Adhesive tape on the end of the tube makes a cylinder just large enough to slip into a rubber tube carrying the desired sample of smoke. After precipitation has taken place, the air passes through a flowmeter to determine the volume of sample taken.

The glass rod which is sealed to the end of the central wire extends somewhat beyond the edge of the aluminum foil thus securing a margin of safety for the deposit of smoke. The appearance of the deposit is usually sufficient to show whether complete precipitation has taken place. At the entering end of the foil there is a sharp line of demarcation between the bare foil and the deposit, corresponding to the junction of the central wire and the glass rod. Beyond this line of demarcation, the deposit gradually tapers off leaving a couple of inches of bare foil at the other end.

The high voltage direct current for the operation of the apparatus was obtained by stepping up from 110 volts, alternating current, and then rectifying with a General Electric Company "Kenotron." It was possible to use in the neighborhood of 15,000 volts without sparking. A mechanical rectifier for the current was tried in place of the Kenotron but for some reason this led to increased sparking.

In general it was found possible to pull a fairly concentrated sample of smoke through the apparatus at a speed of about 5 liters per minute and obtain complete precipitation.

The use of the apparatus, in following the behavior of smokes, will be considered in a subsequent article.

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THE EQUATION OF STATE FOR LIQUIDS AND VAPORS. I. THE VAPOR PHASE OF ETHYL ETHER.

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CONTENTS.—1. Theoretical Considerations. 2. The Experimental Method. 3. Preparation of the Material. 4. Discussion of the Older Data. 5. The Newly Measured Isometrics of Ethyl Ether. 6. Interpretation of All Experimental Data Relating to the Vapor Phase. 7. Summary.

1. Theoretical Considerations.

Many experimental researches have been carried out for the purpose of supplying data bearing on the pressure-volume relation of substances. These researches may be said to have been inspired for the most part by the desire to supply a basis for testing adequately certain equations of state or for providing a more extended body of data upon which, perhaps by purely empirical means, a satisfactory equation might be built up.

The evident importance to steam engineering, refrigerating engineering, and other industries involving the use of fluids, of discovering the mathematical form of the equation of state would be difficult to overestimate. By means of it the properties of the technically used substances, such as water, ammonia, sulfur dioxide, methyl chloride, among others, could be accurately computed from a small body of experimental data, providing thereby accurate tables by which the performance of machines using the substances could be controlled. Useful as it would be, however, for practical purposes to possess the form of the equation of state for substances, the benefit to chemistry and physics would be of tremendously greater importance. A proper understanding of the specific heats of substances, and of the general chemical equilibria of reactions is impossible without the relation; to say nothing of the stimulus to the development of the dynamical theory of fluids which would follow the establishment of the mathematical form of the equation.

As an example of the service to chemistry that would be rendered by an exact equation of state, reference may be made to the problem of calculating from a few equilibria measurements made under attainable experimental conditions the equilibria at other temperatures and at high pressures. In the ammonia synthesis, for example, it is desirable to operate at pressures amounting to 100 atmospheres or more. The assumption of the perfect gas laws which suffice to treat the equilibrium at one atmosphere is of no real value when the pressure amounts to 100 atmospheres or more. An exact equation for each of the substances[1] would evidently permit the discarding of the present expedient of experimental trial and permit the setting up of the equilibrium equations predicting the actual state of affairs in a hydrogen, nitrogen, ammonia mixture at any temperature and pressure.

The necessary thermodynamic basis has been provided by Gibbs for classifying and understanding chemical equilibria; and the Gibbs equations await, as has been indicated, the solution of the equation of state enigma before they can be used in connection with the general numerical solution of physico-chemical problems. Gibbs himself gave much attention to the problem of the equation of state; and the visible result of his work appears in the "Elementary Principles in Statistical Mechanics." The solution of the equation of state problem will inevitably owe much to the general dynamic treatment given by Gibbs; but it must also have for its basis a clearly defined conception of the atom and the molecules, about which so much has been revealed by the recent studies on radioactivity, specific heat, radiation, spectroscopy and ionization. Yet even

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[1] It is evident that the interaction constants would be required to completely solve the problem. Interaction constants are understood to be the constants appropriate to two unlike molecules, such as hydrogen and nitrogen molecules in a mixture, as distinguished from the constants peculiar to a gas composed of hydrogen and nitrogen molecules alone.

if by some means the essential structure of an atom or molecule could be given with the nature of its attractive forces for molecules of the same kind, the task of arriving at the equation of state by rigorous mathematical analysis would appear at present insurmountable. Even with the impetus given by the "Elementary Principles in Statistical Mechanics," so well formulated by Gibbs, the time when such a problem will be satisfactorily solved in the mathematical sense seems very remote.

When, however, the mathematical form of the equation representing the gaseous and the liquid phase is obtained, even approximately, it will inevitably be found that there are relations between the constants peculiar to each substance which are connected with atomic structure of the molecule. These relations between the constants will, of course, automatically lessen the body of the data needed to secure the constants of further substances and even contribute a share towards understanding better the nature of chemical reactivity. It is, indeed, becoming ever more clearly evident that those mild chemical reactions referred to as association or the formation of molecular compounds are different only superficially from the ordinary chemical reactions. That there is, however, a long and unknown road to be traveled before a satisfactory kinetic understanding of chemical reactions is obtained, at least as it relates to the properties of the molecules themselves, is not to be denied. It is, nevertheless, the instinctive impulse to attempt to base the explanation of chemical as well as physical actions upon the properties and dynamic interactions of the molecules, and even the properties of the molecules themselves upon the properties of the atoms from which they are built up.

There are, fortunately, methods of thought and study, which, while not so satisfying as the direct methods of mathematical development, are capable of yielding useful results in attempting to discover a desired mathematical relation. Many of the general laws of nature which are already a part of the existing body of knowledge were in the first instance entirely matters of inspiration. The "law" has then subsequently been arrived at by the application of a straightforward mathematical deduction. The process of guessing the solution of a problem and then justifying the solution, required, however, that it be submitted to a searching test by comparison with experience.

Many equations of state have been given. In fact more than a hundred, for the greater part wholly empirical, have been proposed since the epochmaking work of van der Waals. The results, however, obtained by van der Waals do not appear to be due to any exact mathematical development of his physical ideas, but rather, as some German writers have commented, to inspiration. Van der Waals made use of a type of molecule that was hard, round and elastic,—properties which recent studies have shown not to correspond to the probable actual molecule. In fact, van der Waals for the most part added to the classical notion of the molecule the idea of an attraction which was great at short distances, but negligible at large distances. The equation of van der Waals, as is now well known, does not fit the experimental facts with sufficient exactness to meet modern requirements. It does, nevertheless, reproduce so perfectly the qualitative behavior of substances that the belief is justified that the basis upon which it rests is not wholly incorrect, but rather not sufficiently complete. It remains then, as a reasonable extension of van der Waals' mode of thought, to adopt a type of molecule and atom which conforms to what may reasonably be conceived to correspond with the actual molecule in accordance with recent discoveries bearing on the structure of molecules and atoms. Our knowledge of the electrical properties of the moving electrons and positive corpuscles, which, according to present views, go to make up the atom, may also be used to develop further a knowledge of the attractive forces existing between molecules.

This further specification of the molecule and atom has greatly enhanced the mathematical difficulties of solving the dynamical problem of an assemblage of such molecules or atoms. Having, however, obtained an equation of state based on the type of molecule and atom already referred to, by a process which may be called mathematically assisted guessing, it is practicable to make a careful comparison of the equation with the available body of experimental data, and by obtaining new data by improved experimental methods, examine more thoroughly the consequences of the equation. For this latter purpose Joule-Thompson coefficients and specific heat measurements under pressure may be used.

All the equations of state which have been proposed may be written in one of the three following forms, denoting by p the pressure, by T the temperature on the thermodynamic scale, and by $f(v)$, $F(v)$, $f(v,T)$, $F(v,T)$ functions of the volume alone or functions of the both volume and temperature:

$$p = T.f_1(v) - F_1(v), \tag{1}$$

$$p = T.f_2(v,T) - F_2(v,T), \tag{2}$$

$$p = T.f_3(v) - F_3(v,T). \tag{3}$$

van der Waals' equation illustrates an equation of the general type (1), where $f_1(v) = R/(v - b)$ and $F_1(v) = a/v^2$. Clausius' equation, on the other hand, is of the intermediate form (3), where $f_3(v,T) = R/(v - b)$, independent of T, and $F_3(v,T) = a/(v + m)T$.

A very evident difference exists between (1) and (2) or (3); for, if the volume be kept at any constant value, the pressure *is* or *is not* a linear function of the absolute temperature. In one case, $(\partial p/\partial T)_v$ is a constant, in the other a function of the temperature.

There has been a great amount of work done to determine whether the simple Equation 1 corresponds to the facts in the case of actual substances. Barus,[1] who studied the behavior of liquids, concluded that within the limits of his experimental errors the pressure at constant volume was a linear function of the temperature. The more refined and detailed study of the pressure, volume, temperature behavior of a variety of substances by Amagat[2] led him to conclude, however, that "*Dans tous les cas, les résultats obtenus pour les liquides par MM. Ramsay et Young, par M. Barus et par moi, ne me paraissent pas contradicoires; dans limits communes de nos recherches, les variations du coefficient sont certainment très faibles, mais je ne les crois pas imputables aux seules erreurs d'observation, et je considere la constance du coefficient de pression comme une loi limite.*"

Ramsay and Young[3] called attention to the fact that their work on ether and Andrews' work on carbon dioxide could be represented by an equation of Type (1), and they listed numerical values of $f_1(v)$ and $F_1(v)$ for various values of the volume, calling attention to their significance as follows: "*Dieser wert von* $(\partial p/\partial T)_v$ *ist identisch mit dem Wert von* b *in unserer Gleichung* $p = bt - a$ *beim kritischen Volum. Bis eine mathematische Funktion endeckt ist, welche* b *als eine Funktion des Volums darstellt, ist das einzige Mittel, das uns zur genauen Bestimmung des wahren Volums, welches* b *entspricht, zu Gebote stand, die Interpolation der ursprünghlichen Kurve, mittelst welcher Werte von* b *ausgeglichen waren.*"

It will be shown, as soon as time permits that when all the data available are critically and systematically examined, there are certain regions where, within the limits of error, the pressure at constant volume appears to be a linear function of the temperature for practically all substances in the gas phase and for the greater number of substances in the liquid phase. Practically all vapors, in fact, at larger specific volumes than about 15 cc. per g. show a linear increase of pressure, the exception being only with associated molecules. Liquid water and the alcohols show an increase of $(\partial p/\partial T)_v$ with increasing temperature; water, a very marked increase, the alcohols a smaller rate of increase. The smaller the constant volume considered, however, in the case of water, the smaller the rate of increase of the coefficient becomes, appearing to approach, in fact, a constant value at very high pressures.

The equation given in a recent paper[4] has been used in connection with a critical examination of all the available data on gases and liquids. This equation[5] is:

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[1] Barus, *Phil. Mag.*, **30**, 338 (1890).

[2] Amagat, *Ann. chim. phys.*, [6] **29**, 505 (1893).

[3] Ramsay and Young, *Z. physik. Chem.*, **1**, 440 (1887).

[4] *Proc. Nat. Acad. Sci.*, **3**, 323 (1917).

[5] The physical basis upon which the equation rests is given in the paper referred to. The van der Waals notion of the molecule or atom is replaced by the conception of an atom having a positive central charge about which electrons are rotating. The

$$p = RT/(v - \delta) - A/(v - l)^2 \qquad (4)$$
$$\delta = \beta e^{-\alpha/v}.$$

This is, however, a particular form valid where only one type of molecule or atom is present. Evidently if association takes place, the constants β, α, A and l will change; and, since the degree of dissociation will depend on volume and temperature, evidently β, α, A and l will be functions of volume and temperature or the degree of association (x). The general equation for a substance would accordingly be:

$$p = RTx/(v - \delta) - (Ax/(v - l)^2. \qquad (5)$$

General Equation 5, as distinguished from (4) which is valid for a one-type system, is seen to correspond to Equation 2, so that $(\partial p/\partial T)_v$ will be a function of the temperature. To anticipate somewhat the results of the study of the experimental data, it may be stated that for many substances which have hitherto been classed as unassociated, for examples, for carbon dioxide, ether, ethylene, and isopentane, there are regions in both the gaseous and liquid phases where the special Equation 4 appears to apply.

In the critical region, on the other hand, $(\partial p/\partial T)_v$ is unmistakably not constant, but a function of the temperature. This circumstance, taken in connection with the change in value of the constants in passing from the liquid phase to the vapor-phase region well below the critical temperature, where Equation 4 appears to be valid compared with the similar region in the liquid phase, has induced the belief that in the vapor phase at large volumes there exists only substantially unassociated molecules and that in the liquid region of so-called normal liquids, substantially completely associated molecules. Water and ammonia, because of the rapid increase of $(\partial p/\partial T)_v$, are clearly then examples of substances which, for some reason peculiar to the water and the ammonia molecule, consist of at least double and single molecules existing together in considerable proportion.

Those interested in the development of the kinetic theory have made many attempts to take account in their calculations of the effect of an association of the molecules. Van der Waals has in particular devoted considerable thought to the matter in a series of papers.[1] Van Laar[2] has

rotating charges produce effects which account for the attraction and for van der Waals constant b. In the case of polyatomic molecules b becomes a quantity whose apparent volume changes in accordance with the electromagnetic effect of the surrounding molecules. The essential ideas of van der Waals are thus extended to a molecule constituted in accordance with what modern physics has learned of atomic structure. It is interesting to note that at sufficiently large volumes, where the electromagnetic effects of surrounding molecules become feeble, Equation 4 becomes identical in form with van der Waals" equation. It should be noted, however, that the constants are not to be obtained from the critical data.

[1] *Verslag Akad. Wetenschappen Amsterdam,* 1910.

[2] *Ibid.,* 1910 and 1911.

attacked the problem in a bold attempt to sketch out a theory which would account, on an association basis, even for the solid phase. For this purpose he assumes that van der Waals equation is rigorously true for a system of molecules of the same type. He then sets up an equation giving the association at any temperature and volume, and investigates the course of the isotherms when van der Waals' constant *b* changes as a consequence of the association. Van Laar's theory is very interesting and certainly indicates the manner by which the general problem can be treated. Doubtless the equation of state for like molecules is not so simple as is assumed by van Laar for the purposes of his development; and there remains also the proof of Gibbs' paradox proposition for a fluid following any equation other than that of a perfect gas. This calculation of the entropy of a mixture of actual gases as distinguished from a perfect gas is of fundamental importance, and this problem must be solved before the equilibrium constant can be calculated for an associating fluid departing from the perfect gas law. Nevertheless the attempt made by van Laar is admirable both for its striking ingenuity and its success as regards the general explanation of complex phenomena connected with changes of phase. Indeed it can scarcely be denied that, where association actually takes place in passing from the gaseous phase to the liquid phase, van Laar's general method of procedure is most logical and fundamental.

It is clear that the attempt to discuss the kinetic theory or the equation of state of substances, known to be only partially associated, before the equation of an unassociated fluid is known, is less promising than to obtain first an equation which represents the behavior of the fluid in the essentially completely dissociated or completely associated state. Once the equation for a system with one kind of molecule is obtained the path will be cleared for the study of the equation of a system containing a mixture of two or more kinds of molecules. The question of how the simple type of system can be recognized is not an easy one to answer; and at this point faith must be put at least temporarily in the validity of the deductions and inferences from the general theory of molecular mechanics. If, for example, there is an attraction between the molecules it is difficult to see how temperature change would affect it; for the attraction, gravitational or electrical, between bodies of material size has been shown to be independent of temperature. Excluding association or dissociation, it is also difficult to perceive how the apparent volume of the atoms can change at constant volume. Accordingly as a working basis it has been assumed that within the region where a system of particles remains of essentially the same kind, the pressure must be a linear function of the temperature.[1]

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[1] Barus, commenting in this connection at the conclusion of his paper of 1890 on the linear temperature function isometrics of liquids, states: "For the time being the above results admit of the following interpretation: whenever a substance passes

Equation 4 already referred to is the equation of state of a one-type molecular system. The process by which it was obtained indicates that there should be a marked difference between the volume correction for a monatomic system and a system of polyatomic molecules. Helium and argon were selected as representatives of a monatomic system, and nitrogen as a representative of a diatomic system. The difference expected between these two systems is that the volume correction term δ of Equation 4 should, for a monatomic system, be constant and independent of the volume, while for a diatomic system this term should be a certain function of the volume. The examination of the Onnes' data on argon and helium and of the nitrogen data of Amagat indicate very clearly that δ is constant for the monatomic fluid, but a volume function in the case of the diatomic fluid. The form of function for δ in the case of a diatomic fluid was, moreover, found to be exact within the limits of experimental error. For the details of this important test of the fundamental basis of the equation the original paper must be consulted.

2. The Experimental Method.

The remaining portion of the present paper describes an examination of the vapor region of ether, using as experimental material the data given by Ramsay and Young,[1] together with the preliminary results of an experimental investigation designed to attack the problem directly. Many sources of possible error required investigation, and modified designs of apparatus were worked out in consequence. The work had to be dropped on account of the war before all the changes and improvements serving to make accurate measurements possible could be made. Since this work it will not be again taken up for a considerable time, it seems best to publish the results, so far as it has progressed.

Observers have almost invariably carried out their measurements of the properties of substances at constant temperature, varying the pressure and the volume. To obtain the pressures and the temperatures corresponding to various constant volumes, graphical methods have been resorted to with the uncertainty which attends drawing the hyperbola-shaped curves. The work of taking observations themselves is evidently by no means an easy task; for the absolute temperature scale must be adhered to, and corrections applied for the temperature dilation and pressure dilation of the container. In addition to these difficulties there exists the problem of providing a pressure-measuring device of requisite sensibility. The air manometer, for example, if used, must be filled with

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from the liquid to the gaseous state, no matter whether this takes place continuously above the critical temperature or discontinuously below it, the underlying cause is a change of molecule from a more complex to a less complex type. As long as the molecule remains unchanged the isometrics are straight."

[1] Ramsay and Young, *Z. physik. Chem.*, **11**, 433 (1887).

dry, carbon dioxide-free air; its percentage accuracy, however, diminishes roughly proportionately to the increase of pressure. Moreover, the isotherms of air must be measured by some absolute method. It is by no means certain that the most accurate work done in this latter connection is as good as one part per thousand.

The difficulty of locating a given temperature on the absolute temperature scale is not easily surmounted. In many, indeed, in most instances, mercury thermometers have been used, and mercury thermometers indicate temperatures which are functions of the differential expansion of the glass and mercury. Glass in unfortunately afflicted with a temperature hysteresis which seriously interferes with accurate work, so that even when all precautions have been taken, and this assurance is often lacking, the mercury thermometer must be compared with some absolute standard which becomes finally the gas thermometer.

The gas thermometer either in its constant volume or constant pressure form requires numerous corrections, after which the departure of the gas from the so-called ideal state requires consideration. It is important to note that for any gas following Equation 2 no corrections for departure from the ideal state are necessary. The readings of a constant volume thermometer filled with such a gas lie on the absolute scale except for the addition of a constant, the constant being the position of the water freezing point on the absolute scale. The constant pressure thermometer in the compensating form devised by Callendar[1] could become an instrument of great precision, but the thermometer has yet to be used with a bulb of material suited for gas thermometry. Glass and porcelain are wholly unsuitable, while even a metallic alloy[2] may prove unfit. Even with an ideal bulb the equation of state of the gas must be known to calculate the deviations of the readings from the thermodynamic scale[3] or reliable and extensive Joule-Thomson measurements are required. The latter would unfortu-

[1] *Proc. Roy. Soc.*, 50, 247 (1891).

[2] "High Temperature Gas Thermometry," *Carnegie Inst. Publication*, 1911.

[3] Buckingham has made the most careful and complete investigation of the application of the existing Joule-Thomson measurements to the corrections necessary for both the constant volume and constant pressure thermometer. The Joule-Thomson measurements are all included between 0° and 100° and three empirical formulas were employed to represent the experimental results. Using these formulas to extrapolate from 100 there results a correction of about 0.7° at 1000° for the constant volume thermometer and nearly 2° for the constant pressure thermometer. Evidently a small trend in the experimental values of the Joule-Thomson measurements will have an enormous effect at an extrapolated point 900° away from the nearest experimental data. It is clear that a study of the Joule-Thomson coefficients of the thermometric gases must be carried out with the refinements now possible and over a large temperature range. One alternative as stated in this paper is to attempt to test the validity of the linear increase of pressure with temperature at constant volume. Another alternative would be to measure the temperature of normal boiling sulfur with the gas thermometer at widely different ice point pressures. If the resulting

nately even then have to be correlated as a function of the temperature empirically.[1]

The most logically exact procedure would seem to be to test the thermometric gas at higher pressures, of the order of five to ten hundred atmospheres, for linear increase of pressure with temperature, using for a temperature scale that provided by the gas thermometer having an ice-point pressure of approximately one-half atmosphere. The pressure differences per degree at eight hundred atmospheres are large enough to be accurately measured, and should the pressure increase at constant volume turn out to be linear for these high pressures where the departures from linearity would be marked, assurance would be had that at the low pressures used in thermometry a strictly linear increase of pressure with rising temperature at constant volume was the fact.

In a recent paper[2] Amagat's work on nitrogen was examined in the pressure range of 100 to 900 atmospheres. This examination seems to prove that Equation 3 is the type of equation which must be used to represent this gas above zero.

The experimental method used in this investigation consists essentially in keeping a definite mass of fluid at a fixed volume and measuring the pressures corresponding to successively higher temperatures. In principle, therefore, the method amounted to an ideal gas thermometer, with the exception, of course, that the physical properties of the fluid made it impossible to determine the ice-point and normal steam-point.

The material of the first piezometer bulbs used was Thüringer glass, and that of the later ones pyrex glass. Pyrex glass has a coefficient of expansion of the order of $^1/_3$ that of the Thüringer glass, and accordingly the correction for the thermal expansion is less. The Thüringer glass piezometer consisted of one bulb of the same general design as shown at S in Fig. 1. The pyrex glass was made up in the three-bulb form, shown at S, each bulb being separated by a portion of capillary divided into millimeters by lines etched into the glass. As the temperature was raised, mercury could be injected by means of the compressor O, E, D and thus compensation made for the expansion of the glass due to temperature and pressure. The volume of the etched capillary portion was, of course, designed to allow volume compensation for the entire temperature range of the measurements. The piezometer and capillaries were calibrated for volume by weighing the mercury which filled the portions.

The coefficient of temperature expansion of soda or pyrex glass is not

temperatures for the boiling sulfur were identical the linearity of pressure increase would appear to be verified. Strictly, however, this would only prove that the Joule-Thomson effect was independent of pressure and only dependent upon the temperature.

[1] Bur. Standards, *Bull.* 3, 237 (1907).

[2] *Proc. Nat. Acad. Sci.*, 3, 323 (1917).

only a temperature function, but is also a pressure function. The temperature coefficient of soda glass at atmospheric pressure was repeatedly determined by means of the mercury weight thermometer method and also by the comparator method. It was, however, found impossible to maintain a sufficiently constant and uniform temperature along the total length of the glass in the particular comparator available, and it was thought best to discard the measurements by this method. The weight thermometer determinations, however, indicated that the temperature coefficient of soda glass is best given by the equation of Onnes, who used an accurate comparator. The weight thermometer method, of course, depends upon a knowledge of the expansion of mercury. The equation given by Onnes is

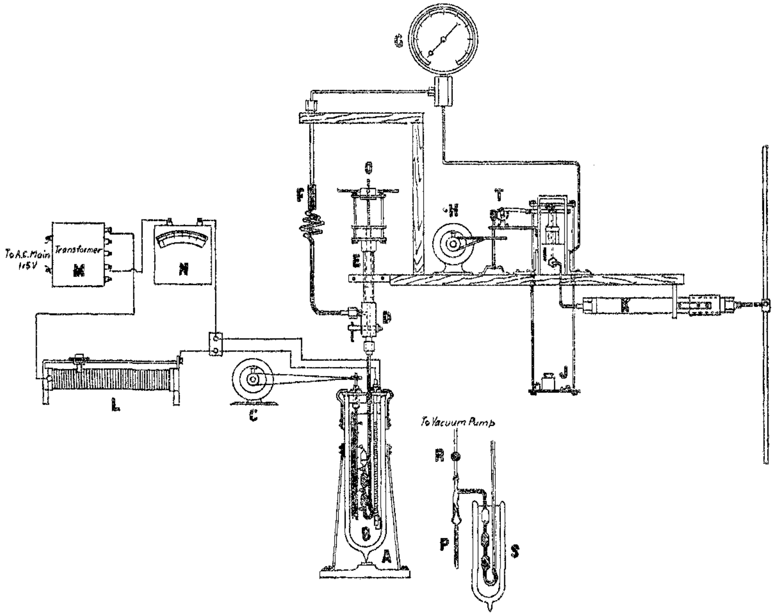

Fig. 1.

$$v_t = v_0 [1 + (27.45 + 3.570 \cdot 10^{-2}.t) \cdot 10^{-6}.t].$$

This cubical coefficient equation was obtained from the actual measurements by Onnes of the linear coefficient on the assumption that the glass is perfectly isotropic and accordingly three times the linear coefficient.

The cubical coefficient of the temperature expansion of pyrex glass was also determined by means of the weight thermometer method, and the Callendar and Moss[1] formula for the expansion of mercury employed in the calculations. The equation for the volume of pyrex glass as a function of the temperature obtained from measurements is

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[1] *Phil. Trans. Roy. Soc. London,* 211, 1 (1911).

$$v_t = v_0[1 + (9.679 + 3.107 \cdot 10^{-3}.t) \cdot 10^{-6}.t].$$

The coefficient of pressure expansion, at least within the range of perfect elasticity, is a function of the temperature. The measurements of the expansion due to pressure at different temperatures, is given by the equation

$$v_t = v_0[1 + 10^{-5}(1.616 + 8.89 \cdot 10^{-4}.t + 7.27 \cdot 10^{-6}.t^2).p].$$

By a combination of the coefficients of expansion due to temperature and to pressure, the volume of soda glass at any temperature and pressure becomes

$$v_t = v_0[1 + (27.45 + 3.57 \cdot 10^{-2}.t)10^{-6}.t + 10^{-5}(1.616 + 8.89 \cdot 10^{-4}.t + 7.27 \cdot 10^{-6}.t^2).p.$$

Lack of time prevented a determination of the pressure expansion of pyrex glass. But since the pressure expansion is relatively small in comparison with the temperature expansion, it was decided, for the present, to employ the same pressure expansion coefficient for pyrex glass as was found for soda glass. The total expansion of pyrex glass, due to temperature and pressure, becomes accordingly

$$v_t = v_0[1 + (9.679 + 3.107 \cdot 10^{-3}.t) \cdot 10^{-6}.t + 10^{-5}(1.616 + 8.89 \cdot 10^{-4}.t + 7.27 \cdot 10^{-6}.t^2)p].$$

The gage I, Fig. 1, used in the measurements of pressure was the same gage that was used by Keyes and Brownlee in their work on the vapor pressure of liquid ammonia and has been described in detail elsewhere.[1] The method of detecting equilibrium of the gage consisted in watching the rise or fall of the mercury-oil meniscus at F, for evidently if there is too great a weight on the scale pan, mercury from the capillary at F will be forced into the piezometer, and if the weight is not sufficient, mercury will pass out of the piezometer and the mercury meniscus will rise at F. The capillary was less than a millimeter in diameter, and accordingly magnified considerably the motion of the gage piston, whose diameter was about 4.7 mm.

The several constant temperatures required for the work were obtained in part by employing boiling liquids. The normal boiling points and the rate of change of temperature per mm. pressure, used in reducing the boiling points to the normal values, are given below.

Substance.	Boiling point (760 mm.).	d(b. p.)/dp.
Bromobenzene	155.93	0.053°
Naphthalene	218.02	0.058
Diphenyl	255.27	0.062
Benzophenone	305.53	0.060
Anthracene	339.66	0.093

The boiling points of the various constant boiling liquids were obtained by means of the platinum thermometer. This necessitated an accurate

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[1] THIS JOURNAL, 40, 25 (1918); *Am. J. Sci.*, 33, 543 (1912).

determination of Δ in the Callendar formula, and as fixed thermometric points, besides the ice and steam points, use was made of the much investigated substances naphthalene and sulfur. Taking the respective boiling temperatures at one atmosphere as 218.02, and 444.44, a very accurate and closely agreeing value of Δ for the platinum thermometer was found (1.50). The form of boiling tube having an inner mantle was employed for water and naphthalene. For the sulfur boiling point, a specially constructed and heat insulated boiling bath was employed. The vapor mantle was employed, but the heating was done electrically, and a 4-inch layer of heat-insulating material employed about the whole boiling bath. The constancy of the sulfur bath was all that could be desired.

A study of the effect of the rate of boiling upon the constancy of the boiling point at a definite atmospheric pressure was made. The boiling point was affected very little by the rate of boiling, but a rate of boiling was soon ascertained, which seemed to give the most constant and most reproducible results. Under these conditions, the change of boiling temperature could not be noticed with a platinum thermometer indicating 0.01°. The form of boiling tube finally employed consisted of a large glass tube in the form of a test-tube, having a diameter of two inches and a length of about 24 inches. On the inside of this large tube was placed a mantle, a smaller glass tube open at the bottom and flaring out at the top to serve as partial cover for the large tube. This inside mantle extended to within about two inches of the surface of the boiling liquid. In this form of boiling tube the inner tube serves as a radiation mantle, and is very necessary if even approximately constant temperatures are to be obtained when a boiling liquid is employed. The precautions needed to secure the best results when boiling liquids are employed as constant temperature baths have, in the past few years, been carefully studied and care was taken to employ all the devices in the present instance. The large tube was surrounded by an asbestos mantle, having on one side a mica window for reading volumes on the piezometer capillaries. The piezometer was centered on the inside of the smaller tube, care being taken not to have any portion of the piezometer in contact with the walls of the mantle. The heating was done with an easily controlled gas burner; the top of the boiling tube being covered with asbestos lids, thus preventing an influx of cool air with consequent escape of the boiling substance vapors.

Owing to the fact that the boiling liquids did not function as perfectly as desired, a novel type of constant temperature bath was finally used. The apparatus consisted of a pyrex Dewar tube filled with liquid paraffin and electrically heated. The details of the arrangement are shown by A, Fig. 1. The heating coil consisted of a long, steel tube, covered with mica, and wound uniformly with resistance wire. The stirrer extended the entire length of the Dewar tube and was constructed of small, flat blades on a stubbs steel shaft. The shaft revolved at about 2400 revolutions per minute, and provided sufficient stirring. The bath liquid consisted of water-white liquid paraffin, which became as fluid as water at about 100°, while the temperature of the bath was read by means of a series of Baudin thermometers which were later checked against the platinum thermometer. The heating was hand regulated, and the accuracy with which this could be done was only limited by the accuracy with which the mercury thermometers could be read. The Dewar flask was not large enough (two inches inside diameter) to permit the introduction of the platinum thermometer along with the piezometer, or the mercury thermometers would not have been employed.

The calibration of the gage by Keyes and Brownlee[1] gave the equivalent of one g. on the scale pan as 0.005441 atmos. The weights of the piston and of the scale pan were, of course, accurately ascertained and the weights employed had been calibrated. For the greater part, the gage was sensitive to a difference of one g. on the scale pan. At the lower pressures, however, this did not seem to always obtain, for at times a difference of 3 to 5 g. on the scale pan were necessary to start the mercury in motion in the observing capillary. This latter effect is due to the close fit of the piston, which at low pressures does not permit sufficient oil to flow up about the piston and effectively lubricates it. In fact, at the higher pressures the piston is probably actually floating in the oil. As an example of the effect of the error of pressure measurement a deficient or excess gram may produce, consider the vapor pressure of ether at 100° (v. p. = 6.4423 atmos.). An error of one g. on the scale pan would mean an absolute error of 0.005441 atmosphere—or an error of one part in 1200. At higher pressures, 20 atmos., where the gage seemed sensitive to one g., the accuracy becomes, on the other hand, about 1 part in 3700.

In addition to the pressure measured on the gage, there must be taken into account the height of the mercury column above the surface of the mercury in the piezometer. This height of mercury, measured by means of a cathetometer, must be corrected for temperature expansion, for the mercury column is at different temperatures at different points. Part is at the temperature of the bath, part at room temperature, and still another part at some intermediate temperature. These lengths of mercury column at the different tempertures could each be corrected separately, and the total corrected height obtained. An accuracy of better than *one* part in 1000 is not probable in determining the pressure due to this column. The atmospheric pressure, which must be added, can be read with an accuracy of 0.02 millimeter. All things considered, the accuracy of the pressure measurements at the lower pressures leaves something to be de-

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[1] *Loc. cit.*

sired. Details for a gage 4 times as sensitive as the present one have been drawn up, but this cannot be employed until after the war. It is believed that with the new gage it will be possible to make the low pressure measurements comparable in accuracy with those now obtainable at the higher pressures with the present gage.

From the total pressure measured must be subtracted the vapor pressure of mercury at the temperature of the measurement. This correction is, of course, very small, becoming at 300°, however, about 0.3 atmos. The coefficient $(\partial p/\partial P)_T$ for mercury where P is the total pressure is extremely small, as it always is when at temperatures considerably away from the critical temperature. The pressure of mercury was subtracted from the total pressure using the data on the vapor pressure of mercury taken from the excellent résumé of Smith and Menzies.[1]

The temperature of the electrically heated oil bath could be determined accurately to at least 0.05–0.1°, since the mercury thermometers could be read with this accuracy. The thermometers were later compared with the platinum thermometer. Nonautomatic regulation of the bath temperature was very satisfactory as tested by the resistance thermometer reading to 0.01°. The vacuum jacketed baths are most satisfactory and are perfectly safe when made of pyrex glass for temperatures as high as 400°. In future work it would be desirable to provide automatic temperature control, particularly where vapor pressures are being measured. In determining $(\partial p/\partial T)_v$, where differences are taken, the additive error might in the present work amount to 0.2°, and this error where $dT = 30°$ would mean an error of one part in 150. There are, however, other sources of error in the other variables, pressure and volume which may affect $(\partial p/\partial T)_v$ more than the latter.

3. Preparation of the Material.

The commercial ether used in the work was treated in the following manner, to remove alcohol, water, and other impurities: The ether was repeatedly shaken with fairly large portions of dil. sulfuric acid in large separatory funnel. Following this, it was shaken with large amounts of pure water, which procedure was certain to remove any alcohol present in the ether. The moist ether was then dried for two weeks in contact with fused calcium chloride and subsequently dried over metallic sodium ribbon for two weeks. After the sodium drying the ether was transferred to the reservoir of Fig. 2 by means of the capillary tube attached to its side, and the tip of the capillary sealed off. In order to free the ether from dissolved gases, the whole ether storage apparatus was pumped by means of the vacuum pump at F, Fig. 2 for a few minutes. The dissolved gases then again established their partial pressure in the apparatus. The whole was again pumped, and this occasional pumping continued

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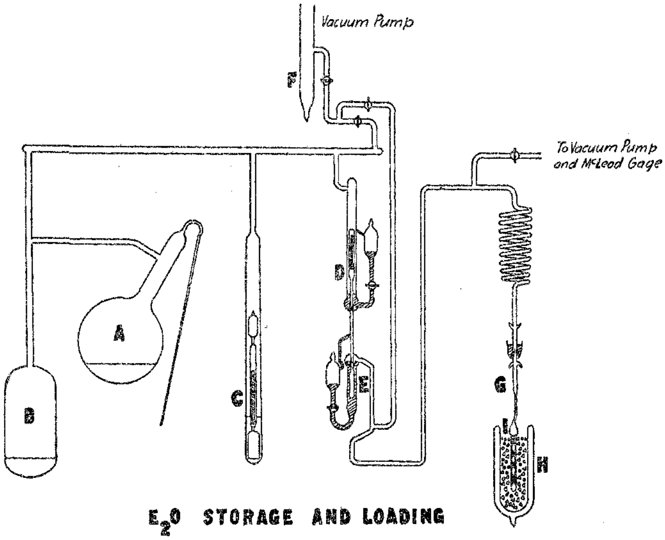
[1] THIS JOURNAL, 32, 1445 (1910).

until all the dissolved gases had been removed. Finally the ether was repeatedly distilled from one bulb to the other and pumped at the end of each distillation (bulbs A and B, Fig. 2). In order to test for the presence of any gaseous impurity, use was made of the method suggested by Young.[1] An inverted bell, C, could be raised by means of a magnetic arrangement, thereby trapping a portion of the gas phase. If the gas phase collapses promptly under the slight hydrostatic head of liquid, it is certain that very little gaseous impurity is present. Another test is offered by the promptness with which the ether distils over into the volumometer at 0°. Any foreign gas present would hinder the prompt distillation of ether through the fine capillary.



E$_2$O STORAGE AND LOADING APPARATUS

Fig. 2.

The volume of the piezometer being the order of 7.5 cc., a specific volume of 50 cc. per g. would require 0.15 g. of ether to be accurately transferred to the piezometer from the storage chamber. It is quite impossible to weigh this quantity of ether, and suitable three-bulb volumometers represented at I, Fig. 2, were constructed with reference to the desired volumes per g. at which it was decided to make measurements in the piezometers. In place of attempting to weigh the quantity of ether, its volume was read off at the temperature of melting ice and the weight obtained from the known density at zero. The ether in the volumometer was so adjusted at the ice-point that the ether meniscus was resting within the graduated capillary portion between the bulbs of the volumom-

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[1] *Phil. Mag.*, 20, 797 (1910).

eter. When this adjustment had been made, the volumometer could be sealed from the loading apparatus and its ether volume read off at the ice-point when the entire volumometer was submerged. The total weight of ether is obtained from the vapor and liquid densities.

The remaining step in transferring the ether to the piezometer is illustrated in Fig. 1, R, S, P. The upper portion of the volumometer is ground to fit the piece R which connects by means of a fine (0.2 mm.) capillary with the piezometer. The upper portion of R connects with a vacuum pump capable of producing a vacuum of 1×10^{-5} mm. or less. The total volume of the space below the stopcock of R is determined with the volumometer inserted in its ground seat by weighing the mercury required to fill the space. The volumometer ground-joint having been properly greased, the piezometer is exhausted by opening the stopcock of R. The piezometer walls must be heated with a hand blast during the exhaustion to remove adsorbed gases, and the mercury boiled vigorously during the exhaustion. Many days of painstaking labor and much data were lost by failing to continue this heating sufficiently to remove the adsorbed gases. For example, it was found that the vapor pressure at 156° was independent of the vapor space previous to heating to 340°, but that subsequently the vapor pressure had increased and rose on diminishing the ratio of vapor to liquid. At first decomposition at the higher temperature was suspected, but when experience in boiling out the piezometer had been attained, it was found that the vapor pressure at 156° was independent of the vapor-liquid volume ratio or the temperature (340°) to which the ether had been heated. The effect on measurements in the vapor phase of this adsorbed gas is enormous as regards its effect on the constants of the equation of state for a trend would be introduced into the data and clearly this would be fatal to the attempt to evaluate the α and l constants. Even the sign of l may easily be changed by a trend in the data which may appear small as judged by the percentage difference in the pressures. In fact, the present experimental work was undertaken to determine whether or not l was positive or negative in sign in the gas phase. The older data for the gas phase of many substances appears to have a negative value, whereas in the liquid phase l corresponds in sign to that implied by the theory.

When the heating and pumping is completed, the stopcock of R may be closed and the piezometer cooled by immersion in liquid ammonia. The drawing, Fig. 1, shows the projection just above the ground-joint of R, and when the volumometer is turned in its ground joint the previously scratched tip of the volumometer is broken off and the ether distills into the piezometer. The capillary above the piezometer is sealed off and the weight of ether computed. The ether weight correction for the vapor left in the volumeter and the connections is easily obtained from the volume of the latter, and the pressure is determined by the temperature of the ether in the piezometer. The magnitude of this correction amounted in the case of the smaller weights of ether to about one part in three hundred. The accuracy with which the quantities of ether could be introduced into the piezometer was the order of one part in 2000.

The density of ether was determined at 0° many times by two manipulators employing independently calibrated volumometers and different ether samples. The form of apparatus employed consisted of a cylindrical bulb of about 5 cc. capacity, to which was attached a graduated capillary stem. A small bulb was also attached at the upper end of the capillary to allow for the expansion of the ether as it warmed to room temperature. The entire apparatus was carefully calibrated with mercury, and the volume at 0° and other temperatures calculated from a knowledge of the coefficient of temperature expansion of the glass. All weights were, of course, corrected to vacuum. At least a dozen measurements were made at zero by the writers, and a number also by Dr. A. W. Kenney, formerly of this laboratory. The results of all the determinations at zero lead to the mean value of 0.73635 for the density of ether at zero. The measurements of Young,[1] Seitz, Altherum, and Lechner,[2] and of Kenney (at higher temperatures), and some measurements at —33° by the writers, were employed to find the relation between the density and the temperature. For this purpose, a graph was made of volume and log $(Tc - T)$ where Tc is the critical temperature. This procedure serves very well if the values near the critical temperature are not desired.

TABLE I.

Density of Liquid Ether.

t.	Spec. vol.	Density (plot).	Density (obs.).	Observer.
+150	1.9308	0.5179	0.5179	Y
+145	1.8892	0.5293		
+140	1.8530	0.5396	0.5385	Y
+135	1.8195	0.5496		
+130	1.7892	0.5589	0.5580	Y
+125	1.7610	0.5678		
+120	1.7340	0.5767	0.5764	Y
+115	1.7095	0.5849		
+110	1.6865	0.5929	0.5942	Y
+105	1.6642	0.6008		
+100	1.6435	0.6084	0.6105	Y
+ 95	1.6230	0.6161		
+ 90	1.6038	0.6235	0.6250	Y
+ 85	1.5862	0.6304		
+ 80	1.5689	0.6373	0.6402	Y
+ 75	1.5521	0.6442		

[1] *Dublin Proceed.*, **12**, 374 (1910).

[2] *Ann. Physik*, **49**, 90 (1916).

TABLE I (*continued*).

t.	Spec. vol.	Density (plot).	Density (obs.).	Observer.
+ 70	1.5363	0.6509	0.6532	Y
+ 65	1.5211	0.6574		
+ 60	1.5061	0.6639	0.6658	Y
+ 55	1.4925	0.6700		
+ 50	1.4780	0.6765	0.6764	Y
+ 45	1.4650	0.6825		
+ 40	1.4524	0.6885	0.6894	Y
+ 35	1.4393	0.6947		
+ 30	1.4270	0.7007	0.7019	Y
+ 25	1.4150	0.7067		
+ 20	1.4031	0.7127	0.7135	Y
+ 15	1.3920	0.7183		
+ 10	1.3800	0.7246	0.7248	Y
+ 5	1.3695	0.7301		
± 0	1.3580	0.73635	0.73620 0.73635	Y K. & F.
— 5	1.3475	0.7421		
— 10	1.3379	0.7474	0.7474	S. A. & L.
— 15	1.3270	0.7535		
— 20	1.3171	0.7592		
— 25	1.3075	0.7648		
— 30	1.2982	0.7702	0.7690	S. A. & L.
— 35	1.2891	0.7757		
— 40	1.2795	0.7815		
— 45	1.2708	0.7869		
— 50	1.2620	0.7923	0.7899	S. A. & L.
— 55	1.2531	0.7980		
— 60	1.2442	0.8037		
— 65	1.2358	0.8091		
— 70	1.2275	0.8146	0.8106	S. A. & L.
— 75	1.2205	0.8193		
— 80	1.2130	0.8244		
— 85	1.2052	0.8297		
— 90	1.1982	0.8345	0.8313	S. A. & L.
— 95	1.1900	0.8403		
—100	1.1826	0.8455	0.8415	S. A. & L.
—105	1.1752	0.8509		
—110	1.1682	0.8560	0.8517	S. A. & L.

The volumes read from the plot for each 5° between 150° and —110° are given in Table I. In the second column will be found the densities, while the third column gives the value of the density assigned by the observers whose initials appear in Col. 5. It is to be noted that the Seitz, Altherum and Lechner values are too low below about 30°. The data of the latter fluctuate considerably, and it is not possible to draw a line of uniform curvature through the values above zero which are relatively more reliable than the low temperature densities of these workers. It is believed the values read from the plot represent the most probable values of the densities which can be assigned at present. The mean value of the density at 0° on the basis of the work of Kenney and the writers is believed to be correct to one part in 4000.

4. Discussion of the Older Data.

Ramsay and Young,[1] in their paper made use of a body of data obtained in a previous piece of experimental work, and by graphical methods obtained the pressures corresponding to the temperatures for various constant volumes. They showed that the pressures are a linear function of the temperature for the constant volumes out to about 300 cc. and make a list of the constants a and b for the series of equations of the type $p = bT - a$. The constant volume pressures and temperatures as given by Ramsay and Young are used to examine the correctness of form of δ and the cohesive pressure term $A/(v - l)^2$ for Equation 4.

In using data of this kind it must be noted that the accuracy with which δ and ϕ may be determined varies [ϕ will be used to designate $A/(v - l)^2$]. The quantity δ for example is obtained as the difference of two quantities, $v - R/[(p_2 - p_1)/(T_2 - T_1)]$, and accordingly for 0.25% uniformly accurate volume and pressure data the error in δ at 15 cc. per g. would be about one %. At 100 cc. per g. δ could be in error by at least 4%, and at 300 cc. per g. about 12%. This is assuming that $(\partial p/\partial T)_v = (p_2 - p_1)/(T_2 - T_1)$ is exact. When the possible errors in $(\partial p/\partial T)_v$ are compounded with the errors in v erratic fluctuations in δ may result at large volumes. The value of ϕ becomes smaller as approximately the square of the volume and in consequence at the larger volumes ϕ may fluctuate very materially. At 300 cc. for example, ϕ is the order of 0.08 atmosphere. Now at 2.50 atmospheres total pressure is the difference between $RT/(v - \delta) = 2.58$ and $p = 2.50$ and therefore an error of 0.25% in p involves an error in ϕ of possibly 12%. It is accordingly clear that the original experimental data taken by the isothermetric method and subsequently manipulated by graphical methods to obtain the isometrics, may in consequence possess a trend. Accordingly too much weight cannot be attached to the apparent deviation of the δ and ϕ equations especially at the larger volumes where differences in nearly equal quantities have to be employed. Ramsay and Young apply their considerations to volumes smaller than the critical, but a careful inspection of the data from which they calculated the isometric leads to the conclusion that $(\partial p/\partial T)_v$ is not a constant much below 15 cc. per g. The data on isopentane by Young as well as pressure–volume–temperature data for other substances confirms this observation. Expressed otherwise it may be stated that for the most part association does not begin to be appreciable in the gas phase until the volume becomes less than 15 cc. per gram.

Obviously elevation of temperature would lessen the association and it

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[1] *Z. physik. Chem.*, 1, 440 (1887).

is the fact that $(\partial p/\partial T)_v$ at smaller volumes than 15 cc. per g. becomes constant as higher temperatures are reached. The 15 cc. per g. statement refers to the saturated temperature which is usually about 20 to 30° below the critical temperature. The so-called normal liquids, as ether, for example, appear on the other hand not to appreciably dissociate into single molecules until about 6 to 10° from the critical temperature.

Returning to the vapor phase data of Ramsay and Young's paper the isometric pressures and temperatures as given by them were employed rather than attempting to redetermine the isometrics graphically. Values of $(\partial p/\partial T)_v = (p_2 - p_1)/(T_2 - T_1)$ were taken and used to compute δ values by means of the Equation 4 where it is seen to be equal to $v - R/((p_2 - p_1)/(T_2 - T_1))$. The logarithms of the various δ's were plotted with the corresponding $1/v$ to prepare Fig. 3. It will be noted that the functional form of δ appears to be exact with a greater scattering of the observational points at the larger volumes. From what has been stated regarding the diminishing precision of evaluation of δ as larger volumes are considered, it is clear that the scattering is of no particular significance.

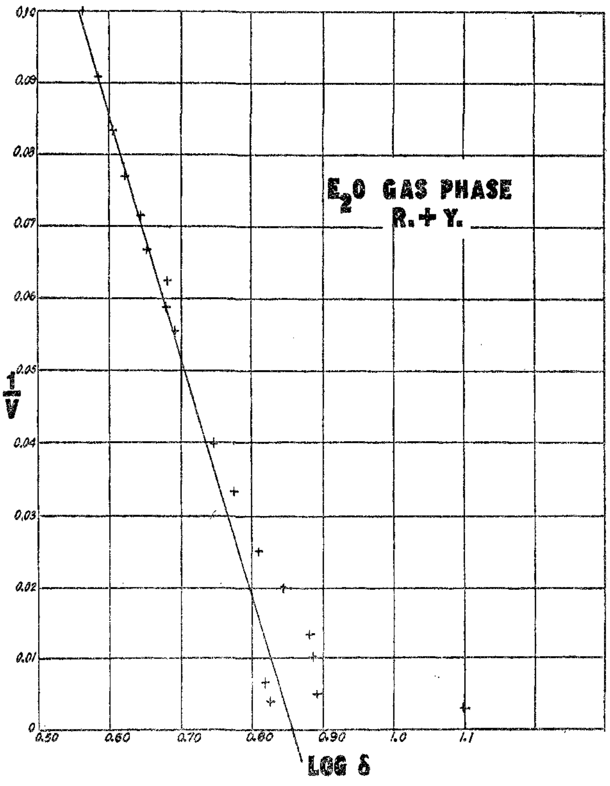

Fig. 3.

Table II gives the observed values of δ with which may be compared the values calculated by the equation for the straight line of the plot. The observed values of $(\partial p/\partial T)_v$ may be compared then with the values of the coefficient calculated by means of the δ equation. Note should be made that the departure or scattering of the large volumes data corresponds to a very small error in the observed $(\partial p/\partial T)_v$ coefficient. There seems no reasonable doubt that the calculated $(\partial p/\partial T)_v$ values at the larger volumes are far more reliable than are the observed values.

Table II.

Ramsay and Young's Data.

Spec. vol.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
12	4.033	4.040	0.13885	0.13910	37.510	37.565
13	4.168	4.221	0.12671	0.12620	32.675	32.660
14	4.396	4.380	0.11459	0.11520	28.634	28.650
15	4.482	4.526	0.10534	0.10575	25.367	25.312
16	4.790	4.657	0.09730	0.09766	22.604	22.531
17	4.756	4.766	0.09047	0.09050	20.215	20.203
18	4.906	4.883	0.08452	0.08442	18.208	18.202
19	4.935	4.982	0.07909	0.07900	16.461	16.475
20	5.077	5.072	0.07425	0.07420	14.976	15.002
25	5.542	5.431	0.05692	0.05660	9.770	9.991
30	5.942	5.685	0.04605	0.04555	7.121	7.024
40	6.436	6.017	0.03300	0.03259	4.132	4.059
50	6.964	6.226	0.02560	0.02531	2.630	2.641
75	7.594	6.516	0.016434	0.016175	1.296	1.199
100	7.687	6.666	0.01199	0.01187	0.700	0.672
150	6.578	6.819	0.00779	0.00774	0.3267	0.3071
200	7.788	6.898	0.00578	0.00573	0.2022	0.1735
250	6.680	6.945	0.00458	0.00456	0.1265	0.1114
300	12.666	6.977	0.00376	0.00378	0.1126	0.0775

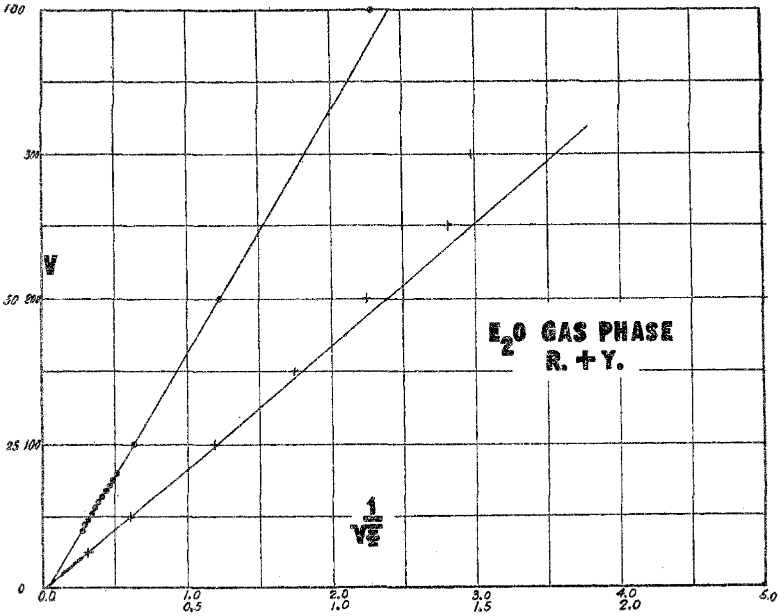

Fig. 4.

The values of observed ϕ listed in Table I have been obtained by means of the equation $\phi = RT/(v - \delta) - p$ where the observed values of p

were used. The calculated values of ϕ result from the straight line of the plot, Fig. 4. In this plot appear two lines, one of which is an enlargement of scale of the other. The equation of $\phi = R/(v - \epsilon)^2$ has been brought into the form which would make evident the corrections of mathematical form of the ϕ equation. The larger scale line passing from 0 to 300 cc. shows that apparently the data beyond 100 cc. depart from the straight line which satisfies the ϕ values below 100 cc. The absolute values of ϕ are very small in this region and they are at most a few multiples of the error in the pressure measurements. The values of ϕ calculated by means of the straight line equation are given in the table.

The equations for δ and ϕ having been obtained a comparison of the calculated pressures may be made. Table III gives the comparison and considering the effects of the simultaneous errors in the pressure, volume and the temperature the differences are nowhere greater than the errors of the original measurements except in the case of the 12 cc. volume where it is believed from the general experience with 11 other substances that association is at this volume appreciable.

TABLE III.

Pressures Observed by Ramsay and Young and Calculated by the Equation of Keyes.

$$p = (RT/(v - \delta)) - (7058.6/(v + 1.7)^2).$$

	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
T.	$v = 12.$		$v = 13.$		$v = 14.$		$v = 15.$	
100	14.422	14.312	14.422	14.419	14.380	14.313	14.126	14.159
150	21.365	21.271	20.722	20.728	20.096	20.071	19.392	19.438
280	39.416	39.362	27.070	37.132	34.995	35.040	33.087	33.187
	$v = 16.$		$v = 17.$		$v = 18.$		$v = 19.$	
100	13.861	13.907	13.597	13.611	13.290	13.310	13.012	13.007
150	18.725	18.790	18.121	18.142	17.525	17.532	16.978	16.958
280	31.375	31.486	29.883	30.923	28.515	28.511	27.246	27.230
	$v = 20.$		$v = 25.$		$v = 50.$		$v = 75.$	
100	12.713	12.687	11.330	11.130	6.820	6.862	4.825	4.814
150	16.418	16.397	14.172	13.961	8.193	8.127	5.646	5.622
175	..	..	..	..	..	..	6.057	6.126
280	26.079	26.044	21.574	21.320	..	..	..	..
	$v = 100.$		$v = 150.$		$v = 200.$		$v = 250.$	
50	..	..	2.230^a	2.268^a	1.658	1.677	1.342	1.362
100	3.725	3.747	..	..	..	..	..	..
150	4.325	4.338	..	..	..	..	..	..
195	..	..	3.316	3.301	2.496	2.508	2.007	2.023
280	5.200	5.210	..	..	..	..	..	..
	$v = 300.$							
50	1.131	1.144						
195	1.677	1.692						
223	1.800	1.797						

[a] Temperature = 59.7.

The equation obtained from the Ramsay and Young data and used in calculating the data contained in Tables II and III is

$$p = 1.1078T/(v - \delta) - 7050.6/(v + 1.7)^2 \qquad (6)$$

$$\log_{10} \delta = 0.85352 - 2.966/v$$

where the units are the atmosphere (76 cm. Hg), cc. per g. and

$$T = (273.1 + t).$$

There are other scattered data due to several observers. In particular there are a number of isotherms due to Battelli. These isotherms are so short and the values so inconsistent among themselves that little use can be made of them for the present purpose.

5. The Newly Measured Isometrics of Ethyl Ether.

The method by which the isometrics of ethyl ether were measured has been described in detail, and the results should give information directly on the question of the linear increase of pressure with temperature as well as further test with greater exactness the correctness of the mathematical form of δ and ϕ.

The completeness of the experimental work leaves much to be desired as regards some details, but on the other hand, what has been accomplished is sufficient to add material evidence concerning the kinetic theory already sketched out. For the time being, the war has interrupted investigations in connection with a selected series of substances whose physical properties were to be carefully measured for the purpose of establishing as completely as possible many of the consequences of the attempt to use modern atomic notions as a basis for the kinetic theory.

It has been shown in the nitrogen-argon paper that there is a fundamental difference between a diatomic system and a monatomic system, in that the apparent molecular volume is a function of the volume in the case of the diatomic substance, and a constant for the monatomic system of particles. The work of Ramsay and Young on ethyl ether has moreover appeared also to confirm substantially the correctness of mathematical form of δ for the case of a multiatomic molecule (15 atoms). The data of Amagat indicates that the same form of Equation 4 applies in the liquid phase, but in this case the constants are a different numerical magnitude than those obtained for the gas phase. The fact, however, that the A constants are in simple ratio $A_1/A_2 = 2$, to one another suggested that perhaps complete doubling[1] of the molecules takes place in the liquid

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[1] It should be emphasized that the simple Equation 4 is true when only one type of molecule is present in the system under consideration. The linear increase of the pressure with the temperature is taken as the test that such a system is under observation, and within the region that this state of affairs is the fact in the gaseous and liquid phase, the δ and ϕ expressions have been determined. It is to these regions that the statements above refer. The limits of the regions have already been stated, but it is clear that if doublets are capable of existence, their presence is never excluded

phase. The δ equation for liquid ether was calculated on this basis, and, using the new experimental data, there now appears to be a simple numerical ratio between the β's and the α's for the two phases. Ramsay and Young's data were not sufficiently accurate to precisely establish the relationship as definitely as desirable.

The difficulty encountered in entirely freeing the ethyl ether itself and the glass walls of the apparatus from permanent gas has been already alluded to. The prompt collapsing of the vapor phase under very small excess pressures is a most delicate test; and in the present work very especial attention was given to preserving the ether in an air-free condition as described. The matter of freeing the walls of the piezometer depends upon experience in carefully boiling out the piezometer before distilling the ether into it. Many puzzling and contradictory data were obtained, of course worthless, due to the absorbed gases. Each series of results obtained represents several repeated measurements on one filling of the apparatus. In fact, each filling of the piezometer was subjected to successive measurements from 150° to 340° and was required to give no increase in pressure on subsequent measurement at 150°. An increase in the pressure was shown to be due to the presence of absorbed gas liberated at the higher temperature; for the ethyl ether does not decompose in contact with mercury and glass when heated for long intervals of time at 340° if completely freed from gas. The presence of oxygen or iron at this temperature, it may be stated, is quite sufficient to bring about decomposition.

Table IV gives the temperature on the absolute scale ($T_0 = 273.14$) and the corrected absolute pressure in atmospheres (760 mm. per atm.) corresponding to the constant volumes from about 53 cc. to about 14 cc. The pressures and temperatures for each constant volume were plotted on coördinate paper and the most representative line drawn corresponding to the data. Heading each series will be found the linear equation which was used to calculate the values in the third column and it is evident that a linear equation represents the measurements with considerable accuracy.

The coefficients of the absolute temperature were used to calculate values of δ and the logarithm of δ was plotted with the reciprocal specific volume. The best straight line on such a diagram has the equation

in the gaseous phase, and conversely single molecules will never be excluded in the liquid phase. The statements completely associated or completely dissociated merely means that insofar as the finiteness of our powers of measurement go, we recognize a system as substantially completely associated or as substantially completely dissociated. It is also difficult to sometimes perceive why a pair or associated particles should remain associated. All that is required is that on the statistical average two particles remain associated and an exchange may be conceived to be in continual progress. This view in fact, since there must inevitably always be a small portion of single molecules present, would seem not alone logical but required.

$\log_{10}\delta = 0.79352 - (2.086/v)$. Evidently this δ equation may be used to calculate the values of ϕ corresponding to each pressure measurement. The values obtained from the calculation have been placed in the plot Fig. 5 in which ϕ and v are the coördinates. It is evident that a straight line adequately represents the data and the value of ϕ is given by the equation: $\phi = 5796.2/v^2$.

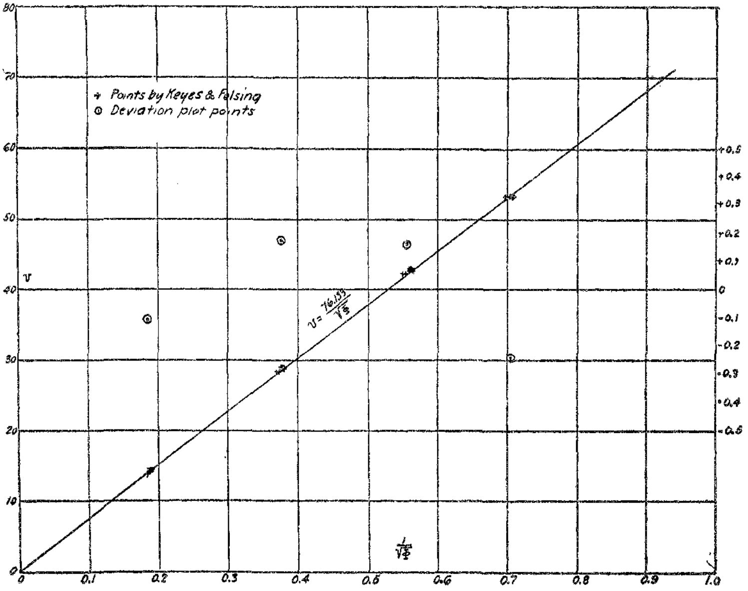

Fig. 5.

Table IV.

Pressure as a Linear Function of the Temperature.

T.	p_{obs}.	p_{calc}.	p.
Series No. 4. $p = 0.02349\,T - 2.1366$. $v = 53.265$ cc.			
429.030°	7.942	7.942	±0.000
491.120	9.406	9.401	—0.005
528.370	10.280	10.276	—0.004
578.630	11.450	11.456	+0.006
613.190	12.264	12.268	+0.004
Series No. 5. $p = 0.02938\,T - 2.980$. $v = 42.727$ cc.			
428.855°	9.619	9.620	+0.001
491.412	11.796	11.457	...
528.270	12.539	12.540	+0.001
578.607	14.073	14.073	—0.054
612.749	14.974	15.022	+0.048
$p = 0.047156\,T - 7.060$. $v = 28.816$ cc.			
428.855°	13.165	13.165	±0.000
491.412	16.630	16.115	...
528.270	17.854	17.853	—0.001
578.607	20.224	20.226	+0.002
612.749	21.939	21.836	—0.103

Table IV (*continued*).

T.	$p_{\text{obs.}}$	$p_{\text{calc.}}$	p.
$p = 0.11852\,T — 31.100$. $v = 14.119$ cc.			
491.412°	28.954	27.142	...
528.270	31.515	31.515	±0.000
578.607	37.481	37.480	—0.001
612.749	41.131	41.527	+0.396
Series No. 6. $p = 0.029715\,T — 3.060$. $v = 42.231$ cc.			
429.117°	9.691	9.692	+0.001
491.215	11.581	11.537	—0.044
528.509	12.645	12.645	±0.000
578.769	14.085	14.139	+0.054
$p = 0.04866\,T — 7.710$. $v = 28.481$ cc.			
429.117°	13.173	13.172	—0.001
491.215	16.285	16.194	—0.091
528.509	18.009	18.009	±0.000
578.769	20.400	20.353	+0.054
$p = 0.11646\,T — 29.549$. $v = 13.955$ cc.			
491.215°	27.662	27.662	±0.000
528.509	32.354	32.005	—0.349
578.769	37.859	37.859	±0.000
Series No. 7*a*. $p = 0.02962\,T — 3.190$. $v = 42.904$ cc.			
428.650°	9.497	9.497	±0.000
489.926	11.349	11.322	—0.027
527.096	12.416	12.416	±0.000
578.215	13.733	13.927	+0.194
$p = 0.04622\,T — 6.750$. $v = 28.936$ cc.			
428.650°	13.064	13.064	±0.000
489.926	15.958	15.896	—0.052
527.096	17.618	17.618	±0.000
578.215	19.863	19.976	+0.113
Series No. 7*b*. $p = 0.029319\,T — 3.116$. $v = 42.902$ cc.			
422.925°	9.333	9.285	—0.048
452.545	10.108	10.153	+0.045
482.847	11.042	11.041	—0.001
541.176	12.743	12.752	+0.009
571.404	13.585	13.638	+0.053
$p = 0.04725\,T — 7.240$. $v = 28.934$ cc.			
422.925°	12.771	12.770	—0.001
452.545	14.218	14.163	—0.055
482.847	15.652	15.588	—0.064
518.305	17.250	17.255	+0.005
541.176	18.289	18.331	+0.042
571.404	19.556	19.846	+0.290
$p = 0.11020\,T — 26.430$. $v = 14.175$ cc.			
452.545	23.463	23.466	+0.003
482.847	26.876	26.801	—0.075
518.305	30.701	30.703	+0.002
541.176	33.225	33.220	—0.005
571.404	36.288	36.546	+0.258

To afford a comparison between the data of Ramsay and Young and those obtained in the present work the Table V has been prepared in which the pressures corresponding to the measured volumes and temperatures are substituted in the equation representing Ramsay and Young's

TABLE V.

Observed Pressures Compared with the Pressures Calculated by Equation Based on the Data of Ramsay and Young.

Series.	Spec. vol.	T.	P (obs.).	P (calc.).		p_2-p_1/t_2-t_1 obs.	$(dp/dT)_v$ calc.
4........	53.265	429.030	7.942	7.781	+0.161	0.02349	0.02357
		491.120	9.406[a]	9.245	+0.161	0.02339	
		528.370	10.280	10.123	+0.147	0.02310	
		578.630	11.450	11.308	+0.142	0.02403	
		613.190	12.264	12.122	+0.142	0.02349	
5........	42.727	428.855	9.619	9.392	+0.227	0.02939	0.03023
		491.412	11.796	11.282	+0.514	0.03045	
		528.270	12.539	12.397	+0.242	0.02641	
		612.749	14.974	14.951	+0.023	0.02875	
5........	28.816	428.855	13.165	12.919	+0.246	0.04716	0.04778
		491.412	16.630	15.908	+0.722	...	
		528.270	17.854	17.668	+0.196	0.04708	
		578.607	20.224	20.047	+0.152	0.05023	
		612.749	21.939	21.705	+0.234	0.04814	
5........	14.119	491.412	28.954	27.835	+1.119	...	0.11398
		528.270	31.515	32.036	−0.521	0.11852	
		578.607	37.481	37.773	−0.282	0.10689	
		612.749	41.131	41.664	−0.533	0.11270	
6........	42.231	429.117	9.691	9.493	+0.198	0.03041	0.03063
		491.215	11.581	11.395	+0.186	0.02853	
		528.509	12.645	12.537	+0.108	0.02863	
		578.769	14.085	14.077	+0.008	0.02919	
6........	28.481	429.117	13.173	13.048	+0.125	0.05010	0.04834
		491.215	16.285	16.057	+0.228	0.04624	
		528.509	18.009	17.863	+0.146	0.04753	
		578.769	20.400	20.299	+0.101	0.04796	
6........	13.955	491.215	27.662	28.031	−0.369	0.12578	0.11563
		528.509	32.354	32.344	+0.010	0.10946	
		578.769	37.859	38.155	−0.296	0.11762	
7........	42.904	428.650	9.497	9.353	+0.144	0.03021	0.03008
		489.926	11.349	11.197	+0.152	0.02865	
		527.096	12.416	12.315	+0.101	0.02579	
		578.215	13.733	13.853	−0.120	0.02822	
7*a*.......	28.936	428.650	13.064	12.869	+0.195	0.04723	0.04754
		489.926	15.958	15.781	+0.177	0.04456	
		527.096	17.618	17.548	+0.070	0.04396	
		578.215	19.863	19.978	−0.115	0.04525	

TABLE V (*continued*).

Series.	Spec. vol.	T.	P (obs.).	P (calc.).		$p_2—p_1/t_2—t_1$ obs.	$(dp/dT)_v$ calc.
7*b*.......	42.902	422.925	9.333	9.182	+0.151	0.02616	0.03008
		452.545	10.108	10.073	+0.035	0.03083	
		482.847	11.042	10.985	+0.057	0.03180	
		518.305	12.170	12.052	+0.118	0.02505	
		541.176	12.743	12.740	+0.003	0.02786	
		571.404	13.585	13.649	—0.064	0.02834	
7*b*.......	28.934	422.925	12.771	12.597	+0.174	0.04885	0.04755
		452.545	14.218	14.005	+0.213	0.04734	
		482.847	15.652	15.446	+0.206	0.04507	
		518.305	17.250	17.132	+0.118	0.04543	
		541.176	18.289	18.219	+0.070	0.04190	
		571.404	19.556	19.657	—0.101	0.04572	
7*b*.......	14.175	542.545	23.463	23.350	+0.113	0.11266	0.11341
		482.847	26.876	26.787	+0.089	0.10786	
		518.305	30.701	30.808	—0.107	0.11039	
		541.176	33.226	33.402	—0.176	0.10132	
		571.404	36.288	36.831	—0.543	0.10806	

data. This procedure affords a comparison of pressures, but since there are three variables, it is not possible from the pressure comparisons alone to draw conclusion with regard to which variables may be most in error either in the new or the old work. There are, however, several interesting observations which may be made from the table. The calculated pressures are somewhat higher in general except at the volume about 14 cc. The volumes observed by Ramsay and Young were not corrected for the stretch of the glass which would cause a drift in the pressures, resulting in too small values as the pressure increased. A better understanding of the differences in the pressures which have caused the change in the constants of the equation of state may be obtained by comparing the equations themselves. Representing by p_r the values of the pressure calculated by the equation based on Ramsay and Young's data and by p_k the values calculated by the equation based on the new data, the difference in pressures is given by the equation

$$p_r - p_k = \Delta p = (RT/v^2)(\delta_r - \delta_k) - (2/v^3)(A_k l_k - A_r l_r)$$

or

$$p = (1.108T/v^2)(\delta_r - \delta_k) - (2.396 \times 10^4)/v^3$$

The following table has been calculated by this equation:

Δp.	V. Cc.	*t*.	*p* approx. atm.	Percentage. Difference.
—0.563	15	300	34.8	—1.62
—0.541	15	150	18.9	—2.85
—0.186	50	150	9.4	—1.95
+0.011	100	150	4.7	+0.23
+0.0013	500	150	0.94	+0.14

It appears that the absolute difference in pressure is nearly independent of temperature as small volumes are approached and that as larger volumes are considered the differences in the pressures given by the two equations becomes more and more inappreciable. Clearly measurements of great uniform precision would be required at large volumes to enable decisions to be made regarding the comparative differences in constants.

6. Interpretation of All Experimental Data Relating to the Vapor Phase.

The equation for ϕ appears to indicate that l is zero, but in the case of carbon dioxide[1] l appears to be one-fourth the magnitude of l in the liquid phase where the units are cc. per gram. If the same rario held between these constants in the case of ether the value of l would be about 0.065. The extent and accuracy of the present work is not sufficient to enable the value to be determined although if in the plot, Fig. 5, the 14 cc. group of data are discarded, the most "representative line" through the remaining data passes above the zero of ordinates and at about 0.07 cc. It may accordingly be the fact that there is sufficient association at 14 cc. to necessitate the rejection of this volume from the plot of the substantially unassociated ether.

Assuming the liquid ether to be associated to double molecules within the region of Amagat's one to one thousand atmospheres gives the following δ equation where the units are cc. per gram:

$$\log_{10} l_2 = 0.48959 - (0.5098/v).$$

The equation for the gas phase based on the present work on the other hand, using the same units and assuming the presence of single $[(C_2H_5)_2O]$ molecules only is

$$\log_{11} \delta e = 0.79352 - (2.086/v).$$

The β and α values obtained from these equations are given in Table VI.

TABLE VI.

β_1.	β_2.	
6.216	3.0874	$\beta_1/\beta_2 = 1.982$
α_1.	α_2.	
4.805	1.174	$\alpha_1/\alpha_2 = 4.094$

$$2\beta_2 = 6.748 \equiv 6.216 = \beta_1$$

$$4\alpha_2 = 4.696 \equiv 4.805 = \alpha_1$$

It is evident that there is apparently a simple numerical relation between the constants of the gas phase δ equation and the liquid phase δ equation provided the assumption is made that the molecules in the liquid phase are associated completely to double molecules. The ratio of the values of the A and l constants cannot be given until further work has been carried out which will enable the value of l to be determined more definitely. In the case of carbon dioxide, however, the ratio$(A_1/A_2)CO_2$ is 2.06 while $(l_2/l_1)CO_2$ is 3.44. The gas phase data is due to Andrews, while the liquid phase data is due to Amagat's data, from one to a thousand atmospheres. The value of the l ratio is probably 4 and if this ratio

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[1] Keyes and Kenney, *Am. Soc. Refrigerating Eng. J.*, 3, 1 (1917).

were assumed, the l_1 calculated from the liquid phase l_2 would be numerically 0.0475 in place of 0.055 obtained directly from Andrews' results. This difference in gas phase l values is well within the limits of accuracy of Andrews' work.

The ratio of the β and α constants has been presented in terms of the units, cc. per g. and atmospheres. When the mol is chosen as the unit β_2 is numerically 457.0, while β_1 is 460. The value of α_2 is 174.0, and that of α_1 is 356.0. The magnitude β would be the limiting "volume effect" of the molecules as infinitely large volumes were approached, assuming no change in the molecular type took place as the substance expanded. The numerical result means, therefore, that if the liquid molecules $[(C_2H_5)_2O]_2$ were expanded to infinite volume the limiting "volume effect" would equal numerically the limiting "volume effect" of the gas phase molecules $[(C_2H_5)_2O]$ when expanded to infinite volume.

In the papers to follow similar investigations of systems with diatomic molecules as well as one with a monatomic molecule will be presented.

7. Summary.

The classical ideas upon which the kinetic theory is based have been discussed as they relate to van der Waals' work, and the attempt has been made to base an equation of state on the atom as it is at present comprehended.

It has been indicated that the proportionality of pressure-increase to temperature-increase at constant volume is the only reliable test for a system with one type of molecule, and that departure from the linear isometric is due to a polymerization or change in the molecular system under consideration.

The older data for ethyl ether have been examined with respect to the new equation of state, and the particular form of mathematical function for $\delta = \beta e^{-\alpha/v}$ shown to be exact as well as the cohesive pressure expression $\phi = A/(v - l)^2$.

The isometrics of ethyl ether have been measured directly and shown to be linear within the limits of accuracy of the measurements. From the constants of these isometrics the δ equation and ϕ equation have been computed and the mathematical form deduced for each shown to be exact.

The data of Amagat on the liquid phase of ethyl ether have been used to determine the equation for δ (liquid phase) on the assumption that two of the vapor phase molecules associate in the liquid phase to form a new moelcular species $[(C_2H_5)_2O]_2$. The ratios of the β constants and α constants have been compared and found to be in simple ratio. For a mol of liquid, β_2 the limiting "volume correction" is numerically equal to β_1 the limiting "volume correction" for the gas phase, while α_2 is numerically one-half as great as α_1 of the gas phase.

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