation of the dissolved substance.

About three years ago Prof. Kahlenberg found that cane sugar is moderately soluble in pyridine; and recently at his suggestion, I undertook to determine the specific rotatory power of such solutions at various concentrations and at different temperatures. This work seemed of particular interest, because of the great importance of cane sugar in every-day life, and also because of its scientific importance in connection with the development of the present theory of solutions. Again, the fact that pyridine is a solvent in which salts, when dissolved, conduct electricity, gave additional interest to the investigation.

A 6.25 percent solution of sugar in pyridine is nearly saturated, consequently the range of concentrations, the rotations of which can be measured, is small. On the other hand, the high boiling-point of pyridine and the low temperature at which it solidifies, make it possible to obtain results through a relatively great range of temperature. Measurements were made at temperatures varying from $-10°$ to $+105.°$ Below $-10°$ satisfactory constancy of temperature could not be obtained during the hot summer weather in which the work was carried on. It would, no doubt, be comparatively easy in winter to measure the rotation at $-50°$ or $-60°$.

The pyridine used was purchased from Kahlbaum. After drying it for several days with fused caustic potash, it was distilled and the portion passing over between 113.5° and 115°, under 737.8 mm pressure, was used in determining the specific rotation. The density of this fraction was 0.9735 at 25°. The density of the distillate above 115° decreased quite rapidly. The purest loaf sugar obtainable in the market was used in the experiments. It was first pulverized in a mortar and then kept for about half an hour at a temperature of 90° to 100° to expel moisture. Three solutions of 8 g of this sugar in 120 g of water gave 66.8, 66.6, and 66.5 respectively as the values for $[\alpha]_D$ at 25°.

To prepare a solution of 8 g of sugar in 120 g of pyridine, it was necessary to heat the pyridine to the boiling-point in a paraffin bath in order to dissolve all the sugar. Although this made a nearly saturated solution, no sugar crystallized out on cooling, even to temperatures below zero. Four such solutions in which the pyridine was distilled at different times, but under approximately the same conditions, gave 83.9, 83.7, 83.8, and 83.6 respectively, as the specific rotation at 25°. The average of these results is 83.75, a value more than 25 percent greater than that obtained for sugar in aqueous solutions.

To find out whether sugar combines chemically with pyridine to form a crystallizable compound, 40.79 g of a 6.74 percent solution was placed under a bell-jar over concentrated sulphuric acid and left until most of the pyridine had been taken up by the acid. While still slightly moist with pyridine the residue weighed 2.7922 g. The calculated amount of sugar in the solution was 2.7492. Apparently no compound is formed. The sugar did not crystallize out from this solution as the pyridine evaporated, but a thick syrup was formed of about one-sixth the original volume. A fine particle of sugar introduced into this syrup caused some small crystals to form, but most of the sugar was deposited as a hard and apparently amorphous mass, which dissolved rather slowly in water. A second attempt to obtain a supersaturated solution in order to measure its rotation failed, crystals being formed on the dish at the surface of the solution.

The polariscope[1] used was of the Landolt-Lippich type with triple field, made by Schmidt and Haensch. The circular scale was divided into quarter degrees and the verniers permitted readings to be made to hundredths of a degree. The tube containing the solution was made of brass and was 1 dcm long. It was mounted in a brass box covered with asbestos, as described by Landolt.[2] To prevent the deposit of moisture at low temperatures on the glass plates closing the ends of the tube, cylindrical glass caps containing calcium chloride below the line of sight were fitted by ground glass joints over the brass screw caps at the ends of the tube. A little vaseline made the joints moisture proof. Sodium light was obtained by suspending common salt in a platinum basket over a Bunsen burner.

All densities were determined with an Ostwald-Sprengel pycnometer of 10.607 cc capacity. Temperatures were measured with a thermometer graduated to fifths of a degree.

The specific rotation was calculated according to the usual formula, $[\alpha]^t_D = \frac{\alpha^t_D \times 100}{l \times p \times d}$, in which $[\alpha]^t_D$ represents the specific rotation for sodium light at the temperature t; α^t_D, the rotation read on the scale of the polariscope; l, the length of the tube in decimeters; p, the number of grams of sugar in 100 g of solution; and d, the density of the solution.

To determine the effect of concentration upon the specific rotation, four solutions of sugar in pyridine, containing, 1, 2, 4, and 6.25 percent of sugar respectively, were used. The 6.25 percent solution was prepared, as already described, by dissolving 8 g of sugar in 120 g of pyridine. Four g of this solution containing 0.25 g of sugar were then diluted with pyridine until the solution weighed 25 g and, hence, contained 1 percent of sugar. Eight g and 16 g of the 6.25 percent solution were then diluted in the same manner to 25 g to make the 2 percent and 4 percent solutions. The rotation was measured at 25° as soon as the solutions were prepared, and again after two days as a test for birotation. After standing for this length of

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[1] This instrument is fully described by Landolt. l. c. p. 321.

[2] l. c. p. 322.

time, none of the solutions gave results which varied more than 0.01°. Each measurement represents the average of five settings of the polariscope.

The following results were obtained :

Percent of sugar	Density of solution	$\alpha_D^{25°}$	$[\alpha]_D^{25°}$
1	0.9805	0.62°	86.7
2	0.9829	1.69	85.9
4	0.9912	3.36	84.7
6.25	1.0010	5.23	83.6

The curve obtained by representing percentages of sugar as abscissas and specific rotations as ordinates (Fig. 1) shows the decrease in specific rotation to be almost proportional to the concentration. The slope of the curve is much greater than that of the curve obtained from Tollens'[1] results for sugar in aqueous solutions of corresponding range in concentration, and it is in the opposite direction.

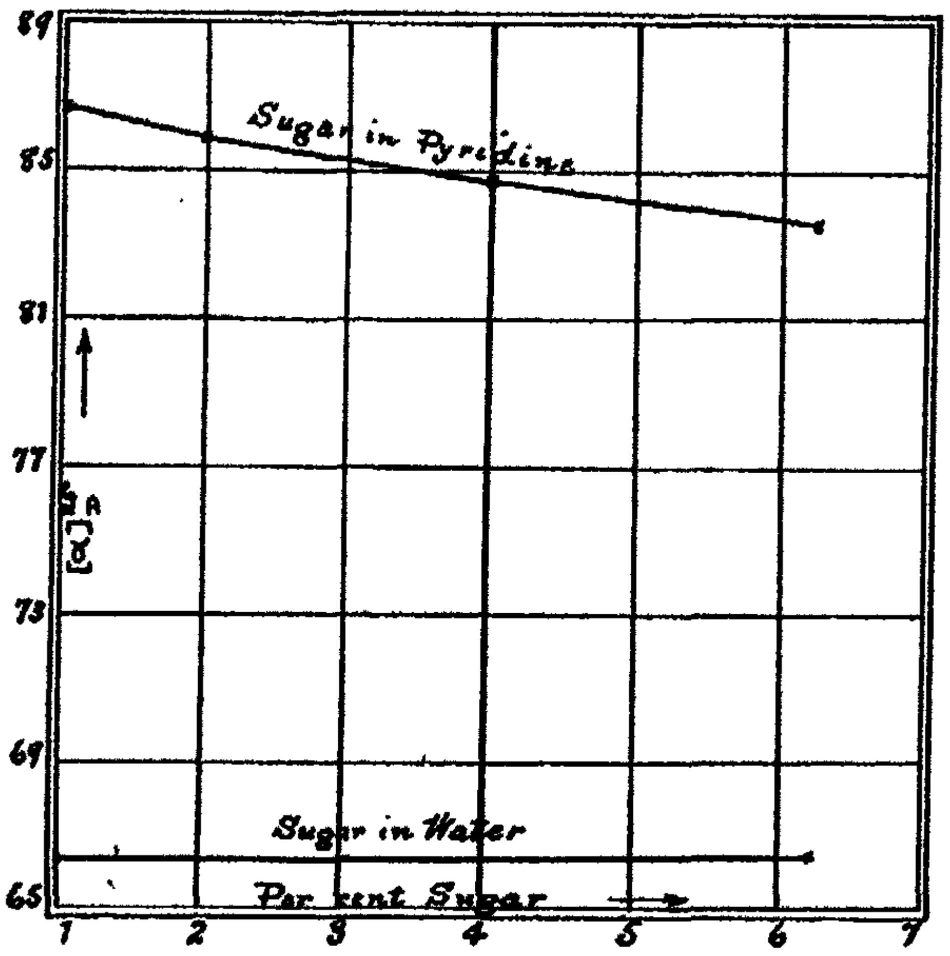

Fig. 1

To calculate the specific rotation of sugar in the pure con-

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[1] Landolt. l. c. p. 173.

dition by the usual method from these results would be useless, since the solubility is too small to give a sufficient range in concentration. It was intended to extend the curve by using supersaturated solutions, but the attempt failed.

Water mixed with the pyridine has a marked effect upon the specific rotation of the dissolved sugar. Two solutions were prepared, one of 8 g of sugar in 120 g of pyridine, the other of 8 g of sugar in 120 g of water. These were mixed in varying proportions, and the rotations of the resulting solutions were measured at 25°. The following table gives the results obtained, and they are also represented graphically in Fig. 2.

Percent of pyridine solution	Percent of water solution	Density	$\alpha_D^{25°}$	$[\alpha]_D^{25°}$
100	0	1.0005	5.24°	83.8
90	10	1.0120	4.93	77.9
80	20	1.0206	4.67	73.2
60	40	1.0263	4.44	69.4
40	60	1.0269	4.31	67.2
20	80	1.0255	4.23	66.0
0	100	1.0224	4.26	66.6

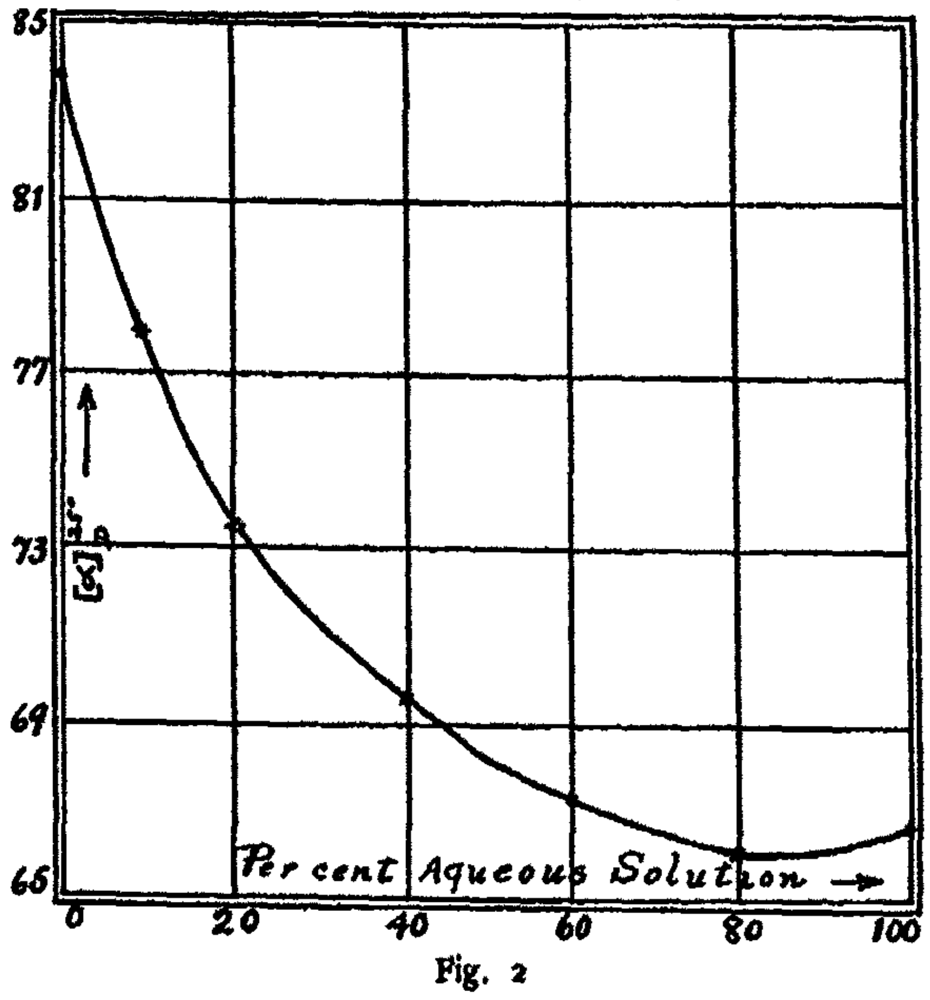

Fig. 2

The mixture containing 10 percent of the pyridine solution shows a slightly lower rotation than a pure aqueous solution; while 10 percent of the aqueous solution lowers the rotation in pyridine more than 7 percent.

The curve obtained by using the densities of these mixtures as ordinates and the proportion of aqueous solution in the mixture as abscissas, is interesting because it shows a maximum density for a mixture containing about 50 percent of each solution. Pyridine forms a compound with water,[1] the formula of which is $C_5H_5N + 3H_2O$, and, apparently, the form of the curve is due, in part at least, to the presence of this hydrate.

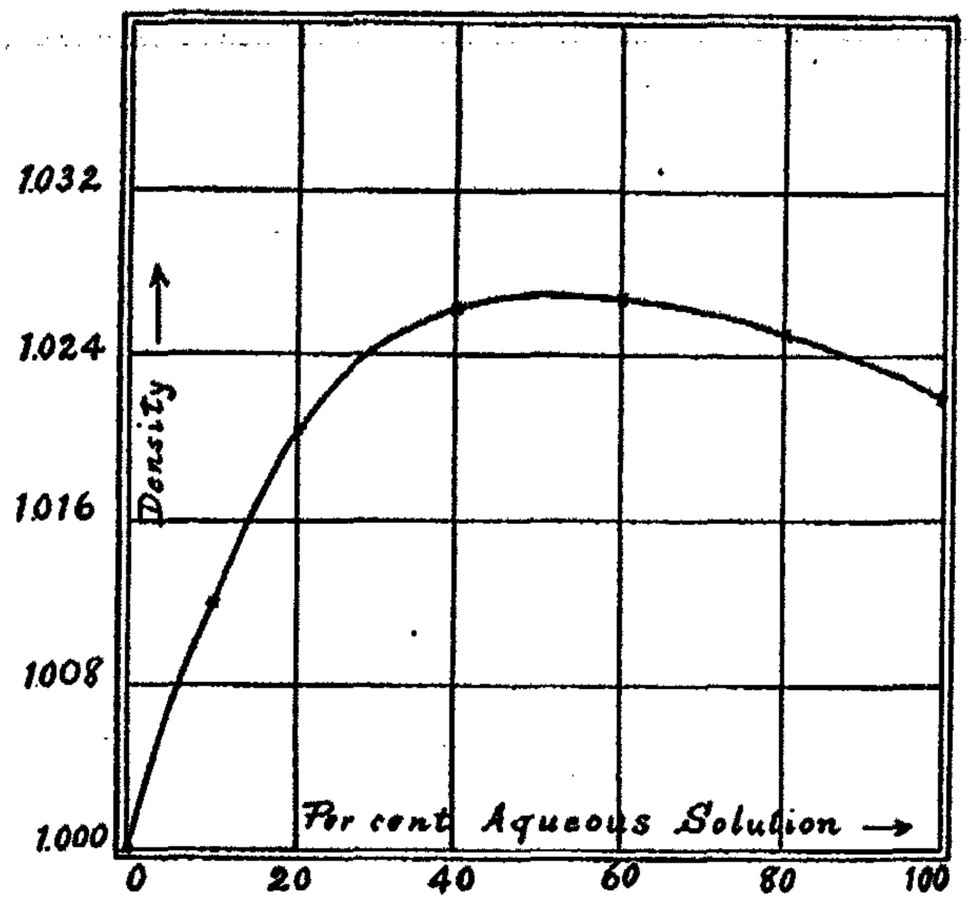

Fig. 3

The effect of temperature was next investigated. For temperatures above 25° the rectangular brass vessel in which the tube of the polariscope was mounted was filled with lard oil after filling the tube with a 6.25 percent solution of sugar in pyridine. The whole was then placed on the open bed of the polariscope and heated with a Bunsen burner to 105°. During the heating the parts of the polariscope were protected as much as possible

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[1] Calm Buchka, "Chemie des Pyridins," p. 50.

with screens of asbestos. The temperature was kept constant within a few tenths of a degree for from 20 to 30 minutes by regulating the gas supply and stirring the oil bath. When all distortion of the field, on account of convection currents in the solution and on account of unequal heating of the glass plates closing the ends of the tube, had disappeared, five readings of the polariscope were taken. The average of these readings gave the rotation, when the zero reading, previously determined, was subtracted. The different readings usually did not vary more than two or three hundredths of a degree. The chief sources of error were the difficulty in keeping a constant temperature during the readings, and the absorption of light by the greenish colored compound formed by the slight action of the pyridine on the brass tube, particularly at high temperatures. As far as could be determined, this action did not alter the rotation appreciably, but the absorption of light was at times a serious annoyance, as it increased the difficulty in obtaining accurate readings. A glass tube would have been preferable to a brass one, but it would have been somewhat difficult work to properly mount such a tube in the apparatus for high temperatures.

After the readings at 105° had been taken, the tube with its surrounding jacket, was removed from the bed of the polariscope and allowed to cool to the temperature of the next observation, when it was replaced and readings were again taken in the same manner as before.

The zero of the polariscope was tested between each set of readings, and was found to remain practically unchanged. To determine the zero, readings were taken with the tube filled with distilled water and also with the tube removed. These agreed within the limit of error in reading the polariscope. To see whether heating the glass plates closing the ends of the tube introduced an error in the rotation, the tube was filled with distilled water and the temperature raised to 90°. At first the lines of the field were distorted and blurred, but, after 15 or 20 minutes, the field became clear again and the average of five readings gave the same result as at 25°.

For temperatures below 25°, ice and water, melting ice, or ice and salt were used, as required, in the box surrounding the tube, and the glass caps containing calcium chloride, previously mentioned, were put in place over the ends of the tube to prevent moisture from collecting and interfering with the transmission of light.

At the end of the high temperature series, the rotation at 25° was found to have increased by about one-hundredth of a degree; possibly this was due to evaporation of the pyridine through the small vertical tube into which the solution expanded. Reheating to 105° gave the same result as at first. The results are tabulated on p. 596. They are also given in graphic form in Fig. 4. A repetition of the series with a new solution gave the same values of the rotation within one or two hundredths of a degree.

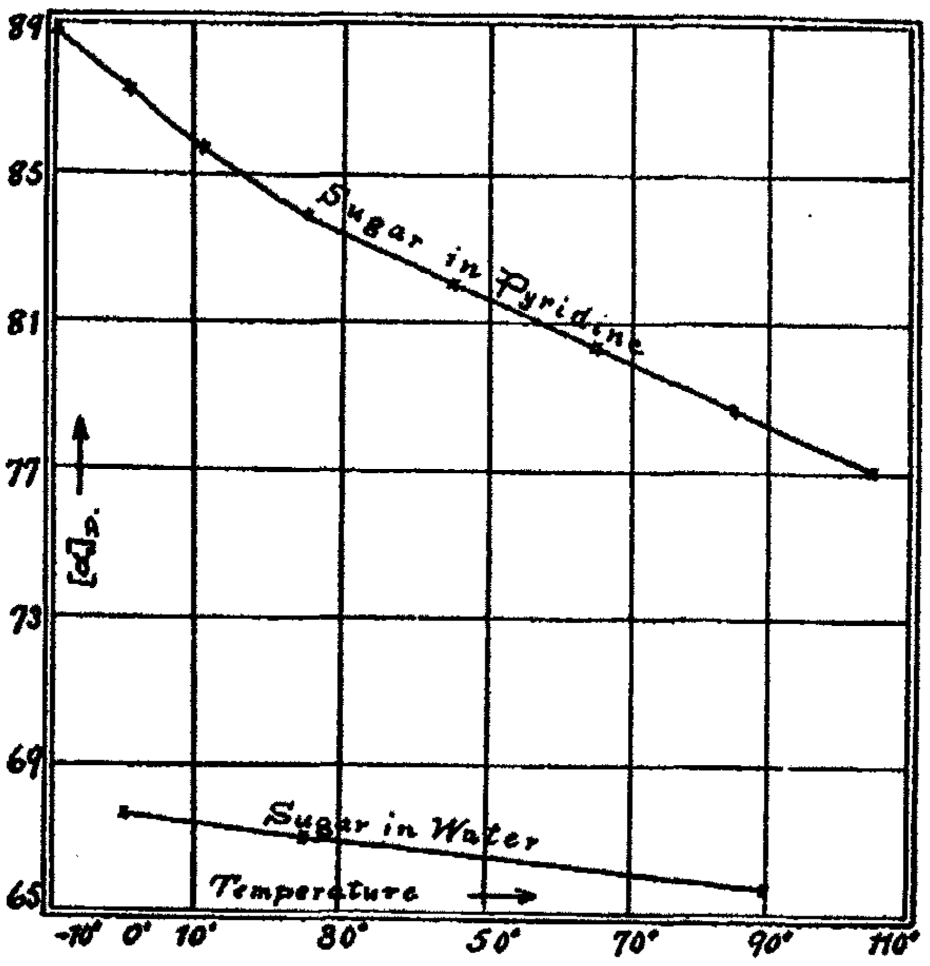

Fig. 4

Corrections have been applied to these results for the change in length of the brass tube with change of temperature. Assuming that the tube was 1 dcm long at 25°, then, since the coefficient of linear expansion of brass is 0.000019, its length will be 1.0015 dcm at 105°, and 0.9993 dcm at – 10°. The corrections are small and do not alter the results as given except the last two, which are decreased by one unit in the first decimal place.

6.25 Percent Solution of Sugar in Pyridine

Temperature	Density	α^t_D	$[\alpha]^t_D$
–10°	1.034	5.73°	88.7
0	1.0248	5.59	87.3
+10	1.0150	5.43	85.6
25	1.0005	5.24	83.8
45	0.9811	5.03	82.0
65	0.9619	4.83	80.3
85	0.9420	4.63	78.5
105	0.9220	4.40	77.0

The temperature curve (Fig. 4) indicates that the rate of change in specific rotation is greatest below 25°. This was the most difficult region in which to maintain constant temperatures in warm weather, and the observations, except the one at 0°, are possibly a little less accurate than those above 25°, but the increased steepness of the curve was verified by a number of concordant measurements.

The comparison curve of sugar in water was drawn from the following results of a series of three measurements of a 6.25 percent solution:

Temperature	Density	α^t_D	$[\alpha]^t_D$
0°	1.0254	4.33°	67.60
25	1.0222	4.28	66.99
90	0.9921	4.07	65.59

The specific rotation of this solution at 25° is unusually high. Considering the curve a straight line, which it probably is not, the temperature coefficient would be about 0.0223, a value considerably greater than 0.0144, which was obtained by Schönrock[1] for temperatures from 12° to 25°. The work done on the

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[1] Landolt. l. c. p. 531.

temperature coefficient of sugar in water seems to have been confined to a very limited range of temperatures. Pellat[1] came to the conclusion that the rotation changed, if the solution was heated much above 30°. A more extended research in this direction would be of interest.

From a comparison of the two curves in Fig. 4, it is evident that the specific rotation of sugar in pyridine decreases much more rapidly as the temperature increases. The same statement may be made in regard to the density of the two solutions. The density of a 6.25 percent aqueous solution at 0° is 1.0254; at 90° it is 0.9921, a difference of 0.0333. The density of a 6.25 percent pyridine solution is 1.0248 at 0°, and 0.9420 at 85°, a difference of 0.0828. This comparison suggests that the property of pyridine, which causes it to expand more rapidly than water with increase of temperature, also influences the specific rotation of the sugar dissolved in it.

To test further the behavior of sugar in this solvent, its molecular weight was determined by the boiling-point method. A modified form of Beckmann's apparatus was used. Instead of a vapor jacket around the glass tube containing the solvent, an asbestos jacket was used and the whole was placed on a sand-bath. A Beckmann thermometer, graduated to hundredths of a degree was fitted into the tube with a cork. Garnets, to the depth of about 2 cm, and a few pieces of platinum were placed in the bottom of the tube. A condenser was attached to the tube by a side neck and the sugar was introduced through the condenser in the usual way. The pyridine used for this determination distilled over between 114.5° and 115° under 737 mm pressure.

As has been pointed out by Innes,[2] it is necessary to boil the pyridine several hours in order to obtain a constant boiling-point. In the first series the boiling was continued 10 hours, in the second series 7 hours. The boiling-point constant used in calculating the results was 29.5. This is about the value ob-

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[1] l. c.

[2] Jour. Chem. Soc. 79, 261 (1901).

tained by the Trouton-Schiff rule, 0.00096 × 388 × 79 = 29.43.[1] Werner's[2] empirical value, 30.07, gives molecular weights about 5 or 6 units higher.

1st Series (9.73 g solvent used)

Sugar	Sugar in 100 g. pyridine	Barometer	Temp. change	Mol. wt.
0.1742 g	1.790 g	737.3	0.163°	324
0.3138	3.225	"	0.275	346
0.5375	5.525	"	0.450	362

2nd Series (14.84 g solvent used)

0.1417 g	0.955 g	739.9	0.110°	256.[3]
0.3612	2.434	"	0.235	305.5
0.5582	3.761	"	0.355	312.6
0.7640	5.148	"	0.465	326.6

Mr. Alva Eighmy, in an unpublished thesis, a copy of which is in the library of the University of Wisconsin, gives a series of determinations of the molecular weight of sugar in pyridine. Mr. Eighmy used 16.45 g of pyridine and continued the preliminary boiling about four hours. He computed the molecular weights, using 30.07 as the constant for pyridine, and obtained the following results:

Sugar	Sugar in 100 g. pyridine	Temp. change	Mol. wt.
0.3387 g	2.059 g	0.215°	287.8
0.4927	2.995	0.305	295.0
0.6818	4.145	0.410	303.7
0.8172	4.986	0.475	324.8

In general, the molecular weights are low, and they would still be below the normal, if calculated by Werner's boiling-point constant for pyridine. The only exception is in the first series, where the quantity of solvent was small and the experimental

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[1] For a complete discussion of the boiling-point constant, see Innes, l. c., and Kahlenberg, Jour. Phys. Chem. 5, 215 (1901).

[2] Zeit. anorg. Chem. 15, 1 (1897).

[3] Probably an experimental error.

errors relatively large. As sugar is a non-electrolyte when dissolved in pyridine, it should give a normal molecular weight according to the dissociation theory. All the results show a marked increase in molecular weight as the amount of sugar in solution is increased.

In conclusion, I wish to express my thanks to Prof. Kahlenberg, at whose suggestion this work was begun, for the interest he has taken in its progress and for the apparatus and material furnished in his laboratory to carry on the investigation.

Further study of sugar solutions in pyridine is contemplated. A determination of the refractive power and the dielectric constant will soon be made.

Laboratory of Physical Chemistry,
University of Wisconsin,
Madison, Wis.,
Sept. 14, 1901.

NEW BOOKS

Rapports présentés au Congrés International de Physique *réuni à Paris en 1900 sous les Auspices de la Société de Physique. Rassemblés et publiés par Ch.-Éd. Guillaume et L. Poincaré. Tome I: Questions générales; Métrologie; Physique mécanique; Physique Moléculaire. xv + 698 pp. Tome II: Optique; Électricité; Magnétisme. 570 pp. Tome III; Electro-optique et Ionisation; Applications; Physique cosmique; Physique biologique. 619 pp. 16 × 25 cm. Paris: Gauthier-Villars, 1900. Price: paper, 18 francs per volume, or 50 francs for the three volumes.*—When the French Physical Society arranged for the International Congress of Physics held in Paris on the occasion of the Exposition of 1900, it was planned to issue a collection of reports to the Congress, in which a large number of distinguished investigators should present accounts of the present state and immediate outlook of the various branches of research in which they are working. The result is these three magnificent volumes, in which are summarized the results attained up to the close of the nineteenth century in most of those branches of physics that are now in a state of active development. The manner in which the editors, Messrs. Ch.-Éd. Guillaume and L. Poincaré, have arranged the reports is sufficiently indicated by the sub-titles cited at the head of this notice. All the papers are in French.

Among the papers to which especial attention might be directed here are the following: H. Poincaré, Relations between experimental physics and mathematical physics; J. S. Ames, The mechanical equivalent of heat; E. H. Griffiths, The specific heat of water; W. Roberts-Austen and A. Stansfield, The constitution of metallic alloys; W. Spring, Properties of solids under pressure; B. Weinberg, Fusion and crystallization according to the researches of G. Tammann; J. H. van 't Hoff, Crystallization at constant temperature; J. Perrin, Osmosis, and semipermeable walls; G. Lippmann, The kinetic theory of gases and the principle of Carnot; E. H. Amagat, Experimental statics of fluids [one-component fluids]; J. D. van der Waals, Statics of fluid mixtures; É. Mathias, The methods of determination of critical constants, and the results to which they have led; S. Arrhenius, The electrolytic dissociation of solutions; L. Poincaré, Remarks on the theories of the voltaic cell; A. Leduc, The electrochemical equivalents of silver, of copper, and of water; J. H. van 't Hoff, The transformations of carburetted iron; H. Becquerel, On the radiation of uranium and on various physical properties of the radiations from radioactive bodies; P. Curie and Mme. Curie, The new radioactive substances and the rays that they emit; J. J. Thomson, Indications relative to the constitution of matter furnished by the recent researches on the passage of electricity through gases.

The interest and importance of this collection of reports is not easily to be overestimated. Everyone interested in the current development of exact science will wish to own the volumes; and they assuredly should be acquired by every library that undertakes to supply scientific information to its readers.

J. E. Trevor

Die partiellen Differential-Gleichungen der mathematischen Physik. *Nach Riemann's Vorlesungen. Fourth, revised, edition. By Heinrich Weber. Part I. 14 × 23 cm; pp. xvii + 506. Braunschweig: Friedrich Vieweg und Sohn, 1900. Price: paper, 10 marks.* — When the forms of the fundamental integral laws of a branch of exact science have been discovered, the entire integral theory of the subject can be developed by the integration of the corresponding differential equations. Physical chemistry, from the nature of its subject matter, is mainly thermodynamics, and thermodynamic theory is as yet differential theory, — experimentation has not yet established the form of any of the thermodynamic 'fundamental functions.' So the theory of differential equations has as yet found but little application in physical chemistry. The chief aim of physicochemical research at the present time seems to be to find the forms of these fundamental functions for systems of different numbers of independently variable components. As these are found, the wholesale integration of the differential equations of the theory will immediately follow. It is thus clear that the theory of differential equations is destined soon to become of very great importance in physical chemistry; and this fact leads us to welcome the appearance of Weber's important work on the physical applications of the theory.

Weber treats the subject as an instrument of physical research, and not as an abstract branch of mathematics. He aims to assemble the mathematical means and methods of the exact sciences, and to do this in a way that presupposes only an acquaintance with the elements of the calculus. His book is a development from the various editions of Riemann's well-known *Vorlesungen*; but it has been wholly reconstructed, only the spirit of the original work being retained.

A good part of the present first volume is occupied by a general introduction to the mathematical means that are employed, an introduction to definite integrals, infinite series, multiple integrals, functions of complex arguments, differential equations, and Bessel functions. A hundred pages are then devoted to the necessary geometrical and mechanical principles. Much of this deals with vector phenomena, and so does not bear upon the problems of physical chemistry. The remainder of the volume is concerned with the applications in electricity and magnetism. Some very interesting physical chemistry appears here in the sections devoted to Electrolytic Conduction and to Electrolytic Displacements respectively. Here, as elsewhere, Weber exhibits a thorough comprehension of the physical problems whose theoretical treatment he discusses. Referring to these matters in his preface, he comments on the notable influence which the progress of physical chemistry is exerting on the development of mathematical physics in general.

In a forthcoming second volume, the applications of the theory of differential equations in the theories of heat conduction, of wave motion, of elasticity, and of hydrodynamics are to be presented. A special treatment of the equations of thermodynamics, is, of course, as yet impossible. But in the meantime the physical chemist can prepare himself for the next great formal advance of his subject; and he cannot do this better than with the aid of Weber's uncommonly good book. *J. E. Trevor*

Lehrbuch der mathematischen Chemie. *By J. J. van Laar. 14 × 22 cm; pp. xiii + 224. Leipzig: Johann Ambrosius Barth, 1901. Price: paper, 7; bound, 8 marks.* — Van Laar is quite right in insisting, in his preface, that the relation of mathematical chemistry to experimental chemistry is wholly comparable with that between mathematical physics and experimental physics; for mathematical chemistry is a topic of mathematical physics, just as experimental chemistry is a branch of experimental physics — in the broad sense of the term. In both cases the mathematical theory is a coordination of the results of experimentation; the object of experimentation is to establish the form of the theory, and the object of theory is to represent in economical form the results of possible experimentation. Among experimentalists there is as yet but little demand for formal expositions of the thermodynamic theory of chemical equilibrium. But this is not surprising, the theory is yet differential theory and the experimentalist wants integral relations. It remains for him to find them, however; he must first furnish the data that will suffice for the determination of the form of some one of the thermodynamic fundamental functions; when this is done the system of integral relations will at once follow, and the theoretical subject will become for the first time comparable with the present elegant formulation of, say, the phenomena of mechanics. Van Laar claims that his book is the first systematic treatise on mathematical chemistry. In a way this may be so, certainly it differs markedly in character from its predecessors; but the claim is hardly likely to pass unchallenged, in view of the existence of Helm's conscientious *Mathematische Chemie* and Duhem's notable four volumes.

Van Laar arranges his material in two parts: a relatively brief thermodynamic introduction, and a series of applications. The introduction is essentially a disquisition upon Planck's thermodynamic potential function, the negative ratio of the thermodynamic potential to the absolute temperature; so the book is hardly an *introduction* to mathematical chemistry, one requires a general knowledge of thermodynamics in order to be able to read it. This circumstance is likely to hinder the success of the book. The greater part of the text is devoted to the "applications"; they are arranged with reference to the number and character of the phases present in the systems under examination. The states successively treated are: vapor, liquid, liquid-liquid, solid, solid-solid, liquid-vapor, solid-vapor, liquid-solid, liquid-solid-vapor. These are the combinations of vapor, liquid, solid, taken successively one, two, and three at a time, and in an order dictated by convenience. The concluding chapter is on the phase rule. This way of doing the thing results in separate treatment of different states of a given system, and in making secondary the all-important classification according to the number of independent components. It would be far better to treat one-component systems in order in their one-, two-, and three-phase states; then to pass to two-component systems, treated in a like order; and to finish with the general case of *n*-components. The phase rule could then be developed, with its increasing complexities, under each head, instead of leaving this most fundamental matter to the last.

Very properly all consideration of kinetic theory is excluded from the work. Another proper feature is the exclusion of all reaction velocity equations, about which nothing is certainly known, except in a negative way. It is not so happy that electrochemical matters have been omitted; but there were personal reasons for this, and it is promised that the gap shall be filled in a possible future edition. Roozeboom has written a few words of praise to introduce the book. He makes the obvious point that only thermodynamic theory affords a prospect of important results in the quantitative study of chemical equilibria.

There is one thing in the text that calls for particular mention. At the outset van Laar assumes (we use an obvious notation)

$$d'Q = \theta d\eta - \Delta,$$

where for irreversible changes Δ is positive; and he then gets

$$dE = -pdv + \theta d\eta - \Delta.$$

Disregarding the risky character of this proceeding, we note that Δ is next replaced by $\Sigma \mu dn$, the sum of the molecular chemical work-equivalent terms. This formulation is surprising, and deserves mention; van Laar seems to regard it as essentially identical with Gibbs's procedure, which is far from being the case. He then writes the equations for the differentials of a series of fundamental functions, and says that these are Gibbs's fundamental equations. This also is not true.

Detailed comment upon the way in which the author has elaborated his programme is hardly necessary: the book works up, in van Laar's well known style, a series of applications of the theory of the thermodynamic potential, using Planck's form of this function. But little can be said for the mechanical execution of the volume; the text is full of italics and underscoring, which make the reader feel that he is being continually shouted at; and the typography is anything but the handsome output that we are accustomed to associate with the name of the publisher. *J. E. Trevor*

Technische Thermodynamik. *By Gustav Zeuner. Zweite Auflage. Zugleich vierte vollständig neu bearbeitete Auflage der "Grundzüge der mechanischen Wärmetheorie." Erster Band: Fundamentalsätze der Thermodynamik; Lehre von den Gasen. 16 × 23 cm; pp. vi + 436. Leipzig: Arthur Felix, 1900. Price: paper, 13 marks.* — Like the widely known first edition of Zeuner's Technical Thermodynamics (1887), this revised edition is arranged in two volumes, the first presenting the general theory of thermodynamics and an account of the thermodynamic behavior of gases, while the second is devoted to the thermodynamics of vapors. The work is designed for the instruction of students of engineering, and follows the arrangement of Zeuner's lectures at the Technical High School at Dresden. It contains many carefully worked out special applications. The present treatise has grown from Zeuner's little *Grundzüge der mechanischen Wärmetheorie*, which appeared in 1859, when thermodynamics was yet in its infancy. Thanks to numerous thorough revisions, the work has maintained the interest and the influence that attached to its first appearance.

In its present form, the book incorporates the results that have been attained during the past dozen years in the extension of the technical applications of thermodynamics. The new matter relates chiefly to the outflow of gases through orifices, and much of it is the outcome of Zeuner's own experimental work. The second volume, which has not yet reached us, is to show extensive changes.

Zeuner begins his exposition with an introductory comment on the development of the idea of the equivalence of heat and work; and he then takes up the first and second laws of thermodynamics, Carnot's function, entropy, and irreversible processes. The remainder of the volume has to do with gases, giving first the general thermodynamics of gases and mixtures of gases, and a "physical part" on reversible and irreversible changes of state and on the flow of currents of gas, and second a "technical part" on the theory of air motors and gas engines. Peculiarly interesting features of the treatment are Zeuner's introduction of the absolute temperature as the integrating divisor of the heat differential, and his elucidation of changes of entropy as the "weight" of additions of heat. Although intended for engineering students, the book has much interest for the student of general thermodynamics. *J. E. Trevor*

Thermodynamik und Kinetik der Körper. *By B. Weinstein. Erster Band. Allgemeine Thermodynamik und Kinetik, und Theorie der idealen und wirklichen Gase und Dämpfe. 14 × 22 cm; xviii + 484 pp. Braunschweig: Friedrich Viewig und Sohn, 1901. Price: paper, 12 marks.* — Notwithstanding the interest that has attended the phenomenal development of thermodynamics during the past twenty-five years, as a result of the work of Gibbs and Helmholtz and their successors, we have as yet no good conprehensive treatise on the modern theory of thermodynamics. Duhem's elaborate work, good as it is, does not pretend to cover the entire ground. In the present work we have an attempt to do so. Only one volume is as yet out (how many are to follow is not announced); it is devoted to general thermodynamic and kinetic theory and the special thermodynamics and kinetics of gases and vapors. The successive topics treated are: Thermal phenomena in general, The two laws of thermodynamics, Characteristic equations, The analytical developments of thermodynamics, Boyle-Gay-Lussac gases, Actual gases. Experimental methods are not considered.

Pure thermodynamics and the consequences of the kinetic hypothesis are pretty thoroughly mixed up together throughout the whole treatment. The reason for this is apparently the author's opinion that the forms of the thermodynamic fundamental functions, which must be known before the thermodynamic theory, which is differential theory, can be converted into the corresponding integral theory, can be provided only by the kinetic theory. Were this belief well founded it would hardly justify the procedure; and it begins to look very much as though it were not well founded, as though the forms of these functions are more likely to be discovered from direct examination of the experimental results than through mediation of the complicated and hypothetical kinetic theory. The detailed results that are presented have been carefully worked up; in fact the strength of the book lies more in a careful elaboration of details than in a grasp of fundamental principles, or even in a logical arrangement of the matter. On the whole, however, the author has done with some thoroughness what he set out to do, and the result will unquestionably be greeted with pleasure by those — and they are many — who do not care to distinguish between inductively developed theory and speculation. The mechanical execution of the book is good, and an exhaustive index is promised.

J. E. Trevor

Essai critique sur l'Hypothèse des Atomes dans la Science contemporaine. *By Arthur Hannequin. Second Edition. 457 pp. Paris: F. Alcan, 1899. Price: paper, 7.50 francs.* — Prof. Hannequin's aim and method in writing this book are sufficiently indicated by quoting the headings of the three sections into which the introduction is divided: I. The hypothesis of atoms is a necessary hypothesis, derived from the very nature of our knowledge. II. The hypothesis of atoms includes contradictions. III. Conclusion, — The atom is a concept and not a thing in itself. The reconciliation of the contradictions which it appears to include is to be looked for in metaphysics.

The treatise is laid out on the lines of the introduction, widened to include a discussion of many phases of the subject, and from several different standpoints.

"It is proposed in the first book, by starting from the first principles of mathematical knowledge and by studying the constitution and the main progress of the physical and chemical sciences, to establish at once the necessity of atomism and its contradictions; in the second book the reconciliation of these last will be sought in metaphysics." It is therefore to the first book that the experimental scientist turns with the most interest, for if the theory of atoms is in itself contradictory, such reconciliation as may be supplied by metaphysics is likely to afford him small consolation.

"The task of science is to reduce everything in the universe to the ultimate conditions of movement and position; geometry and mechanics thus become the sovereign sciences; the one because it is the science of position and figures in space; the other because it is the science of changes, with time, in situation and position. Extension and duration are then for science, the matter found at the end of all its reductions and all its physical research."

"Mechanics in a sense is only a geometry of movable extension."

"Geometry is thus the first of our creations; and, it may be added, in the hands of modern science it is the common storehouse whence are drawn the theorems of general and molecular mechanics, and hence all the mathematical laws of physical and natural phenomena." But the principle which limits, defines, and renders intelligible geometrical ideas, is the principle of number, without which we could know nothing of extension; and it is this principle applied to physics which leads to the atom.

"Physical atomism is therefore not imposed on science by reality, but by our method and the nature of knowledge; it would be a mistake to think that it necessarily implies the real discontinuity of matter; it implies merely that we make it so, — i. e. discontinuous, — that we may comprehend it. It has, in a word, its origin in the universal use of number which places its mark on all that it touches, so that if the use of number in geometry is anything else but a convenient process, if it is its essential and indispensable method, and if number is really the concept from which all our geometrical knowledge proceeds, then we need not look elsewhere for the principle of atomism, nor for the reason of its predominance in modern science."

In stating, as the author does, that "atomism", i. e. the theory of the discontinuity of matter, "is, as it were, the soul of modern science," and that it "presides at the birth of modern chemistry and is found at every step in its progress," he goes a good deal farther than many chemists will be willing to follow him, considering how many of the advances in modern chemistry are entirely independent of any idea as to the structure of matter.

The contradictions into which the theory of atomism leads are as follows: The first, that which is derived from the idea of infinitesimals always capable of reduction, "the flagrant contradiction of the divisible indivisible atom". The second, that which is based on the difficulties encountered when the transformations of energy are considered in the light of any one of the theories regarding the nature of atoms. The author shows that neither the theory of hard nuclei nor that of vortex rings in a frictionless medium will meet the difficulties of the case. To the lay mind in the matter of metaphysics neither of these objections affords proof that matter may not consist of small particles such as the chemist postulates them, even though their exact character is not yet defined.

There is however a good deal in the book which makes suggestive reading even for the layman, and it all has that good style which is the mark of French work in science and philosophy no less than in other fields. For the chemical material the author has drawn mainly from Berthelot and Wurtz and from Lothar Meyer's Modern Theories, thermochemistry receiving a liberal treatment as it always does at the hands of the countrymen of Berthelot.

It is not possible here to trace the development of the argument; enough has been done if some idea has been given of the author's aim and standpoint.

The later chapters, under such headings as "Being", "Appearance", etc., are devoted to working out the scheme of the book from a more purely metaphysical point of view, and in a way which does not lend itself to review; to clearing up the contradictions involved in the idea of atoms, on the theorem: "The atom is a concept, and not a thing in itself". *A. P. Saunders*

Die Determinanten. *Eine Darstellung ihrer Theorie und Anwendungen, mit Rücksicht auf die neueren Forschungen. By Ernesto Pascal. Authorized translation by Hermann Leitzmann. 14×21 cm; pp. xvi + 266. Leipzig: B. G. Teubner, 1900. Price: cloth, 10 marks.* — Our warrant for noticing the appearance of a treatise on the theory of determinants lies in the fact that these functions play an important part in the development of the Gibbsian theory of chemical equilibrium. The book before us is a translation of Pascal's well-known *I determinanti*, of 1896, and it appears as the third volume of Teubner's magnificent *Sammlung von Lehrbüchern auf dem Gebiete der mathematischen Wissenschaften, mit Einschluss ihrer Anwendungen.* It is divided into two parts: an introductory part of thirty-five pages, on what the beginner requires to know about the elementary properties of determinants, and about minors, expansion and multiplication of determinants, and reciprocal determinants; and an account of the results of special investigations on the expansion and differentiation of determinants, and on the various special types of these functions, including the Jacobians and Hessians that appear so constantly in the thermodynamic theory of chemical equilibrium. The text is essentially an analytical treatment of the theory, the geometrical applications being only casually touched upon.

The book is not a heavy treatise, like Gordan's *Invariantentheorie*, going exhaustively into details; it is rather an exposition in outline of the major features of the subject. And it is extremely well done: the topics are judiciously chosen, are well arranged, and are made clear in each case in but few words. The translation reads easily; and the mechanical execution leaves little to be desired. *J. E. Trevor*

Differential and Integral Calculus for Beginners. *Adapted to the use of Students of Physics and Mechanics. By Edwin Edser. 12 × 18 cm; pp. vi + 253. London: Thomas Nelson and Sons, 1901. Price: cloth, 2s. 6d.* — Students beginning the study of mathematical physics frequently wish to use a short introductory treatise on the calculus, in connection with their work. This is particularly true of students of chemistry who begin the study of physical chemistry. The present book has been written to supply the sort of simple introduction that is desired. Its subject-matter is so arranged that only the usual acquaintance with elementary algebra and geometry is presupposed. The author begins with a general account of functions of one variable, adding a synopsis of the trigonometric formulas to be used, with their proofs. He then gives a geometrical explanation of the significance of a derivative, deduces the rules for differentiation, outlines the geometry of complex quantities, and gives applications to maxima and minima problems and to the expansion of functions. On passing to the integral calculus, the idea of integration is explained as simply as possible, various applications to geometrical, mechanical, and physical problems are given, and double and triple integrations are described. The book closes with a short chapter on differential equations (in one variable), hyperbolic functions being here introduced in an elementary way. Everything that is presented is clearly stated and carefully illustrated; the book wil doubtless serve its purpose very well. Its most noticeable lack is the omission of all consideration of partial derivatives. The book is well printed, but in very small type. *J. E. Trevor*

Sur l'influence des corrections á la grandeur b dans l'équation d'état de M. van der Waals; *et sur les dates critiques d'un corps simple. By J. J. van Laar. Reprinted from the Archives Teyler. Haarlem: Les Hèritiers Loosjes, 1901.* — Supposing the quantity b of van der Waals's characteristic equation to be an arbitrary function of the volume, the author equates $\partial p/\partial v$ to zero, and writes the condition for this equation to have two equal roots. This gives an equation

$$f(v_c, b_c, b_c', b_c'') = 0, \qquad (1)$$

where the letters refer to the critical values and the accents to derivatives. On eliminating b_c, b_c', b_c'', between this equation and van der Waals's equation for $b = f(b_\infty, v)$, an equation

$$f(b_\infty/v) = 0 \qquad (2)$$

is found. Van der Waals's values for the coefficients in (1), however, give impossible results in (2); but the values given by Boltzmann lead to $v_c = 2b_\infty$, which is the result that is indicated by experiment. Boltzmann's coefficients, however, do not accord with the experimental value of the "critical coefficient" $p_c v_c / R\theta_c = 0.27$. On the other hand, the characteristic equation proposed by Dieterici in 1899 gives $v_c = 2b$, and $p_c v_c / R\theta_c = 0.27$, in agreement with both requirements.

The formula proposed by Onnes for $b(v)$ is shown to yield the necessary values for b for hydrogen and carbon dioxide with a remarkable accuracy, but it disagrees with the critical data as much as do the formulas of van der Waals and of Boltzmann. So the net result is that only the characteristic equation of Dieterici agrees with the critical data, and at the same time accords with the compression data of Amagat as well as does the equation of van der Waals.

In the remainder of the paper it is shown that the equation

$$p[v - f(p)] = R\theta$$

holds good for hydrogen for pressures greater than 1500 atmospheres; and a revised derivation, from a dynamical theorem of Boltzmann, is given of the characteristic equation of Reinganum (1899). Finally, expressions for a and b are obtained by comparison of the equation of Reinganum with that of van der Waals.

J. E. Trevor

A School Chemistry. *By John Waddell. 13 × 19 cm; pp. viii + 278. New York: The Macmillan Company, 1900. Price $0.90.* — The plan of this introductory textbook is well indicated by the following extracts from its preface. "To many young students it would be a matter of surprise that chemistry does not hang upon the atomic theory, that a number of the most brilliant and epoch-making discoveries were made without its assistance, that analyses were carried on and manufactures engaged in before the theory was enunciated. … The beginner is liable to consider that he has made great advance when he has learned to call water H_2O, though the probability is that he has no idea why the formula is given, and has very vague notions as to its real meaning and significance. The endeavor is made in this little book … to show how facts lead to theory, and theory aids in investigation and in the discovery of further facts. The subject is presented in what seems to me the correct perspective, theory being subordinated to fact. The order in which the various topics are taken up appears to me to be the most simple. Water is first discussed, as being one of the most common substances, and one with whose properties the pupil is already somewhat familiar. Thereafter follows the consideration of hydrogen and oxygen, the latter leading up to the study of air and its constituents. Throughout the book the arrangement is equally simple. … No mention of the atomic theory is introduced until the study of a large number of facts has afforded an intelligible basis for it."

The book is a small one, well adapted for use in schools or in a short college course. The space devoted to the metals is correspondingly short, only forty-five pages. Directions for over a hundred good illustrative experiments, to be performed by the student, are interpolated. The book is an excellent one for the purposes for which it was written.

J. E. Trevor

The Elementary Principles of Chemistry. *By A. V. E. Young. 12 × 19 cm; pp. xiv + 252. New York: D. Appleton and Company, 1901.* — This college textbook is distinguished by the unusual arrangement of its material. The first chapter treats very extensively of the definition and identification of substances by their properties, and distinguishes between elements, compounds, and mixtures, and between acids, bases, and salts. The second presents the laws of combination, and those of gas-volumetric proportions, of the conservation of energy in chemical changes, and of constant heat sums; the third introduces the system of combining weights, chemical equations, and stoichiometry; the fourth the laws of gases; the fifth the rôle of the combining weight in the laws of Gay-Lussac, Dulong and Petit, Mitscherlich, and Raoult; the sixth the determination of equivalent and combining weights, and formulas; and the seventh the atomic theory, isomers, polymers, metamers, and stereoisomers. In the concluding chapter we find the descriptive chemistry of the elements, in the order H, Li, Gl, B, C, N, O, (the atmosphere), A, F, Na, (valence), Mg, Al, Si, P, S, Cl, K, Ca, Cr, Mn, Fe, Ni, Co. The whole is concluded by an account of the periodic law. Thus it will be seen that the more abstract matters are treated first, and thereupon the descriptive chemistry of the chief elements of the first three rows of the periodic table, in the order in which they appear in the table. The book is accompanied by a pamphlet of suggestions to teachers. *J. E. Trevor*

Chemical Lecture Experiments. *By Francis Gano Benedict. 12 × 18 cm; pp. xiii + 436. New York: The Macmillan Company, 1901. Price: $2.00.* — An extensive collection of carefully worked up experiments for the lecture table. The author states that the preparation of the book received its impulse from the brilliant experimental lectures of Cooke and of Victor Meyer. All experiments requiring elaborate apparatus are excluded; and descriptions of apparatus and manipulation are given in considerable detail. The elements are treated mainly in the order of their arrangement in the periodic table. The book will doubtless be of great assistance to teachers of introductory chemistry, both in schools and in colleges. *J. E. Trevor*

Essays on the Theory of Numbers. *By Richard Dedekind. Translated by W. W. Beman. 13 × 19 cm; pp. 115. Chicago: The Open Court Publishing Company, 1901. Price: cloth, $0.75 net.* — The newest volume in the Open Court Company's interesting series of popular mathematical works is an authorized translation, by W. W. Beman, of Dedekind's two essays: Continuity and Irrational Numbers (1872), and The Nature and Meaning of Numbers (second edition, 1893) When giving a course of lectures on the elements of the differential calculus, in 1858, Dedekind felt the necessity of a rigorous arithmetic definition of continuity. He found it in the principle that: If all points of the straight line fall into two definite classes, such that every point of the first class lies to the left of every point of the second class, then there exists one, and only one, point which produces this division. Starting from this principle, he gives a simple and clear discussion of the continuity of the straight line, of the creation of irrational numbers, and of the continuity of the domain of real numbers; and he adds an account of the bearing of his principle on operations with real numbers, and on the infinitesimal analysis. The little essay, covering only twenty-seven small pages, is a model of clear and beautiful reasoning.

The remainder of the present volume is occupied by the essay, The Nature and Meaning of Numbers (second edition, 1893). In the preface to the first edition, of 1887, Dedekind says: "My answer to the problems propounded in the title of this paper is, then, briefly this: numbers are free creations of the human mind; they serve as a means of apprehending more easily and more sharply the difference of things. It is only through the purely logical process of building up the science of numbers and by thus acquiring the continuous number-domain that we are prepared accurately to investigate our notions of space and time by bringing them into relation with this number-domain created in our mind. If we scrutinize closely what is done in counting an aggregate or number of things, we are led to consider the ability of the mind to relate things to things, to let a thing correspond to a thing, or to represent a thing by a thing, an ability without which no thinking is possible. Upon this unique and therefore absolutely indispensable foundation, as I have already affirmed in an announcement of this paper, must, in my judgment, the whole science of numbers be established." The essay itself aims to make clear how this establishment is to be effected. It is written in a way that presupposes no technical philosophic or mathematical training.

In the publisher's announcement, the book is said to be accompanied by a portrait of Dedekind. We do not find this portrait in our copy.

J. E. Trevor

An Introduction to Science. *By Alex. Hill. (Temple Edition No. 1.) 9 × 14 cm; pp. 140. New York: The Macmillan Company. Price: cloth, $0.40.*—This book is the introductory volume of Macmillan's new "Temple Primers, forming an International Primer Cyclopaedia." It is a neatly gotten up little volume, bound in limp cloth. The series is to present condensed information introductory to great subjects, written by leading authorities, adapted at once to the needs of the general public, and forming introductions to the special studies of scholars and students. The present volume contains a general discussion of the philosophy of science, and particular consideration of the age of the earth, the ultimate constitution of matter, and several questions of natural history. Much may be expected of the series as a whole; but the ideas advanced in this initial volume are not closely allied to the helpful general views that men of science are familiar with in the writings of Helmholtz, Mach, Hertz, and others.

J. E. Trevor

Die Fortschritte der Physik. *Dargestellt von der physikalischen Gesellschaft zu Berlin. Im Jahre 1899. 16 × 23 cm. Zweite Abtheilung: Physik des Aethers; redigirt von Richard Börnstein und Karl Scheel. pp. lii + 935. Price: paper, 34 marks. Dritte Abtheilung: Kosmische Physik; redigirt von Richard Assmann. pp. xliii + 544. Price: paper, 20 marks. Braunschweig: Friedr. Vieweg und Sohn, 1900.*—The present volumes complete the *Fortschritte* for 1899. The large second volume, on the "Physics of the Ether", embraces the work of the year in light, heat, and electricity and magnetism. The chapters on heat and on electrochemistry summarize, of course, a great part of the current work in physical chemistry. The final volume deals with the progress of astrophysics, astronomy, and meteorology. This comprehensive collection of adequate reviews continues to maintain its high degree of excellence. *J. E. Trevor*

Les Tourbillons cellulaires dans une Nappe liquide *propageant de la chaleur par convection, en régime permanent. Thèse. Par Henri Bénard. 15 × 23 cm; pp. 88. Paris: Gauthier-Villars, 1901. Price: 3 francs.* — The author has heated thin disks of various liquids from below, and has observed, in various ingenious ways, the convection currents that arise. He finds these currents to consist of small filaments of liquid, distributed with remarkable regularity. The thesis is accompanied by a number of reproductions of photographs of the upper surfaces of the liquids. The phenomena are curious and very beautiful. *J. E. Trevor.*

Production et Emploi des Courants alternatifs. *By L. Barbillion. Scientia, No. 11. 103 pp. (1901).*

La Série de Taylor et son prolongement analytique. *By J. Hadamard. Scientia, No. 12. 102 pp. (1901). — Limp boards; 13 × 20 cm. Paris: C. Naud. Price: 2 francs each.* — The above two numbers of the *Scientia* series of monographs have reached us. No. 11, Production and Employment of Alternating Currents, recapitulates the theory of electromagnetic induction, gives a theoretical study of alternating currents, and treats of the theory of generators, motors, and transformers in some detail. No. 12, Taylor's Series and its Annlytic Extension, is an elaborate monograph on the work of the past few years in the development of the subject in question. *J. E. Trevor*

Die Erweiterung unserer Sinne. *Akademische Antrittsvorlesung gehalten May 19, 1900. By Otto Wiener. 16 × 25 cm; pp. 43. Leipzig: Johann Ambrosius Barth, 1900. Price: paper, 1.20 marks.* — In this inaugural lecture before the University of Leipsic, Wiener adduces a number of illustrations of the statement that instruments of observation provide extensions of our senses. He adds the comment that the sensations obtained are interpreted by physical theory, and that the object of the physicist is to make this theory both as comprehensive and as uniform as possible. *J. E. Trevor*

Elements of Physics. *By Henry A. Rowland and Joseph S. Ames. 13 × 19 cm; pp. v + 263. New York: American Book Company. Price: bound, $1.00.* — This is a small introductory textbook on general physics. Its treatment is everywhere brief and simple. Some use is made of algebra, but none of the calculus. The book is well illustrated, largely by diagrams. It contains many dogmatic statements about matters of hypothesis. Brief descriptions of a set of lecture experiments, for use in connection with the text, are appended. *J. E. Trevor*

England's Neglect of Science. *By John Perry. 13 × 21 cm; pp. 113 London: T. Fisher Unwin, 1900. Price: bound 2s. 6d.* — This little book is a collection of spirited and extraordinarily sensible articles and addresses in aid of the present crusade against existing methods of elementary and technical education in England. It is contended that the teaching of mathematics and physics should be kept more in touch with drawing and experiment than is usually the case, and should follow a more natural order. In mathematics, much abstraction and rigor should be eliminated from the early work. It is made obvious that engineering students, in particular, should acquire a working acquaintance with mechanical and electrical science, together with a practical facility in the use of the mathematical means that are necessary for its economical employment. Failure in this respect is responsible for the fact that English engineers, in the mass, are not in touch with the technical development of the time. In regard to his ideas of educational reform, Professor Perry says: "I claim that these notions are natural to any man of experience who can think for himself, and who is not materially interested in the maintenance of existing methods of education." *J. E. Trevor*

Die mechanische Wärmetheorie. *By G. Gross. Vol. I. 14 × 22 cm; pp. xiii + 254. Jena: Hermann Costenoble. Price: paper, 8 marks.* — This book is a short introductory treatise on thermodynamics, written by an engineer for engineers. It is intended to serve as an introduction to the larger works on the subject. After some general comment on thermodynamic processes, the author discusses the history of the discovery of the equivalence of heat and work, the achievements of Carnot and of Clapeyron, the reorganization of the subject by Clausius and the method of exposition of Zeuner, and the kinetic gas theory. He then makes an effort to elucidate the mutual transformations of heat and work by means of a study of the behavior to be attributed to a single gas-molecule enclosed in a cylinder under a piston. Chemical thermodynamics are not considered. *J. E. Trevor*

Gustav Theodor Fechner. *By Wilhelm Wundt. 15 × 23 cm. Leipzig: W. Engelmann, 1901. Price: paper, 2 marks.* — This extremely interesting address is the oration delivered by Wundt, before the Royal Saxon Society of Sciences, on the occasion of the commemoration of Fechner's hundredth birthday. It gives a detailed and sympathetic account of Fechner's career, first as a physicist, and then as a professional philosopher after the severe illness that separated his life so completely into two different parts; and it gives a thoughtful description of the growth of the curious philosophical ideas which Fechner developed and defended. Some delightful personal recollections add greatly to the charm of the whole. The pamphlet is accompanied by a heliogravure of the bronze bust of Fechner in the Rosenthal at Leipsic. *J. E. Trevor*

Ueber die Grundlagen der exacten Naturforschung. *By A. Fock. 15 × 23 cm; pp. 125. Berlin: Mayer and Müller, 1900. Price: paper, 3 marks.* — A general examination of the method and means employed in the development of the exact sciences. The author examines in detail the ideas of time, space, mass, force, and energy. His view appears to be about as follows. The objective changes of things give rise to subjective changes, which appear as representations (*Vorstellungen*) and sensations. But these parallel processes do not seem, in every stage, to be immediately connected. So we must undertake to transform our representations and states of consciousness into pictures and symbols, with reference to the measured quantities and free from purely subjective additions, in such wise that the pictures obtained shall remain in agreement with the changes of the objective world. *J. E. Trevor*

REVIEWS

The object of this department of the Journal is to issue, as promptly as possible, critical digests of all Journal articles that bear upon any phase of Physical Chemistry.

General

The reputed importance of the theory of invariants in chemistry. *E. Study. Zeit. phys. Chem.* 37, *546* (*1901*). —The author claims that Alexejew's application of the theory of invariants to chemistry (5, 265, 406) is purely formal and is worse than useless. *W. D. B.*

One-Component Systems

On the position of the volume and energy surface of a crystal and its melt. *G. Tammann. Arch. néerl.* (*2*) 5, *108* (*1900*). —Benzophenone was the substance taken and the author has determined the change of volume along the cryobaric curve and has calculated the heat of fusion. The volume change decreases about 0.5 percent per degree as the freezing-point rises, while the heat of fusion increases about 0.2 percent per degree. *W. D. B.*

On a new manometer and on the gas law between 1.5 and 0.01 mm mercury. *Lord Rayleigh. Zeit. phys. Chem.* 37, *713* (*1901*). —The author describes a manometer of his invention with which it is possible to measure to about 1/2000 mm Hg. With this new instrument he has studied the pressure-volume relations for nitrogen, hydrogen and oxygen. All three follow Boyle's law very closely between 1.5 and 0.01 mm Hg and the author's results contradict those of Bohr for oxygen. *W. D. B.*

On the expansion of platinum, platinum iridium, palladium, silver, nickel, iron, steel and constantan at high temperatures. *L. Holborn and A. Day. Sitzungsber. Akad. Wiss. Berlin*, 1900, *1009*. —The measurements were made on rods 1/2 meter long and 5–6 mm diameter. The rods were heated over the whole length as uniformly as possible. The measurements ran to 500° with constantan, to 750° with iron and steel, to 875° with silver, and to 1000° with the other metals. With the non-magnetic metals the expansion can be fairly accurately expressed by a quadratic equation. It is interesting to note that the formula of Benoît for platinum, deduced from experiments between 0° and 75°, gives the result at 1000° with an error of only one percent. *W. D. B.*

On the air thermometer at high temperatures. *L. Holborn and A. Day. Drude's Ann.* 2, *505* (*1900*). —This is a continuation of the author's previous work on the subject (4, 142) in the way of studying more in detail certain more important requirements. The coefficient of expansion of platinum-iridium, the material out of which the bulb of the thermometer is made, is determined accurately from 10° to 1150°, and the effect of pressure on the enclosed gas when the bulb is hot is tested by comparing measurements at constant pressure and constant volume. The agreement appears to be excellent, and points to there being little error from this cause. A comparison of the platinum-platinum-rhodium thermocouple with the air thermometer gives the simple parabolic equation

$$e = -310 + 8.048t + 0.00172t^2$$

with the hot junction at t° and the cold junction at 0° C. This holds from 250° upwards.

The main object of the paper is to determine accurately, with the air thermometer, three points between 300° and 1100° which would serve as reference points for the calibration of thermojunctions. A series of metals from cadmium, 321.7°, to pure copper, 1084.1°, are given. *H. T. B.*

Two-Component Systems

On the nature of lead amalgams. *H. Fay and E. North, 2nd. Am. Chem. Jour.* 25, *216* (*1901*). — Addition to mercury of lead up to sixty-five percent has no effect on the freezing-point. Addition of mercury to lead lowers the freezing-point, the relation being linear to nearly sixty-five percent lead where the curve must become practically vertical, since the authors cannot tell whether the freezing-point for this mixture is + 177.3° or — 37.8°. The phenomena are accounted for, with the exception of this astonishing change in the curve, by the hypothesis of a solid solution with Pb_2Hg for its last term, this compound being practically insoluble in mercury. *W. D. B.*

Relations between surface tension and solubility. *G. A. Hulett. Zeit. phys. Chem.* 37, *385* (*1901*). — The solubility was determined by means of conductivity measurements. A normal saturated solution of gypsum contains 15.33 millimols at 25°; the size of the solid particles in equilibrium with this solution is 2μ. When the particles are only 0.3μ the solubility becomes 18.2. With solid barium sulphate of a diameter 1.8μ the solution contains 2.29 mg/liter. This increases to 4.15 when the size of the particles is reduced to 0.1μ, and becomes still greater when the barium sulphate is ground up with quartz powder.

Since mercuric oxide did not affect the conductivity of the water used, the solubility of this substance was determined colorimetrically. The concentration with coarse red oxide was 50 mg/liter; with fine powder it was 150. *W. D. B.*

Precipitation of salt on evaporating dilute solutions. *F. W. Skirrow and H. T. Calvert. Zeit. phys. Chem.* 37, *217* (*1901*). — If the vapor-pressure of the system, salt, solution and vapor, is always less than one atmosphere, solid salt cannot be obtained by boiling off the solvent under atmospheric pressure. Caustic soda and water is a case in point. Solid salt may of course be obtained by evaporating at pressures lower than the saturation pressures. *W. D. B.*

The crystallization of copper sulphate. *A. J. Hopkins. Amer. Chem. Jour.* 25, *413* (*1901*). — The following general principles are assumed.

" In a solution, supersaturated in absolute quiet, no crystals will form.

"In a solution, supersaturated in absolute quiet, the number of crystal points formed by the first disturbance (if the disturbance is succeeded by quiet) is the same as the number of crystals finally formed.

"The ratio between the number of crystals formed and the weight of the crystal deposit determines the size of the crystals.

"For a given volume of solution and given size of crystals and weight of crystal deposit, the diameter of the crystallizing dish determines the space between the crystals."

The author's object was to obtain crystals of copper sulphate 20–30 mm in length and he succeeded. Obviously the important thing was to regulate the number of crystals formed. This was done by sudden, temporary surface-cooling. The real secret is that the author has worked intelligently and carefully. He has avoided dust, local variations of temperature, etc., and has consequently obtained splendid results. *W. D. B.*

Mixtures of hydrochloric acid and methyl ether. *J. P. Kuenen. Arch. néerl. (2) 5, 306 (1900); Zeit. phys. Chem. 37, 485 (1901).* — It was not possible to make a complete study of the *p-v-t* relations of mixtures of hydrochloric acid and methyl ether because the two react perceptibly above 100°. The relations so far as they could be determined are those required by the theory of van der Waals for systems in which a maximum boiling-point occurs. The author thinks that the contraction in the vapor may possibly be a sign of a strong affinity only, and not proof of the existence of a compound. *W. D. B.*

Note on the use of pyridine for molecular weight determinations by the ebullioscopic method. *W. R. Innes. Jour. Chem. Soc. 79, 261 (1901).* —When the constant for pyridine is taken as 29.5, normal molecular weights are obtained for benzophenone, phenanthrene, diphenylamine, succinic acid, tartaric acid, salicylic acid, resorcinol tartaric ditoluidide and β-naphthol. *W. D. B.*

The molecular weight of aluminum compounds. *E. P. Kohler. Amer. Chem. Jour. 24, 385 (1900).* — Boiling-point determinations for aluminum acetylacetone and aluminum acetoacetic ester in carbon bisulphide and freezing-point determinations for aluminum chloride and aluminum bromide in nitrobenzene point to the formula AlX_3. With aluminum bromide, aluminum iodide, aluminum bromide plus benzene sulphonchloride, aluminum bromide plus benzoyl chloride, aluminum bromide plus benzophenone, and aluminum bromide plus *p*-dibrombenzene in carbon bisulphide give results pointing definitely to the formula Al_2X_6. This same result is obtained for aluminum chloride in nitrobenzene. *W. D. B.*

On the absorption of gases by glass powder. *P. Mülfarth. Drude's Ann. 3, 328 (1900).* — Gases are quite readily absorbed by glass powder, the absorption being less at higher temperatures. It becomes complete in from one to two hours for dry powder, the presence of moisture merely retarding the absorption. Carbon dioxide is studied most completely, but in addition a number of other gases are treated. The results appear to be only relative. *H. T. B.*

Solubility of gases in organic solvents. *G. Just. Zeit. phys. Chem. 37, 342 (1901).* — The author has determined the solubility at 20° and 25° of hydrogen, nitrogen, carbon monoxide and carbon dioxide in from fifteen to forty-four solvents. In general, the gases are least soluble in glycerol, water, aniline, and carbon bisulphide, while they are quite soluble in the acetates. With carbon monoxide and nitrogen the ratio of the solubilities in different solvents varies very little with the solvent; but this is not true of the other two gases. The solubility of nitrogen, hydrogen and carbon monoxide increases with rising temperature; that of carbon dioxide decreases. Experiments were also made with mixed liquids. *W. D. B.*

Some thermodynamic relations between the values which characterize the state of a solution. *N. Schiller. Arch. néerl.* (*2*) 5, *118* (*1900*). — Among other equations the author deduces one

$$\frac{\sigma}{x} - \frac{\sigma_0}{x_0} = C\xi^{\frac{1}{2}},$$

where σ is the specific volume of the pure solvent when under the pressure p; σ_0 the specific volume of the solvent in a solution of the concentration ξ; x_0 and x are corresponding values for the coefficients of elasticity; while C is a constant. *W. D. B.*

Permanent changes in glass and the displacement of the zero in thermometers. *L. Marchis. Zeit. phys. Chem.* 37, *553* (*1901*). — Reviewed (3, 109) from the author's doctor thesis.

On accurate thermometry. *L. Marchis. Zeit. phys. Chem.* 37, *605* (*1901*). — The author discusses the ageing of thermometer tubes, the determination of the fundamental interval, the measurement of any given temperature, and the long-continued measurement of the same temperature, all from the point of view of Duhem's theory. *W. D. B.*

Attempt at a theory of colloidal solution. *F. G. Donnan. Zeit. phys. Chem.* 37, *735* (*1901*). — The author looks upon the so-called solution of colloids as a case of mechanical or molar breaking down which stops well short of molecules or atoms. *W. D. B.*

Poly-Component Systems

On the equilibrium between mix-crystals and the vapor phase. *H. W. Bakhuis Roozeboom. Arch. néerl.* (*2*) 5, *360* (*1900*). — A discussion of the vapor pressure relations with different types of mix-crystals. *W. D. B.*

On the vapor pressure of mix-crystals of some isomorphous hydrated salts. *P. Hollman. Zeit. phys. Chem.* 37, *193* (*1901.*) — The vapor pressures were determined by standing the crystals over sulphuric acid of known strengths. The pairs studied were potassium iron and aluminum alums; potassium chromium and aluminum alums; zinc and magnesium sulphates; copper and manganese sulphates; zinc and copper sulphates; magnesium and copper sulphates; zinc and manganese sulphates. In all cases the vapor pressure curve decreases at both ends of the curve, passing through a minimum if a continuous series of mix-crystals is realizable. *W. D. B.*

Some isomeric halogen compounds of thallium and the constitution of

double salts. *A. S. Cushman. Amer. Chem. Jour.* 24, *222* (*1900*). — The author has prepared an orange compound and a red compound to which he ascribes the formula $TlCl_3 3TBr$ and $TlBr_3 3TlCl$. The orange compound is stable, the red relatively instable. The author states that by adding thallium trichloride or thallium tribromide to the solutions he can obtain $TlCl_3 3TlCl$, $TlCl_3 3TlBr$, $TlBr_3 3TlCl$ or $TlBr_3 3TlBr$. The author's apparent ignorance of the phase rule handicaps him very seriously and he talks about carefully-adjusted conditions without giving any clue as to what those conditions are. Under no circumstances does he appear to have worked at constant temperatures. These double salts show slow hydrolysis in solution. *W. D. B.*

Preliminary report on the passivity and on the rendering passive and active of iron. *H. L. Heathcote. Zeit. phys. Chem.* 37, *368* (*1901*). — Iron is made passive at 15°-17° by nitric acid of a specific gravity 1.25, but not by a 1.2 acid. Iron with a colored film on the surface is not passive, but can be made so. Even in concentrated nitric acid iron dissolves, though very slowly. A number of interesting experiments were made to test the length of time the passivity lasts under different conditions. With iron as cathode a pulsating phenomenon could be observed. The author calls attention to the possible analogy between the transmission of passivity from one end of a rod to the other and the transmission of a stimulus along a nerve. *W. D. B.*

Osmotic Pressure and Diffusion

On the relation between osmotic pressure and osmotic work. *C. Dieterici. Zeit. phys. Chem.* 37, *220* (*1901*). — A reply to Noyes (5, 268). *W. D. B.*

Resorption of one solution by another. *M. Oker-Blom. Zeit. phys. Chem.* 37, *744* (*1901*). — When two different solutions are separated by a membrane permeable to one of the solutes and not to the other, the flow will be through the membrane to the solution containing the solute which cannot pass the membrane, irrespective of the initial concentrations. This process is to be called resorption. *W. D. B.*

Velocities

The effect of non-electrolytes on the saponification of ethyl acetate. *C. Kullgren. Zeit. phys. Chem.* 37, *613* (*1901.*) — The non-electrolytes were cane sugar, glycerol, methyl and ethyl alcohols, acetone. All decrease the reaction velocity, sugar by far the most. With sugar it seems probable that the decrease is due chiefly, perhaps entirely, to the formation of sodium saccharate. In order to explain the phenomena in the other cases the author assumes an active and an inactive ethyl acetate. *W. D. B.*

Catalysis in concentrated solutions. *J. M. Crafts. Jour. Am. Chem. Soc.* 23, *250* (*1901*). — The author has studied the catalytic action of concentrated acids on the hydrolysis of the sulphonic acids. In one case the reaction velocity increased thirty-five fold on changing from nineteen to thirty-eight percent hydrochloric acid, while an addition of zinc chloride increased this latter rate threefold. *W. D. B.*

The paralysis of platinum catalysis by poisons. *R. W. Raudnitz. Zeit.*

phys. Chem. 37, *551* (*1901*).—The author proves that the catalysis of hydrogen peroxide goes on at an undiminished rate if the prussic acid be removed in any way. This shows that no irreversible change is caused by the poison.

W. D. B.

Inorganic ferments, III. *G. Bredig and W. Reinders. Zeit. phys. Chem.* 37, *323* (*1901*).—This paper, the third of the series, deals with the action of colloidal gold on hydrogen peroxide. The same general phenomena are found with the gold solutions as have been observed with platinum solutions (4, 326; 5, 416).

W. D. B.

Catalysis in the reaction between hydrogen peroxide and hydriodic acid. *J. Brode. Zeit. phys. Chem.* 37, *257* (*1901*).—The following conclusions are drawn:—

Allied reactions show but little similarity in their behavior towards catalytic agents.

The concentration functions of catalytic agents are usually linear.

The acid functions vary with each catalytic agent.

The combination of different catalytic agents may produce an additive, an increased, or a diminished effect.

The action of a catalytic agent may be much intensified by the presence of a substance which by itself has practically no catalytic action.

In the case studied, the catalytic agent does not act specifically on each component.

The order of the reaction is not changed by hydrogen as ion but is by the special catalytic agents.

From the form of the equation found it is believed that the effect of the special reaction is due to intermediate reactions.

W. D. B.

The catalysis of detonating gas by colloidal platinum. *C. Ernst. Zeit. phys. Chem.* 37, *448* (*1901*).—Colloidal platinum does not lose its activity even after changing large quantities of hydrogen and oxygen into water. The product is water only, neither ozone nor hydrogen peroxide being detected. The reaction velocity is proportional to the amount of platinum. When neither gas is present in excess, the rate of change is proportional to the concentration of the mixed gases; but when either is in excess it acts as a diluent. The explanation offered for this is that the rate of absorption by the platinum is really the thing measured. The temperature coefficient is very small and becomes negative at higher temperatures.

W. D. B.

Studies on solutions of tin salts, I., II. *S. W. Young. Jour. Am. Chem. Soc.* 23, *21*, *119* (*1901*).—In the first paper the author measures the conductivity of stannous chloride in aqueous solution and then again in presence of hydrochloric acid or potassium chloride. Evidence is obtained of the formation of double compounds. The second paper deals with the oxidation of stannous chloride by oxygen. The rate is probably approximately proportional to the concentration of the tin salts, but catalytic disturbances were very disturbing. Rubber, sulphur, hydrogen sulphide, alcohol, and the salts of copper and iron accelerate the reaction. Brucine, morphine, nicotine, mannite, aniline, potassium cyanide and the salts of chromium and manganese retard the reaction. *W. D. B.*

Reaction velocity and solubility. *W. D. Bancroft. Arch. néerl.* (*2*) 5, *46* (*1900*). — The form of the reaction velocity equation is one between functions of the chemical potentials. Since the chemical potential varies with the solubility, the reaction velocity must also. *W. D. B.*

Electromotive Forces

Investigations on normal cells and especially the Weston cadmium cell. *W. Jaeger and S. Lindeck. Drude's Ann.* 5, *1*; *Zeit. phys. Chem.* 37, *641* (*1901*). — Cadmium cells with 13 or 12 percent amalgam behave perfectly well even when kept a long time at zero; cells with a 14.3 percent amalgam may be used as standards above 10°. The authors deny the accuracy of the Barnes formula for the temperature coefficient (4, 344). The authors also deny the existence of two forms of $CdSO_4 8/3H_2O$. They may be entirely right in all their claims, but there is a distinctly "official" tone to their statements, and the world at large certainly did not know the peculiarities of the 14.3 percent cadmium amalgam until Cohen called attention to them. *W. D. B.*

On the determination of the work corresponding to affinity. *E. Cohen. Arch. néerl.* (*2*) 5, *295* (*1900*). — Reviewed (5, 410) from Zeit. phys. Chem. 36, 517 (1901).

The calculation of the degree of dissociation of strong electrolytes, II. *S. Arrhenius. Zeit. phys. Chem.* 37, *316* (*1901*). — A reply to Nernst and Jahn (5, 328, 329, 418). *W. D. B.*

On Mr. Jahn's measurements of the electromotive force of concentration cells. *R. A. Lehfeldt. Zeit. phys. Chem.* 37, *308* (*1901*). — The author trips himself up by trying to express things in too general a form and reaches the obviously erroneous conclusion that Nernst's formula is right provided the degree of dissociation is a function of the total concentration. This lands him in a difficulty from which the only chance of escape appears to lie in the assumption of large variations from the gas laws. *W. D. B.*

The degree of dissociation and the dissociation equilibrium of highly dissociated electrolytes, II. *H. Jahn. Zeit. phys. Chem.* 37, *490* (*1901*). — The author now admits that the Nernst formula for concentration cells is "slightly inaccurate" when applied to solutions which do not follow the dilution law. He clings to the conclusion that the Nernst formula is necessarily right when the dilution law holds because it reduces to the Helmholtz formula for infinite dilution [Cf. 5, 276, 329]. One might as well say that it is immaterial whether we assume that the sun moves round the earth or that the earth moves round the sun, because these two hypotheses lead to the same conclusions in case neither sun nor earth moves. The disturbing influence of the undissociated salt becomes zero when the undissociated salt is not there. *W. D. B.*

Comment on R. Luther's paper: "On the electromotive behavior of substances with several oxidation stages." *E. Abel. Zeit. phys. Chem.* 37, *623* (*1901*). —

The author points out that only one or two of Luther's measurements (5, 329) can be looked upon as experimental proof of the theoretical deductions.

W. D. B.

An electrometric method for detecting very small amounts of electrolytes whose ions have different migration velocities. *M. Oker-Blom. Zeit. phys. Chem.* 37, *665* (*1901*). — If one takes calomel electrodes with potassium chloride solutions of different strengths and separates the solutions by a piece of moistened filter paper, the electromotive force of the combination will change measurably if the solute in the filter paper is an electrolyte, the ions of which have different migration velocities. *W. D. B.*

Thermoelectromotive forces. *A. Abt. Drude's Ann.* 2, *266* (*1900*). — On account of the author's researches on the magnetic properties of certain ores, it was found desirable to study the thermoelectromotive properties of the same materials for temperature difference of 100°. Metallic oxides and sulphides in contact with each other, as well as with the pure metals, are studied.

It is found that the electromotive force of a galenite-pyrite couple is 13.4 times as large as a bismuth-antimony couple, and a chalcopyrite-pyrite couple 10.8 times as large. *H. T. B.*

A simple method to determine the neutral point of a thermocouple. *A Abt. Drude's Ann.* 3, *320* (*1900*). — There is nothing new in the method beyond perhaps a more complete thermal shielding of the solder joins. The apparatus described is simple and no doubt efficacious. The thermoelectric properties of a brass-lead, iron-silver and zinc-iron couple are given.

H. T. B.

Thermodynamics of thermojunctions. *C. Liebenow. Drude's Ann.* 2, *636* (*1900*). — A reply to Voigt's criticism of the author's theory (4, 58), which, it is claimed, he has entirely misunderstood. *H. T. B.*

Liebenow's thermodynamic theory of thermoelectricity. *W. Voigt. Drude's Ann.* 3, *155* (*1900*). — The author challenges the sufficiency of the premise upon which Liebenow founded his theory of thermoelectricity (4, 58). He rightly points out that because it fits in with the final results is not alone sufficient justification of its correctness. *H. T. B.*

Theory of the thermoelectricity of electrolytes. *A. H. Bucherer. Drude's Ann.* 3, *204* (*1900*). — The effort is made to develop a theory for the force resulting from temperature differences in electrolytes on thermodynamic grounds, sufficient to accord with the known facts.

The final expression deduced, which was also developed by Duane from the Nernst theory is

$$E = \frac{4.35 \times 10^{-5}}{Y} \int_{T_1}^{T_2} (2N - 1)\, R\, dT,$$

where Y = the valency of the metallic element to the non-metallic part of the electrolyte, and N = the transport number. *H. T. B.*

Electrolysis and Electrolytic Dissociation

The migration velocity of ions in dilute solutions. *H. Jahn. Zeit. phys.*

Chem. 37, *673* (*1901*). — The following values were obtained at 18° for the transference numbers of the cation in very dilute solution: HCl 0.826; HNO_3 0.830; KCl 0.497; KBr 0.496; NaCl 0.396; NaBr 0.396; LiCl 0.330; $BaCl_2$ 0.447; $CdCl_2$ 0.430; $CdBr_2$ 0.430; CdI_2 0.443; $AgNO_3$ 0.471; $CuSO_4$ 0.375.

W. D. B.

A method of preparing normal, seminormal, decinormal, etc., sulphuric acid of exact strength. *R. K. Meade. Jour. Am. Chem. Soc.* 23, *12* (*1901*). — The author weighs out exactly the desired amount of copper sulphate, dissolves in water, and precipitates the copper electrolytically. Comment is superfluous.

W. D. B.

The production of alloys of tungsten and molybdenum in the electric furnace. *C. L. Sargent. Jour. Am. Chem. Soc.* 22, *783* (*1900*). — Tungsten does not alloy readily with bismuth, tin or manganese; nor does molybdenum with copper or tin. Tungsten alloys readily with cobalt, chromium, nickel or copper, and molybdenum with cobalt, chromium, nickel, bismuth or manganese.

W. D. B.

Alloys made in the electric furnace. *L. P. Hamilton and E. F. Smith. Jour. Am. Chem. Soc.* 23, *151* (*1901*).—A brief description of the furnace used and of some alloys made in it. *W. D. B.*

On the electrical resistance of pure metals. *E. van Aubel. Arch. néerl.* (*2*) 5, *49* (*1900*). — It is pointed out that measurements at different times of the electrical conductivity of different samples of supposedly pure metals show such large discrepancies in the case of bismuth, tin and nickel that we really do not know the values or the temperature coefficients for any one of these metals.

W. D. B.

On the electrical conductivity of solutions of alkali iodates and a formula for calculating conductivity. *F. Kohlrausch. Sitzungsber. Akad. Wiss. Berlin*, 1900, *1002*. — Up to *n*/20 solutions, the conductivity of the alkali halides can be represented by the formula $\frac{\Lambda_0 - \Lambda}{\Lambda^p} = cm^{\frac{1}{3}}$, where m is the molecular concentration, and c and p are constants. No reference is made to Storch's formula.

W. D. B.

Variations of the conductivity of a gas by a continuous electric current. *J. Stark. Drude's Ann.* 2, *62* (*1900*). — From a consideration of the large quantity of work that has been done recently on the conductivity of gases from the ionic standpoint, the author deduces certain conclusions in regard to the variation of the specific resistance in a gas subjected to a continuous discharge. A curve is given, typifying his conclusions. *H. T. B.*

A theoretical determination of the ratio of the heat to electrical conductivity in metals from Drude's electron theory. *M. Reinganum. Drude's Ann.* 2, *398* (*1900*). — The author points out that Drude's calculation of the ratio of the heat to electrical conductivity in metals, may be made without the assumption of the two approximate values involved, i. e. the Loschmidt value of the number of the molecules, and Thomson's value of the electrical charge. A slight change in the equation, in accord with Drude's theory (5, 420), enables the calculation to be made in terms of the velocity of a molecule of hydrogen and the well-known electrochemical equivalent of hydrogen.

The ratio so obtained is found to be 0.7099×10^{-10}, which agrees with the lowest value found experimentally by Jaeger and Diesselhorst, which is 0.706×10^{-10}.

According to further conclusions, Giese's original conception of the actual transport of the electrons in metals seems to be supported. *H. T. B.*

Electrical conductivity in gases through which cathode rays pass. *J. C. McLennan. Zeit. phys. Chem.* 37, *513* (*1901*). — The conductivity produced in a gas by cathode rays is similar to that caused by Röntgen or uranium rays and can be accounted for by the hypothesis that positive and negative ions are produced in the gas into which the radiations pass.

If cathode rays strike isolated metallic conductors surrounded by air at atmospheric pressure, the conductors assume a slight negative charge, irrespective of their previous condition. The dissipation of previous charges, if any, is due to the action of the ionized air around the conductor and the value of the negative residual charge depends on the conductivity of this air.

The ionization of a gas caused by rays coming through an aluminum window from a Lenard tube is due to cathode rays and not to Röntgen rays.

Lenard's results on the absorption of cathode rays, determined by fluoroscopic methods were confirmed by a study of the ionization which these rays cause in gases.

When cathode rays of a given intensity pass through a gas, the number of ions produced per cubic centimeter is proportional to the density of the gas and independent of its chemical composition.

With cathode rays, as with Röntgen rays, there is a definite ratio between the number of ions produced and the amount of radiant energy absorbed.

W. D. B.

An electrically heated and electrically controlled thermostat. *S. W Young. Jour. Am. Chem. Soc.* 23, *327* (*1901*). — The regulating and heating is electrical. To keep a thirty-liter bath at 25° calls for about three-quarters of an ampere. The temperature can be held to about two one-hundredths of a degree.

W. D. B.

Dielectricity and Optics

On fluorescence and after-glow in nitrogen, produced by electrical discharge. *P. Lewis. Drude's Ann.* 2, *459* (*1900*). — The fluorescence, noted by the author, extending beyond the discharge tube into the connecting tube, is called β-fluorescence, as distinguished from α-fluorescence produced in the discharge tube alone. The paper is mainly valuable as a collection of observational data on the subject. *H. T. B.*

On cathode rays. *P. Villard. Comptes rendus,* 130, *1614* (*1900*). — Two filaments from an incandescent lamp are made the poles, and the anode remains dark while the cathode becomes luminous owing to the greater amount of heat evolved there. The heat and therefore the incandescence is greatest where the most cathode rays are emitted. *W. D. B.*

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REVIEWS

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OXIDATION OF FERROUS SOLUTIONS BY FREE OXYGEN

BY J. W. MCBAIN

As early as 1858 Schönbein attempted to solve the problem of the "mechanism" of slow processes of oxidation. In the last few years the question has been revived by the experiments of van 't Hoff, Ewan, Jorissen, Ostwald's pupils, and others, and quite recently the problem has been given an entirely new interest by the astonishing results of Bredig[1] and his collaborators, which appear to open another gate to the large field of research connecting physiology and physical chemistry. It was with the object of extending the quantitative data concerning slow oxidation that the following experiments were carried out in which the rates of oxidation of ferrous sulphate, chloride and acetate solutions under various conditions have been studied.

From the point of view of the analytical chemist also the following results may be of interest in demonstrating the extreme slowness with which dilute ferrous sulphate solutions undergo oxidation and the consequent superfluity of the elaborate precautions often prescribed for the preparation of volumetric iron solutions.

Experiments

In the earlier experiments a ferrous solution through which air was caused to bubble, was titrated from time to time by decinormal permanganate and the extent of oxidation estimated by difference. Owing to the unexpected slowness of the reaction, however, the effects of evaporation and of impurities accumulated from the air (which were only partially avoided by previous washing and saturation), rendered the method impracticable, and it was finally abandoned in favor of the following procedure.

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[1] Zeit. phys. Chem. 31, 258 and later.

Numbers of glass-stoppered bottles were completely filled with the solution to be oxidized containing a known and controllable quantity of dissolved oxygen, and the contents of these analyzed at intervals by a method described below. The process of filling the bottles requires some explanation. The solutions to be used were thoroughly freed from air by boiling, cooled in vacuo and placed in flasks or burettes, fitted with carbon dioxide attachments.[1] Water, saturated with oxygen (purified by passing through a KOH-Tower), was kept in a glass reservoir, to the bottom of which the lower end of a graduated cylindrical vessel was attached. The upper end of the latter was connected with the oxygen space above the water in the reservoir and a current of oxygen passed through this space while the pipette was being used. By means of a three-way tap the measure could be filled and emptied repeatedly, while the water was always in contact with oxygen at atmospheric pressure.

The solutions to be investigated were made up in a tall, cylindrical stoppered bottle of 500 cc capacity. After filling the bottle with carbon dioxide, a quantity of boiled water was introduced, and then measured quantities of the heavier solutions (ferrous sulphate, etc.) added so as to form a layer below the water. A measured amount of oxygen water was next run in between the two layers, it being in this way prevented from losing oxygen to the carbon dioxide space above by the protecting layer of water. Finally the bottle was filled completely with boiled water, immediately closed, and stirred by means of a glass float. The contents were rapidly siphoned into smaller bottles, using only the lower layers from the large bottle and allowing each small bottle to overflow before inserting its stopper. The bottles were transferred to a thermostat and kept under water to prevent the formation of bubbles by

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[1] A number of the first experiments were rendered useless by traces of sulphur dioxide given off by the CO_2-Kipp, which had a marked influence on the rate of reaction. In all the experiments described, the gas which was prepared from marble and hydrochloric acid, was passed through water, cotton wool, permanganate of potash and ferrous sulphate solutions, which effectually removed the impurity.

evaporation round the stoppers. It may be added that the solutions were generally about one-fifth saturated with oxygen so that the chance of losing oxygen to the air while filling the small bottles was reduced to a minimum.

In some few cases another method was employed; namely, shaking the liquid in a large closed bottle with air or oxygen. This is satisfactory when the same solution is used in different experiments, but with different liquids the concentration of the oxygen would vary with the solubility, which is difficult to determine accurately.

Analysis

In the solutions made up in the manner described above, the concentration of the oxygen was about 0.001 normal, and this represents the maximum concentration of ferric solution formed by oxidation. It is obvious, therefore, that to obtain accurate measurements of the ferric iron, any "method of difference" by ferrous determinations would be out of the question. Fortunately a very satisfactory direct determination of the ferric iron was afforded by colorimetric readings of the sulphocyanate. This method has been pronounced unsatisfactory by Krüss and Moraht.[1] Lapicque,[2] on the other hand, has advocated it as a practical method, and the following results entirely support the latter view.

A very serviceable colorimeter was improvised from two test-tubes with thin flattened bottoms. The one containing a standard red solution was provided with a side tube sealed at the extreme lower end, leading through a short rubber connection to a larger tube suspended by a string. The height of the latter could be adjusted by turning a handle round whose axis the suspension was wound. The two test-tubes were fixed side by side above an oblique cardboard surface illuminated by a screened arc light. The colored solutions in the tubes were viewed through two small holes, and the height of the standard liquid was adjusted till the shade in the two test tubes appeared identical.

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[1] Zeit. anorg. Chem. 1, 399 (1892).

[2] Bull. Soc. Chim. Paris, (3) 7, 113 (1892).

The height of the standard liquid was then read off by a millimeter scale, the adjustment repeated, and the average of six or eight readings taken. Readings were taken in quick succession, and though individual readings often differed by 5 pct, the averages generally agreed to within 1 pct, while by careful and extended repetitions, averages were obtained differing by as little as 0.1 pct.

The standard color was made from equal volumes of 0.625 normal ammonium sulphocyanate and 0.005 normal ferric chloride in normal sulphuric acid solution. These are mixed afresh for each analysis, as the color slowly fades on standing. The heights of the columns used varied from 5 to 60 mm, and it was found that under the conditions followed the depth of color was exactly proportional to the concentration of the ferric iron. One mm indicated a concentration of about 0.000003 normal ferric salt. Ferrous sulphate and acetic acid do not affect the color. Changing from 0.02*n* H_2SO_4 to 1.0*n* H_2SO_4 decreases the color by 8 pct. Normal hydrochloric acid decreases the color by 2 pct. The color was frequently standardized by comparison with a ferric solution of known composition, and the influence of all materials occurring in the solutions to be analyzed was determined and allowed for where necessary. As apparently noticed by Lapicque,[1] different brands of sulphocyanate produce slightly different depths of color, but solutions from the same specimen give consistent results. A solution to be analyzed was diluted with half its volume of normal sulphocyanate, and a constant volume taken for the colorimeter. In cases where the ferric iron would correspond to a longer column than 60 mm, the solution was diluted before adding the sulphocyanate.

The test measurements gave very accurate and consistent results — far more so than those of Lapicque. This was no doubt due to the fact that the standard color had exactly the same tint as the solution to be analyzed, while Lapicque used a colored glass for comparison. It was found that a solution matched by a red dye gave different results, depending on

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[1] Bull. Soc. Chim. Paris, (3) 7, 115 (1892).

whether the eye was tired or not. The alterations due to temperature moreover have less influence on the results in this method, for both solutions are affected to roughly the same extent.

Results

Preliminary experiments were made to test the influence of light and of carbon dioxide on the rates of oxidation. These were both found to be without appreciable effect. Two identical sets of bottles were made up. Both sets were placed in a glass trough of water exposed to sunlight, and one of the sets was covered with an opaque vessel.

Composition of solution: 0.1*n* $FeCl_2$, 1.0*n* HCl, approx 0.001*n* O_2.
Temperature: 21.5° C.

Light, in 47.55 hrs 0.000296*n* Fe''' formed, or, per hr 0.00000623*n*.
Dark, in 47.88 hrs 0.000300*n* Fe''' formed, or, per hr 0.00000627*n*.

A similar result was found with ferrous sulphate.

Identical sets of ferrous sulphate, one made up with carbon dioxide and the other without, also gave identical results.

Composition of solution: 0.1*n* $FeSO_4$, 0.2*n* H_2SO_4, approx 0.001*n* O_2.
Temperature: 30° C.

With CO_2, in 16.03 hours 0.000227*n* Fe''' formed, or per hour, 0.00001416*n*.

Without CO_2, in 15.57 hours 0.000224*n* Fe''' formed, or per hour, 0.00001427*n*.

1. Oxidation of ferrous sulphate

The stock solutions for making up the following set of reactions were *n* $FeSO_4$, 5*n* H_2SO_4, and oxygen water saturated at 20.2° and 753 mm barometer with 96.4 pct oxygen. In each of the following experiments, except *f*, where double the quantity was used, 100 cc of this oxygen water were made up in the manner described above to a total volume of 535 cc.

The ferrous sulphate was recrystallized from ordinary crystals, very thoroughly washed with dilute sulphuric acid, sucked partially dry by the filter pump and put rapidly into boiling water, in a large round-bottomed flask. After boiling a few moments longer, a rubber stopper was inserted and the flask cooled. The vacuous space was afterwards filled with carbon dioxide.[1]

The results of the determinations are given on the following pages. All concentrations are expressed in normalty, except ferric and oxygen concentrations, which are given in millionths of normality, for which the sign "mil" is used. (One mol of iron salt and ¼ mol of oxygen per liter are normal solutions.) Time is expressed in hours and decimals.

The constant K is calculated from the expression for a monomolecular reaction,

$$K = 1/\theta \log \frac{A}{A - X},$$

since oxygen is the only substance whose concentration is appreciably altered by the reaction. θ is the time in hours from the first reading; log is the sign of the ordinary logarithm; A is the concentration of the oxygen at the first reading, expressed in millionth normality, and X is the ferric iron produced in the same units.

The constancy of the constants, and still more the identity of the K in experiment *a* and *f* where the initial concentration is doubled, show that the rate is proportional to the oxygen concentration. (See also under § 2.) The values assigned to A require a word of explanation. It was hoped that by measuring the oxygen water added, the value of A could be calculated from Winkler's[2] solubility determinations; but in all cases where the end point was actually reached (as in the fast reactions) the value obtained by subtracting the ferric iron originally in the ferrous solution from the observed final reading was consistently several percent lower than that calculated from Winkler's data, and consequently the former number was used in calculating the results of all experiments made up at the same time from the

---

[1] Solutions prepared by dissolving iron wire in sulphuric acid could not be employed for the reactions; for not only the black residue, but also some soluble impurity — possibly phosphine — produced irregular results. A solution prepared in this way, containing a trace of ferric iron, was found after a few days to have completely reduced itself.

[2] Ber. chem. Ges. Berlin, 22, 1764 (1889).

TABLE I.

Ferrous sulphate. Temperature = 30° C

Composition of solution	Interval = θ	Fe'''	X	K
a. $FeSO_4$ 0.0935*n*	0	48 mil	0	....
	6.0	172	124	0.0104
H_2SO_4 1.0*n*	12.3	291	243	0.0108
	13.17	303	255	0.0107
O_2 922 mil = A	72.5	745	697	0.0085
	72.75	769	721	0.0091
				0.0103
b. $FeSO_4$ 0.0184*n*	0	15	0	....
	12.48	24	9	0.000312
H_2SO_4 1.0*n*	75.46	74	59	0.000378
	116.9	105	90	0.000378
O_2 925 mil = A	117.1	105	90	0.000378
	294.4	247	232	0.000423
				0.000374
c. $FeSO_4$ 0.463*n*	0	228	0	....
	0.10	293	65	0.315
H_2SO_4 1.0*n*	0.383	421	193	0.264
	0.383	426	198	0.271
O_2 930 mil = A	0.642	599	371	0.344
	1.09	747	519	0.325
	2.30	1007	779	0.343
	19.0	1158	930 end[1]	....
	19.3	1156	928 "	....
				0.310
d. $FeSO_4$ 0.0938*n*	0	43	0	....
	5.63	199	156	0.0142
H_2SO_4 0.02*n*	11.13	333	290	0.0146
	12.38	351	308	0.0141
O_2 917 mil = A	23.8	563	520	0.0150
	24.13	571	528	0.0151
	71.23	816	773	0.0110
	288	958	917 end	....
				0.0140

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[1] Used to determine A for the other experiments.

TABLE I.—(*Continued*).

Composition of solution	Interval = θ	Fe'''	X	K
e. $FeSO_4$ 0.0915*n*	0	43 mil	0	....
	5.6	194	153	0.0140
H_2SO_4 0.10*n*	10.7	306	263	0.0136
	11.75	335	292	0.0140
O_2 923 mil = A	24.91	462	519	0.0143
	71.47	824	781	0.0112
	71.22	816	773	0.0110
	288	966	923 end	....
				0.0130
f. $FeSO_4$ 0.0915*n*	0	48	0	....
	5.4	264	216	0.0101
H_2SO_4 1.0*n*	11.0	452	404	0.0098
	12.25	481	433	0.0095
O_2 1852 mil = A	72.0	1506	1458	0.0093
	72.17	1513	1465	0.0094
				0.0096
g. (Blank expt.)	0	45	0	
$FeSO_4$ 0.0921*n*	72	53	6	
	288	60	15	
H_2SO_4 1.0*n*				
O_2 0.0				
h. $FeSO_4$ 0.0185*n*	0	9	0	....
	21.0	40	31	0.000700
H_2SO_4 0.10*n*	67.67	105	96	0.000699
	68.15	104	95	0.000687
O_2 929 mil = A	114.8	153	144	0.000637
	170.9	243	234	0.000736?
				0.000692
j. $FeSO_4$ 0.0185*n*	0	9	0	....
H_2SO_4 0.02*n*	67.57	108	99	0.000731
O_2 929 mil = A	67.92	109	100	0.000727
	114.8	170	161	0.000719
				0.000726
k. $FeSO_4$ 0.0935*n*	0	40	0	....
H_2SO_4 0.02*n*	7.8	414	374	0.0281
Na_2SO_4 1.0*n*	9.45	469	429	0.0280
O_2 930 mil = A	20.78	724	684	0.0276
	21.20	730	690	0.0275
	69.42	920	880	0.0181
				0.0278 (omitting salt)

same oxygen water. Since the first readings were not made exactly at the time of mixing, the values for A were put equal to the oxygen calculated from the fast sets, less the difference between the first reading and the ferric iron originally present.

The most striking facts brought out by the above results are the enormous influence of the concentration of the ferrous sulphate on the rate and the comparatively slight, and retarding influence of the sulphuric acid. The proportionality of the rate to the concentration of the oxygen was referred to above. The relations between K are set forth in the following summary, in which the *approximate* concentrations are given for clearness. The letters after the constants refer to the experiments.

TABLE II.

	n H_2SO_4	Ratio	*n*/10 H_2SO_4	Ratio	*n*/50 H_2SO_4	Ratio
n/2 $FeSO_4$	0.31(*c*)	840	....		....	
n/10 $FeSO_4$	0.01(*a*)	27	0.013(*e*)	20	0.014(*d*)	20
n/50 $FeSO_4$	0.00037(*b*)	1	0.00069(*h*)	1	0.00073(*j*)	1

The constants are very nearly proportional to the squares of the concentration of the ferrous sulphate, even between such wide limits as *n*/2 and *n*/50. The effect of acid is almost nothing between *n*/50 and *n*/10, while increasing the acid to *n*/2 decreases the constant in the ratio of about 2 : 3. The reaction, therefore, in the ordinary sense, is trimolecular, or the rate

$$\frac{dX}{d\theta} = K'C^2_{FeSO_4} \cdot (A - X).$$

Replacing *n*-sulphuric acid by *n*-sodium sulphate increases the constant. (Ex. *k*.)

2. Additional experiment on the effect of the concentration of oxygen

Two large bottles were one-quarter filled with a solution of ferrous sulphate containing sulphuric acid (Table III.). In one was placed air and in the other oxygen containing something less than 10 pct nitrogen, so that the relative concentration of the dissolved oxygen in the two experiments was about 1 : 4.5. The bottles were placed on a shaking table in a room of constant temperature. Owing to the small amount of oxidation the concentrations remained practically constant during the experiment.

TABLE III.

Comp'n. of solution: 0.68n $FeSO_4$, 0.68n H_2SO_4. Temp. = 14.5° C

	Interval in hrs	Fe'''	X	Ratio
Air	0	57 mil	0	
	17.5	6550 "	6490	1
Oxygen	0	57 mil	0	
	17.8	31000 "	30940	4.77

The result of this experiment is a confirmation of the conclusion drawn above, that the rate of oxidation is proportional to the concentration of the oxygen.

3. Ferrous chloride

The next set of experiments was made up with ferrous chloride and hydrochloric acid. In spite of all care, however, the constants in each case showed a steady decrease, which in duplicate experiments (*a*, *aa*, and *aaa*) was quite consistent. The ferrous chloride was prepared by dissolving soft iron wire in hydrochloric acid and twice recrystallizing. The oxygen water was saturated with 97 pct oxygen at 19.9° and 753 mm bar and, except in Exp. *f*, 100 cc diluted to 525 cc. The results are given in the following table, to which the same remarks apply as to Table I.

TABLE IV.

Composition of solution	Interval = θ	F'''	X	K
a. $FeCl_2$ 0.0942n HCl 1.0n O_2 959 mil = A	0	54 mil	0	....
	4.95	209	155	0.0155
	8.87	287	233	0.0136
	21.88	459	405	0.0109
	24.01	480	426	0.0106
	47.7	657	603	0.0092
aa. $FeCl_2$ 0.0926n HCl 1.0n O_2 962 mil = A	0	51	0	....
	2.95	154	103	0.0167
	5.66	217	166	0.0166
	19.14	410	359	0.0105
	31.07	543	492	0.0100
aaa. $FeCl_2$ 0.0870n HCl 1.0n O_2 958 mil = A	0	55	0	....
	3.18	162	107	0.0159
	19.42	413	358	0.0104

TABLE IV.—(*Continued*).

Composition of solution	Interval $=\theta$	F'''	X	K
b. $FeCl_2$ 0.0184*n*	0	13 mil	0	....
HCl 1.0*n*	28.03	150	137	0.00236
O_2 968 mil = A	96.28	304	291	0.00161
	145.0	345	332	0.00127
c. $FeCl_2$ 0.47*n*	0	280	0	....
	0.194	422	142	0.388
HCl 1.0*n*	0.422	509	229	0.305
	0.942	700	420	0.292
O_2 893 mil = A	1.606	830	550	0.259
	2.367	937	651	0.244
	18.8	1174	894 end	....
	19.1	1173	893 "	....
	19.4	1173	893 "	....
d. $FeCl_2$ 0.0946*n*	0	42	0	....
HCl 0.02*n*	5.13	68	26	0.00230
O_2 971 mil = A	29.68	169	127	0.00205
	98.27	408	366	0.00209
	166.8	565	523	0.00201
e. $FeCl_2$ 0.0942*n*	0	41	0	....
HCl 0.10*n*	8.53	93	52	0.00280
O_2 972 mil = A	29.22	195	154	0.00256
	98.33	447	406	0.00239
f. $FeCl_2$ 0.0906*n*	0	66	0	....
HCl 1.0*n*	3.68	280	214	0.0140
O_2 1920 mil = A	19.37	722	656	0.0094
g. $FeCl_2$ 0.1*n*	0	41	0	....
HCl 1.0*n*	20.20	54	13	....
O_2 0.0 (blank ex)	167	63	22	....
h. $FeCl_2$ 0.0174*n*	0	9	0	....
HCl 0.1*n*	32.88	40	31	0.000428
O_2 972 mil = A	96.0	69	60	0.000289
j. $FeCl_2$ 0.0185*n*	0	9	0	....
HCl 0.02*n*	31.3	31	22	0.000320
O_2 972 mil = A	94.47	61	52	0.000253
	144.2	75	67	0.000216
k. $FeCl_2$ 0.0934*n*	0	44	0	....
HCl 0.02*n*	3.03	106	62	0.00947
KCl 1.0*n*	8.97	210	166	0.00910
O_2 969 mil = A	20.55	398	354	0.00961
	31.63	464	420	0.00780

The constants are summarized below, as in Table II., the first values being arbitrarily chosen.

TABLE V.

	n HCl	Ratio	*n*/10 HCl	Ratio	*n*/50 HCl	Ratio
n/2 $FeCl_2$	0.39(*c*)	24	....		....	
n/10 $FeCl_2$	0.016(*a*)	1	0.0028(*e*)	6.5	0.0023(*d*)	7
n/50 $FeCl_2$	0.0024(*b*)	1/7	0.00043(*h*)	1	0.00032(*j*)	1

As far as can be judged from the somewhat uncertain values, the rate appears to be proportional to the square of the concentration of the iron in the strong solutions, but between *n*/10 and *n*/50 the relation is nearer a direct proportionality. Contrary to the results with ferrous sulphate, the acid, when concentrated, increases the rate, but between *n*/10 and *n*/50 no effect is apparent. Experiments *a* and *f* show that the rate is proportional to the first power of the oxygen concentration, as in the sulphate.

4. Ferrous acetate

To test the effect of concentration and free acid in the case of the salt of a weak acid, a set of solutions of ferrous acetate was arranged. The preparation of pure ferrous acetate presents many difficulties. The following procedure was adopted. To a boiling solution of ferrous sulphate of known composition a boiling solution of barium acetate — prepared by neutralizing a known weight of barium carbonate with pure acetic acid — was added, in quantity just insufficient to completely precipitate the ferrous sulphate. The barium sulphate was allowed to settle in a vacuum for 36 hours. The clear liquid was then siphoned off into an exhausted receiver, while carbon dioxide was allowed to enter the flask. The solution was analyzed and used as it was, without attempting to remove the trace of harmless ferrous sulphate. In the experiments with dilute acetic acid, the difficulty of determining the ferric salt formed was much increased by the separation of ferric hydrate or basic acetate, which had to be redissolved in boiling sulphuric acid and cooled in vacuo before preparing for the colorimeter. The results follow in Table VI., and their summary in Table VII.

TABLE VI.

Ferrous acetate

Composition of solution	Interval=θ	Fe'''	X	K
a. $Fe(C_2H_3O_2)_2$ 0.061n	0	68	0	....
	0.405	360	202	0.343
$C_2H_4O_2$ 1.0n	0.88	610	542	0.350
	1.04	672	604	0.349
O_2 1066 mil = A	1.56	726	658	0.267
	2.46	742	674	0.176
b. $Fe(C_2H_3O_2)_2$ 0.0206n	0	42	0	....
$C_2H_4O_2$ 1.0n	3.39	142	100	0.0123
O_2 1090 mil = A	16.49	400	358	0.0105
	41.97	562	520	0.0067
c. $Fe(C_2H_3O_2)_2$ 0.060n	0	152	0	....
$C_2H_4O_2$ 0.02n	0.096	680	528	3.49
O_2 982 mil = A	0.41	1014	862	2.23
	18	1132	980 end	....
d. $Fe(C_2H_3O_2)_2$ 0.0205n	0	40	0	....
$C_2H_4O_2$ 0.02n	0.375	116	76	0.0837
O_2 1090 mil = A	2.184	414	373	0.0833
	2.75	522	482	0.0922
e. $Fe(C_2H_3O_2)_2$ 0.101n	0	45	0	....
$C_2H_4O_2$ 0.02n	1.71	138	93	0.0227
H_2SO_4 0.6n	15.93	552	507	0.0171
O_2 1089 mil = A	40.87	878	833	0.0154
f. $Fe(C_2H_3O_2)_2$ 0.0196n	0.028	620	510	9.7(?)
$C_2H_4O_2$ 0.02n	19	1128	1088 end	....
$NaC_2H_3O_2$ 1.0n				
O_2 1090 mil = A				

TABLE VII.

	n $C_2H_4O_2$	Ratio	n/50 $C_2H_4O_2$	Ratio
6/100n $Fe(C_2H_3O_2)_2$	0.35(*a*)	28	3.49(*c*)	41
2/100n $Fe(C_2H_3O_2)_2$	0.0123(*b*)	1	0.084(*d*)	1

Here, more than ever, is seen the enormous influence of the concentration of the ferrous salt, indeed the rate, both with n and n/50 acetic acid, is roughly proportional to the *cube* of the concentration of the ferrous acetate, and the reaction appears to be *tetra molecular*. The acid has a retarding influence, as in the sulphates, only here the effect is more marked. The addition of sodium acetate (Exp. *f*) greatly increases the rate, though the value of the constant in this experiment, in which the whole reaction was complete in the first few moments, can not be relied upon. Experiment *e* (K = 0.023 to 0.015), which contains a large excess of sulphuric acid, and is therefore roughly comparable with Exp. *a* of Table I. (K = 0.01), with the addition of free acetic acid, shows that the acetic acid itself has no very marked catalytic influence on the rate.

5. Discussion of the results

The hope of being able to collate the above results by any simple assumption as to the "mechanism" of the reaction has not been realized. The equation by which the action of oxygen on ferrous sulphate is usually expressed

$$4FeSO_4 + 2H_2SO_4 + O_2 = 2Fe_2(SO_4)_3 + 2H_2O,$$

predicts a marked acceleration in the rate of oxidation on increasing the concentration of the acid, whether the undissociated molecules or the ions be assumed to take part in the reaction. This equation, moreover, would supply no reason for the great difference between the sulphates or chlorides, and the acetates. The hypothesis involving the fewest contradictions appears to be that the minute quantity of hydrolyzed ferrous salt is the part oxidized. On the very rough assumption that the ferrous salt, hydrochloric acid and sulphuric acid are completely dissociated, the concentration of the undissociated $Fe(OH)_2$ would be proportional to the first power of the $FeSO_4$, the first power of the $FeCl_2$, or the cube of the $Fe(C_2H_3O_2)_2$, and would be very much greater with the acetate than with the sulphate and chloride. Moreover, the hydrolyzed part would in each case be strongly decreased by increasing the concentration of the acid, which might account for the retardation in the case of the sulphate and acetate. The comparatively small influence of the acids might be explained by assuming that the effect on hydrolysis is partly compensated for by the acids themselves taking part in the reaction. Although in the case of the sulphates the rate was roughly proportional to the square of the concentration, yet in the weaker solutions, where the above assumptions would be more nearly true, the ratio showed a decided falling off.

6. Influence of temperature

Comparison of the results obtained from the sulphates (§ 1) with those of some earlier rates carried out at 15°, which, however, on account of impure carbon dioxide, are only approximately correct, shows that the influence of temperature is within the limits usually observed for other reactions. In the oxidation of $n/10$ $FeSO_4 + n\ H_2SO_4$ the rate is increased between three- and fourfold for a rise of temperature of 15°.

In this connection two experiments will be described, which may be of interest to analysts. They show the needlessness of some of the precautions usually prescribed for the preparation of volumetric solutions of ferrous sulphate from iron wire. In these experiments about 75 cc of dilute sulphuric acid (approx. $3n$) were put into small Erlenmeyer flasks and heated over a Bunsen flame. A continuous stream of air was bubbled through during the operation. 1.4 grams of iron wire were used in each case.

	A	*B*
	P.M.	P.M.
Flame lighted and air current started	12:00	12:34
Flame withdrawn	12:05	12:45
Iron added and flame replaced	12:06	12:46
Iron dissolved and air stopped	12:25	12:53
A was cooled immediately under the tap, *B* was boiled for twenty seconds, placed under the tap and the air current started again at		12:54
Completely cold at	12:26	12:55
After diluting to 250 cc, analysis of ferric iron showed	0.000044*n*	0.000051*n*
Percent of total iron oxidized	0.044%	0.051%

This procedure *without* the bubbling air gives an oxidation of the total iron of about 0.03 pct. The essential precautions to prevent oxidation are: (1) To have the acid boiling before adding the iron. (2) To cool as rapidly as possible. (3) To dilute as much as possible. (See results of the experiments on ferrous sulphate, § 1.) It may be noted here that numbers of materials, such as rubber stoppers, filter paper, the hand, etc., exert a slight accelerating influence, so that contact with such substances should be avoided.

7. Summary

The main facts established by the above results are: (1) The oxidation of weak ferrous sulphate and chloride solutions by free oxygen is unexpectedly slow. (2) The rate of oxidation of ferrous sulphate is proportional to the concentration of the oxygen and roughly to the square of the concentration of the ferrous iron. (3) The rate of oxidation of the chloride varies directly with the concentration of the oxygen and roughly with that of the ferrous iron. (4) The rate of oxidation of ferrous acetate is approximately proportional to the cube of its concentration. (5) The influence of free acid in no case reaches direct or inverse proportionality to the concentration. In the cases of sulphate and acetate, addition of the acid retards the rate. (6) Incidentally the applicability of a colorimetric determination of ferric iron has been demonstrated.

In conclusion, I wish to express my sincerest thanks to my instructor, Dr. F. B. Kenrick, for suggesting this research, and for his advice and assistance throughout the work.

University of Toronto,
Chemical Laboratory,
June 25, 1901.

SOME APPLICATIONS TO CHEMISTRY OF J. J. THOMSON'S WORK ON THE STRUCTURE OF THE ATOM[1]

BY FELIX LENGFELD

The work of Thomson is so full of suggestion to the chemist that it seems important to call attention to a few of the points in which it enables us to elucidate and round out some generally accepted theories, more particularly the ionic theory, the solution tension theory, and the periodic law. Applied to the ionic theory, we find that a salt like sodium chloride dissociates in solution, not into positively charged sodium and negatively charged chlorine atoms, but into chlorine atoms plus one corpuscle and sodium atoms minus one corpuscle. The chlorine ion has therefore a greater mass, the sodium ion a smaller mass than the corresponding atom. The corpuscle being electronegative, the chlorine ion is electronegative to the chlorine atom and the sodium ion electropositive to the sodium atom. The atom can be regenerated only by restoring the lost or removing the extra corpuscle, and this is done in many chemical reactions and in electrolysis. In the latter we may suppose that the chlorine ions give up their corpuscles to the anode, that these diffuse in the system outside of the electrolyte from the anode to the cathode, there to replace those taken up by the sodium ions. Or the chlorine ion may be neutralized at the anode, and though the neutral chlorine atom of n corpuscles is stable, that of $n + 1$ corpuscles may be unstable and lose the extra corpuscle. This would diffuse through the solution and at the cathode take up a negative charge and add to the sodium ion, or replace in the cathode the corpuscles that have been taken up by the sodium. We can thus explain the heavy charges of the ions, whose origin has seemed to many the weak spot of the ionic theory.

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[1] Thomson, Phil. Mag. 44, 293; 46, 528; 48, 547; 50, 279. See also Am. Chem Jour. 25, 340; Crew, Astrophysical Journal, 11, 170, and Townsend, Proc. Roy. Soc. 65, 192.

Few theories have been more fruitful than the solution tension theory, and yet it is hard to see why the metal should send ions into the solvent, and Nernst himself recognized this difficulty at the beginning.[1] When a metal plate is placed in water the plate becomes negative, the solution positive, yet there is little reason to think that the positive metal ions exist as such in the plate before contact with the solvent, or that the metal molecule consists of positive and negative ions, of which the former go into solution, leaving an excess of the latter. The difficulty vanishes if we suppose that diatomic metal molecules go into solution and there split largely into positive ions (1 atom minus 1 corpuscle) and negative ions (1 atom plus 1 corpuscle).[2] The negative ions being less soluble than the positive deposit upon the zinc, which becomes negative, the solution becoming positive. The latter is saturated with positive metal ions, with negative ions and with metal molecules. As in other saturated solutions, the product of positive and negative ions is a constant. The addition of a salt of the metal must therefore by increasing the positive ions diminish the negative. As, however, there is equilibrium between negative ions in the solution and in the plate, a diminution of these in the solution must be attended with a corresponding decrease in their concentration in the plate which becomes less negative. At the same time the concentration of positive ions in the plate must increase to keep pace with the increase in the solution, and this may become so great that the positive ions in the plate will predominate and the latter become positive. If the negative ions of the plate are partially destroyed (as for instance by connecting a zinc plate with a more positive copper plate), negative ions come from the solution to maintain equilibrium, but more positive ions go into solution, so that more of the metal (zinc) dissolves. If positive ions of the plate are destroyed, the opposite effect is produced and, as the

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[1] Zeit. phys Chem. 4, 153 (1899).

[2] Professor Stieglitz, of this laboratory, has held for several years that chlorine in aqueous solution dissociates into positive and negative ions, and only stress of other work has prevented him from carrying out experiments planned to prove his theory.

positive ions are much more soluble than the negative ions, metal is precipitated. Thus the phenomena attending the solution of metals, even in the primary cell, are similar to those connected with the solution of a salt. It may be urged that we know nothing regarding the negative metal ion, and that many metals are apparently monatomic. We know nothing, however, regarding the molecular weights of the solid metals and the data regarding their molecules in solution are not sufficiently definite to exclude the possibility of a not inconsiderable proportion of diatomic molecules.

A chemist may be pardoned for dilating upon the slight hint thrown out by Thomson's work, as to a possible manner in which the atoms may be built up of corpuscles and obey the periodic law. If the hydrogen atom is composed of hundreds and the uranium atom of tens of thousands of corpuscles, it seems as if there should be thousands of elements between the two. Or if the elements are built up of corpuscular molecules, each of which consists of a large number of corpuscles, the relation of the atomic weights, or rather of the differences of atomic weights, to one another should be simpler than shown by determination of those constants.

It seems possible that the arrangement of the corpuscle in the atom is that of Mayer's group of magnets floating in a magnetic field. Of the thousands of possible atoms, comparatively few were stable under the conditions of formation.[1] They were formed, and unless unstable under present conditions, are our elements. Some readily lose or take up one, two, or more corpuscles and form the univalent, bivalent, etc., elements. Others neither take nor give up corpuscles and may form the helium argon group. Accepting the Mayer arrangement, each atom is made up of nucleus and periphery, certain properties depending on the shape, size, etc., of the nucleus, others on the periphery. The group properties might depend on the nucleus and chlorine, bromine and iodine or sulphur, selenium and tellurium have the same or similar nuclei. The peripheries of

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[1] Crookes. Am. Chem. Jour. 9, 232; Jour. Chem. Soc. 1889, 284.

sulphur and chlorine, though both members of the same period, need not be the same, but the variation in periphery from sulphur to selenium would be of the same order as from chlorine to bromine. Thus if one element with a nucleus N have a greater atomic weight than another element with the nucleus M, peripheral changes would be such that in general all elements with nucleus N would have greater atomic weights than corresponding elements with nucleus M. But the changes being merely of the same order, this need not always be the case, and we might have exceptions like tellurium and iodine. The peripheral change from selenium to tellurium may be so much greater than that from bromine to iodine as to account for the greater atomic weight of the former and yet remain of the same order. Or it may be that all members of one family have the same nucleus, and all members of one period the same periphery, but then we can account for the irregular variations in the atomic weights only by supposing that the weight of the atom is not the sum of the weights of the corpuscles and that the law of the conservation of mass does not apply to bodies smaller than atoms. Of course many of the suggestions put forward in this paper are purely speculative, but Thomson's work promises to bring into the field of experiment much that has been speculative, and it would not be surprising if it led to a scientific study of that most fascinating of all problems — the transformation of the elements.

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SOLUBILITY OF GYPSUM IN AQUEOUS SOLUTIONS OF CERTAIN ELECTROLYTES[1]

BY FRANK K. CAMERON AND ATHERTON SEIDELL

The results obtained in the study of the solubility of gypsum in aqueous solutions of sodium chloride[2] were of such a character as to make it appear desirable to obtain data for other solutions of a similar kind. The work was therefore continued and a description of the investigation is here recorded. The solubility of gypsum was therefore determined in solutions of magnesium chloride, calcium chloride, sodium sulphate, and in solutions of sodium chloride when calcium carbonate in the solid phase was also in contact with the solution.

All these determinations were made at temperatures from 23° C to 26° C. The temperature of the laboratory held quite constantly within these limits and, as slight changes of temperature were found to affect the solubility of gypsum in these solutions but very little, it was not deemed necessary to use a constant temperature bath.

It is desirable, for some reasons, both scientific and technical, that determinations should be made at other temperatures, especially above 40° C; but the exigencies of the public service hardly seemed to warrant their being made at this time.

Instead of gypsum, precipitated calcium sulphate, obtained from The Baker and Adamson Chemical Co. and labeled c. p., was used in these experiments. It was found by examination of a few solutions that, as was the case in sodium chloride solutions described in the preceding paper, the same results were obtained with gypsum and with precipitated calcium sulphate; but that the solutions came to equilibrium more rapidly when the latter was used. The other salts used in the investigation were chemically pure materials obtained from the same firm.

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[1] Published by permission of the Secretary of Agriculture. See Bul. 18, Division of Soils, U. S. Department of Agriculture.

[2] Jour. phys. Chem. 5, 556 (1901).

The general method of procedure was the same in all cases. A series of solutions of various concentrations with respect to the readily soluble salt was prepared, and enough calcium sulphate added to insure an excess of this substance in the solid phase. The solutions were then set aside for periods of from one to six weeks, with occasional vigorous shaking.

The solutions were generally of about 700 cc volume and were contained in liter Florence flasks fitted with rubber stoppers, to prevent evaporation of the solvent. When ready for analysis, they were allowed to settle, and appropriate portions of the clear supernatant solutions were drawn off with a pipette, and whenever this procedure seemed advisable, they were filtered. The analytical operations were conducted according to the conventional methods and call for no special comment. The amount of calcium sulphate which had dissolved was calculated from the amount of sulph-ions found in the solution. The results obtained are presented graphically in Fig. 1, the ordinates represent reacting weights per liter of calcium sulphate, and the abscissas represent reacting weights per liter of the more soluble salt used.

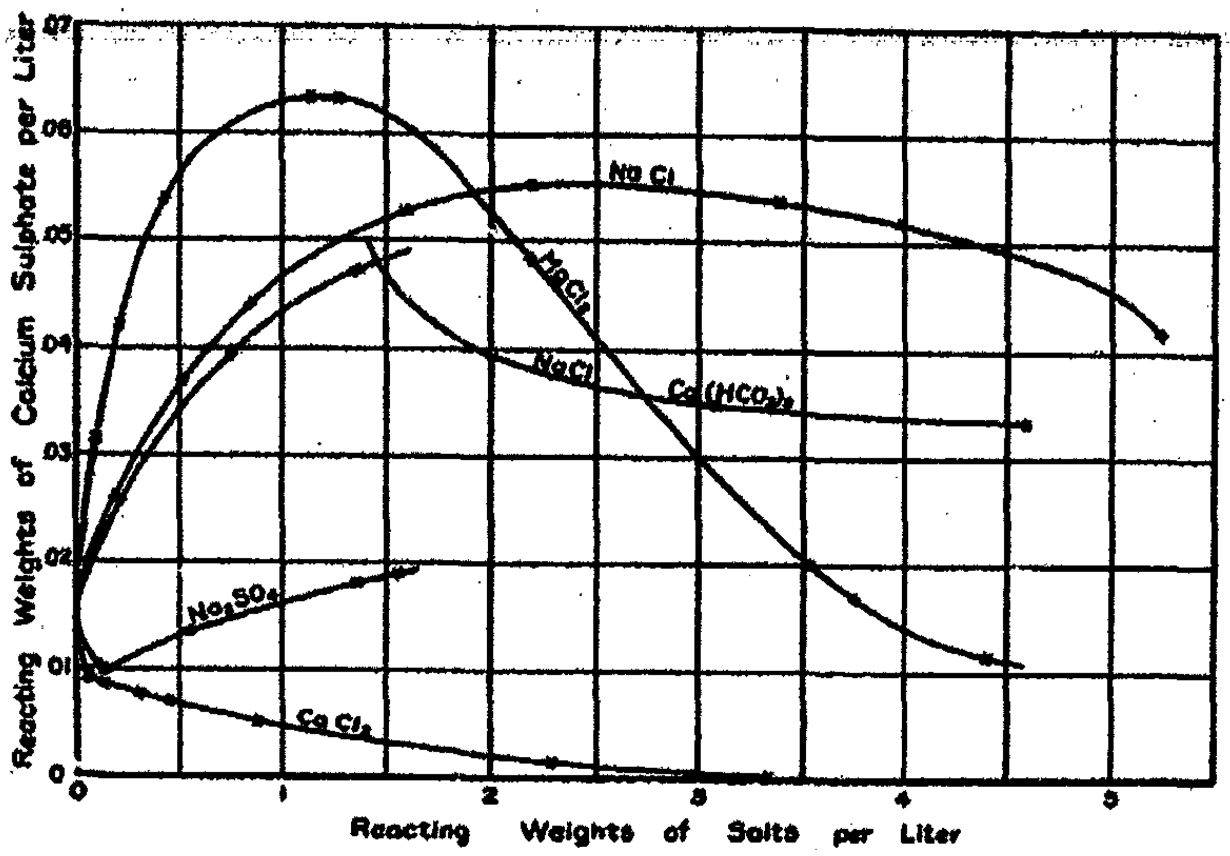

Fig. 1

For some reasons it seemed more advisable to give the results in terms of calcium sulphate found in the solution rather than in amounts of gypsum found to be soluble. These latter can always be readily obtained by multiplying the given results by the factor 1.2647.

Although the temperature was not quite the same for these different series of determinations, in all these series it was found that such small differences of temperature as are involved here have such a small influence on the solubility of the calcium sulphate that these curves may fairly be considered as entirely comparable.

Solubility of calcium sulphate in magnesium chloride solutions

It was found that the curves illustrating this case showed unusually well-marked maximum points. Therefore it was deemed advisable to determine the curve with reference to a constant weight of the solvent water as well as to a constant volume of the solution. The data obtained at 26° C are given in the accompanying table, which is self-explanatory. The results, referred to a constant volume of solution, are presented graphically.

TABLE I.

Solubility of calcium sulphate in aqueous solutions of magnesium chloride at 26° C

H_2O (grams per liter)	$CaSO_4$		$MgCl_2$	
	Grams per liter	Reacting wts. per liter	Grams per liter	Reacting wts. per liter
997.924	2.082	0.0154	0.000	0 0000
996.520	4.258	0.0315	8.501	0.0900
994.489	5.692	0.0421	19.175	0 2030
989.143	7.588	0.0561	46.640	0.4938
972.218	8.622	0.0638	121.381	1.2850
949.950	6.567	0.0486	206.985	2.1912
908.678	2.774	0.0205	336.986	3.5674
878.588	1.385	0.0102	441.128	4.6699

TABLE I.—(*Continued*).

$CaSO_4$		$MgCl_2$	
Grams per 1000 grams of water	Reacting weights per 1000 grams of water	Grams per 1000 grams of water	Reacting weights per 1000 grams of water
2.086	0.0154	0.000	0.0000
4.273	0.0316	8.531	0.0903
5.724	0 0423	19.860	0.2102
7.674	0.0568	47.170	0.4993
8.867	0.0656	124.800	1.3212
6.913	0.0511	217.900	2.3068
3.553	0.0263	370.900	3.9265
1.577	0.0116	502.000	5.3144

By interpolation on the curves it appears that the maximum solubility for calcium sulphate is about 8.8 grams per liter in a solution containing about 105 grams per liter of magnesium chloride. In this solution, therefore, there is more than four times as much calcium sulphate as in a saturated solution of this substance alone. Calculated as gypsum, this maximum solubility is 11.129 grams per liter, or 4.23 times as much as is soluble in pure water. Beyond the maximum point the solubility of the calcium sulphate decreases quite rapidly as the concentration with respect to magnesium chloride increases, this decreasing solubility being much more rapid than in the corresponding curve for the solubility of gypsum in sodium chloride solutions. This decrease in solubility continues until in a solution containing about 370 grams magnesium chloride per liter the solubility of gypsum is the same as in pure water. Therefore, even in the presence of this salt, which does not yield a common ion, the solubility of gypsum is less at high concentrations than in pure water.

The curve plotted from the data obtained on the basis grams of salt per 1,000 grams of the solvent is of the same general nature as the curve plotted on the basis of a constant volume of solution, and shows about equally well the character of the phenomena involved. The former lies slightly above the latter, and it does not seem worth while to chart it here. Attention is called to it for it also shows, in a most striking way, the real existence of a maximum point on the solubility curve. It would seem that this pair of electrolytes may be particularly well adapted to the further study along the general lines indicated by the investigation here described.

Another point of interest in the curves for this pair of electrolytes is the wavy character for the higher concentrations with respect to magnesium chloride. To what this may be due can not be said at present, but it shows that in all probability complex molecular or ionic changes must take place in the solution at these higher concentrations and that the subject is much in need of further investigation.

By referring to Fig. 1 it will be observed that the maximum point on the curve for magnesium chloride occurs at about half the concentration that it does on the curve for sodium chloride; that is, at about the same concentration for chlorine in the two cases, since a reacting weight of magnesium chloride contains twice as much chlorine as does a reacting weight of sodium chloride. But the total amount of calcium sulphate is different in the two cases, showing that magnesium and sodium have markedly different properties, at least in degree, under such circumstances.

Solubility of calcium sulphate in calcium chloride solutions

In the preparation of the calcium chloride solutions for this series of experiments it was found that the solutions were more or less turbid, due to undissolved calcium hydrate originally present in the supposed chemically pure calcium chloride used. A few drops of methyl orange solution were therefore added in each case, and then hydrochloric acid, until the indicator showed the solutions to be neutral. The solutions became perfectly clear and free from suspended matter. The calcium sulphate was then introduced and the usual procedure followed.

In this case the two salts will yield a common calcium ion, and in consequence the solubility of the calcium sulphate will be much decreased by the presence of the calcium chloride. This is shown by the accompanying table of results, obtained on a series of experiments made at 25° C. It is even more strikingly brought out by the graphical representation of the results. The observations on this pair of electrolytes made by Tilden and Shenstone[1] and by Lunge[2] agree in general with the results given here.

TABLE II.

Solubility of calcium sulphate in aqueous solutions of calcium chloride at 25° C

$CaSO_4$		$CaCl_2$	
Grams per liter	Reacting weights per liter	Grams per liter	Reacting weights per liter
2.056	0.01521	0.000	0.00000
1.244	0.00921	7.489	0.06801
1.181	0.00874	11.959	0.10860
1.096	0.00811	25.770	0.23401
1.080	0.00799	32.045	0.29100
1.016	0.00752	51.530	0.46794
0.841	0.00622	97.023	0.88106
0.465	0.00344	192.705	1.74996
0.203	0.00150	280.303	2.54543
0.032	0.00024	367.850	3.34045

The solubility of the calcium sulphate decreases very rapidly as the concentration with respect to calcium chloride increases, until a concentration of about 20 grams per liter of this latter salt is reached. From this point the solubility of the calcium sulphate decreases more slowly, but steadily, until by extrapolation on the curve it would seem that the solution containing 375 grams per liter of calcium chloride would dissolve practically no calcium sulphate.

Just why there should be so marked a change in the solubility of the calcium sulphate in solution concentrations of about 2 percent calcium chloride does not admit of explanation as

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[1] Proc. Roy. Soc. 38, 335 (1885).

[2] Jour. Soc. Chem. Ind. 4, 31 (1885).

yet. It is possible that at concentrations above this the calcium chloride may partially dissociate in such a way as to form complex ions containing both calcium and chlorine,[1] and thus diminish the proportional effect of calcium as ions in the solutions forcing back the dissociation of the calcium chloride, and consequently the retarding effect upon the solubility of the calcium sulphate. It seems probable, however, that the density of the solvent itself may have an important rôle in this connection.

The solubility of calcium sulphate in sodium sulphate solution

In this case it is to be expected that the two electrolytes would yield the common sulph-ion, therefore the solubility of gypsum should decrease as the concentration with respect to sodium sulphate increases. Such was found to be the case up to a concentration of about 17.5 grams per liter of sodium sulphate, when the solubility of the calcium sulphate was about 1.38 grams per liter, or 1.745 grams per liter of gypsum. At this point, as the concentration with respect to sodium sulphate increases, there is a sudden change in the direction of the curve and the solubility of the calcium sulphate steadily increases until, in a liter of solution containing 230 grams of sodium sulphate, there will be dissolved 2.5 grams of calcium sulphate — a quantity markedly larger than will be dissolved by pure water. The data obtained for this pair of electrolytes are given in Table III.

Apparently we have to deal with two solubility curves which intersect at the minimum point. Possibly at concentrations with respect to sodium sulphate greater than that at the minimum point the dissociation of the sodium sulphate takes place in part according to the scheme:

$$Na_2SO_4 \rightleftarrows \overset{+}{Na} + \overline{NaSO_4}$$

rather than entirely as indicated thus:

$$Na_2SO_4 \rightleftarrows \overset{+}{Na} + \overset{+}{Na} + \overline{SO_4}.$$

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[1] Noyes. Phys. Rev. 12, 15 (1901) ; Jour. Am. Chem. Soc. 23, 37 (1901); Zeit. phys. Chem. 36, 61 (1901).

If this be so, it is tantamount to introducing a substance into the solution which does not yield a common ion with calcium sulphate, and which therefore may be expected to increase the solubility of the latter. We thus have the sodium sulphate exerting two effects on the solubility of the calcium sulphate, depending on the way in which it dissociates. These two effects are opposite in direction, and in consequence the resulting effect will be dependent on the relative amounts of the dissociation in the two different ways, which is dependent in turn upon the concentration of the solution with respect to the sodium sulphate itself.

TABLE III.

Solubility of calcium sulphate in aqueous solutions of sodium sulphate at 22° C

$CaSO_4$		Na_2SO_4	
Grams per liter	Reacting weights per liter	Grams per liter	Reacting weights per liter
2.084	0.0154	0.000	0.0000
1.583	0.0117	2.771	0.0196
1.433	0.0106	13.820	0.0979
1.408	0.0104	16.360	0.1159
1.569	0.0116	39.310	0.2786
1.841	0.0136	77.320	0.5480
2.185	0.0162	133.000	0.9425
2.414	0.0178	193.800	1.3734
[a]2.578	[a]0.0190	[a]222.580	[a]1.5773

From this point of view one would expect the existence in the solution of a double salt, possibly of the composition $Ca(NaSO_4)_2$. Such a salt is, probably, the mineral glauberite, found in nature. Fritzsche[1] describes a hydrated double sulphate ($CaSO_4.Na_2SO_4.2H_2O$), obtained by heating gypsum with a small amount of water and a large excess of Glauber salt ($Na_2SO_4.10H_2O$). The substance was a well characterized one,

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[1] Jour. prakt. Chem. 72, 291 (1857).

[a] Both calcium sulphate and sodium sulphate as solid phases were in contact with the solution.

crystallizing in fine needles, which, on heating, quickly lost the water it contained, yielding the anhydrous double salt. It was expected, therefore, that this salt, or its hydrate, might be obtained by evaporating solutions of sodium sulphate saturated with respect to calcium sulphate. Such solutions were prepared and allowed to evaporate spontaneously at room temperature. No evidence of the presence of the double salt, however, could be detected in the residue after evaporation of the water. It should be remembered that in those areas where this double calcium sulphate has been observed in nature, the ground temperatures are frequently very high and the equilibrium condition of the solution may well be very different from those obtaining at 25° C.[1]

An experiment was then made to see if the composition of the solid phase would affect the composition of a solution in contact with both salts in the solid phase. Four vessels were prepared. In each was placed 100 cc of water and 40 grams of sodium sulphate and 1, 2, 5, and 10 grams of calcium sulphate, respectively, insuring the presence of both salts in the solid phase. The vessels were then placed in a shaking apparatus and shaken constantly for four days. The contents were allowed to settle and the supernatant solutions quickly decanted upon folded filters. Aliquot portions of the filtrates were analyzed for calcium and sulphates. It was found that the composition of the solid phase apparently did not effect the composition of the solution, practically identical results being obtained in all four analyses. The solution in contact with both salts in the solid phase was found to contain 222.5810 grams per liter of sodium sulphate and 2.5783 grams per liter of calcium sulphate. It is desirable that some one, with time and opportunity for it, should

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[1] van 't Hoff and Chiaraviglio [Sitzungsber. Akad. Wiss. Berlin, 1899, 810] have shown that gypsum and the decahydrate of sodium sulphate will form glauberite at 25° C. if the solution be saturated with respect to both these salts and sodium chloride as well. This last substance is commonly, though perhaps not always, found in those areas from which glauberite has been reported as occurring in nature. These authors have also shown that glauberite and gypsum exist together as solid phases only when solid sodium sulphate, decahydrate, is not also present.

take this matter up and investigate the system throughout a range of temperature. It is a subject of considerable practical importance in several technical operations, as well as in geological and soil studies.

It follows from these experiments that, considerable amounts of sodium sulphate being in the solution, the solubility of calcium sulphate or gypsum may be relatively great, instead of falling to a very small figure; and the amount of gypsum in contact with the solution in the solid phase will not have any effect in determining the amount that will go into solution at ordinary temperatures, even though sodium sulphate also be present in the solid phase.

Solubility of calcium sulphate in aqueous solutions of sodium chloride and in the presence of solid calcium carbonate

In order to obtain light on some problems which had been referred to this laboratory for explanation, it was determined to study the solubility of calcium sulphate in sodium chloride solutions when calcium carbonate in the solid phase was also in contact with the solution. The solubility of this latter salt is dependent upon the partial pressure of the carbon dioxide in the gaseous phase in contact with the solutions. Therefore, air which had been previously washed in dilute sulphuric acid was bubbled through the solutions for fifty-one days, or until they came to equilibrium.[1] The addition of phenolphthalein to the solution did not show the presence of normal carbonates in any of the solutions. The amounts of bicarbonates found, in the equivalents of calcium hydrogen carbonate dissolved, are given in Table IV.

The variation in the solubility of the calcium carbonate in the solutions of sodium chloride when gypsum was also present in the solid phase will be discussed in more detail in a following paper. The effect of the presence of the calcium carbonate upon the solubility of the calcium sulphate is most strikingly

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[1] It is very probable that these solutions had come to final equilibrium within eighteen days, but the passage of air through them was continued to make certain that such a condition had been reached.

brought out in the graphic presentation of the results. From a point representing no sodium chloride in solution up to a concentration for this latter salt of somewhat more than 80 grams per liter, the curve follows very closely the curve representing the solubility of calcium sulphate in the presence of sodium chloride alone. The solubility of calcium sulphate steadily increases with increasing concentration of sodium chloride, but at a somewhat diminishing rate from that which obtains when no calcium carbonate was present. As the amount of sodium chloride increases beyond 80 or 100 grams to the liter, the solubility of the calcium sulphate steadily decreases and apparently follows a new curve, the two curves probably intersecting as charted and not forming a continuous curve with a maximum point, as in the case when there is no calcium carbonate present.

TABLE IV.

Solubility of calcium sulphate in aqueous solutions of sodium chloride in contact with solid calcium carbonate

$CaSO_4$		$Ca(HCO_3)_2$		NaCl	
Grams per liter	React'g wts. per liter	Grams per liter	Reacting wts. per liter	Grams per liter	Re'c'g wts. per liter
1.9298	0.0143	0.0603	0.000375	0.000	0.0000
2.7200	0.0201	0.0724	0.000450	3.628	0.0625
3.4460	0.0255	0.0885	0.000550	11.490	0.1979
5.1560	0.0381	0.1006	0.000625	39 620	0.6824
6.4240	0.0475	0.0603	0.000375	79.520	1.3696
5.2720	0.0390	0.0563	0.000350	121.900	2.0995
4.7860	0.0354	0.0482	0.000300	193.800	3.3379
4.4620	0.0330	0.0402	0.000250	267.600	4.6090

It thus appears that while the solubility of gypsum in solutions of sodium chloride would be but little affected by the presence of calcium carbonate up to 8 or 9 percent solutions, beyond this point its solubility would be considerably diminished. But in solutions nearly saturated with respect to sodium chloride the gypsum would be about twice as soluble as in pure water, even though calcium carbonate be present.

It is interesting to note that while the solubility of calcium sulphate is only about 2.1 grams per liter in pure water, it reaches a maximum solubility of about 7.5 grams per liter in solution containing 140 grams per liter of sodium chloride. But this solubility would be reduced to about 5 grams per liter if calcium carbonate were present, and in the presence of this latter substance the maximum solubility of calcium sulphate is about 6.35 grams per liter in a solution containing only about 80 to 90 grams per liter of sodium chloride.

Summary

By reference to Fig. 1 it will be seen that up to the tenth-normal solution the solubility curves in all cases follow, qualitatively at least, the direction indicated by an application of the mass law to the hypothesis of electrolytic dissociation. This is still true for calcium chloride solutions at high concentrations, but in the other cases here recorded it is not true, and it would have been quite impossible to have predicted the character of these solubility curves *à priori*.

The phenomena which have been described in this paper lend support to the view that ionic complexes are formed in solutions of high concentration. Noyes,[1] in a recent publication, has brought forward evidence to show that such ionic complexes are probably in solutions of the chlorides of the alkaline earths, even at quite high dilutions. The investigations in recent years lend much evidence pro and con to the view that such complexes exist, not only in aqueous solutions, but in other solvents.[2] Of great interest in this connection is the fact brought out by Walden[3] that binary electrolytes in general dissociate much more readily than do ternary or quartenary electrolytes. Since it is to be presumed that ternary electrolytes were present in all the solutions studied in this investigation, it is not so surprising, therefore, that abnormal results were observed at the higher concen-

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[1] loc. cit.

[2] See Jones. Am. Chem. Jour. 25, 232 (1901).

[3] Zeit. anorg. Chem. 25, 209 (1900).

trations. It seems most probable that all these facts are dependent upon, or at least causally connected with, the considerable condensation of the solvent which takes place when solutes, especially electrolytes, go into the solution; and that much of interest for the general theory of solutions could be obtained by a systematic investigation from this point of view.

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NEW BOOKS

Die heterogenen Gleichgewichte, vom Standpunkte der Phasenlehre. *Erstes Heft: Die Phasenlehre: Systeme aus einer Komponente. By H. W. Bakhuis Roozeboom. 14 × 22 cm; pp. xiii + 217. Braunschweig: Friedrich Vieweg und Sohn, 1901. Price: paper, 5.50 marks.* — The first volume deals solely with one-component systems; the second is to be devoted to two-component systems, and the third to poly-component systems. In a forty-five page introduction the author first traces the historical development of the conception of a definite relation between pressure and temperature; he next deduces the phase rule and then discusses the chief characteristics of invariant, monovariant, divariant, and polyvariant systems

As the title of the book indicates, one-phase systems are not discussed. In the volume before us, the author first discusses the boundary curves for liquid and vapor, solid and vapor, solid and liquid. The triple point at the intersection of these three curves is next considered. We then pass back to the equilibrium between two stable solid phases and the triple point with solid, solid and vapor in equilibrium. A chapter on flowing crystals follows, in which it is shown that these are properly to be considered as a solid phase and that the first inversion point is one for solid, solid and vapor. Next comes a chapter on instable triple points in the case of enantiotropic systems, and then one on the behavior of monotropic substances. The volume closes with a chapter on the triple point, solid, solid, liquid, one on the triple point solid, solid, solid, and a final chapter in which the general question of uniform and non-uniform pressure is considered.

There are a number of special points in the treatment which are of great interest. Under the equilibrium between liquid and vapor there is a discussion of the question of polymerization in liquid or vapor in its bearing on phase rule problems. It is a question of reaction velocity and of time. If the rate at which equilibrium is reached be sufficiently high, the system will behave in every respect like a one-component system and the existence of two or more modifications in liquid or vapor can be shown only by a study of such properties as vapor density, surface tension, heat of vaporization, etc. If the rate of change be low and the time of observation be long, we shall again find the properties of one-component systems, while a more rapid study will betray some of the characteristics of two-component systems. Ramsay's experiments on the isothermal compression of acetic acid seem to show that the time factor is here not absolutely negligible. With some of the enol and keto substances the time factor becomes an important item, while with acetaldehyde it is practically impossible to treat the system as containing only one component unless one adds a catalytic agent. With some of the di-substituted benzene compounds, we are not yet able to make them act experimentally like a one-component system. There is thus a continuous gradation from one-component systems in which the presence of two or more modifications in liquid or vapor cannot be shown by phase rule methods to one-component systems which require a knowledge of the theory to enable us to recognize them as such.

There is a very thorough discussion of the equilibrium between solid and liquid. The author considers that the evidence is distinctly against the existence of a critical point; but he does not look upon Tammann's hypothesis of a closed curve as established. The suggestion is made that cases may occur in which the pressure-temperature curve for solid and liquid does not cut the corresponding curve for liquid and vapor. Under such circumstances a solid phase can be obtained only by cooling under pressure.

Owing to the fact that some solids, azoxyanisol for instance, are more fluid than some liquids, such as glass, the author suggests that it might be well to drop the terms solid and liquids, substituting therefor the terms crystalline and amorphous. This hardly seems a wise suggestion. Quite apart from the fact that we have no noun corresponding to the adjective amorphous, it must be remembered that gases are amorphous and that we are introducing more of an ambiguity than we eliminate. It does not seem to the reviewer to be asking too much to have solid connote crystalline structure and to separate the conception of distinct mobility from the term liquid.

The author criticizes Ostwald's generalization that in case of sudden change that form first appears which involves least loss of free energy. The conclusion reached is that "the observations show merely that this sometimes occurs."

A few years ago, no case was known of a triple point with three solid phases in equilibrium. Owing to Tammann's investigations we can now cite three cases with an approximate degree of accuracy:

Ammonium nitrate at a temperature of 64.2° and a pressure of 930 atm; silver iodide at a temperature of about 100° and a pressure of about 2950 atm; ice at a temperature of −37° and a pressure of 2240 atm.

The thermodynamic relations introduced in this volume consist practically of the relation between pressure, temperature, and heat effect.

The reviewer would have been pleased if stress had been laid on the inadequate state of our knowledge in regard to allotropic forms of the elements. One or two elements have been studied with some care and we know something about the conditions of equilibrium. On the other hand one has only to turn over the pages of the monographs by Meslans and by D. Berthelot to see what a mass of inaccurate observations are on file. From the view-point of systematic chemistry it certainly seems as though a careful study of the simplest cases is desirable, either as a preliminary to a study of compounds or as an introduction to the question of a possible transmutation of the elements.

Wilder D. Bancroft

Vorträge für Aerzte über physikalische Chemie. *By Ernst Cohen. 16 × 24 cm; pp. viii + 249. Leipzig: Wilhelm Engelmann, 1901.* — In the preface the author says:

"The fact that a large number of investigations are described in the medical literature of to-day, which are based on modern physico-chemical conceptions, makes it necessary for the physician to have some knowledge of these theories and methods if the researches together with their practical results are not to remain a sealed book to him.

"These lectures are in no sense a text-book of physical chemistry. I have endeavored to make clear the close connection between this new branch of chemistry and the biological science, while I have also met the wishes of my listeners by discussing the most important methods in detail."

This course of physical chemistry for physicians was given in Amsterdam and consisted of seventeen lectures. The subjects of these lectures were as follows: reaction velocity; inversion of cane sugar and catalysis in general; action of ferments; equilibrium phenomena (three lectures); viscosity of liquids; osmotic pressure; determination of the molecular weights of dissolved substances; electrolytic dissociation (two lectures); applications of the theory of electrolytic dissociation (three lectures); electromotive phenomena (two lectures).

To the professional physical chemist the interesting portions of this volume are of course those containing the applications to biological problems. The whole chapter on ferments comes under this head. In the chapter on reaction velocity and temperature we find again the action of ferments, also the slow action of some poisons at low temperatures and the very interesting problems as to the variation of the dose with the temperature of the patient. In the chapters on equilibrium we find a discussion of the behavior of oxyhaemoglobin with reference to oxygen and to carbon monoxide. The chapter on viscosity introduces us to the question of the relation between the viscosity of blood and the other characteristics of the organism. The phenomenon of osmotic pressure was first studied quantitatively by a botanist, and quite recently it has been shown in France that the sprouting of seeds and the general development of the young plant is enormously affected by the strength of the solution in which it grows. The use of the "physiological saline solution" in surgical cases rests on the same principle, though one would rather like to know whether or why it is not better to use a somewhat stronger solution.

Among the applications of the electrolytic dissociation theory we find the study of the toxic action of solutions, the solvent action of salts, and the important question of the solvent. The importance of hydrochloric acid in at least one artificial food now on the market can best be explained by physical chemical observations.

The volume closes with a quotation from Loeb: "In order to accomplish our task we must make adequate use of comparative physiology as well as physical chemistry. Pathology in particular will be benefitted by such a departure."

The author has done his work well and has written a very interesting and profitable book. We must be careful however not to claim too much for it nor for physical chemistry. While it is unquestionable that a knowledge of physical chemistry would prove serviceable to every student of biological problems, it is not probable that such a knowledge would work an immediate and overwhelming revolution. In medicine and biology it is practically impossible to control all the conditions, and progress is consequently relatively slow. Then, too, it must be remembered that the physical chemist has not solved all his own problems yet. The electrolytic dissociation theory has swept everything before it up to now; but the facts are piling up in an ominous way and the difficulties must soon be faced and not dodged. *Wilder D. Bancroft*

Elektrochemisches Praktikum. *By Richard Lorenz. 13 × 19 cm; pp. xiv + 234. Göttingen: Vandenhoeck und Ruprecht, 1901. Price: bound, 6 marks.* — This is by long odds the best laboratory manual for electrochemistry that has been written, and it is, in most respects, a satisfactory book. There are five sections: preliminary exercises; preparations; quantitative analysis; electromotive forces; the electrolytic cell.

Under the first section we get: standardization of an ammeter by means of a copper voltameter; standardization of an ammeter by means of an oxyhydrogen voltameter; comparison of the acid and the alkaline voltameter; preparation of a resistance; determination of the resistance of an electrolytic cell; determination of the resistance capacity of a dip electrode; calculation of the resistance of an electrolytic cell; the electrolytic cell and Ohm's law; determination of polarization by means of a voltmeter; plotting an energy curve by means of polarization discharge through a voltmeter; electrolysis of oxalic acid with constant current; current density; gas-analytical study of a reaction; decomposition of salt with a diaphragm.

Under the second section we find the preparation of potassium chlorate, potassium perchlorate, potassium persulphate, metallic hydroxides, potassium permanganate, potassium chromate, lead disulphate; the electrolytic refining of cadmium, zinc, and mercury; the preparation of iodoform, sodium, and calcium carbide; the reduction of nitrobenzene to azobenzene; the electrolysis of fused lead chloride.

Under section three are chapters on copper, silver, nickel, zinc, cadmium, iron, antimony, tin, mercury, and lead.

The special exercises in section four are: preparation of a standard Clark cell, and of a standard Weston cell; determinations of electromotive force by three methods; electromotive force of cells of the Daniell type; measurement of a concentration cell; precipitation of some metals by hydrogen sulphide; oxidation and reduction cells; determination of single potentials by means of the normal electrode

Under section five are experiments on: transference of the ions: charging and discharging an accumulator; determination of decomposition voltages; separation of silver from copper under definite potential difference; successive reduction of nitrobenzene.

This summary of the contents shows the ground covered by the book. There is just one fault to be found with the treatment. Too little attention is paid to conditions. The copper voltameter is given as an absolute instrument without limitations. Only one experiment is given on the preparation of potassium chlorate or perchlorate. The student actually makes both these substances, but that is all he does. He does not learn what happens if he varies the conditions and consequently he does not learn the importance of determining the best conditions and of holding to those absolutely. He does not learn the difference between the behavior of calcium chloride and of potassium chloride nor the cause of this difference. So it goes throughout. It is of no great value to the student to make a number of preparations, though it does him no harm. It is of great importance to him to learn the fundamental principles and how to solve a new problem.

Another weakness is the indefiniteness of the directions. Take the case of nitrobenzene for instance. No particular size of cathode is specified. The current density is given and the student is told to carry the reaction through to complete reduction. If the cathode surface is 100 cm^2, this calls for a run of over eleven hours at a hundred percent efficiency. That may be practical in Zürich, but it is not in this country. In any case it is unnecessary. So far as may be experiments should be finished in three hours and the quantities of solution should be so arranged as to call for the minimum number of platinum electrodes. This can be done. The reviewer has done it to a limited extent himself. It must be done if a manual of this sort is to have the widespread influence to which its general excellence entitles it. *Wilder D. Bancroft*

High-temperature Measurements. *By H. Le Chatelier and O. Boudouard. Translated by George K. Burgess. 12 × 18 cm; pp. xi + 230. New York: John Wiley and Sons, 1901. Price: bound, $3.00.* — A review of the original French edition has already appeared (4, 394). We now have an English translation, which is as it should be. The book is of such importance that it should be readily accessible to all. The publishers might well have studied the French original in the matter of general appearance. Wider margins would cost but little more and would add enormously to the appearance of the volume.

Wilder D. Bancroft

Research Papers from the Kent Chemical Laboratory of Yale University. *Edited by Frank Austin Gooch. Vols. I. and II. 14 × 21 cm, pp. Vol. I. xiv + 411. Vol. II. x + 415. New York: Charles Scribner's Sons, 1901. Price: cloth, $7.50, net.* — "With the approval of the President and Fellows of Yale University, a series of volumes has been prepared by a number of the Professors and Instructors, to be issued in connection with the Bicentennial Anniversary, as a partial indication of the character of the studies in which the University teachers are engaged." As the title indicates, these two volumes are the contribution from the Kent Chemical Laboratory. There are one hundred and eight papers, covering the period from 1888 to 1901. Of these, eighty-nine are classified by the editor under the heading of analysis and some of the others might easily have been included without straining a point. The record is a brilliant one, but the field covered is narrow. *Wilder D. Bancroft*

Heinrich Hertz — *für die Willensfreiheit? Eine kritische Studie über Mechanismus und Willensfreiheit. By Richard Manno. 15 × 23 cm; pp. 67. Leipzig: Wilhelm Engelmann, 1900. Price: paper, 1.50 marks.* — A philosophical study. It presents, successively, an analysis of the idea of mechanism, an examination of the content of the principles of mechanics, and a formulation and interpretation of the ideas of causality and of necessity.

J. E. Trevor

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