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THE INTERNAL HEAT OF VAPORIZATION.

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If a liquid is heated the temperature of the liquid rises until the boiling point of the liquid is reached. When the liquid has attained this temperature no amount of further heating will serve to raise the temperature of the liquid in the least—the liquid merely changes into vapor—the temperature of the liquid and the temperature of the vapor being both the same and remaining perfectly constant until all of the liquid has been vaporized. The heat that was necessary to vaporize the liquid after the boiling point was reached is known as the heat of vaporization of the liquid. As we have stated, the liquid and its vapor are at precisely the same temperature and both are under identically the same pressure (the atmospheric pressure), which has also remained constant throughout the process of vaporization. If no heat were added at that temperature and pressure none of the liquid would vaporize. Hence the added "heat of vaporization" is evidently necessary merely to change the substance from the condition of liquid to that of vapor under the given temperature and pressure.

During this change from the condition of liquid to that of vapor the substance has changed from the volume, which we will call v, occupied by the liquid, to the usually much larger volume occupied by the vapor, which larger volume we will call V. The total change in volume is $V - v$. This change in volume has occurred in spite of the fact that the external atmospheric pressure was continually acting as a weighted piston whose resistance had to be overcome (that is, the piston had to be pushed back), as the liquid expanded to vapor. Work was necessary to overcome this external pressure as the liquid expanded. If we represent the pressure by P, the work done will be measured by $P(V - v)$. Calling the energy so used E_e, and using the constants previously adopted[1] (the pressure being expressed in millimeters of mercury and the volumes being expressed in cubic centimeters), we will have

$$(1) \qquad E_e = 0.0_431833 \, P(V - v) \text{ calories.}$$

This equation represents the amount of the total heat of vaporization that was necessary to do external work. If from the "total heat of vaporization," which we will call L, we subtract that part of the heat which went to do the purely "external work," E_e, we will have, in all cases, a certain residual heat which must have been used in doing internal work as the substance expanded. This heat we will call the "internal heat of vaporization" and denote by the symbol λ. We may therefore write,

$$(2) \qquad L - E_e = \lambda.$$

Now it must be remembered that the boiling point of a liquid changes with the external pressure to which the liquid is subjected. If the external pressure is lessened—as by the use of an air pump—the boiling point of the liquid is lowered. If the external pressure be increased—as by the use of a suitable compressor—the boiling point of the liquid is raised. A liquid may, by suitably regulating the external pressure, be made to boil at any temperature between its freezing point and its critical temperature. What has been said above holds true for any boiling point of any liquid. But if the same weight of a liquid be taken it will be found that the volume of the liquid and the volume occupied by its vapor change with the temperature and pressure and therefore at each boiling point P, V, and v have all changed. E_e has therefore changed, and it will be found that both L and λ have also changed. We undertake in this paper to study these changes with the hope of throwing some light upon their cause and upon the theory of liquids in general.

Since many readers of this article doubtless do not care for a detailed mathematical discussion of the changes involved, we will first briefly outline the results of the investigation. Then later we give, or give reference to, such details as will enable the work and the conclusions to be critically studied.

We have used the three following equations for calculating the internal heat of vaporization.

$$(3) \qquad \lambda = 0.0_431833 \left(\frac{dP}{dT} T - P\right)(V - v) \text{ calories.}$$

$$(4) \qquad \lambda = \mu'(\sqrt[3]{d} - \sqrt[3]{D}) \text{ calories.}$$

$$(5) \qquad \lambda = C.\ R\, T \ln V/v = 4.77\, C(T/m)(\log d/D) \text{ calories.}$$

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[1] *J. Physic. Chem.*, 8, 384 (1904).

In these equations:

λ is the internal heat of vaporization of one gram of the liquid.

T is the absolute temperature.

P is the vapor pressure in millimeters of mercury.

V is the volume of one gram of the saturated vapor.

v is the volume of one gram of the liquid.

d is the density of the liquid.

D is the density of the saturated vapor.

μ' is a constant for any particular substance. These constants are given in Table 2, under the heading "Average μ'."

C is a constant for any particular substance. These constants are given in Table 2, under the heading "Average C."

R is the constant of the gas equation, $PV = RT$, and is equal to $1.9878/m$.

m is the molecular weight of the substance.

Thirty-eight substances were investigated and the values obtained from all three equations are given in Tables 3 to 40, at the end of this article (equation 3 under the heading "Ther," equation 4 under the heading "Mills," and equation 5 under the heading "Dieterici). Whenever, except with the associated substances, the value obtained from equation 4, or from equation 5, differed from the value obtained from equation 3 by more than one calorie the divergent value is marked with an asterisk above and to the right. Even a brief examination of the results as shown in the tables proves conclusively that the equations are in substantial accord with each other, and a more thorough examination (see later) shows that most of the divergences are due either directly to experimental error or to the multiplication of such error by the calculations. Equation 3 is certainly true and the other two equations must similarly represent the truth.

The three equations represent, therefore, three facts, and each equation must be capable of a certain physical interpretation and is worthy of study not alone as a mathematical problem but as a representation of a physical reality. We will consider in turn the meaning of the three equations.

Interpretation of Equation 3, $\lambda = 0.0_431833\left(\frac{dP}{dT}T - P\right)(V - v)$.

This equation is the well known thermodynamical equation first discovered by Clausius and later independently discovered by Clapeyron. Its derivation and application are discussed in all works on thermodynamics and in most of the larger works on physics and physical chemistry. It can be derived from the first and second laws of thermodynamics and if those laws are true the equation must be true. (At least this seems to be the universal opinion. The author himself has never felt quite sure that the equation really rests upon those two laws *alone*.)

The equation is a very general one and makes no supposition as to the nature of the substance or as to the cause of the change. The equation applies equally as well to the calculation of the "heat of fusion," the "heat of volatilization," or to the heat given out during a change of state, as for instance the change of monoclinic into rhombic sulphur. The equation has been abundantly verified, both directly and indirectly, and we believe that its absolute truth is now practically universally admitted.

While the truth of the equation itself cannot be regarded as doubtful, yet in order to calculate λ by its use the values of P, V, v, and dP/dT at the temperature T must be obtained, and the accuracy of the values of λ finally obtained will depend upon the accuracy of the individual observations and upon the way in which the errors of observation that occur are compounded or magnified in the calculations. It is necessary, therefore, to form some idea of the errors which may be thus introduced.

Excepting some of the data for water, the necessary measurements for the first thirty-one substances given were made by Sir Wm. Ramsay and Dr. Young, or by Dr. Young himself, or by Dr. Young and his coworkers. References to the data as published, and most of the original data, are given in the series of papers by the author on Molecular Attraction, to which reference is given later. But the volumes of the saturated vapor of most of the substances, and the smoothed values of the pressure of some eight of the substances, have recently been revised by Dr. Young, and these revisions have not yet been published, but are to be published shortly, together with the complete data, in the Proceedings of the Royal Dublin Society.

Regarding the data for these first thirty-one substances we would point out:

1. At 0° (except for ethyl oxide and methyl and ethyl alcohols) and at 30° for bromobenzene and iodobenzene, the calculated volume of the vapor had to be used. The error introduced by this calculation varies with the reduced temperature[1] ($273/T_c$) for the substance in question and makes the value of the constant at 0° too large. The error thus introduced may even reach two per cent., as with isopentane.

2. The calculation of the dP/dT introduces the largest error into the constant, and is especially uncertain at the end points of the vapor pressure curve. This point has already been discussed[2] and it is useless to repeat that discussion here. In addition to this source of error, we have also pointed out[3] that the Biot formula, from which the dP/dT is derived, cannot be made to fit the observed pressures exactly in the neighbor-

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[1] Young, "Stoichiometry," p. 342, etc.

[2] *J. Physic. Chem.*, 8, 394–397 (1904).

[3] *Ibid.*, 9, 406–411 (1905).

hood of the critical temperature but always gives too low results. This error is greatly magnified in the calculation of the dP/dT and results invariably in giving too low values for the constant as the critical temperature is approached. *The values at 0° (30° for bromobenzene and iodobenzene), and in the immediate neighborhood of the critical temperature, must, therefore, be excluded from consideration because of errors introduced by the calculation.*

3. As regards diisobutyl, we have some reason for believing the substance impure.[1] Until further investigation can definitely settle this point, the values given for this substance should not be given too great weight.

4. Excepting, therefore, the values at 0° (30° for bromobenzene and iodobenzene) and in the neighborhood of the critical temperature, and the values for diisobutyl, we believe that the remaining values of the internal heat of vaporization given for these substances under the heading "Ther" are substantially true—the error caused by inaccurate measurements and by the multiplication of such errors in the calculation never exceeding 2 per cent. and only very rarely exceeding 1.5 per cent. Usually the error is less than 1 per cent.[2]

As regards the last seven substances shown in the tables, the data obtainable are not always trustworthy. The observed or thermodynamically calculated heats of vaporization may be very considerably in error. For a detailed discussion of these results see a former paper.[3]

Hence the values of the internal heat of vaporization obtained from equation 3 and marked "Ther," or from direct observations and marked "Observed," in the tables can, with due regard to the facts above stated, be regarded as accurate, and can be used as a standard by which the truth of equations 4 and 5 can be judged.

Interpretation of Equation 4, $\lambda = \mu'(\sqrt[3]{d} - \sqrt[3]{D})$.

The author, in a series of eight papers,[4] deduced and studied this equation. The entire series of papers needs revision and the author hopes to publish such revision later, giving all of the data and calculations fully. The internal heats of vaporization as given in this paper under the heading "Mills" are revised values and have not heretofore been published. *We believe that these internal heats of vaporization, except for the associated substances, water, the alcohols, and acetic acid, agree with the thermodynamical or observed heats of vaporization throughout, to within*

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[1] *J. Physic. Chem.*, **13**, 526 (1909).

[2] For further details concerning the calculations and results see *J. Physic. Chem.*, **8**, 386–397 (1904); **13**, 512 (1909).

[3] *Ibid.*, 10, 1 (1906).

[4] *Ibid.*, **6**, 209 (1902); **8**, 383 (1904); **8**, 593 (1904); **9**, 402 (1905); 10, 1 (1906); **11**, 132 (1907); **11**, 594 (1907); **13**, 512 (1909).

the limit of experimental error. The results speak for themselves and in only a very few instances is the above conclusion open to the least doubt. If these divergences are carefully examined in the light of our comments and references upon the accuracy of the thermodynamical results, we believe that all of the divergences will be conceded as more probably due to errors of experiment as compounded and magnified by the calculations.

Accepting the equation therefore as true, what does the equation really mean? The equation was deduced[1] theoretically by the author from certain assumptions. Since the equation is true it is highly probable that these assumptions as to the molecules and molecular forces, do, to some extent at least, represent the truth, and since they have led to a true relation they are worthy of study and of a certain amount of respect. These assumptions may be briefly stated as follows:

1. The total energy *per se* of a molecule must be the same in the liquid as in the gaseous state, the temperature being the same. If at a given temperature a given weight of gas represents more energy than the same weight of the substance as a liquid, the extra energy of the gas must be energy of position only (assuming no intramolecular change).

Expressing the above belief in a different form, we may say that the energy necessary to change a liquid into a gas must be spent solely in overcoming the external pressure and in altering the distance apart of the molecules (unless the molecule breaks apart also or nears the point of disruption). Hence the internal heat of vaporization must be spent solely in overcoming the molecular attraction as the molecules move further apart.

2. The molecular attraction between two molecules varies inversely as the square of the distance apart of the molecules.

3. The molecular attraction does not vary with the temperature.

4. The molecules in the liquid and in the gaseous condition are evenly distributed throughout the volume occupied by them, and the number of molecules does not change.

5. The attractive forces, whatever their nature, whether chemical, molecular, magnetic, electrical, or gravitational, which proceed from a particle are definite in amount. If this attraction is exerted upon another particle the amount of the attraction remaining to be exerted upon other particles is diminished by an exactly equivalent amount. (This assumption was not originally made. So far as the molecular attraction is concerned, it is believed, as will appear later, to be a necessary consequence of the facts developed.)

The above assumptions are, none of them, purely gratuitous assumptions made to fit the case in hand. They seemed to the author proba-

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[1] *J. Physic. Chem.*, 11, 132 (1907).

bly true before the equation at present under discussion was discovered, and the equation would not have been discovered had not the assumptions first been made from evidence quite outside of the equation. The evidence in their favor cannot be given and discussed fully in the present paper but a few comments are warranted by the general importance of the assumptions.

The first assumption followed from a study of the kinetic theory of gases, the specific heat of gases, and the application of the gas law, $PV = RT$, to solutions. If the gaseous pressure was produced by the motion of the molecules and a similar pressure (as osmotic pressure) was produced in solution, it seemed reasonable to suppose that the osmotic pressure was in some way due to an equal molecular motion. The molecules of the dissolved substance could not have an average kinetic energy of translational motion different from the molecules of the solvent. Hence the conclusion that the *average translational energy of gaseous and liquid molecules at the same temperature must be equal.*

Now a study of the specific heat of gases showed that the total energy of a gaseous molecule, exclusive of the energy which holds the molecule together and of extraneous forces, is proportional to the translational energy. When the causes for this relation were considered, it seemed a reasonable inference that the *total energy of a molecule of a liquid would similarly be found to be proportional to its translational energy.* Therefore the first assumption follows.

The second assumption was made because all of the attractive forces, whose law of variation with the distance we know, obey the inverse square law. This is true of electrical, magnetic, and gravitational forces. Also the intensity of sound, of light, and of heat vary inversely as the square of the distance from the origin. It seemed to the author, whatever the nature of the molecular attractive force—be it wave motion or emanation—that the intensity of the force must decrease directly in proportion to the increase in the surface of the wave or emanation front, and since and because this surface increases as the square of its distance from the origin, the attractive force must decrease proportionately, and therefore obey the inverse square law.

The third assumption that the molecular attractive force did not vary with the temperature seemed the most natural assumption, for none of the other attractive forces, chemical, magnetic, electrical, or gravitational, are affected by temperature changes so far as is known.

The fourth assumption that the molecules in the liquid and in the gaseous condition are evenly distributed throughout the space occupied by them is probably always more or less untrue. But if the molecules are shifted from their ideal position by reason of the attractive force, the particles would gain in kinetic energy exactly so much as they would lose in potential energy. We may therefore, without error, consider them to be shifted back into their position of even distribution, and the fundamental supposition upon which the mathematical work is based, is that the molecules of a liquid and the molecules of its vapor have *per se* the same energy when they are in this ideal position of even distribution throughout the space occupied by them.

Except for associated substances or substances undergoing decomposition, it is generally believed, and the belief rests upon considerable experimental evidence, that the number of molecules in the liquid and in the gaseous condition are the same. The equation is not true where this condition is violated.

The fifth assumption.—On the one hand, if one assumes that the molecular attraction follows the law of gravitation, as proposed by Newton, namely, force $= \mathrm{K}mm'/\mathrm{S}^2$, where m and m' are the masses of the attracting bodies, S is their distance apart, and K is a constant (though not the same constant as the gravitational constant), then the resultant attraction caused by the large number of molecules must apparently increase as we proceed outward from an interior centrally chosen particle. This follows because the number of molecules increases as the cube of the distance from the centrally chosen molecule, whereas the attraction varies only inversely as the square of that distance. Hence the resultant attraction of any mass upon a particle exterior to the mass, when regarded as proceeding from the center of that mass, must vary as the mass. The molecular sphere of action could not, therefore, be small, but would embrace the entire mass taken. Now the evidence that the molecular sphere of action is small is beyond dispute. Moreover, the gravitational law for the molecular attractive force necessitates that it should require very much more than twice as much heat to vaporize 2 grams of a liquid as to vaporize 1 gram. We know that only twice as much heat is required.

On the other hand, we have overwhelming evidence[1] that the equation,

$$\frac{\mathrm{L} - \mathrm{E}_e}{\sqrt[3]{d} - \sqrt[3]{\mathrm{D}}} = \text{constant},$$

does represent a true law, and that one factor of the molecular force does vary inversely as the square of the distance apart of the molecules. The paradox must be explained. It cannot be ignored.

It seems reasonable to suspect the cause of the paradox to be due to the numerator of the function representing the law of the force, $f = \mathrm{K}mm'/\mathrm{S}^2$, and not to the denominator. Therefore the fifth assumption was made as offering a solution of the paradox. The derivation of the equation,

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[1] *J. Physic. Chem.*, 13, 512 (1909).

the seeming contradiction, and the explanation as offered of this contradiction, are more fully discussed in the sixth paper[1] above cited.

While it seems to the author that all of the above assumptions are conditions that must be fulfilled if the equation $\lambda = \mu'(\sqrt[3]{d} - \sqrt[3]{D})$ is true, we do not mean at all to say that the equation as stated really represents all of those conditions. The equation rests upon those conditions and was derived logically from them, but the meaning of the equation itself is more restricted. Taking into consideration the theory by which the equation was derived, it is certainly probable that the equation will represent, under all circumstances, the work done against the force of molecular attraction in moving molecules further apart. Now, the further the molecules are moved apart the less becomes the value of D, and D will finally become zero when the molecules have been moved an infinite distance apart. Making, therefore, D equal to zero, and remembering that the distance apart of the molecules which we will call s, is proportional to $1/\sqrt[3]{nd}$, where n is the number of molecules and is therefore a constant, we can write

$$(6) \qquad \lambda_{\infty} s = \text{constant}$$

as the very simple form assumed by the law under discussion. This statement means simply this:

In any normal substance the internal heat given out as the molecules approach each other, multiplied by the distance apart of the molecules, is equal to a constant.

The equation $\lambda_{\infty} s$ = constant and the above statement are true, because the molecular attraction varies inversely as the square of the distance apart of the attracting particles and because the total amount of attractive force possessed by a molecule is a constant.

The author believes that the above equation and italicized sentences express the physical reality represented by the equation under discussion, $\lambda = \mu'(\sqrt[3]{d} - \sqrt[3]{D})$.

Interpretation of Equation 5, $\lambda = C. \mathrm{RTln}\, V/v$.

In the series of papers cited above upon molecular attraction, a very thorough study has been made of an equation proposed by H. Crompton:[2]

$$(7) \qquad L = 2\ \mathrm{RTln}\, V/v = 2\ \mathrm{RTln}\, d/D.$$

The equation was derived by Mr. Crompton on theoretical grounds and we quote his argument verbatim:

"Imagine a saturated vapor in so attenuated a state that the gas law, PV = RT, applies to it. Assume that it were possible at constant temperature and by compression alone to reduce the volume of the vapor

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[1] *J. Physic. Chem.*, **11**, 132 (1907).

[2] *Proc. Chem. Soc.*, **17**, 61 (1901).

V to the volume which the liquid it forms would normally occupy v, *without any change in state occurring, and the substance during this compression continuing to obey the gas law.* The work done in bringing about this change in volume would be

$$\int_v^V P dv = \int_v^V \frac{RT}{v} dv = RT \log_e \frac{V}{v},$$

and, as no change in temperature occurs, heat equivalent to this work will be given out during compression.

"The vapor now occupies the volume of the liquid but it is not yet liquid. It is by assumption a gas under high pressure, and if the pressure is now reduced to its original amount, the gas would expand to its original volume. To form the liquid the substance must be brought to such a state that it would be possible to reduce the pressure to the normal vapor pressure of the liquid, without any corresponding change in volume. Assuming that no change in molecular aggregation occurs, the substance must then be deprived of the potential energy of expansion of the gas, that is, of the energy that would enable the molecules of the substance to occupy their original volume on a return to the original pressure. This energy is equal to that expended in compressing the material, namely, $RT \log_e V/v$. If this is removed in the form of heat, the total heat given out during the production of the liquid from the vapor is $2RT \log_e V/v$, and this is the latent heat of evaporation."

Crompton applied this equation to carbon dioxide, nitrous oxide, and sulphur dioxide, and obtained results apparently confirming his idea, although it was noted that the calculated results were usually somewhat too high.

The author, in the papers above cited, extended the investigation of Crompton's equation to thirty-eight substances, over wide ranges of temperature and pressure, and reached the following conclusion regarding the equation:

The relation gives values for the heats of vaporization uniformly too high at low vapor pressures, but at high vapor pressures, in the neighborhood of the critical temperature, the equation is accurate.

Moreover, it was shown[1] that the equation of Crompton, 7, could be combined with the thermodynamical equation below,

$$(8) \qquad L = 0.0_4 31833 \frac{dP}{dT} T(V - v) \text{ calories,}$$

and would give as a result,

$$(9) \qquad \frac{dP}{dT} = \frac{2 \times 62445}{m} \cdot \frac{\ln V/v}{V - v}.$$

This equation is not true at all temperatures, owing to the inaccuracy

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[1] *J. Physic. Chem.*, **8,** 625 (1904); **9,** 402 (1905).

of Crompton's equation, but at the critical temperature it should be true. At the critical temperature the fraction $\frac{\ln V/v}{V - v}$ assumes the indeterminate form 0/0. Evaluating by differentiating the numerator and denominator we find the limit approached at the critical temperature to be $1/V_c$. Therefore, at the critical temperature, we have

$$\frac{dP}{dT} = \frac{124890}{mV_c} = \frac{2R}{V_c}. \tag{10}$$

We give in Table 2 the values for the dP/dT at the critical temperature thus obtained. Equation 10 means that the change of vapor pressure with the temperature at the critical temperature is just twice what it would be for a perfect gas occupying the critical volume. Dieterici[1] had himself observed this relationship, unknown to the author, giving the result as an empirical fact.

Prof. C. Dieterici[2] recently proposed the equation of the form

$$\lambda = C.\ RT\ln V/v = 4.577\ C(T/m)(\log d/D) \text{ calories,} \tag{5}$$

resembling, as will be seen, very closely the equation proposed by Crompton.

The relationship above given was discussed and investigated for isopentane by Dieterici, and was further applied to benzene, ether, sulphur dioxide, carbon dioxide, and water, in a dissertation published by A. Richter.[3] Except when within a few degrees of the critical temperature, the factor C was found by them to be remarkably constant for ether, benzene, and isopentane, where the observations of Dr. Sydney Young were used. For carbon dioxide and sulphur dioxide the deviations are greater, due probably to the use of less exact data, and for water the divergency from constancy is quite marked, a divergence which was to be expected from the well recognized exceptional behavior of water, due probably to the association of its molecules.

The above equation 5 seemed to us to offer a possible explanation of the flaw in Crompton's equation and argument. Our interest in the equation was increased by the fact that Dieterici, in undertaking to calculate the constant C of the equation, made use of equation 10,

$$\left(\frac{dP}{dT} = \frac{2R}{V_c}\right),$$

and thereby (though apparently unwittingly) admitted the truth of Crompton's equation at the critical temperature, since we have shown that equation 10 is an immediate consequence of Crompton's equation. We determined, therefore, to investigate thoroughly the relation proposed by Dieterici. Since Dr. Young had meanwhile revised much of

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[1] *Ann. der Physik*, **12**, 144 (1903).

[2] *Ibid.* [4], **25**, 569 (1908).

[3] "Ueber die innere Verdampfungswärme," Rostock, 1908.

the data used by Dieterici and Richter, it was necessary also to revise their calculations.

The internal heat of vaporization we had already calculated, except in the few places where direct measurements were available, from equation 3. Combining equation 3 with equation 5, we obtain

$$(11) \qquad C = \frac{0.0_4 31833 \left(\frac{dP}{dT} T - P\right)(V - v)}{\frac{4.577}{m} T \log_{10} d/D}$$

This equation was tested for thirty-eight substances over wide ranges of temperature. A summary of the values obtained for C are given in Table 1 (pp. 1111-1114).

In this table all values of C differing by more than 2 per cent. from the average value of the uncrossed results shown at the top of the column are marked with an asterisk above and to the right. All values of C differing from this average value of C by more than 1 per cent. are marked with a plus or minus, above and to the left, to show the nature of the divergence. We have already pointed out the errors introduced into the calculation of C by equation 3 (pages 1102 and 1103) and an inspection of Table 1 in the light of that discussion shows, I think beyond any question, that nearly all of the variation of C from constancy is due to the errors thus introduced in calculating the internal heat of vaporization from the data. This idea is greatly strengthened by a comparison of Table 1 with the values for the constant μ' of equation 4, as given in a previous paper.[1] At only one point, 0° (30° for bromobenzene and iodobenzene), is there an essential difference of behavior shown by the results of these two tables. At this point the divergences, shown by Table 1, are more marked, are always negative, and appear to increase as the vapor pressure is lowered. On the other hand, the divergences in μ' shown at this point are usually, though not always, positive. This same difference is shown very clearly by a comparison of the internal heats of vaporization as calculated from equations 3, 4 and 5, and given in Tables 3 to 40, at the end of this article. It will be seen that at very low vapor pressures the values obtained from equation 5, marked "Dieterici," are usually too high. We have already pointed out (p. 1102) that errors at 0° were introduced by using the calculated density of the vapor, and also by the unusually large multiplication of error in calculating the dP/dT from the Biot formula near its end point. Neither of these causes is sufficient to explain the divergence shown by equation 5.

The errors introduced by using the calculated density of the vapor can be estimated from the observations given by Young in his work on Stoi-

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[1] *J. Physic. Chem.*, **13**, 512 (1909).

TABLE I.—VALUES OF C IN EQUATION II.

	Ethyl oxide.	Di-iso-propyl.	Di-iso-butyl.	Isopentane.	Normal pentane.	Normal hexane.	Normal heptane.	Normal octane.	Hexa-methylene.	Benzene.	Fluo-benzene.
Av. C.	1.724	1.725	1.813	1.688	1.707	1.752	1.814	1.858	1.694	1.690	1.711
Temp.											
0°	1.718	— 1.672*	— 1.669*	1.696	1.697	— 1.680*	— 1.685*	— 1.694*	— 1.606*	— 1.601*	— 1.599*
20	1.714	..	..	1.680	..	..	..	..	..	..	..
40	1.712	..	..	1.682	1.699	..	..	..	..	..	..
60	1.718	1.726	..	1.678	1.707	1.734	..	..	..	..	..
80	1.721	1.734	..	1.682	1.710	1.753	1.800	..	1.709	1.693	1.724
100	1.732	1.727	— 1.791	1.691	1.711	1.759	1.809	..	1.710	1.691	+ 1.733
120	1.737	1.725	— 1.779*	1.692	1.724	1.767	1.808	— 1.813*	1.702	1.678	1.724
140	+ 1.749	1.721	— 1.763*	1.694	1.713	1.760	1.800	— 1.826	1.691	1.684	1.710
160	+ 1.742	1.720	— 1.769*	1.691	1.708	1.752	1.801	— 1.833	1.685	1.693	1.702
180	— 1.700	1.722	— 1.794	— 1.648*	1.696	1.751	1.823	1.841	1.689	1.701	1.699
200	..	1.723	1.810	..	..	1.755	+ 1.835	1.848	1.680	1.697	1.696
220	..	— 1.679*	1.831	..	..	1.735	+ 1.847	1.866	1.692	1.698	1.706
240	..	..	+ 1.858*	..	..	..	+ 1.858*	1.873	1.696	1.693	1.715
260	..	..	+ 1.877*	..	..	..	1.820	+ 1.895	1.699	1.691	1.724
280	..	..	..	..	..	..	..	+ 1.889	..	— 1.665	— 1.688
Critical temp.	193.8°	227.35°	276.8°	187.8°	197.2°	234.8°	266.85°	296.2°	280.0°	288.5°	286.55°

TABLE I.—VALUES OF C IN EQUATION II (*Continued*).

	Chloro-benzene.	Bromo-benzene.	Iodo-benzene.	Carbon tetrachloride.	Stannic chloride.	Methyl formate.	Ethyl formate.	Methyl acetate.	Propyl formate.	Ethyl acetate.	Methyl propionate.
Av. C.	1.714	1.691	1.687	1.667	1.741	1.706	1.747	1.784	1.774	1.812	1.803
Temp.	—	—	—	—	—		—	—	—	—	—
0°	1.583*	1.603*	1.558*	1.592*	1.579*	1.717	1.695*	1.703*	1.679*	1.721*	1.703*
20	..	..	..	..	..	..	..	..	..	..	..
40	..	..	..	..	..	1.720	..	..	..	..	..
60	..	..	..	..	..	1.713	1.757	1.778	..	..	..
80	..	..	..	1.662	..	1.706	1.758	1.790	1.785	1.798	1.791
100	..	..	..	1.664	1.742	1.702	1.756	1.784	1.777	1.816	1.796
120	..	..	..	1.662	1.749	1.714	1.754	1.786	1.774	1.821	1.800
	—										
140	1.681	..	..	1.658	1.746	1.706	1.750	1.790	1.776	1.819	1.803
		—									
160	1.697	1.658	..	1.665	1.745	1.696	1.743	1.792	1.766	1.806	1.805
			—			—					
180	1.711	1.675	1.658	1.663	1.748	1.677	1.739	1.778	1.765	1.813	1.805
						—	—				
200	1.713	1.688	1.679	1.664	1.735	1.616*	1.718	1.771	1.775	1.821	1.818
							—	—			
220	1.723	1.701	1.697	1.674	1.739	..	1.663*	1.731*	1.788	1.806	1.818
	+									—	
240	1.733	1.698	1.701	1.683	1.739	..	..	..	1.789	1.755*	1.788
				+					—		
260	1.731	1.707	1.696	1.685	1.736	..	..	..	1.740	..	..
280	..	..	..	1.657	1.733	..	..	..	..	..	..
Crit. temp.	359.1°	397.0°	448.0°	283.15°	318.7°	214.0°	235.3°	233.7°	264.85°	250.1°	257.4°

TABLE 1.—VALUES OF C IN EQUATION 11 (*Continued*).

Temp.	Propyl acetate.	Ethyl propionate.	Methyl butyrate.	Methyl isobutyrate.	Water.	Methyl alcohol.	Ethyl alcohol.	Propyl alcohol.	Acetic acid.	Carbon disulphide.	Chloroform.	Acetone.
Av. C.	1.850	1.837	1.824	1.814	...	...	...	...	...	1.516	1.706	1.754
0°	— 1.718*	— 1.718*	— 1.709*	— 1.711*	1.529	1.680	1.758	1.847	...	1.502	— 1.676	— 1.728
20	..	..	..	..	1.559	1.735	1.855	..	0.857	1.516	1.696	1.750
40	..	..	..	..	1.581	1.784	1.948	..	0.925	1.524	1.716	1.754
60	..	..	..	..	1.601	1.825	2.018	..	0.986	1.528	+ 1.735	+ 1.786
80	..	..	..	..	1.620	1.858	2.080	2.103	1.047	1.525	..	..
100	1.834	1.844	— 1.779*	1.807	1.637	1.877	2.124	2.135	1.101	1.517	+ 1.771*	+ 1.802*
120	1.848	1.846	— 1.790	1.805	1.648	1.896	2.140	2.137	1.177	1.503	..	..
140	1.845	1.832	— 1.802	1.813	1.659	1.906	2.157	2.148	1.198	— 1.482*	..	..
160	1.853	1.823	— 1.804	1.810	1.670	1.918	2.170	2.117	1.231	..	..	..
180	1.856	— 1.817	1.809	1.811	1.684	1.919	2.161	2.102	1.275	..	..	..
200	1.858	1.827	1.828	1.825	1.702	1.927	2.127	2.073	1.326	..	..	..
220	1.862	1.843	1.834	1.828	1.723	1.876	2.094	2.030	1.373	..	..	..
240	1.857	1.854	+ 1.849	1.824	1.726	..	2.011	1.948	1.431	..	..	..
260	1.835	1.848	+ 1.860	1.800	1.717	..	..	1.879	1.481	..	..	..
280	..	..	— 1.737*	..	..	..	..	..	1.517[1]	..	..	..
Crit. temp.	276.2°	272.9°	281.3°	267.55°	370.0°	240.0°	243.1°	263.7°	321.65°	273.05°	260.0°	237.5°

[1] At 300° = 1.513; at 320° = 1.442

TABLE I.—VALUES OF C IN EQUATION II (*Continued*).

	Ammonia.	Sulphur dioxide.	Carbon dioxide.	Nitrous oxide.
Av. C.	1.622	1.707	1.762	1.513
Temp.				
—30°	1.608	. .	— 1.738	. .
—20	1.615	. .	+ 1.789	1.503
—10	. .	1.712	. .	. .
0	1.622	1.712	1.760	+ 1.637*
20	1.629	— 1.679	— 1.682*	1.521
40	1.634	1.697	. .	. .
60	. .	— 1.670*	. .	. .
80	. .	+ 1.750*	. .	. .
100	. .	+ 1.734	. .	. .
120	. .	+ 1.736	. .	. .
140	. .	+ 1.818*	. .	. .
Crit. temp.	131.0°	156.0°	31.35°	38.8°

chiometry, p. 342, etc. These errors are greatest when the vapor pressure is comparatively high, as with ethyl ether, isopentane, and normal pentane, and yet for these very substances, as shown in Table 1, the values of C at 0° are nearest the normal average value. The error introduced by the Biot formula is irregular, would not always make C at 0° negative, and in most cases could not be large enough to explain the divergence shown. As concerns equation 5, or the denominator of equation 11, an error in the measurement of the density or the volume of the saturated vapor or liquid is reduced in its proportionate effect upon λ or upon C. In the case of benzene we have, from the extended investigation of Griffiths and Marshall,[1] the value of 100.10 for the internal heat of vaporization at 0°. Comparing this value with the values "Ther" (99.16), "Mills" (100.05), and "Dieterici" (104.67), it will be seen that no reasonable supposition of error in the measurements can bring the latter result into accord with the facts.

To our very great disappointment we are obliged, therefore, to draw the conclusion that *at very low vapor pressures, the equation* λ = C.R Tln V/*v* *proposed by Dieterici is not exactly true. The remarkable, and apparently exact, agreement with the facts given by this equation at higher temperatures deserves the closest attention and study.* The equation undoubtedly marks an important step forward and must aid greatly in understanding the theory of liquids.

[1] *Phil. Mag.*, 41 (1896).

The relations between equations 4 and 5 are very suggestive. Equation 4 can be written, when V = infinity, $\lambda\sqrt[3]{v}$ = constant, reminding one of Boyle's law, PV = constant. The two equations are, of course, not simultaneous, and yet the equation of Dieterici, $\lambda = \mathrm{CR\ T}\ln V/v$, bears an evidently simple relation to the gas law, PV = RT, and is in turn related to each of the above equations. In Dieterici's equation λ would become infinite when V = 0 unless T were also equal to 0. We do not yet see clearly the true meaning of these relationships nor can we yet give a theoretical basis for the equation of Dieterici, or explain the physical meaning lying behind the equation. The argument of Crompton is undoubtedly wrong and yet his reasoning and its results, taken in connection with the equation of Dieterici, are exceedingly suggestive We very much desire that some one should throw further light upon the cause and meaning of these relationships.

Some Necessary Consequences of the Equations.

We would examine more closely the relationship between the three equations used for calculating the internal heat of vaporization, namely

$$(3)\qquad \lambda = 0.0_4 31833 \left(\frac{d\mathrm{P}}{d\mathrm{T}}\,\mathrm{T} - \mathrm{P}\right)(\mathrm{V} - v)\ \text{calories,}$$

$$(4)\qquad \lambda = \mu'(\sqrt[3]{d} - \sqrt[3]{\mathrm{D}})\ \text{calories,}$$

$$(5)\qquad \lambda = \mathrm{CR\ T}\ln\frac{\mathrm{V}}{v} = \mathrm{C}\,\frac{4.577}{m}\,\mathrm{T}\log_{10}\frac{d}{\mathrm{D}}\ \text{calories.}$$

Combining equation 3 with equation 4 we obtain

$$(12)\qquad \mu' = 0.0_4 31833 \left(\frac{d\mathrm{P}}{d\mathrm{T}}\,\mathrm{T} - \mathrm{P}\right)(\mathrm{V}v^{1/3} + \mathrm{V}^{2/3}v^{2/3} + \mathrm{V}^{1/3}v),$$

which at the critical temperature becomes

$$(13)\qquad \mu' = 0.0\,955\,\mathrm{V}_c^{4/3}\left(\frac{d\mathrm{P}}{d\mathrm{T}}\,\mathrm{T}_c - \mathrm{P}_c\right).$$

Solving equation 12 for P we obtain

$$(14)\qquad \mathrm{P} = \frac{d\mathrm{P}}{d\mathrm{T}}\,\mathrm{T} - \frac{31414u'}{\mathrm{V}v^{1/3} + \mathrm{V}^{2/3}v^{2/3} + \mathrm{V}^{1/3}v}$$

This equation is accurate, but the right-hand member being the difference of two nearly equal quantities, greatly magnifies errors of observation and makes the equation unsuitable for calculating the pressure.

At the critical temperature equation 14 gives

$$(15)\qquad \mathrm{P} = \frac{d\mathrm{P}}{d\mathrm{T}}\,\mathrm{T}_c - \frac{10471\mu'}{\mathrm{V}_c^{4/3}}.$$

We have called attention[1] to the similarity of equation 15 to the equation proposed by Ramsay and Young,[2]

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[1] *J. Physic. Chem.*, **8**, 622 (1904).

[2] *Phil. Mag.*, May, 1887; *Ibid.*, August, 1887; *Ibid.*, April, 1899; *Proc. Phys. Soc.*, 1894–95; *Ibid.*, 15; *Ibid.*, 17.

$$(16) \qquad P = bT - a,$$

where $b = \dfrac{dP}{dT}$ and a is a constant. It is interesting also to view equation 14 as a combination of two equations, one for the liquid and the other for the vapor, both similar in form to equation 16.

Combining next equation 3 with equation 5 we obtain

$$(17) \qquad C = \frac{0.0_431833\left(\dfrac{dP}{dT}\,T - P\right)(V - v)}{R\,T \ln V/v},$$

which at the critical temperature becomes

$$(18) \qquad C = \frac{0.0_431833\left(\dfrac{dP}{dT}\,T_c - P_c\right)V_c}{RT_c} = \frac{mV_c\left(\dfrac{dP}{dT}\,T_c - P_c\right)}{62445T_c}.$$

Combining this equation with equation 13 we obtain, also at the critical temperature,

$$(19) \qquad C = \frac{\mu'}{3RT_cV_c^{1/3}} = \frac{\mu'\sqrt[3]{d_c}}{3RT_c} = \frac{m\mu'\sqrt[3]{d_c}}{3 \times 1.9878T_c} = \frac{m\mu'\sqrt[3]{d_c}}{5.9634T_c},$$

an important result. This equation may also be obtained directly by combining equations 4 and 5 and obtaining

$$(20) \qquad C = \frac{\mu'(\sqrt[3]{d} - \sqrt[3]{D})}{R\,T\ln V/v} = \frac{\mu'}{RT}\cdot\frac{V - v}{\ln V/v(Vv^{1/3} + V^{2/3}v^{2/3} + V^{1/3}v)},$$

which at the critical temperature becomes

$$(21) \qquad C = \frac{\mu'V_c}{3RT_cV_c^{4/3}} = \frac{\mu'\sqrt[3]{d_c}}{3RT_c} = \frac{m\mu'\sqrt[3]{d_c}}{3 \times 1.9878T_c}$$

Several years ago[1] we deduced theoretically and investigated the relation

$$(22) \qquad \frac{m\mu'\sqrt[3]{d_c}}{T_c} = \text{constant}.$$

The theoretical basis for this equation we found in the belief that at the critical temperature the kinetic energy of the molecules was just sufficient to overbalance the molecular attraction and would cause the molecules to fly apart were the pressure removed. Now the kinetic energy, E_K, of the molecules at the critical temperature is

$$(23) \qquad E_K = {}^3/_2RT_c = \frac{2.982T_c}{m} \text{ calories},$$

and the energy necessary to overcome the molecular attraction and cause the molecules to fly apart to an infinite distance is, from equation 6, since $D = 0$,

$$(24) \qquad \lambda_\infty = \mu'\sqrt[3]{d_c} \text{ calories}.$$

Equation 19 may therefore be written

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[1] *J Physic. Chem.*, 6, 228 (1902); 8, 630 (1904); 10, 33 (1906).

$$(25)\quad C = \frac{\mu' \sqrt[3]{d_c}}{2E_K} = \frac{\text{energy necessary to overcome molecular attraction}}{2 \times \text{kinetic energy of molecules}}$$

We give below, in Table 2, the substances investigated, their molecular weight, critical data, the average contains μ' and C and finally the values $\frac{m\mu' \sqrt[3]{d_c}}{5.9634T_c}$ under the heading "Equation 19, C′."

It will be seen that the values of C so calculated are larger (with the exception of carbon disulphide, where the data is most uncertain) than the average values of C. We give under the heading $\frac{C'}{C}$ the ratio of the two values. Since equation 21 is not exactly true, it is plainly evident that either equation 4 or equation 5, or both are not exactly true at the critical temperature. Unfortunately, the errors introduced into the calculations near the critical temperature by the use of the Biot formula for obtaining the $\frac{dP}{dT}$ make it impossible to decide with certainty as to the cause of the trouble, and a very careful examination of the smoothed $\frac{dP}{dT}$ obtained directly from the observed pressures near the critical temperature still leaves us in doubt. However, a careful review of all the data inclines us to the belief that the values of μ' in equation 4 decrease slightly near the critical temperature with some substances, and also that the values of C in equation 5, proposed by Dieterici, increase slightly as the temperature is raised. Such decrease and such increase is, when an individual substance is considered, within the possible limit of experimental error, and probably no certain conclusion can be drawn until a method of directly and accurately measuring the $\frac{dP}{dT}$ at and near the critical temperature is devised and carried out. The suspected slight variation in C and in μ' with the temperature may be due to slight changes in molecular association or to slight changes within the molecule. It is at least suggestive that larger changes in the direction indicated do take place with the liquids whose molecules are known to be associated, as with water, the alcohols, etc., as shown in the tables.

If equation 21 be changed so that it becomes

$$(26)\qquad C = \frac{m\mu' \sqrt[3]{d_c}}{6.112T_c},$$

the average values of C for non-associated liquids at all temperatures can be calculated from the average values of μ' with an error usually less than 1 per cent. and nearly always less than 2 per cent.

If now we make the further supposition that the equation of Cromp-

TABLE 2.—RELATIONS AT THE CRITICAL TEMPERATURE.

		Critical data.					
		Temperature.					
Substance.	Molecular weight, m.	Centigrade.	Absolute.	Pressure.	Density.	Volume.	Theoretical critical density, D_c.
Ethyl oxide	74.08	193.8	466.8	27060	0.2622	3.814	0.06876
Di-isopropyl	86.112	227.4	500.4	23345	0.2411	4.148	0.06434
Di-isobutyl	114.144	276.8	549.8	18660	0.2366	4.227	0.06203
Isopentane	72.10	187.8	460.8	25020	0.2343	4.268	0.06270
Normal pentane	72.10	197.2	470.2	25100	0.2323	4.305	0.06167
Normal hexane	86.112	234.8	507.8	22510	0.2344	4.266	0.06114
Normal heptane	100.13	266.9	539.9	20415	0.2341	4.272	0.06060
Normal octane	114.144	296.2	569.2	18730	0.2327	4.297	0.06013
Hexamethylene	84.096	280.0	553.0	30250	0.2735	3.656	0.07368
Benzene	78.05	288.5	561.5	36395	0.3045	3.284	0.08100
Fluobenzene	96.09	286.55	559.55	3391	0.3541	2.824	0.09323
Chlorobenzene	112.49	359.1	632.1	33910	0.3654	2.737	0.09666
Bromobenzene	156.99	397.0	670.0	(33910)	0.4853	2.061	0.1273
Iodobenzene	203.89	448.0	721.0	(33910)	0.5814	1.720	0.1536
Carbon tetrachloride	153.8	283.15	556.15	34180	0.5576	1.793	0.1513
Stannic chloride	260.8	318.7	591.7	28080	0.7419	1.348	0.1981
Methyl formate	60.032	214.0	487.0	45030	0.3489	2.866	0.08891
Ethyl formate	74.05	235.3	508.3	35590	0.3232	3.094	0.08302
Methyl acetate	74.05	233.7	506.7	35180	0.3252	3.075	0.08230
Propyl formate	88.064	264.85	537.85	30440	0.3093	3.233	0.07980
Ethyl acetate	88.064	250.1	523.1	28880	0.3077	3.250	0.07788
Methyl propionate	88.064	257.4	530.4	30030	0.3124	3.201	0.07983
Propyl acetate	102.08	276.2	549.2	25210	0.2957	3.382	0.07504
Ethyl propionate	102.08	272.9	545.9	25210	0.2965	3.373	0.07549
Methyl butyrate	102.08	281.25	554.25	26000	0.3002	3.331	0.07669
Methyl isobutyrate	102.08	267.55	540.55	25750	0.3012	3.320	0.07788
Water	18.016	370.0	643.0	...	..	...	...
Methyl alcohol	32.032	240.0	513.0	59760	0.2722	3.674	0.05974
Ethyl alcohol	46.048	243.1	516.1	47850	0.2755	3.630	0.06835
Propyl alcohol	60.064	263.7	536.7	38120	0.2734	3.658	0.06830
Acetic acid	60.032	321.6	594.6	43400	0.3506	2.852	0.07020
Carbon disulphide	76.14	273.05	546.05	55379	0.377	2.652	0.1236
Chloroform	119.358	260.0	533.0	41724	..	...	0.1496
Acetone	58.048	237.5	510.5	45600	..	...	0.08301
Ammonia	17.064	131.0	404.0	85880	..	...	0.05810
Sulphur dioxide	64.07	156.0	429.0	59964	0.520	1.923	0.1434
Carbon dioxide	44.00	31.35	304.35	55404	0.464	2.155	0.1283
Nitrous oxide	44.08	38.8	311.8	58900	0.454	2.203	0.1334

TABLE 2 (*Continued*).

Substance.	$\frac{D_c}{d_c}$.	2.3026R.	Equation 10, $\frac{dP}{dT}$.	$\sqrt[3]{d_c}$.	$V_c^{4/3}$.	Equation 23, E_K.	$\mu'\sqrt[3]{d_c}$.
Ethyl oxide	0.262	0.06178	441.9	0.6401	5.958	18.79	66.42
Di-isopropyl	0.267	0.05315	349.6	0.6224	6.666	17.33	60.70
Di-isobutyl	0.263	0.04010	258.8	0.6185	6.834	14.36	54.17
Isopentane	0.268	0.06347	405.7	0.6165	6.922	19.06	65.01
Normal pentane	0.266	0.06347	402.3	0.6147	7.004	19.45	67.58
Normal hexane	0.261	0.05315	339.9	0.6166	6.919	17.58	63.39
Normal heptane	0.259	0.04571	291.9	0.6163	6.933	16.08	60.79
Normal octane	0.259	0.04010	254.5	0.6151	6.987	14.87	57.30
Hexamethylene	0.270	0.05442	406.0	0.6491	5.634	19.61	67.27
Benzene	0.267	0.05864	487.0	0.6728	4.879	21.45	73.49
Fluobenzene	0.264	0.04763	460.1	0.7075	3.990	17.36	60.60
Chlorobenzene	0.265	0.04069	405.6	0.7149	3.829	16.75	58.38
Bromobenzene	0.263	0.02915	386.0	0.7858	2.623	12.72	43.59
Iodobenzene	0.265	0.02245	356.0	0.8346	2.061	10.54	36.20
Carbon tetrachloride	0.272	0.02976	452.7	0.8231	2.179	10.78	36.22
Stannic chloride	0.267	0.01755	355.2	0.9053	1.489	6.76	24.00
Methyl formate	0.255	0.07624	725.6	0.7040	4.070	24.19	84.38
Ethyl formate	0.257	0.06181	545.0	0.6863	4.508	20.47	73.52
Methyl acetate	0.254	0.06181	548.2	0.6877	4.470	20.41	75.35
Propyl formate	0.259	0.051975	438.5	0.6763	4.781	18.21	66.81
Ethyl acetate	0.254	0.051975	436.3	0.6751	4.813	17.71	66.75
Methyl propionate	0.256	0.051975	442.9	0.6785	4.718	17.96	67.18
Propyl acetate	0.254	0.044835	361.7	0.6662	5.076	16.04	62.04
Ethyl propionate	0.256	0.044835	352.7	0.6668	5.059	15.95	61.07
Methyl butyrate	0.256	0.044835	367.2	0.6696	4.973	16.19	61.14
Methyl isobutyrate	0.259	0.044835	368.4	0.6703	4.954	15.79	59.29
Water	...	0.2541	..	..	...	106.42	...
Methyl alcohol	0.220	0.14288	1061.1	0.6481	5.669	47.77	...
Ethyl alcohol	0.249	0.09939	747.0	0.6507	5.579	33.43	...
Propyl alcohol	0.250	0.07620	568.3	0.6490	5.637	26.65	...
Acetic acid	0.201	0.07624	729.2	0.7051	4.044	29.54	...
Carbon disulphide	c.328	0.06011	618	0.7224	3.670	21.39	59.53
Chloroform	...	0.038345	..	..	...	13.32	...
Acetone	...	0.07885	..	..	...	26.22	...
Ammonia	...	0.26822	..	..	...	70.58	...
Sulphur dioxide	0.276	0.07143	1013	0.8041	2.393	19.97	68.73
Carbon dioxide	0.277	0.10402	1317	0.7742	2.783	20.62	73.67
Nitrous oxide	0.294	0.10383	1286	0.7686	2.866	21.09	67.87

TABLE 2 (*Continued*).

Substance.	Average, μ'.	Equation 27, μ'.	Average, C.	Equation 19, C'.	Equation 28, C''.	$\frac{C'}{C}$.	C — C''.
Ethyl oxide	103.76	102.0	1.724	1.767	1.738	1.025	—0.014
Di-isopropyl	97.53	96.5	1.725	1.751	1.733	1.015	—0.008
Di-isobutyl	87.58	80.7	1.813	1.886	1.737	1.040	0.076
Isopentane	105.46	107.0	1.688	1.705	1.732	1.010	—0.044
Normal pentane	109.94	109.4	1.707	1.737	1.734	1.018	—0.027
Normal hexane	102.80	99.2	1.752	1.803	1.739	1.029	0.013
Normal heptane	98.64	90.8	1.814	1.890	1.741	1.042	0.073
Normal octane	93.16	84.2	1.858	1.926	1.741	1.037	0.117
Hexamethylene	103.63	104.5	1.694	1.715	1.730	1.012	—0.006
Benzene	109.26	110.5	1.690	1.713	1.733	1.014	—0.043
Fluobenzene	85.65	85.2	1.711	1.745	1.736	1.020	—0.025
Chlorobenzene	81.66	81.3	1.714	1.743	1.735	1.017	—0.021
Bromobenzene	55.47	56.3	1.691	1.713	1.737	1.013	—0.046
Iodobenzene	43.37	43.8	1.687	1.717	1.735	1.018	—0.048
Carbon tetrachloride	44.01	45.3	1.667	1.680	1.728	1.008	—0.061
Stannic chloride	26.51	25.9	1.741	1.775	1.733	1.019	0.008
Methyl formate	119.86	119.8	1.706	1.744	1.745	1.022	—0.039
Ethyl formate	107.14	103.9	1.747	1.796	1.743	1.028	0.004
Methyl acetate	109.59	103.6	1.784	1.846	1.746	1.035	0.038
Propyl formate	98.79	93.7	1.774	1.834	1.741	1.034	0.033
Ethyl acetate	98.88	91.7	1.812	1.885	1.746	1.040	0.066
Methyl propionate	99.02	92.4	1.803	1.870	1.744	1.037	0.059
Propyl acetate	93.12	84.1	1.850	1.934	1.746	1.045	0.104
Ethyl propionate	91.59	80.8	1.837	1.914	1.744	1.042	0.093
Methyl butyrate	91.31	84.3	1.824	1.888	1.744	1.035	0.080
Methyl isobutyrate	88.45	82.0	1.814	1.877	1.741	1.035	0.073
Water	555.1	...	...	...	...	...	...
Methyl alcohol	305.04	262.4	...	...	1.780	...	...
Ethyl alcohol	240.90	179.9	...	...	1.751	...	...
Propyl alcohol	199.20	143.7	...	...	1.750	...	...
Acetic acid	..	150.7	...	...	1.799	...	...
Carbon disulphide	82.41	98.8	1.516	1.392	1.672	0.9182*	—0.156
Chloroform	57.97	...	1.706	...	...	...	...
Acetone	150.8	...	1.754	...	...	...	...
Ammonia	381.86	...	1.622	...	...	...	...
Sulphur dioxide	85.48	85.4	1.707	1.721	1.724	1.008	—0.017
Carbon dioxide	95.16	91.8	1.762	1.786	1.723	1.014	0.039
Nitrous oxide	88.3	93.6	1.513	1.609	1.706	1.063*	—0.193
						1.025	

ton does give true results at the critical temperature, then we will have, as already shown,

$$(10) \qquad \frac{dP}{dT} = \frac{2R}{V_c} = \frac{124890}{mV_c}$$

The values of the $\frac{dP}{dT}$ obtained from this equation are given in Table 2.

Substituting these values in equation 13, we obtain the values of μ' given in Table 2 under the heading "Equation 27,"

$$(27) \quad \mu' = 0.0_4955V_c^{4/3}\left(\frac{2R}{V_c}\,T_c - P_c\right) = V_c^{1/3}\left(\frac{11.924T_c}{m} - 0.0_4955P_cV_c\right)$$

Comparing these values with the values of "Average μ'" in the adjacent column, the agreement is seen to be close, but is not always within the limit of error of the data used. There is some evidence[1] that the differences are proportionate to the curvature of the Cailletet and Mathias line of rectilinear diameter.

If we similarly substitute in equation 18 the above value of $\frac{dP}{dT}$ we obtain

$$(28) \quad C = \frac{\left(\frac{2 \times 62445T_c}{V_c} - P_c\right)V_cm}{62445T_c} = 2 - \frac{P_cV_cm}{62445T_c} = 2 - \frac{D_c}{d_c},$$

where D_c is the theoretical critical density and d_c is the actual critical density. We give the values of D_c, the ratio of $\frac{D_c}{d_c}$ and also the value of $2 - \frac{D_c}{d_c}$ in Table 2 (the latter under the heading, "Equation 28, C''"). The differences between these calculated values of C and the average values of C we give under the heading C—C'' These differences are sometimes larger than can be attributed to experimental error, as was to be expected, since equation 27 had already shown that probably equation 10 was not always exactly true.

Of course, from equation 28 the conclusion is readily drawn that

$$(29) \qquad \frac{P_cV_cm}{T_c} = \text{constant}.$$

This conclusion we had previously[2] drawn from equations 21 and 27 and it had long before been pointed out by Young.

Considering next equation 7, $L = 2RT\ln V/v$, and equation 5, $\lambda = CRT\ln V/v$, we have, also making use of equations 19 and 28,

$$(30) \qquad \frac{\lambda}{L} = \frac{C}{2} = \frac{m\mu'\sqrt[3]{d_c}}{6 \times 1.9878T_c} = 1 - \frac{D_c}{2d_c}.$$

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[1] Contained in a letter to the author from Dr. Young.

[2] *J. Physic. Chem.*, 9, 415 (1905)

This relation may easily be thrown into the form

$$(31)\qquad \frac{E_e}{L} = \frac{D_c}{2d_c} = \frac{P_cV_cm}{124890T_c}$$

This relation is very nearly true at the critical temperature, but is, of course, not accurate at lower temperatures owing to the use of equation 7.

It is probable that there are some interesting relations between the facts cited above and the Cailletet and Mathias law of rectilinear diameters. Assuming that the mean of the densities of the liquid and saturated vapor do lie exactly on a straight line we can write that law in the form

$$(32)\qquad \frac{D+d}{2} = \frac{d_0}{2} - T\tan\alpha,$$

where d_0 is the theoretical density of the liquid at the absolute zero and is very nearly four times the critical density. α is the angle which the line of mean densities makes with the temperature axis. The law above is not exactly true, as has been shown by Young,[1] but the deviations are not very great. Solving now equation 32 for T we can write

$$(33)\qquad T = \frac{d_0 - (D+d)}{2\tan\alpha},$$

and at the critical temperature,

$$(34)\qquad T_c = \frac{d_c}{\tan\alpha}.$$

These values of T can be substituted in the equations above and will give equations that are approximately true, only. Of particular interest is the substitution in equation 19, giving

$$(35)\qquad C = \frac{\tan\alpha.\ m\mu'\sqrt[3]{d_c}}{5{\cdot}9634d_c} = \frac{\tan\alpha.\ m\mu'V_c^{2/3}}{5{\cdot}9634},$$

and in equation 5, giving

$$(36)\quad \lambda = CR.\frac{d_0 - (D+d)}{2\tan\alpha}\ln d/D = \frac{\mu'}{6d_c^{2/3}}\left\{d_0 - (D+d)\right\}\ln d/D,$$

which is a second expression for the heat of vaporization in terms of the densities only (compare with equation 4). This equation is only approximate, and to give an idea of the approximation we select, at haphazard, benzene at 100° for trial. $\mu' = 109.23$, $V_c^{2/3} = 2.208$, $d_0 = 4d_c = 1.2180$, $D_{100} + d_{100} = 0.7974$, $\ln\frac{d_{100}}{D_{100}} = 5.127$. Hence, $\lambda = 86.69$. The thermodynamical value formerly obtained is 82.37. The error is due to the fact that equation 32 is not exactly true.

In conclusion we would express our sincerest thanks to Dr. Sydney

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[1] *Phil. Mag.*, 50, 291 (1900).

Young for furnishing us, in advance of its publication, with the revised data used in this paper, and for the kindness he has shown, and the trouble he has taken, in facilitating the work in various ways. Without the splendid series of measurements due to his labors this work would have been wholly impossible, and we take this opportunity to acknowledge our indebtedness to his work and to express our very great appreciation of its wonderful accuracy and of its value to science.

TABLE 3.—ETHYL ETHER.

Heat of Vaporization.

			Internal.		
Temp.	Total.	External.	Ther.	Mills.	Dieterici.
0°	92.52	7.11	85.41	83.95*	85.70
20	87.54	7.50	80.04	79.93	80.52
40	82.83	7.81	75.02	75.55	75.53
60	78.44	8.04	70.40	70.97	70.63
80	73.50	8.10	65.40	65.97	65.53
100	68.42	8.02	60.40	60.49	60.14
120	62.24	7.71	54.53	54.34	54.11
140	55.33	7.20	48.13	47.52	47.44
160	46.07	6.26	39.81	39.48	39.38
180	31.87	4.51	27.36	27.86	27.73
190	19.38	2.79	16.59	17.68*	17.4
193	11.36	1.65	9.71	10.90*	10.65
193.8	0	0	0	0	0

TABLE 4.—DI-ISOPROPYL.

Heat of Vaporization.

			Internal.		
Temp.	Total.	External.	Ther.	Mills.	Dieterici.
0°	85.11	6.30	78.81	78.66	81.27*
60	76.20	7.34	68.86	68.58	68.81
80	72.64	7.56	65.08	64.69	64.75
100	68.14	7.60	60.54	60.48	60.47
120	63.57	7.54	56.03	55.69	56.04
140	58.45	7.33	51.12	51.11	51.22
160	52.70	6.92	45.78	45.69	45.90
180	45.86	6.26	39.60	39.42	39.65
200	37.15	5.23	31.92	31.74	31.94
220	22.14	3.19	18.95	19.49	19.46
225	14.57	2.11	12.46	13.21	13.12
227.35	0	0	0	0	0

TABLE 5.—DI-ISOBUTYL.

Heat of Vaporization.

			Internal.		
Temp.	Total.	External.	Ther.	Mills.	Dieterici.
0°	80.99	4.75	76.24	74.97*	82.80*
100	68.12	6.10	62.02	62.16	62.78
120	64.01	6.18	57.83	58.86*	58.96*
140	59.78	6.19	53.59	55.31*	55.09*
160	56.23	6.19	50.04	51.57*	51.26*
180	53.05	6.15	46.90	47.64	47.39
200	48.83	5.92	42.91	43.22	42.99
220	43.80	5.48	38.32	38.17	37.93
240	37.37	4.78	32.59	32.08	31.80
260	27.93	3.62	24.31	23.81	23.46
274	14.24	1.85	12.39	12.56	12.20
276.8	0	0	0	0	0

TABLE 6.—ISOPENTANE.

Heat of Vaporization.

			Internal.		
Temp.	Total.	External.	Ther.	Mills.	Dieterici.
0°	88.86	7.51	81.35	79.98*	80.96
20	83.41	7.74	75.67	75.90	76.02
40	79.12	8.02	71.10	71.53	71.37
60	74.35	8.15	66.20	66.85	66.59
80	69.80	8.21	61.59	61.89	61.80
100	64.83	8.11	56.72	56.49	56.63
120	58.62	7.73	50.89	50.49	50.77
140	51.07	7.03	44.04	43.52	43.89
160	41.27	5.88	35.39	34.97	35.31
180	24.65	3.61	21.04	21.45	21.55
185	16.47	2.42	14.05	14.75	14.74
187	10.43	1.54	8.89	9.55	9.49
187.4	8.07	1.19	6.88	7.51	7.43
187.8	0	0	0	0	0

Table 7.—Normal Pentane.

Heat of Vaporization.

Temp.	Total.	External.	Internal.		
			Ther.	Mills.	Dieterici.
0°	93.36	7.51	85.85	84.91	86.35
40	84.31	8.15	76.16	76.57	76.50
60	80.07	8.38	71.69	71.94	71.71
80	75.33	8.47	66.86	66.96	66.72
100	69.94	8.37	61.57	61.56	61.40
120	64.48	8.15	56.33	55.72	55.77
140	56.58	7.50	49.08	48.83	48.90
160	47.42	6.53	40.89	40.76	40.87
180	35.01	4.99	30.02	30.20	30.23
195	15.66	2.28	13.38	14.32	14.18
197.15	3.11	0.45	2.66	2.96	2.90
197.2	0	0	0	0	0

Table 8.—Normal Hexane.

Heat of Vaporization.

Temp.	Total.	External.	Internal.		
			Ther.	Mills.	Dieterici.
0°	90.98	6.30	84.68	83.99	88.32*
60	80.82	7.23	73.59	73.83	74.35
80	77.55	7.51	70.04	69.89	70.01
100	73.48	7.66	65.82	65.63	65.54
120	69.29	7.73	61.56	61.12	61.02
140	63.84	7.55	56.29	56.15	56.03
160	57.63	7.18	50.45	50.58	50.46
180	50.93	6.63	44.30	44.39	44.30
200	42.75	5.75	37.00	37.02	36.93
220	30.37	4.19	26.18	26.62	26.43
230	19.73	2.75	16.98	17.81	17.55
234	10.44	1.46	8.98	9.79	9.58
234.8	0	0	0	0	0

Table 9.—Normal Heptane.

Heat of Vaporization.

Temp.	Total.	External.	Internal.		
			Ther.	Mills.	Dieterici.
0°	89.86	5.42	84.44	83.58	90.92*
80	79.44	6.78	72.59	72.18	73.14
100	75.80	6.99	68.81	68.65	69.00
120	71.69	7.11	64.58	64.85	64.81
140	67.12	7.11	60.01	60.74	60.47
160	62.65	7.04	55.61	56.34	56.00
180	58.52	6.90	51.62	51.67	51.35
200	53.17	6.54	46.63	46.39	46.09
220	46.46	5.89	40.57	40.16	39.83
240	37.45	4.85	32.60	32.24	31.83
260	21.90	2.88	19.02	19.43	18.95
266.5	8.50	1.12	7.38	8.02	7.73
266.85	0	0	0	0	0

Table 10.—Normal Octane.

Heat of Vaporization.

Temp.	Total.	External.	Internal.		
			Ther.	Mills.	Dieterici.
0°	89.46	4.75	84.71	80.94*	92.88*
120	71.43	6.33	65.10	65.50	66.72*
140	68.28	6.50	61.78	62.11	62.86*
160	64.75	6.58	58.17	58.48	58.94
180	60.91	6.55	54.36	54.59	54.85
200	56.61	6.40	50.21	50.32	50.49
220	52.03	6.13	45.90	45.67	45.70
240	45.97	5.60	40.37	40.12	40.03
260	39.14	4.89	34.25	33.74	33.57
280	28.26	3.59	24.67	24.58	24.26
290	19.10	2.44	16.66	17.06	16.68
296.2	0	0	0	0	0

Table 11.—Hexamethylene.

Heat of Vaporization.

Temp.	Total.	External.	Internal.		
			Ther.	Mills.	Dieterici.
0°	96.22	6.45	89.77	90.70	94.59*
80	86.72	8.09	78.63	78.12	77.94
100	83.07	8.36	74.71	74.37	73.98
120	78.78	8.51	70.27	70.39	69.93
140	74.24	8.56	65.68	66.15	65.78
160	69.71	8.51	61.20	61.70	61.52
180	65.15	8.36	56.79	56.92	56.94
200	59.37	7.95	51.42	51.66	51.83
220	53.56	7.41	46.15	45.87	46.21
240	45.76	6.49	39.27	38.89	39.21
260	35.16	5.07	30.09	29.78	30.00
270	26.72	3.87	22.85	22.90	22.97
279	11.78	1.71	10.07	10.63	10.54
280	0	0	0	0	0

Table 12.—Benzene.

Heat of Vaporization.

Temp.	Total.	External.	Internal.		
			Ther.	Mills.	Dieterici.
0°	106.11	6.95	99.16	100.05	104.67*
80	95.45	8.75	86.70	86.74	86.56
100	91.41	9.04	82.37	82.78	82.30
120	86.58	9.19	77.39	78.53*	77.93
140	82.82	9.37	73.45	74.12	73.71
160	78.94	9.46	69.48	69.55	69.35
180	74.62	9.41	65.21	64.66	64.79
200	68.81	9.06	59.75	59.24	59.51
220	62.24	8.48	53.76	53.12	53.51
240	54.11	7.58	46.53	46.04	46.44
260	43.82	6.27	37.55	37.21	37.52
280	27.43	3.98	23.45	23.75	23.79
288.5	0	0	0	0	0

TABLE 13.—FLUOBENZENE.

Heat of Vaporization.

Temp.	Total.	External.	Internal.		
			Ther.	Mills.	Dieterici.
0°	87.78	5.64	82.14	82.75	87.87*
80	80.07	7.11	72.96	72.00	72.42
100	77.10	7.39	69.71	68.72	68.80
120	73.03	7.51	65.52	65.18	65.04
140	68.75	7.56	61.19	61.44	61.23
160	64.37	7.51	56.86	57.48	57.28
180	60.17	7.37	52.80	53.28	53.18
200	55.35	7.12	48.23	48.67	48.66
220	50.37	6.72	43.65	43.64	43.79
240	44.07	6.04	38.03	37.76	37.93
260	35.65	4.99	30.66	30.33	30.44
280	20.82	2.95	17.87	18.21	18.12
286.55	0	0	0	0	0

TABLE 14.—CHLOROBENZENE.

Heat of Vaporization.

Temp.	Total.	External.	Internal.		
			Ther.	Mills.	Dieterici.
0°	89.89	4.83	85.06	82.92*	92.11*
140	73.36	6.88	66.48	67.61*	67.77*
160	71.26	7.12	64.14	64.76	64.79
180	68.96	7.29	61.67	61.76	61.77
200	65.83	7.33	58.50	58.54	58.53
220	62.89	7.34	55.55	55.18	55.24
240	59.49	7.24	52.25	51.54	51.67
260	55.15	6.98	48.17	47.53	47.70
270	52.56	6.76	45.80	45.35	45.50
359.1	0	0	0	0	0

TABLE 15.—BROMOBENZENE.

Heat of Vaporization.

Temp.	Total.	External.	Internal.		
			Ther.	Mills.	Dieterici.
30°	67.41	3.84	63.57	61.21*	67.06*
160	55.21	5.10	50.11	50.89	51.10
180	53.80	5.28	48.52	48.91	48.99
200	52.22	5.42	46.80	46.84	46.88
220	50.46	5.51	44.95	44.61	44.68
240	47.96	5.49	42.47	42.25	42.29
260	45.72	5.46	40.26	39.78	39.89
270	44.34	5.41	38.93	38.43	38.57
397	0	0	0	0	0

TABLE 16.—IODOBENZENE.

Heat of Vaporization.

Temp.	Total.	External.	Internal.		
			Ther.	Mills.	Dieterici.
30°	56.42	2.96	53.46	52.38*	57.89*
180	46.69	4.15	42.54	43.34	43.28
200	45.80	4.32	41.48	41.75	41.69
220	44.78	4.46	40.32	40.19	40.08
240	43.27	4.54	38.73	38.56	38.40
260	41.40	4.56	36.84	36.80	36.64
270	40.29	4.53	35.76	35.86	35.70
448	0	0	0	0	0

TABLE 17.—CARBON TETRACHLORIDE.

Heat of Vaporization.

Temp.	Total.	External.	Internal.		
			Ther.	Mills.	Dieterici.
0°	51.87	3.52	48.35	48.88	50.61*
80	46.00	4.36	41.64	42.08	41.75
100	44.15	4.51	39.64	40.07	39.69
120	42.08	4.60	37.48	37.94	37.58
140	39.92	4.65	35.27	35.71	35.46
160	37.95	4.67	33.28	33.41	33.32
180	35.40	4.57	30.83	30.89	30.90
200	32.61	4.39	28.22	28.13	28.28
220	29.45	4.10	25.35	25.04	25.25
240	25.56	3.65	21.91	21.45	21.70
260	20.07	2.92	17.15	16.78	16.97
280	10.43	1.53	8.90	8.92	8.95
283.15	0	0	0	0	0

TABLE 18.—STANNIC CHLORIDE.

Heat of Vaporization.

Temp.	Total.	External.	Internal.		
			Ther.	Mills.	Dieterici.
0°	35.38	2.08	33.30	33.70	36.71*
100	31.76	2.75	29.01	28.75	29.00
120	30.54	2.84	27.70	27.50	27.58
140	29.12	2.91	26.21	26.17	26.14
160	27.69	2.94	24.75	24.77	24.68
180	26.29	2.96	23.33	23.31	23.23
200	24.51	2.92	21.59	21.72	21.66
220	22.82	2.84	19.98	20.02	20.00
240	20.86	2.71	18.15	18.15	18.18
260	18.50	2.48	16.02	16.02	16.07
280	15.60	2.15	13.45	13.48	13.51
318.7	0	0	0	0	0

TABLE 19.—METHYL FORMATE.

Heat of Vaporization.

Temp.	Total.	External.	Internal.		
			Ther.	Mills.	Dieterici.
0°	122.23	9.03	113.20	109.50*	112.45
40	111.25	10.09	101.16	99.87*	100.34
60	105.11	10.37	94.74	94.44	94.37
80	98.81	10.50	88.31	88.61	88.30
100	92.30	10.47	81.83	82.35	82.03
120	86.22	10.35	75.87	75.68	75.50
140	77.97	9.87	68.10	68.14	68.09
160	68.36	9.08	59.28	59.57	59.61
180	56.48	7.84	48.64	49.38	49.47
200	38.80	5.62	33.18	35.10*	35.04*
210	22.98	3.40	19.58	21.99*	21.74*
213.5	10.34	1.54	8.80	10.41*	10.22*
214.0	0	0	0	0	0

TABLE 20.—ETHYL FORMATE.

Heat of Vaporization.

Temp.	Total.	External.	Internal.		
			Ther.	Mills.	Dieterici.
0°	106.83	7.33	99.50	97.96*	102.52*
60	95.82	8.63	87.19	86.17*	86.70
80	90.91	8.86	82.05	81.56	81.54
100	85.74	8.99	76.75	76.59	76.34
120	80.26	8.98	71.28	71.29	70.97
140	74.18	8.81	65.37	65.52	65.24
160	67.21	8.41	58.80	59.13	58.92
180	59.44	7.80	51.64	51.98	51.89
200	49.28	6.74	42.54	43.36	43.27
220	34.47	4.88	29.59	31.29*	31.07*
230	22.79	3.28	19.51	21.43*	21.15*
234	13.91	2.02	11.89	13.54*	13.29*
235.3	0	0	0	0	0

TABLE 21.—METHYL ACETATE.

Heat of Vaporization.

Temp.	Total.	External.	Internal.		
			Ther.	Mills.	Dieterici.
0°	109.34	7.33	102.01	100.99*	106.86*
60	98.59	8.65	89.94	89.08	90.19
80	94.07	8.94	85.13	84.39	84.86
100	88.39	9.04	79.35	79.30	79.35
120	82.87	9.04	73.83	73.82	73.72
140	76.83	8.89	67.94	67.85	67.72
160	69.96	8.53	61.43	61.27	61.17
180	61.00	7.77	53.23	53.62	53.42
200	50.56	6.67	43.89	44.45	44.22
220	34.87	4.74	30.13	31.44*	31.06
230	20.99	2.89	18.10	19.74*	19.33*
233	11.70	1.62	10.08	11.44*	11.11*
233.7	0	0	0	0	0

TABLE 22.—PROPYL FORMATE.

Heat of Vaporization.

Temp.	Total.	External.	Internal.		
			Ther.	Mills.	Dieterici.
0°	99.63	6.16	93.47	91.64*	98.76*
80	87.49	7.64	79.85	78.68*	79.37
100	82.66	7.82	74.84	74.64	74.72
120	78.14	7.96	70.18	70.40	70.18
140	73.74	8.04	65.70	65.91	65.63
160	68.29	7.90	60.39	60.99	60.67
180	62.80	7.65	55.15	55.70	55.41
200	56.91	7.23	49.68	49.83	49.64
220	49.62	6.50	43.12	42.92	42.77
240	39.45	5.28	34.17	34.10	33.89
250	31.99	4.32	27.67	27.98	27.67
260	21.02	2.85	18.17	18.89	18.52
264.85	0	0	0	0	0

TABLE 23.—ETHYL ACETATE.

Heat of Vaporization.

Temp.	Total.	External.	Internal.		
			Ther.	Mills.	Dieterici.
0°	100.61	6.16	94.45	91.36*	99.43*
80	85.78	7.53	78.25	77.71	78.88
100	82.15	7.79	74.36	73.56	74.20
120	77.53	7.89	69.64	69.05	69.31
140	72.24	7.82	64.42	64.17	64.18
160	65.91	7.55	58.36	58.72	58.55
180	59.87	7.19	52.68	52.84	52.56
200	52.71	6.60	46.11	46.10	45.88
220	42.63	5.52	37.11	37.57	37.24
240	27.17	3.62	23.55	24.78*	24.32
247	17.12	2.30	14.82	16.24*	15.80
249	12.03	1.62	10.41	11.73*	11.34
250.1	0	0	0	0	0

TABLE 24.—METHYL PROPIONATE.

Heat of Vaporization.

Temp.	Total.	External.	Internal.		
			Ther.	Mills.	Dieterici.
0°	100.87	6.16	94.71	95.92*	100.24*
80	87.07	7.58	79.49	78.87	80.03
100	82.75	7.78	74.97	74.74	75.27
120	78.27	7.90	70.37	70.33	70.48
140	73.42	7.90	65.52	65.60	65.54
160	68.15	7.76	60.39	60.45	60.31
180	62.05	7.42	54.63	54.77	54.56
200	55.67	6.95	48.72	48.49	48.32
220	47.14	6.10	41.04	40.89	40.70
240	34.41	4.58	29.83	30.41	30.07
250	24.30	3.28	21.02	22.16*	21.75
256	12.70	1.72	10.98	12.23*	11.88
257.4	0	0	0	0	0

TABLE 25.—PROPYL ACETATE.

Heat of Vaporization.

			Internal.		
Temp.	Total.	External.	Ther.	Mills.	Dieterici.
0°	96.03	5.32	90.71	86.95*	97.66*
100	79.80	6.87	72.93	72.39	73.57
120	76.33	7.10	69.23	68.66	69.30
140	71.84	7.16	64.69	64.63	64.86
160	67.66	7.18	60.48	60.36	60.38
180	62.80	7.04	55.76	55.67	55.57
200	57.23	6.72	50.51	50.48	50.28
220	50.78	6.20	44.58	44.56	44.29
240	42.40	5.34	37.06	37.29	36.91
260	30.70	3.96	26.74	27.46	26.95
270	20.57	2.67	17.90	19.28*	18.73
275	11.73	1.53	10.20	11.31*	10.90
276.2	0	0	0	0	0

TABLE 26.—ETHYL PROPIONATE.

Heat of Vaporization.

			Internal.		
Temp.	Total.	External.	Ther.	Mills.	Dieterici.
0°	95.00	5.31	89.69	85.46*	95.84*
100	79.23	6.90	72.33	70.83*	72.06
120	75.17	7.07	68.10	67.09*	67.75
140	70.19	7.09	63.10	62.99	63.26
160	65.16	7.00	58.16	58.61	58.62
180	59.94	6.80	53.14	53.84	53.71
200	54.66	6.48	48.18	48.65	48.44
220	48.54	5.96	42.58	42.67	42.43
240	40.23	5.06	35.17	35.21	34.85
260	27.84	3 56	24.28	24.59	24.13
265	23.15	2 97	20.18	20.64	20.16
270	15.65	2.01	13.64	14.40	13.96
272.9	0	0	0	0	0

TABLE 27.—METHYL BUTYRATE.

Heat of Vaporization.

			Internal.		
Temp.	Total.	External.	Ther.	Mills.	Dieterici.
0°	95.79	5.32	90.47	85.59*	96.56*
100	77.80	6.73	71.07	71.40	72.85*
120	74.31	6.93	67.38	67.79	68.65*
140	70.84	7.09	63.75	63.95	64.52
160	66.53	7.08	59.45	59.79	60.00
180	62.00	6.96	55.04	55.30	55.49
200	57.41	6.75	50.66	50.44	50.56
220	51.31	6.26	45.05	44.81	44.82
240	44.14	5.54	38.60	38.15	38.07
260	34.44	4.42	30.02	29.64	29.43
270	26.96	3.48	23.48	23.52	23.20
275	21.26	2.76	18.50	18.90	18.56
280	11.16	1.45	9.71	10.53	10.19
281.3	0	0	0	0	0

TABLE 28.—METHYL ISOBUTYRATE.

Heat of Vaporization.

			Internal.		
Temp.	Total.	External.	Ther.	Mills.	Dieterici.
0°	91.16	5.32	85.84	82.05*	90.95*
100	74.77	6.76	68.01	67.34	68.25
120	70.65	6.88	63.77	63.59	64.01
140	66.82	6.97	59.85	59.60	59.82
160	62.12	6.89	55.23	55.27	55.34
180	57.19	6.68	50.51	50.57	50.56
200	52.03	6.35	45.68	45.45	45.40
220	45.16	5.70	39.46	39.26	39.16
240	36.06	4.67	31.39	31.44	31.22
260	21.91	2.89	19.02	19.50	19.18
265	14.53	1.92	12.61	13.35	13.02
266.5	10.76	1.42	9.34	10.07	9.78
267.55	0	0	0	0	0

Table 29.—Water.[1]

Heat of Vaporization.

			Internal.		
Temp.	Total.	Ex-ternal.	Ob-served.	Mills.	Dieterici.
0°	595.8	30.8	565.0	545.7	....
20	584.8	32.3	552.5	540.4	....
40	573.5	34.3	539.2	533.1	....
60	561.8	36.4	525.4	523.8	....
80	549.8	38.4	511.4	513.0	....
100	537.5	40.4	497.1	500.5	....
120	523.0	42.0	481.0	486.8	....
140	508.5	43.5	465.0	471.8	....
160	494.2	45.0	449.2	455.5	....
180	479.7	46.1	433.6	437.7	....
200	465.3	47.1	418.2	418.8	....
220	449.4	47.3	402.1	398.3	....
240	429.5	47.8	381.7	377.0	....
260	402.5	46.8	355.7	353.6	....
270	390.3	45.6	344.7	340.9	....
370	0	0	0	0	....

Table 30.—Methyl Alcohol.

Heat of Vaporization.

			Internal.		
Temp.	Total.	Ex-ternal.	Ther.	Mills.	Dieterici.
0°	289.17	16.77	272.40	272.6	....
20	284.54	18.03	266.51	265.1	....
40	277.78	18.87	258.91	256.9	....
60	269.41	19.75	249.66	247.2	....
80	258.96	20.43	238.53	236.4	....
100	246.01	20.82	225.19	224.3	....
120	232.00	20.95	211.05	210.8	....
140	216.12	20.74	195.38	195.9	....
160	198.34	20.15	178.19	179.3	....
180	177.16	19.01	158.15	160.3	....
200	151.84	16.97	134.87	137.4	....
220	112.53	12.92	99.61	105.6	....
230	84.47	9.87	74.60	82.3	....
236	61.66	7.27	54.39	61.6	....
238.5	44.23	5.27	38.96	45.8	....
240.0	0	0	0	0	....

Table 31.—Ethyl Alcohol.[1]

Heat of Vaporization.

			Internal.		
Temp.	Total.	Ex-ternal.	Ther.	Mills.	Dieterici.
0°	220.9	11.7	209.2	216.4	....
20	220.6	12.6	208.0	211.0	....
40	218.7	13.4	205.3	204.6	....
60	213.4	14.2	199.2	196.9	....
80	206.4	14.8	191.6	188.4	....
100	197.1	15.3	181.8	178.9	....
120	184.2	15.4	168.8	168.0	....
140	171.1	15.4	155.7	155.6	....
160	156.9	15.2	141.7	142.3	....
180	139.2	14.3	124.9	127.2	....
200	116.6	12.6	104.0	109.0	....
220	88.2	9.9	78.3	84.6	....
240	40.3	4.7	35.6	41.1	....
242.5	22.1	2.6	19.5	23.9	....
243.1	0	0	0	0	....

Table 32.—Propyl Alcohol.[1]

Heat of Vaporization.

			Internal.		
Temp.	Total.	Ex-ternal.	Ther.	Mills.	Dieterici.
0°	194.4	9.0	185.4	181.8	....
80	173.0	11.5	161.5	161.0	....
100	164.0	11.8	152.2	153.4	....
120	153.0	12.0	141.0	145.0	....
140	142.4	12.0	130.4	135.9	....
160	129.0	11.9	117.1	125.7	....
180	116.3	11.4	104.9	114.4	....
200	102.2	10.8	91.4	101.9	....
220	85.3	9.6	75.7	87.0	....
240	63.4	7.5	55.9	67.8	....
260	33.5	4.2	29.3	37.2	....
263.7	0	0	0	0	....

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[1] Owing to molecular association neither μ' nor C are constant.

TABLE 33.—ACETIC ACID.[1]
Heat of Vaporization.

Temp.	Total.	Ex-ternal.	Internal.		
			Ther.	Mills.	Dieterici.
20°	84.05	4.88	79.17	...	....
40	87.02	5.17	81.85	...	....
60	89.69	6.12	83.57	...	....
80	91.59	6.71	84.88	...	....
100	92.32	7.23	85.09	...	....
120	94.38	7.79	86.59	...	....
140	91.83	8.21	83.62	...	....
160	89.63	8.49	81.14	...	....
180	87.71	8.70	79.01	...	....
200	85.55	8.83	76.72	...	....
220	82.02	8.77	73.25	...	....
240	78.18	8.64	69.54	...	....
260	72.26	8.26	64.00	...	....
280	63.48	7.51	55.97	...	....
300	48.97	6.00	42.97	...	....
310	37.77	4.71	33.06	...	....
320	20.92	2.65	18.27	...	....
321.65	0	0	0	...	....

TABLE 34.—CARBON DISULPHIDE.
Heat of Vaporization.

Temp.	Total.	Ex-ternal.	Internal.		
			Ther.	Mills.	Dieterici.
0°	90.00	7.24	82.76	82.94	83.55
20	88.02	7.71	80.31	80.22	80.31
40	85.64	8.10	77.54	77.26	77.10
60	82.87	8.42	74.45	74.05	73.87
80	79.70	8.67	71.03	70.68	70.59
100	76.14	8.85	67.29	67.12	67.23
120	72.18	8.94	63.24	63.38	63.77
140	67.83	8.95	58.88	59.44	60.23*
150	65.50	8.92	56.58	57.43	58.38*
273.05	0	0	0	0	0

TABLE 35.—CHLOROFORM.
Heat of Vaporization.

Temp.	Total.	Ex-ternal.	Internal.		
			Ther.	Mills.	Dieterici.
0°	67.00	4.55	62.45	62.39	63.56*
20	65.08	4.94	60.14	60.31	60.47
40	63.13	5.26	57.87	58.02	57.52
60	61.13	5.53	55.60	55.55	54.66
100	57.01	6.00	51.01	50.14	49.13*
260.0	0	0	0	0	0

TABLE 36.—ACETONE.
Heat of Vaporization.

Temp.	Total.	Ex-ternal.	Internal.		
			Ther.	Mills.	Dieterici.
0°	140.50	8.68	131.82	131.77	133.81*
20	137.33	10.17	127.16	127.25	127.48
40	133.44	11.05	121.39	122.31	121.35
60	128.82	11.60	117.22	116.87	115.11*
100	117.37	12.20	105.17	104.81	102.34*
237.5	0	0	0	0	0

TABLE 37.—AMMONIA.
Heat of Vaporization.

Temp.	Total.	Ex-ternal.	Internal.		
			Ther.	Mills.	Dieterici.
—30°	324.0	27.5	296.5	296.9	299.1*
—20	316.0	28.2	287.8	288.6	289.1*
0	300.0	29.8	270.2	271.2	270.2
20	284.0	31.2	252.8	252.6	251.7*
40	268.0	32.4	235.6	233.6*	233.9*
131	0	0	0	0	0

TABLE 38.—SULPHUR DIOXIDE.
Heat of Vaporization.

Temp.	Total.	Ex-ternal.	Internal.		
			Ther.	Mills.	Dieterici.
—10°	94.70	8.14	86.56	84.69*	86.34
0	91.76	8.20	83.56	82.31*	83.33
20	83.80	8.11	75.69	76.95*	76.93*
40	79.04	8.31	70.73	71.44	71.16
60	71.65	8.18	63.47	65.34*	64.85*
80	69.89	8.62	61.27	59.44*	59.76*
100	61.61	8.10	53.51	52.25*	52.66
120	51.26	6.97	44.29	43.20*	43.56
140	37.69	5.02	32.67	30.57*	30.68*
150	25.15	3.21	21.94	19.90*	19.77*
155	12.85	1.59	11.26	10.02*	9.88*
156	0	0	0	0	0

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[1] Owing to molecular association neither μ' nor C are constant.

TABLE 39.—CARBON DIOXIDE.
Heat of Vaporization.

			Internal.		
Temp.	Total.	External.	Observed.	Mills.	Dieterici.
—30°	75.2	9.86	65.34	65.74	66.25
—20	69.0	8.70	60.30	59.60	59.38
0	56.2	7.84	48.36	48.25	48.41
20	35.0	5.22	29.78	31.33*	31.20*
25	26.0	3.93	22.07	24.50*	24.32*
30	11.0	2.15	8.85	13.71*	13.55*
31.35	0	0	0	0	0

TABLE 40.—NITROUS OXIDE.
Heat of Vaporization.

			Internal.		
Temp	Total.	External.	Observed.	Mills.	Dieterici.
—25°	66.90	12.00	54.90	58.62*	54.77
—20	65.04	11.88	53.16	56.88*	53.52
0	58.2	9.68	48.52	47.20*	44.83*
20	40.0	7.09	32.91	34.22*	32.74
30	22.5	5.13	17.37	24.54*	23.55*
38.8	0	0	0	0	0

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ON THE DEPENDENCE OF VALENCE UPON VOLUME IN CERTAIN TRIVALENT ELEMENTS.

BY A. LUDWIG.

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In a paper on the melting point of carbon, published in the year 1902,[1] the cessation of the electrical conductivity during the melting of carbon under a high gas pressure was thought to be an indication of the passage of a less dense form of carbon into the more dense form of diamond. On account of the relatively high inversion temperature, more than 3000°, and the necessarily extreme pressure, a more complete study of this reaction appeared for the moment almost impossible. It seemed much more promising to investigate the volume changes of some other conducting material which would be easier to melt. The element bismuth appeared to me particularly adapted for this purpose, not only on account of its low melting point, 265°, but also on account of its relatively large increase of density (about 3 per cent.) on melting. I was aware that neither Spring[2] nor Kahlbaum[3] succeeded in producing a permanent change in the volume of bismuth, even with very high pressures (over 10,000 atmospheres). But as those scientists applied the pressure at ordinary temperature only, I undertook to heat the metal up to the melting point and to prevent its expansion in passing into the solid state by the application of very high pressures.

The material used for the purpose was 99.6 per cent. pure bismuth, with traces of antimony, lead, copper and iron.

Tammann[4] calculates the lowering of the melting temperature for bismuth through pressure from the formula

$$\Delta t = 0.00386\ (p - 1).$$

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[1] *Z. Elektrochem.*, 8, 273–281 (1902).

[2] *Ber.*, 16, 2724 (1883).

[3] *Z. anorg. Chem.*, 46, 217 (1905).

[4] *Ibid.*, 40, 54 (1904).