(6) The most striking feature of the experimental results is, that for all concentrations investigated, the molecular lowering of vapor tension is the same. Thus the lowering of a 0.2 *M* solution is 0.110 mm., while that of the 2.0 *M* solution is 1.1102 mm. Similar results have been obtained by Tower and Germann[1] from a study of the vapor tension of alcoholic solutions of potassium bromide and lithium chloride. Whether this phenomenon can be explained by the combination of the solvent and solute, as suggested by Tower and Germann, cannot be decided until the rigid applicability of Raoult's law has been tested with some non-electrolyte over the same range of concentration. This the authors purpose doing as soon as possible.

BALTIMORE, MD.

THE EQUATION OF STATE FOR GASES AND LIQUIDS.

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Van der Waals' equation, $(p + a/v^2)(v - b) = RT$, has for thirty years been accepted by chemists and physicists as a most valuable guide in the study of the behavior of gases and liquids. On the other hand, the limitations of the equation of the distinguished Hollander have also come to be generally recognized. From any two of the three quantities, critical temperature, critical pressure and critical volume, the theory of van der Waals enables us to calculate a and b. But if from the values of a and b so obtained, we calculate the third critical quantity, our result will be widely at variance with the facts. This is also evident when we remember that the theory of van der Waals requires that the critical density shall be 2.67 times that of an "ideal" gas under the same conditions of temperature and pressure, whereas in all cases hitherto investigated the ratio is much larger, usually about 3.7. Most of the modifications of the equation attempt to meet this condition of affairs, but are unable to raise the ratio above three.

Now there seems to be no doubt that the general ideas underlying the theory of van der Waals are of great value, enabling us to obtain a better insight into the nature of gases and liquids. It would seem to be worth while inquiring whether another method of deriving the equation of state is not theoretically sounder and more justifiable.

Van der Waals' method of applying a correction to the volume of the gas seems to be correct in principle, although the correction represented by the letter b may not be a "constant." Leaving out of account the surface layer of unknown thickness, the pressure throughout the fluid should undoubtedly be represented by the expression $RT/v - b$. Owing, however, to unbalanced molecular forces in the surface layer directed to-

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[1] THIS JOURNAL, 36, 2449 (1914).

wards the interior, the external pressure will be less than $RT/v - b$ by the pressure due to the unbalanced molecular forces. Van der Waals assumes this molecular pressure to be represented by a/v^2 and thus obtains his equation

$$p = \frac{RT}{v - b} - \frac{a}{v^2}.$$

Now it may well be that in order to obtain the external pressure, we should, instead of subtracting a term from $RT/v - b$, multiply it by a function, which will of course always be less than unity. This is the result that Dieterici[1] has obtained, and I shall indicate as briefly as possible his method of reasoning.

In the interior of a fluid the attractive forces between the molecules are balanced; only near the surface are the molecules subject to an unbalanced force directed towards the interior. Molecules with sufficiently low velocities moving towards the surface will be unable to reach it, while all molecules moving from the surface towards the interior will be assisted by the force directed inward. The result will be that the density of the surface layer will decrease from the interior towards the surface, where its value will depend on the external pressure. Only molecules having a velocity greater than a certain value will be able to penetrate this inhomogeneous layer and exert a pressure on the walls of the containing vessel. If we can determine what fraction of the total number of molecules has a velocity greater than a fixed value, then the external pressure (p) will be that fraction of the pressure in the interior, $RT/v - b$. Now if α be the most probable speed, and s be the speed a molecule must possess in order to be able just to penetrate to the surface, then the fraction we are considering is calculated to be e^{-s^2/α^2}, where e is the base of the natural logarithms. If we introduce the speed c, the square root of the mean of the squares of the speeds, we have $c^2 = {}^3/_2\alpha^2$ and our fraction becomes $e^{-\frac{^1/_2 s^2}{^1/_3 c^2}}$. If m be the mass of a molecule and n the number of molecules, the expression may be written $e^{-\frac{^1/_2 nms^2}{^1/_3 nmc^2}} = e^{-\frac{^1/_2 nms^2}{RT}}$. Now ${}^1/_2 ms^2$ is the work done by a molecule against the molecular forces in reaching the wall; we can therefore write the following equation:

$$p = \frac{RT}{v - b} e^{-A/RT} \tag{1}$$

where A is a measure of the work done by the molecules in penetrating to the surface. If now we make an assumption as to how A depends on the volume, we shall obtain an equation of state. Dieterici assumes that A is proportional to the density or $A = a/v$ and thus obtains the Dieterici equation of state

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[1] *Ann. Physik. u. Chem.*, 11, 700 (1899).

$$p = \frac{RT}{v - b} e^{-a/vRT} \tag{2}$$

The object of this paper may be said to be to study this equation in detail and to apply it to a number of well-investigated substances. The results obtained seem worthy of consideration. Dieterici himself showed that his equation reproduces the critical state very well, and in particular gives 3.695 as the value of the ratio RT_c/p_cv_c, in close agreement with the actual results obtained by Young and others. As far as I can learn from the available literature, Dieterici did not get much farther and has not persuaded chemists and physicists to adopt his form of the equation of state. One great difficulty in testing the equation lies in the fact that the "constants" a and b are really variables. This has been generally recognized in recent years and the view has been expressed that they are both temperature and volume functions. I hope to show that they are mainly functions of the temperature and that their variation with change in volume is probably small.

Before proceeding to study Dieterici's equation further, it might be well to show its relation to the original one of van der Waals. Dieterici's equation can be written, when the volume v is large as compared with b in the form

$$p = \frac{RT}{v - b}\left(1 - \frac{a}{vRT}\right) = \frac{RT}{v - b} - \frac{a}{v(v - b)},$$

which is virtually identical with the van der Waals $p = RT/(v - b) - a/v^2$. It is evident then that all the results obtainable from the van der Waals equation will be deducible from the Dieterici equation when only low pressures are considered. When a gas is under high pressure and, in particular, when the gas is in the critical state, the two equations will differ considerably. And it is to be noted that it is just here that the van der Waals equation loses its validity, while the Dieterici equation reproduces the critical results in most cases with accuracy.

Critical State.

The values of p, v, and T at the critical state in terms of a, b and R are obtained by putting $(dp/dv)_T = 0$ and $(d^2p/dv^2)_T = 0$. If we plot the Dieterici equation having the pressures as ordinates and the volumes as abscissae, we shall get for different values of T the isothermal curves. The geometrical interpretation of $(dp/dv)_T = 0$ is that, when this condition holds, we have a horizontal tangent; that is, the curve has at this point a maximum or minimum value or a point of inflexion. If the second derivative also vanishes for the same values of v, the point is a point of inflexion. And that is the critical point. Assuming that a and b are independent of the volume, we obtain the following results:

$$\left(\frac{dp}{dv}\right)_{\mathrm{T}} = -e^{-a/v\mathrm{RT}}\,\frac{(\mathrm{RT}v^2 - av + ab)}{v^2(v-b)^2} = -\frac{p}{v-b}\left(1 - \frac{a(v-b)}{v^2\mathrm{RT}}\right) \qquad (3)$$

$$\left(\frac{d^2p}{dv^2}\right)_{\mathrm{T}} = e^{-a/v\mathrm{RT}}\left[\frac{2\mathrm{RT}}{(v-b)^3} + \frac{a^2}{\mathrm{RT}v^4(v-b)} - \frac{2a}{v^3(v-b)} - \frac{2a}{v^2(v-b)^2}\right] \qquad (4)$$

Now $(dp/dv)_{\mathrm{T}}$ will vanish when v is infinitely great, a value which does not concern us here; when v is equal to zero, which is a physically impossible value since v cannot be less than b; and finally when $\mathrm{RT}v^2 - av + ab = 0$. From this equation we obtain

$$v = \frac{a \pm \sqrt{a^2 - 4ab\mathrm{RT}}}{2\mathrm{RT}}. \qquad (5)$$

This result shows us that there are always two horizontal tangents, real or imaginary or coincident. The two tangents coincide at the critical point and Equation 5 tells us that at this point $a^2 - 4ab\mathrm{RT} = 0$. At the critical point, $a = 4b\mathrm{RT}_c$ and therefore the critical temperature T_c is equal to $a/4b\mathrm{R}$; at the same time, from Equation 5 we find that the critical volume v_c is equal to $a/2\mathrm{RT}_c$ and therefore equal to $2b$. Substituting these values in the Dieterici equation of state, we obtain

$$p_c = \frac{\mathrm{RT}_c}{e^2b} = \frac{2\mathrm{RT}_c}{e^2v_c} = \frac{a}{4e^2b^2} = \frac{a}{29.56b^2}.$$

Hence $\mathrm{RT}_c/p_cv_c = e^2/2 = 3.695$.

These results could of course have been obtained by combining $(dp/dv)_{\mathrm{T}} = 0$ with $(d^2p/dv^2)_{\mathrm{T}} = 0$, but the method adopted is somewhat simpler. In any case, one can easily satisfy himself that the values obtained for v_c and T_c will make both derivatives vanish.

It may be interesting to compare these results with those derived from the original van der Waals equation.

$$\left.\begin{array}{ll}
\text{Van der Waals.} & \text{Dieterici.} \\
v_c = 3b & v_c = 2b \\
\mathrm{T}_c = 8a/27\mathrm{R}b & \mathrm{T}_c = a/4\mathrm{R}b \\
p_c = a/27b^2 & p_c = a/4e^2b^2 = a/29.56b^2
\end{array}\right\} \qquad (6)$$

That the isothermals as given by the Dieterici equation will have the same general appearance as those given by that of van der Waals will be evident if we consider that the condition for a horizontal tangent is given by Equation 5. At the critical temperature the two values of v coincide; above this temperature, $a^2 - 4ab\mathrm{RT}$ is negative, the two values of v become imaginary; that is, there is no horizontal tangent. Below the critical temperature, however, there are two real and unequal values of v, corresponding to each of which there is a horizontal tangent on the theoretical isothermal. In other words, the isothermal curve has a maximum and a minimum value. For certain values of p, then, horizontal lines may be drawn cutting the isothermal curve in three points, giving three values of v corresponding to the same pressure. It is clear then that the theoretical isothermals as given by the Dieterici equation are quite similar in their general appearance to those of van der Waals.

The following results are set down here, partly for reference, partly so that they may be compared with the well-known deductions from the equation of van der Waals:

$$p = \frac{\mathrm{RT}}{v - b} e^{-a/v\mathrm{RT}} \tag{2}$$

$$\left(\frac{dp}{dv}\right)_{\mathrm{T}} = -\frac{e^{-a/v\mathrm{RT}}}{v^2(v-b)^2}(\mathrm{RT}v^2 - av + ab) = -\frac{p}{v-b}\left[1 - \frac{a(v-b)}{v^2\mathrm{RT}}\right] \tag{3}$$

$$\left(\frac{dp}{d\mathrm{T}}\right)_v = \frac{\mathrm{R}}{v-b}\left(1 + \frac{a}{v\mathrm{RT}}\right)e^{-a/v\mathrm{RT}} = \frac{p}{\mathrm{T}}\left(1 + \frac{a}{v\mathrm{RT}}\right) \tag{7}$$

$$\left(\frac{dv}{d\mathrm{T}}\right)_p = \frac{v-b}{\mathrm{T}}\left(\frac{1 + a/v\mathrm{RT}}{1 - a(v-b)/v^2\mathrm{RT}}\right) = \frac{\mathrm{R}}{p} \cdot e^{-a/v\mathrm{RT}} \cdot \frac{(1 + a/v\mathrm{RT})}{1 - a(v-b)/v_2\mathrm{RT}} \tag{8}$$

Where u represents the energy of the gas,

$$\left(\frac{du}{dv}\right)_{\mathrm{T}} = \mathrm{T}\left(\frac{dp}{d\mathrm{T}}\right)_v - p = \frac{ap}{v\mathrm{RT}} = \frac{a\,e^{-a/v\mathrm{RT}}}{v(v-b)} = \frac{a}{v^2} \text{ (approx.)} \tag{9}$$

$$C_p = C_v + \mathrm{R}e^{-a/v\mathrm{RT}}\frac{(1 + a/v\mathrm{RT})^2}{1 - a(v-b)/v^2\mathrm{RT}} = C_v + \mathrm{R} + \frac{2a}{v\mathrm{T}} \text{ (approx.)} \tag{10}$$

Assuming a and b to be functions of T,

$$\left(\frac{dp}{d\mathrm{T}}\right)_v = \frac{p}{\mathrm{T}}\left[1 + \frac{a}{v\mathrm{RT}} + \frac{\mathrm{T}}{v-b}\cdot\frac{db}{d\mathrm{T}} - \frac{1}{\mathrm{R}v}\cdot\frac{da}{d\mathrm{T}}\right]. \tag{7(a)}$$

The value of the product pv at constant temperature varies with the pressure p. The law governing this relation can be deduced from the Dieterici equation and is as follows:

$$\left(\frac{d(pv)}{dp}\right)_{\mathrm{T}} = \frac{v^2(b\mathrm{RT} - a) + abv}{v^2\mathrm{RT} - av + ab} \tag{11}$$

This expression is positive when $b\mathrm{RT} > a$, or $b > a/\mathrm{RT}$, as must be the case with hydrogen at ordinary temperatures and even at as low a temperature as —147°. If, however, a/RT is greater than b, the expression is at first negative for small values of p, becomes equal to zero and finally positive when p is sufficiently increased or v sufficiently diminished. When the expression becomes zero, we have a minimum value of pv. The condition for this minimum is obtained by putting $v^2(b\mathrm{RT} - a) + abv$ equal to zero. Neglecting the impossible value, $v = 0$, we arrive at the following relations which hold when pv has its minimum value:

$$v = ab/(a - b\mathrm{RT}) \qquad (12)$$

$$pv_{(\mathrm{min.})} = \frac{a}{b} e^{1 - a/b\mathrm{RT}} \qquad (13)$$

$$p = \frac{a - b\mathrm{RT}}{b^2} e^{1 - a/b\mathrm{RT}} \qquad (14)$$

Equations 12, 13 and 14 can be used in calculating the values of a and b, above the critical temperature.

When a is greater than $b\mathrm{RT}$, as we have seen, pv at first diminishes as p increases; when a is less than $b\mathrm{RT}$, pv increases with p. When $a = b\mathrm{RT}$, *i. e.*, when $\mathrm{T} = a/\mathrm{R}b$, the minimum pv would occur when v = infinity and $p = 0$; in other words, at this temperature the minimum just fails to appear and the pv curve would be a horizontal straight line for a short distance. Under these conditions, the gas would follow Boyle's law with great accuracy. If a and b were independent of the temperature, we should be able to calculate the temperature at which a gas would obey Boyle's law accurately as equal to four times the critical temperature. Since a and b are functions of the temperature, the temperature calculated in this manner will be usually quite in error. In cases where this temperature is known accurately for any gas, we have a means of finding the value of the ratio a/b at this temperature, for the relation $a = b\mathrm{RT}$ may be written

$$a/b = \mathrm{RT}. \qquad (15)$$

As an example, Young, on page 34 of his "Stoichiometry" states that at about 52°, $d(pv)/dp$ for nitrogen is equal to zero. Accordingly at this temperature, the ratio $a/b = 325/273 = 1.19$, when the unit mass of nitrogen is that which occupies unit volume at zero, and a pressure of one atmosphere.

Equation 11 can be simplified for the case that the pressures obtaining are small and the volumes large. We obtain, then,

$$\frac{d(pv)}{dp} = \frac{v^2(b\mathrm{RT} - a)}{v^2\mathrm{RT}} = b - \frac{a}{\mathrm{RT}}$$

or

$$\frac{p_2v_2 - p_1v_1}{p_2 - p_1} = b - \frac{a}{\mathrm{RT}}. \qquad (16)$$

This equation may also be obtained directly from the Dieterici equation, which for low pressures may be written, $pv = \mathrm{RT} + pb - a/v$.

Hence $p_2v_2 - p_1v_1 = (p_2 - p_1)b - (1/v_2 - 1/v_1)a = (p_2 - p_1)(b - a/\mathrm{RT})$ and finally Equation 16.

PV Curve at the Critical Temperature.

Some interesting results are obtained by applying Equations 12, 13 and 14 when the gas is at the critical temperature. In this case, when pv has its minimum value, the following relations hold:

$$\left.\begin{aligned} v &= {}^4/_3\, b = {}^2/_3\, v_c \\ p &= 3a/4e^3b^2 = 3/e\, p_c = 1.104\, p_c \\ pv_{\text{min.}} &= a/e^3b = 2/e\, p_cv_c = 4/e^3\, \mathrm{RT}_c = 0.736\, p_cv_c = 0.1991\, \mathrm{RT}_c \end{aligned}\right\} \qquad (17)$$

The above results may be expressed in words as follows: At the critical temperature, the minimum value of pv is about $^3/_4$ of its value in the critical state, and about $^1/_5$ of its "theoretical" value; the corresponding volume is $^2/_3$ of the critical volume, and the corresponding pressure is about 10% greater than the critical pressure. It might also be added that Dieterici's equation for the critical isothermal becomes

$$p = a/4b(v - b)\ e^{-4b/v} \qquad (18)$$

which for low pressures is equivalent to

$$p(v + 3b) = \mathrm{RT}_c.$$

Negative Pressures Impossible.

Returning to a consideration of Equation 5, we said that the two values of v given by this equation correspond to the maximum and minimum pressures on any theoretical isothermal. As is well known, on using van der Waals' equation, the theoretical minimum pressure is frequently negative, since the term a/v^2 may easily become greater than the term $\mathrm{RT}/(v - b)$. Using the Dieterici equation, the external pressure (for that is what p refers to) becomes zero only at the absolute zero of temperature and under no circumstances becomes negative. Young,[1] describes an experiment by Worthington,[2] in which a sealed tube completely full of a pure liquid is cooled slowly. He finds that in some experiments the thick-walled tube actually collapsed owing to what he calls the enormous tension. Now on both van der Waals' theory and on that of Dieterici, it is assumed that there is no attractive force between the molecules of the fluid and the wall. The only force assumed at the boundary is that due to the bombardment of the wall by the molecules which reach the surface. The hydrostatic pressure may be here neglected. In the absence of any adhesive force between the fluid and the wall, a negative external pressure is inconceivable. For, assume that under given conditions, the pressure directed towards the interior and due to molecular attraction is equal to p_0. The pressure on any imaginary unit area in the interior will still be given

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[1] "Stoichiometry," 1908, p. 205.

[2] *Phil. Trans.*, (*A*) 183, 355 (1892).

by $RT/(v-b)$. Van der Waals' equation requires us to imagine that under certain circumstances p_0 is greater than $RT/(v-b)$. What would be the result? The result would be that more molecules would move from the surface layers to the interior than in the opposite direction. This would mean that the volume of the fluid would decrease until $RT/(v-b)$ became greater than p, since $RT/(v-b)$ must be greater than p_0 in order that the number of molecules moving in the two directions shall be equal. For molecules moving towards the surface layer have to overcome a force, while those moving into the interior from the surface are moving in the same direction as the force. The phenomena described by Worthington then cannot be explained on the fundamental assumptions either of van der Waals or of Dieterici which do not consider any attractive forces between the fluid and the wall.

Maximum and Minimum Pressures.

We obtain the theoretical maximum and minimum pressures on any isothermal curve by substituting in the Dieterici equation the two values of v from Equation 5. Thus:

$$p_{\text{max.}} = \frac{2R^2T^2}{a - bRT + \sqrt{a^2 - 4abRT}}\, e^{-\frac{2a}{a + \sqrt{a^2 - 4abRT}}} \qquad (19a)$$

$$p_{\text{min.}} = \frac{2R^2T^2}{a - bRT - \sqrt{a^2 - 4abRT}}\, e^{-\frac{2a}{a - \sqrt{a^2 - 4abRT}}} \qquad (19b)$$

Also

$$p_{\text{max.}} \times p_{\text{min.}} = \frac{R^2T^2}{b^2}\, e^{-a/bRT}$$

and therefore

$$\sqrt{p_{\text{max.}} \times p_{\text{min.}}} = \frac{RT}{b}\, e^{-a/2bRT} \qquad (19c)$$

According to Equation 19*c*, the geometric mean of the maximum and minimum pressure on any isothermal is the pressure corresponding to the volume $2b$. At the critical temperature, this volume would be the critical volume and the pressure, the critical pressure. At a lower temperature, the value of $2b$ will be different from the critical volume, since we shall see that b is a function of the temperature. We shall now proceed to discuss a method of determining the value of b at different temperatures.

Determination of *b* at Different Temperatures.

If a substance is at a temperature lower than its critical temperature, experience teaches us that a certain portion of the theoretical isothermal curve is not realizable. Instead of the pressure increasing to a maximum, falling to a minimum and then increasing indefinitely as the volume is decreased, the pressure increases to a certain value and then remains constant until the gas is completely condensed into liquid. If this line of constant pressure be drawn in our *pv* diagram, it will cut the theoretical isothermal in three points; and we know from thermodynamics that the two areas bounded by the isothermal and the horizontal line, one above this line and the other under it, are equal. Two of the points correspond to the volumes of the liquid and the saturated vapor, the third point on our continuous isothermal corresponds in practice to a state in which both liquid and vapor are present. Let v_1, v_2 and v_3 represent the volumes of the liquid, vapor and the third intermediate volume, all corresponding to the pressure of the saturated vapor. We have then the equations

$$p_s = \frac{RT}{v_1 - b} e^{-\frac{a}{v_1 RT}} = \frac{RT}{v_2 - b} e^{-\frac{a}{v_2 RT}} = \frac{RT}{v_3 - b} e^{-\frac{a}{v_3 RT}}. \qquad (20)$$

Evidently the product of the second and third expressions is equal to the square of the fourth. We thus obtain

$$\frac{1}{(v_1 - b)(v_2 - b)} e^{-\frac{a}{RT}\left(\frac{1}{v_1} + \frac{1}{v_2}\right)} = \frac{1}{(v_3 - b)^2} e^{-\frac{a}{RT} \cdot \frac{2}{v_3}}.$$

Now if we make the assumption that $1/v_1 + 1/v_2 = 2/v_3$, then, of course, $(v_1 - b)(v_2 - b) = (v_3 - b^2)$. From these two relations the following results are easily deduced:

$$v_3 = 2b \qquad (21a)$$

$$1/b = 1/v_1 + 1/v_2 \qquad (21b)$$

$$v_1 = \frac{bv_2}{v_2 - b};\ v_2 = \frac{bv_1}{v_1 - b} \qquad (21c)$$

$$\frac{v_2}{v_1} = \frac{v_2 - b}{b} = \frac{b}{v_1 - b} \qquad (21d)$$

$$\left(\frac{v_2}{v_1}\right)^2 = \frac{v_2 - b}{v_1 - b} \qquad (21e)$$

And finally, for the pressure at which liquid and vapor are in equilibrium, since $v_3 = 2b$, we obtain

$$p_s = \frac{RT}{b} e^{-\frac{a}{2bRT}}. \qquad (22)$$

Comparing Equations 22 with 19*c*, we see that the pressure at which liquid and vapor are in equilibrium at any temperature is equal to the geometric mean of the maximum and minimum pressures on the theoretical isothermal for that temperature. Making use of Equation 21*b*, and letting d_1 and d_2 stand for the densities of liquid and saturated vapor, Equation 22 may be written as follows:

$$p_s = \left(\frac{1}{v_1} + \frac{1}{v_2}\right) RT \,.\, e^{-\frac{a}{2RT}\left(\frac{1}{v_1} + \frac{1}{v_2}\right)} \qquad (23)$$

$$p_s = (d_1 + d_2)\, RT \,.\, e^{-\frac{a(d_1 + d_2)}{2RT}} \qquad (24)$$

The above results have been obtained on the assumption that $2/v_3 = 1/v_1 + 1/v_2$. Any of the equations numbered 21 would of course be an equivalent assumption, such as, for example, that $v_3 = 2b$. Our assumption may also be written in the form $d_3 = (d_1 + d_2)/2$, *i. e.*, the third point on the theoretical isothermal cut by the line of constant pressure would represent a density which is the arithmetic mean of the densities of liquid and the saturated vapor. Now what grounds are there for this assumption? In the first place, at the critical temperature, v_1, v_2 and v_3 are all equal to $2b = v_c$. As the temperature is decreased, v_1 decreases fairly rapidly and v_2 increases quite rapidly, while the intermediate volume, v_3, might be expected to change very slowly. And in fact, if a *pv* diagram containing a number of isothermals below the critical temperature be examined, it will be seen that the point where the line of constant pressure cuts the descending portion of the isothermal represents a volume which does not differ much from the critical volume; that is, v_3 does not differ very much, as the temperature decreases, from $v_c = 2b_c$, where b_c is the value of b at the critical temperature. It seemed very plausible to assume that v_3 is equal to $2b$ at every temperature, although not necessarily equal to $2b_c$.

Another circumstance which led me to the assumption that $2/v_3 = 1/v_1 + 1/v_2$ was a consideration of the law of Cailletet and Mathias,[1] according to which the mean of the densities of liquid and saturated vapor is a linear function of the temperature, a statement therefore which would hold for d_3 or $(d_1 + d_2)/2$. Expressed in our symbols, then, $d_3 = d_0 + \alpha T$, where α is always very small. The fact that $(d_1 + d_2)/2$ is so nearly constant, varying only slightly and uniformly with the temperature seemed to me to be of great significance. If the mean of the densities of liquid and saturated vapor is given by such a simple relation, it seemed plausible to assume that this mean is identical with that given by the third point on the theoretical isothermal. Additional support to the assumption is given by the fact that we found the geometric mean of the maximum and minimum pressures on any theoretical isothermal to be equal to $\frac{RT}{b}.e^{-\frac{a}{2bRT}}$ (cf. Equation 19*c*). Now this is exactly the same pressure which we calculate to be the pressure of saturated vapor, when we assume that $v_3 = 2b$. It seems fair to assume that this result is not simply a chance mathematical agreement, but that it corresponds to some physical reality. However insufficient the grounds for this assumption may be, I have adopted it in this paper.

Young[2] has shown that in the equation representing the law of Cailletet and Mathias, which may be written in the form $s_T = s_0 + \alpha T$, the value

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[1] *Compt. rend.*, **102**, 1202 (1886).

[2] "Stoichiometry," p. 228.

of $(-\alpha T_c/s_c)$ is approximately unity for a large number of substances. In this equation, $s_T = (d_1 + d_2)/2$ and s_c is the critical density, and s_0 would be equal to half the density of the liquid at absolute zero, since at this temperature the density of the vapor would be zero. If the law of Cailletet and Mathias is assumed to hold accurately down to absolute zero and if the value of $(-\alpha T_c/s_c)$ is exactly unity, one can easily deduce that at the absolute zero, the density of a substance would be four times the critical density. Again, since $s_T = (d_1 + d_2)/2 = 1/2b$, we can obtain the following result:

$$b_T = \frac{b_c}{(2 - T/T_c)} \tag{25}$$

This result holds only for those substances for which the law of Cailletet and Mathias is valid and for which $(-\alpha T_c/s_c)$ is approximately unity.

It might be added that Thorpe and Rücker's formula[1] for estimating the critical temperature is easily deducible, if we assume the law of Cailletet and Mathias and that $(-\alpha T_c/s_c)$ is approximately unity. For if d_1 and d_2 *now* represent the densities of a liquid at the two temperatures T_1 and T_2, sufficiently below the critical temperature, the densities of saturated vapor may be neglected and we obtain $d_1 = 2s_{T_1}$. Accordingly $d_1 = 2s_c(2 - T_1/T_c)$ and $d_2 = 2s_c(2 - T_2/T_c)$, from which we easily obtain

$$\frac{T_2 d_1 - T_1 d_2}{2(d_1 - d_2)} = T_c.$$

Now Thorpe and Rücker's formula is

$$T_c = \frac{T_2 d_1 - T_1 d_2}{A(d_1 - d_2)},$$

where A varies from 1.926 to 2.030 for 24 substances with a mean value of 1.974.

Determination of *a*.

From the relation

$$p_s = \frac{RT}{v_1 - b} e^{-\frac{a}{v_1 RT}} = \frac{RT}{v_2 - b} e^{-\frac{a}{v_2 RT}}$$

we obtain

$$a_1 = \frac{v_1 v_2}{v_2 - v_1} RT \log_e \frac{v_2 - b}{v_1 - b},$$

or since, according to Equation 21*e*, $(v_2 - b)/(v_1 - b) = (v_2/v_1)^2$,

$$a_1 = \frac{2v_1 v_2}{v_2 - v_1} RT \log_e \frac{v_2}{v_1}. \tag{26}$$

Expressed in terms of the densities d_1 and d_2, Equation 26 becomes

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[1] Quoted in Young's "Stoichiometry," p. 183.

$$a_1 = \frac{2RT}{d_1 - d_2} \log_e \frac{d_1}{d_2}. \qquad (26a)$$

I have called the "a" of Equations 26 and 26a, a_1, since a can be calculated in several other ways. From the set of Equations 20, we obtain the following (since $v_3 = 2b$):

$$a_2 = 2bRT \log_e RT/pb \qquad (27)$$

$$a_3 = v_1RT \log_e RT/p(v_1 - b) \qquad (28)$$

$$a_4 = v_2RT \log_e RT/p(v_2 - b) \qquad (29)$$

An investigation of Equations 26–29 will show that Equation 29 is likely to be the least accurate. In the first place $p(v_2 - b)$ is very nearly equal to RT, so that the logarithm of their quotient, which is the same as the difference of their logarithms, will be greatly affected by small errors in the assumed values of p and v_2. As regards an error in the value of p, its effect on a_4 will be v_2/v_1 times as great as on a_3. Then there is no doubt that usually v_1 is determined more accurately than v_2.

Another method which I have used in calculating a and b for hydrogen is based on Equation 7 or 7a. By Equation 7

$$1 + \frac{a}{vRT} = \frac{dp/dT}{p/T} = \frac{Tdp}{pdT} = \frac{d \log p}{d \log T}. \qquad (30)$$

If the variation of a and b with the temperature be taken into account, we have

$$1 + \frac{a}{vRT} + \frac{T}{v-b}\frac{db}{dT} - \frac{1}{vR}\frac{da}{dT} = \frac{d \log p}{d \log T}. \qquad (30a)$$

If in any particular case, a and b are independent of the temperature, or if the expression $\left(\frac{T}{v-b}\frac{db}{dt} - \frac{1}{vR}\frac{da}{dT}\right)$ is equal to zero, then the simpler Equation 30 may be employed in determining a, and hence b.

Latent Heat of Vaporization.

In order to determine the latent heat of vaporization, we must calculate the work that is done when the liquid expands isothermally from the volume v_1 to the volume v_2. This takes place in practice under the constant external pressure of saturated vapor, p_s. The same work will be done if the expansion is supposed to follow the course of the theoretical isothermal curve. The total work will be expressed by the definite integral

$$L = \int_{v_1}^{v_2} \frac{RT}{v-b} . dv = RT \log_e \frac{v_2 - b}{v_1 - b} = 2RT \log_e \frac{v_2}{v_1}, \qquad (31)$$

if we make use of Equation 21e. $RT/(v - b)$ represents the pressure throughout the fluid except in the surface layer which is negligible. Accordingly $\frac{RT}{v-b}\, dv$ represents the total work done when the volume increases by the increment dv. Equation 31 includes the external work, the amount of which is $p(v_2 - v_1)$. Hence the internal heat of vaporization would be

$$I = 2RT \log_e \frac{v_2}{v_1} - p(v_2 - v_1). \qquad (31a)$$

Comparing Equation 31 with Equation 26, we see that we may write

$$L = 2RT \log_e \frac{v_2}{v_1} = \frac{a}{v_1} - \frac{a}{v_2} \qquad (32)$$

The expression $a/v_1 - a/v_2$ is accordingly a measure of the total heat of vaporization, whereas according to the theory of van der Waals it measures the internal heat of vaporization only. Equation 32 agrees with the assumption made by Dieterici in deriving his original equation that the work done by the molecules in penetrating the surface layer is equal to a/v. According to Kendall,[1] Dieterici has proposed a formula, $I = cRT \log v_2/v_1$ for the internal heat of vaporization. I have not yet been able to obtain a copy of the article in which this formula is deduced; it is, however, to be noted that it is Dieterici's formula for the internal heat of vaporization which is similar to mine for the total effect.

Joule-Thomson Effect.

Our methods of arriving at values of a and b may be summarized as follows: At the critical temperature, a and b can be calculated from the critical data according to equations numbered 6. Above the critical temperature, so long as pv still has a minimum value, use may be made of Equations 12, 13 and 14. Below the critical temperature, Equations 21b and 26 to 29 are to be employed. And of course Equations 30 and 30a are valid at all temperatures and can be used where the data are sufficiently accurate. Another method of finding a relationship between a and b is based on the Joule-Thomson effect. If ΔT be the change in temperature, Δp the change in pressure, in the Joule-Thomson experiments, we have the following relation:[2]

$$\Delta T = \frac{T(dv/dT)_p - v}{c_p} \cdot \Delta p \qquad (33)$$

If we substitute for $(dv/dT)_p$, the value given by Equation 8, we obtain the following approximate result:

$$\Delta T = \frac{2a/RT - b}{c_p} \cdot \Delta p \qquad (34)$$

Equation 34 will hold most accurately when only low pressures are employed. It is identical with the formula derived by van der Waals from his original equation, as we should expect. If the ration $\Delta T/\Delta p$ is de-

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[1] THIS JOURNAL, 36, 1620 (1914).

[2] Planck, "Thermodynamik," 1905, p. 123.

termined accurately at any temperature, we have a means of calculating $2a/RT - b$; while by using Equation 16 we can obtain the value of $b - a/RT$. Hence we can find a and b. Further discussion of these points will appear when we apply our equations to the experimental results.

Applications.

In this paper I have taken —273.09° C. as the absolute zero of temperature and 22412 cc. as the volume of a gram-molecule of an ideal gas under the pressure of one atmosphere.[1] The value assumed for the constant R for a mol is 62372 when a mm. of mercury is the unit of pressure, 82.07 when the unit of pressure is one atmosphere. The unit of volume is always one cubic centimeter. When the equations apply to a mass of gas whose volume is considered to be unity when the pressure is one atmosphere and the temperature is 0° C., the value of R is approximately 1/273.

Isopentane.—Tables I and II contain the results of applying our equations to isopentane. The data for the specific volumes of liquid and saturated vapor are by Young as given in Landolt-Börnstein's *Tabellen.*[2] The observed pressures are also by Young and are taken from an article by Dieterici.[3] The results refer to 1 g. of the substance; pressures are given in millimeters of mercury. Accordingly the value of the constant R is 62372/72.09. The orthobaric volumes of liquid and vapor are represented by v_1 and v_2, respectively; b is calculated using Equation 21b, and a_1, a_2, a_3, and a_4 by means of Equations 26 to 29.

TABLE I.—ISOPENTANE; UNIT MASS = 1 g.

t ° C.	v_1. cc.	v_2. cc.	b. cc.	$a_1 \times 10^{-6}$.	$a_2 \times 10^{-6}$.	$a_3 \times 10^{-6}$.	$a_4 \times 10^{-6}$.
0	1.5642	909	1.5615	4.713	4.704	4.708	2.223
20	1.6140	426.6	1.6079	4.583	4.582	4.582	4.450
40	1.6700	224.4	1.6577	4.461	4.466	4.467	4.434
60	1.7334	127.6	1.7102	4.354	4.353	4.354	4.310
80	1.8051	77.700	1.7641	4.248	4.236	4.242	3.987
100	1.8947	49.505	1.8248	4.150	4.120	4.135	3.747
110	1.9455	39.793	1.8548	4.093	4.059	4.075	3.727
120	2.0036	32.196	1.8862	4.036	3.991	4.012	3.650
130	2.0721	26.103	1.9197	3.977	3.922	3.948	3.604
140	2.1542	21.151	1.9551	3.916	3.860	3.881	3.564
150	2.2497	17.141	1.9887	3.850	3.771	3.806	3.512
160	2.3776	13.719	2.0264	3.778	3.690	3.726	3.480
170	2.5549	10.710	2.0628	3.687	3.599	3.633	3.459
180	2.8588	7.9491	2.1026	3.579	3.503	3.528	3.436
183	3.0202	7.0522	2.1146	3.535	3.473	3.491	3.432
186	3.3025	5.9666	2.1258	3.476	3.441	3.449	3.428
187.8	4.2680	4.2680	2.1340	3.404	3.423	3.423	3.423

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[1] Young, "Stoichiometry," **1908**, p. 39.

[2] **1912**, p. 158.

[3] *Ann. Physik*, **9**, 176 (1903).

TABLE II.—ISOPENTANE; UNIT MASS = 1 g.

t ° C.	p (obs.).	$p = \frac{\mathrm{RT}}{b} e^{-\frac{a_1}{2b\mathrm{RT}}}$.	% error.	$a_1 \times b \times 10^{-6}$.	L (calc.).	L (Young).
0	257.7	254.7	1.2	7.35	95.8	86.8
20	572.6	571.9	0.1	7.36	90.0	82.9
40	1131	1134	0.3	7.40	84.5	78.8
60	2036	2034	0.1	7.45	78.9	74.4
80	3401	3364	1.1	7.50	73.2	69.8
100	5355	5222	2.5	7.58	67.1	64.6
110	6586	6406	2.7	7.59	63.7	61.7
120	8040	7762	3.4	7.62	60.1	58.5
130	9707	9317	4.0	7.63	56.2	54.8
140	11620	11091	4.5	7.65	52.0	50.7
150	13804	13080	5.2	7.66	47.3	46.5
160	16285	15369	5.6	7.65	41.8	41.0
170	19094	18061	5.4	7.61	35.0	34.2
180	22262	21259	4.5	7.53	25.5	24.5
183	23288	22434	3.7	7.47	21.3	20.2
186	24350	23862	2.0	7.38	15.0	13.9
187.8	25005	25287	1.1	7.26	0	0

A study of Table I shows that the value of a decreases from about 4.7×10^6 at 0° C. to 3.4×10^6 at 187.8° C., the critical temperature. The values of a_1, a_2 and a_3 agree very well throughout, whereas in the case of a_4, its values near 0° and near the critical temperature agree with those of a_1, a_2 and a_3, but at intermediate temperatures, a_4 is considerably less than a_1, a_2 and a_3. I am not able wholly to account for this divergence, although there is no doubt that some of the discrepancy may be due to errors in the assumed values of p and v_2. As has been previously remarked, an error in the value of p would have greater effect on the calculated value of a_4 than on that of a_3 or a_2. Note that a_1 is calculated without any use of the value of p. Its value is determined entirely by v_1, v_2 and T. In Table II the values of p at the different temperatures have been calculated, using Equation 22 and a_1. The column is headed $p = \frac{\mathrm{RT}}{b} e^{-\frac{a_1}{2b\mathrm{RT}}}$, but exactly the same values are obtained when we use the equations

$$p = \frac{\mathrm{RT}}{v_1 - b} e^{-\frac{a_1}{v_1\mathrm{RT}}} \quad \text{or} \quad p = \frac{\mathrm{RT}}{v_2 - b} e^{-\frac{a_1}{v_2\mathrm{RT}}}.$$

It is to be noted that we should of course obtain the observed values of p, if instead of a_1 we had used a_2, a_3, or a_4 in the corresponding equations. Since a_2 and a_3 do not differ very much from a_1, it is evident that a small error in the value of a will seriously affect the calculated values of p, except when the equation $p = \frac{\mathrm{RT}}{v_2 - b} e^{-\frac{a}{v_2\mathrm{RT}}}$ is used to calculate p, in which case a considerable error in a produces only a small change in p.

If we compare the calculated with the experimental values of p, we notice that the maximum error amounts to 5.6% at about 30° below the critical temperature. This error is, of course, considerable, but still hardly sufficient to invalidate the views here presented or to render them unworthy of discussion.

In Column 5 of Table II are given the values of the product $ab \times 10^{-6}$, and it will be at once evident that this product exhibits a noteworthy constancy throughout the whole temperature interval studied. Now for the two dozen or so substances which Young has investigated and for which he found $(-\alpha T_c/s_c)$ to be nearly equal to unity, we deduced Equation 25, *viz.*, $b_T = b_c/(2 - T/T_c)$. If the product ab be supposed to be absolutely constant, we should have

$$a_T = a_c(2 - T/T_c). \qquad (25a)$$

It must be clearly borne in mind that these results are supposed to hold only under the stated conditions and only below the critical temperature. Applied above this temperature, Equations 25 and 25a would lead to results which are contrary to all experimental evidence. For at a temperature equal to twice the critical, b would become infinity and a would vanish.

In Column 6 of Table II are given the results obtained for the heat of vaporization of one gram of isopentane at the pressure of saturated vapor. "L" includes the external work done during the increase of volume. I have not access to the original data of Young, but have put in Column 7 of Table II the results as quoted by Dieterici[1] for the internal heat of vaporization, to which I have added the calculated values of the external work, given by $p(v_2 - v_1)$. In calculating L, we have used Equation 32, according to which, $L = 2RT \log_e d_1/d_2 = a_1 (1/v_1 - 1/v_2)$. Assuming the values as quoted by Dieterici to be correct, our formula gives too high results, especially at low temperatures. Near 0° C., the error amounts to 10% and becomes as low as 1.7% at 150° C., increasing thereafter as we approach the critical temperature.

I have studied fluorobenzene, normal hexane, carbon tetrachloride with results quite similar to those obtained in the case of isopentane. I shall not take up space discussing them but proceed to a consideration of carbon dioxide.

Carbon Dioxide.—The results in Tables III and IV refer to one gram of carbon dioxide, but the unit of pressure is one atmosphere and the unit of volume one cubic centimeter. According to Amagat,[2] from whom the data are taken, the critical temperature is 31.35° C. The fifth column of Table IV contains values of the heat of vaporization obtained by Dieterici[3] from Amagat's experimental results.

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[1] *Ann. Physik*, **9**, 176 (1903).

[2] *Ann. chim. phys.*, [6] **29**, 118–136 (1893).

[3] *Loc. cit.*

TABLE III.—CARBON DIOXIDE; UNIT MASS = 1 g.

t° C.	v_1. cc.	v_2. cc.	b. cc.	a_1. Atm.–cc².	a_2. Atm.–cc².	a_3. Atm.–cc².	a_4. Atm.–cc².
0	1.094	10.41	0.9900	2806	2731	2758	2414
5	1.126	8.772	0.9980	2751	2680	2712	2443
10	1.168	7.518	1.0109	2719	2636	2671	2412
15	1.229	6.329	1.0292	2673	2595	2632	2404
20	1.306	5.262	1.0463	2647	2549	2586	2400
25	1.422	4.167	1.0602	2581	2493	2522	2408
27	1.490	3.759	1.0670	2557	2472	2498	2408
28	1.532	3.547	1.0699	2543	2461	2484	2407
29	1.587	3.301	1.0717	2523	2449	2468	2409
30	1.672	2.994	1.0729	2494	2436	2449	2414
31	1.866	2.551	1.0777	2465	2427	2432	2420
31.35	2.155	2.155	1.0775	2447	2421	2421	2421

TABLE IV.—CARBON DIOXIDE; UNIT MASS = 1 g.

t° C.	P (obs.). Atm.	$P = \frac{RT}{b} e^{-\frac{a_1}{2bRT}}$.	L (calc.). Calories.	L (Dieterici).
0	34.3	31.9	55.7	55.0
5	39.0	36.4	51.6	51.0
10	44.2	40.9	47.7	47.5
15	50.0	46.0	42.7	42.5
20	56.3	51.7	37.0	36.4
25	63.3	58.7	29.0	28.5
27	66.2	61.7	25.1	24.8
28	67.7	63.3	22.9	23.1
29	69.2	65.1	20.0	20.2
30	70.7	67.4	16.0	16.0
31	72.3	70.1	8.6	8.6
31.35	72.9	71.3	0	0

The results in Table III are somewhat similar to those for isopentane. Again a_1, a_2 and a_3 show general agreement, but the values of a_4 seem to be irregular, in no case diverging very much from the value at the critical temperature. Table IV shows again that the pressures calculated by our formula are usually too low, while on the other hand our calculated values of L agree very well with those of Dieterici.

The experiments of Amagat on the compressibility of carbon dioxide allow us to calculate a and b above the critical temperature. Amagat has given for a series of temperatures up to 258° C. the minimum values of pv as well as the corresponding pressures. His data are reproduced in Table V. Equations 12 and 13, which concern us here, may be written as follows:

$$a = v(a/b - \mathrm{RT}) \tag{12}$$

$$\frac{a}{b\mathrm{RT}} e^{1 - \frac{a}{b\mathrm{RT}}} = \frac{pv}{\mathrm{RT}} \tag{13}$$

Using Equation 13 for any temperature and its corresponding value of *pv*, the value of $a/b\mathrm{RT}$ may be calculated by a rather laborious trial method; thence the value of a/b is obtained, then a from Equation 12 and finally b. A study of Amagat's results and his diagrams will show that although the minimum value of *pv* may be determined with some accuracy, the value of the corresponding *p*; and hence of *v*, cannot be estimated so precisely. An error in locating the minimum of the curve, especially at high temperatures where the curves are rather flat, will not affect the value of *pv* very much, but will seriously influence the value of *p* and *v*. Hence at the highest temperatures, the values of the pressures as given by Amagat must be allowed to be less accurate than those at lower temperatures. Hence the ratio a/b is probably more accurately determined than a and b.

In Table V the unit mass of carbon dioxide is that which has a volume of 1 cc. at 0° C. when the pressure is one atmosphere. In order to compare the results of Table III with those of Table V, the values of a and b in the former table must be divided by $(505.9)^2$ and 505.9, respectively, since one gram of carbon dioxide occupies 505.9 cc. at 0° C. and one atmosphere. If we select the values of a and b at 20° and 30° in Table III, we shall obtain in the new units: at 20°, $a = 0.009960$, $b = 0.002068$; at 30°, $a = 0.009518$, $b = 0.002121$. These values agree very well indeed with those in Table V obtained in quite a different way.

TABLE V.—CARBON DIOXIDE: $v = 1$ AT 0° C. WHEN $p = 1$ ATMOSPHERE.

t ° C.	p. Atm.	pv. Minimum.	$v \times 10^6$. cc.	$a/b\mathrm{RT}$.	a/b.	$a \times 10^6$. Atm.–cc.	$b \times 10^6$. cc.
20	56.8	0.1475	2597	4.497	4.868	9829	2019
30	76	0.2185	2875	4.027	4.508	9741	2161
40	101	0.3083	3053	3.604	4.168	9192	2206
50	125	0.3965	3172	3.294	3.931	8683	2209
60	143	0.4830	3378	3.050	3.752	8519	2270
70	162	0.5690	3512	2.847	3.608	8218	2278
80	179	0.6500	3631	2.683	3.500	7972	2278
90	196	0.7310	3730	2.538	3.404	7694	2260
100	210	0.8140	3876	2.403	3.312	7495	2263
137	245	1.0850	4429	2.053	3.109	7078	2271
198	255	1.4920	5851	1.661	2.891	6733	2329
258	218	1.8100	8303	1.456	2.857	7433	2602

The results shown in Table V indicate that a continues to decrease above the critical temperature, while b, if it increases at all, increases very slowly. The values for a and b at 258° and probably also at 198° are likely subject to a considerable error, as has already been pointed out. Our results justify us therefore in saying that above the critical temperature and up to 200° C. b remains essentially constant in the case of carbon dioxide.

I may state here that results quite similar to those for carbon dioxide are obtained with ethylene, when Equations 12, 13 and 14 are applied to Amagat's results. In the case of ethylene also, b seems to remain fairly constant from 10° to 198°, while a decreases as the temperature rises.

An application of the set of Equations 17 may be made to carbon dioxide. According to these equations, at the critical temperature, the value of the minimum pv is $\frac{2}{e}\, p_c v_c$, the corresponding pressure is $1.104\ p_c$ and the volume is $^2/_3\ v_c$ or $^4/_3\ b_c$. Now interpolating in Table V between 30° and 40°, we find for 31.35°, $p = 79.4$, $pv = 0.2302$, $v = 0.002899$, while in the same units, $p_c = 72.9$, $v_c = 0.004260$. $b_c = 0.002130$. The calculated values for minimum pv would be: $p = 80.4$, $pv = 0.2286$. $v = 0.002840$, agreeing very well with the interpolated values.

Hydrogen.—In discussing hydrogen, we shall take as unit mass that quantity of hydrogen which occupies one cubic centimeter at 0° C. and the pressure of one atmosphere. According to Witkowski,[1] the behavior of this gas at 0° C. is given accurately by the equation

$$pv = 0.999384 + \frac{0.0006154}{v} + \frac{0.000000706}{v^2}$$

The Dieterici equation at low pressures may be written

$$pv = \mathrm{RT} + bp - a/v^2.$$

If we imagine the pressure to be reduced indefinitely and the volume correspondingly increased, we find by comparing this equation with that of Witkowski that at 0° C. $\mathrm{RT} = 0.999384$ and hence $\mathrm{R} = 0.0036595$. To avoid any misconception, it might be explained that the reason this value of R differs from $1/273.09 = 0.0036618$, is because our unit mass of hydrogen which occupies one cubic centimeter under standard conditions, would occupy only 0.999384 cc. if it were a "perfect" gas. Hence the value of R is smaller to that degree.

The critical temperature and pressure of hydrogen have been determined by a number of investigators. Bulle[2] has recently obtained the following values: $\mathrm{T}_c = 31.95 \pm 0.1°$ and $p_c = 11.0$ atmospheres. Since $\mathrm{T}_c = a/4\mathrm{R}b$ and $p_c = a/4e^2b^2$, we obtain from Bulle's data, $a/b = 0.4677$, $a = 0.000673$, and $b = 0.001439$. The minimum values of pv have been determined by Witkowski[3] and by Kamerlingh Onnes and Braak.[4] The earlier results of Witkowski agree fairly well with those of Onnes and Braak, although Witkowski states that his determinations of the pressures corresponding to a minimum pv may be several atmospheres in error. The results obtained by applying Equations 12, 13

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[1] *Bull. acad. Cracovie*, 6, 305–338 (1905).

[2] *Physik. Z.*, 14, 860–2; *C. A.*, 7, 3877 (1913).

[3] *Loc. cit.*

[4] *Comm. Phys. Lab., Leiden*, No. 97 (1907); quoted in Young's "Stoichiometry," p. 24.

and 14 to the data of Witkowski and of Onnes and Braak are set forth in Tables VI and VII, respectively. Both tables would indicate that the ratio a/b is approximately constant in the temperature interval under investigation. The results from Witkowski's data seem to show a decrease of both a and b with rise of temperature, while the presumably more accurate data of Onnes and Braak exhibit a and b as essentially constant from —217° C. to —183° C. The values of a and b in Tables VI and VII should be compared with those I have calculated from the critical data. In both tables the values of a are considerably smaller than that of a at the critical temperature; but whereas Witkowski's data indicate smaller values of b, those of Onnes and Braak give us values not appreciably different from the value of b at 32° absolute. We shall, however, shortly produce evidence indicating that, above —183° C. at least, a and b for hydrogen do decrease with rise of temperature. Before proceeding to this, I desire to illustrate how well the Dieterici equa-

TABLE VI.—HYDROGEN DATA OF WITKOWSKI. $v = 1$ AT 0° C. WHEN $p = 1$ ATM.

t ° C.	p. Atm.	pv. Min.	a/bRT.	a/b.	$a \times 10^6$. Atm.-cc².	$b \times 10^6$. cc.
—183	32	0.3270	1.1334	0.3737	449	1203
—190	43.5	0.2970	1.2329	0.3749	484	1290
—205	55	0.2273	1.4920	0.3718	507	1363
—212	54.8	0.1926	1.6496	0.3688	511	1384

TABLE VII.—HYDROGEN DATA OF ONNES AND BRAAK. $v = 1$ AT 0° C. WHEN $p = 1$ ATM.

t ° C.	p. Atm.	pv. Min.	a/bRT.	a/b.	$a \times 10^6$. Atm.-cc².	$b \times 10^6$. cc.
—182.75	33.36	0.32630	1.1707	0.3870	552	1426
—195.20	47.69	0.27338	1.3175	0.3756	519	1382
—204.62	52.10	0.22935	1.4816	0.3712	531	1431
—209.6	53.73	0.20394	1.6011	0.3720	530	1425
—212.73	53.63	0.18780	1.6827	0.3717	528	1421
—217.32	51.57	0.16335	1.8234	0.3721	532	1430

TABLE VIII.—HYDROGEN. DATA OF WITKOWSKI.

p (Atm.) Witkowski.	t = —183° C. p (calc.).	t = —190° C. p (calc.).	t = —205° C. p (calc.).	t = —212° C. p (calc.).
1	1.004	1.005	1.006	1.009
5	5.008	5.010	5.014	5.026
10	9.997	9.995	10.003	10.016
15	14.995	14.990	14.986	15.013
20	20.013	20.007	19.989	20.089
25	25.011	24.999	25.023	25.065
30	30.002	30.005	30.058	30.088
35	35.003	35.000	35.093	35.139
40	40.024	40.007	40.079	40.167
45	45.028	45.003	45.036	45.126
50	50.020	49.997	50.005	50.026
55	54.997	54.977	55.000	54.998
60	59.955	59.958	60.007	60.052

tion reproduces the Witkowski data. Witkowski[1] gives a table containing the values of pv at a series of temperatures from 100° C. to —212° C. and up to a pressure of 60 atmospheres. In Table VIII I have given the results of calculating the pressures corresponding to volumes as given by Witkowski and at the temperatures —183°, —190°, —205°, and —212° C. I have used the equation $p = \frac{\mathrm{RT}}{v - b} e^{-\frac{a}{v\mathrm{RT}}}$, where R is equal to 0.0036595, and the values of a and b for each temperature are taken from Table VI. The agreement of the calculated pressures with those given by Witkowski is certainly very excellent. It is to be noted that the values of a and b which have been employed have not been deduced from the whole course of the pv curve, but in each case from its minimum value only.

According to Equation 7a, we have the relation

$$\left.\begin{aligned}\left(\frac{dp}{d\mathrm{T}}\right)_v &= \frac{p}{\mathrm{T}}\left(1 + \frac{a}{v\mathrm{RT}} + \frac{\mathrm{T}}{v-b}\cdot\frac{db}{d\mathrm{T}} - \frac{1}{v\mathrm{R}}\frac{da}{d\mathrm{T}}\right)\\ &= \frac{\mathrm{R}}{v-b}e^{-\frac{a}{v\mathrm{RT}}}\left(1 + \frac{a}{v\mathrm{RT}} + \frac{\mathrm{T}}{v-b}\frac{db}{d\mathrm{T}} - \frac{1}{v\mathrm{R}}\frac{da}{d\mathrm{T}}\right)\end{aligned}\right\} \qquad (7a)$$

If a and b are constants, or if the expression $(\mathrm{T}/(v - b).\, db/d\mathrm{T} - 1/v\mathrm{R}\; da/d\mathrm{T})$ vanishes, we have the simpler equations

$$\left(\frac{dp}{d\mathrm{T}}\right)_v = \frac{p}{\mathrm{T}}\left(1 + \frac{a}{v\mathrm{RT}}\right) = \frac{\mathrm{R}}{v-b}e^{-\frac{a}{v\mathrm{RT}}}\left(1 + \frac{a}{v\mathrm{RT}}\right). \qquad (7)$$

In most cases, where v is not too small, we could write

$$\left(\frac{dp}{d\mathrm{T}}\right)_v = \frac{\mathrm{R}}{v-b}. \qquad (7b)$$

I have assumed that the expression $\frac{\mathrm{T}}{v-b}\frac{db}{d\mathrm{T}} - \frac{1}{v\mathrm{R}}\frac{da}{d\mathrm{T}}$, in what follows, is very small, compared with $a/v\mathrm{RT}$ in the case of hydrogen, at least throughout the temperature interval —183° C. to 100° C. The grounds for this will be discussed later. I have accordingly used Equation 7 to determine a and b, calculating $(dp/d\mathrm{T})_v$ and P/T from the Witkowski data. In his memoir, Witkowski gives the pressures at the series of temperatures, 100°, 0°, —77°, —104°, —147°, —183°, —190°, —205°, and —212° C., corresponding to a series of volumes from 1 to 1/60 in terms of the volume at 0° C. and one atmosphere. The method I employed to obtain an accurate estimate of $(dp/d\mathrm{T})_v$ at each temperature will be clear from the following example: Corresponding to the volume $v = 1/40$, Witkowski gives for the temperatures —77°, —104°, and —147° C. the pressures 29.33, 25.22 and 18.63, respectively. An equation of the second degree in T was found algebraically which would re-

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[1] *Loc. cit.*

produce the pressures at the three temperatures. From this equation, the values of $(dp/dT)_v$ at —104° was easily calculated. Geometrically, having pressures as ordinates and temperatures as abscissae, a parabola was found which would go through the three points and the slope at the intermediate point was the value sought. The parabola, of course, in no case departs much from a straight line. To find $(dp/dT)_v$ at —147° C., the data for —104°, —147° and —183° were used and so on for all the other temperatures. It is evident that the values we have obtained for $(dp/dT)_v$ will, in all probability, be more accurate at higher temperatures than at lower ones. The pressures at 0° C. are more than four times as great as at —205° C., and as $(dp/dT)_v$ is obtained by a different method, the probable error at —205° will be four times as great as at 0° C., assuming that the pressures in both cases have been determined with the same relative accuracy. I have determined $(dp/dT)_v$, and hence a and b, using the data for the volumes 1/60, 1/50, 1/40, 1/30 and 1/20 for the temperatures already named, excluding the highest and the lowest one. Here again the accuracy of the calculated result will, for obvious reasons, be inversely proportional to the volume selected. This will be illustrated by the results obtained at the various volumes, although there is a surprising agreement in nearly all cases.

In Table IX are given the detailed results for $v = 1/60$, while Table X contains only the final results for a, b, and a/b, with the averages in the last column, excluding from the average the results for $v = 1/20$, which are likely to be least accurate. Table XI is simply a summary of these average values together with the values for 100° C., obtained by a rather uncertain extrapolation. As emphasized previously, the results at low temperatures are probably less trustworthy than those at higher temperatures. An examination of these tables shows that a and b decrease with rise of temperature. With regard to the ratio a/b, the same statement may actually be true, in spite of the fact that from —205° to —147° the tables indicate a slight increase with the temperature. The results at low temperatures are, however, subject to such error that it is unsafe to indulge in much generalizing. An important point to be noted, however, is that the values of a, b, and also a/b, as found by the present method for —183°, —190° and —205° C., agree remarkably well with those given in Tables VI and VII, found by a quite different method. The equation of state for a gas at low pressures can be written in the form $pv = RT + p(b - a/RT)$, which at 0° C. is equivalent to $pv = RT + p(b - a)$, since RT is approximately unity. Comparing this with Witkowski's empirical equation already given, we find the value of $(b - a)$ at 0° C. to be 0.0006154. From Table XI we obtain a result in very satisfactory agreement with this value, *viz.*, $(b - a) = 0.000622$.

TABLE IX.—HYDROGEN. $v = 1$ AT 0° C. WHEN $p = 1$ ATM.
$v = {}^1/_{60}$.

t° C.	p. Atm.	p/T.	$\left(\frac{dp}{dT}\right)_{v = 1/60}$.	a/vRT.	$a \times 10^6$. Atm.-cc².	$b \times 10^6$. cc.	a/b.
100	(85.422)	...	...	...	...	....	....
0	62.331	0.22824	0.23136	0.01367	228	851	0.2679
—77	44.49	0.22688	0.23229	0.02385	285	910	0.3132
—104	38.21	0.22597	0.23337	0.03231	333	993	0.3353
—147	28.10	0.22286	0.23505	0.05471	421	1120	0.3759
—183	19.64	0.21800	0.23679	0.08619	473	1273	0.3716
—190	17.98	0.21639	0.23720	0.09668	490	1306	0.3752
—205	14.42	0.21178	0.24110?	0.13844	575	1621	0.3547
—212	12.72	...	...	...	...	....	....

TABLE X.—HYDROGEN. a AND b MULTIPLIED BY 10^6.

		$v = 1/60$.	$v = 1/50$.	$v = 1/40$.	$v = 1/30$.	$v = 1/20$.	Mean, excluding those for $v = 1/20$.
0°	a	228	226	232	213	249	225
	b	851	849	854	834	864	847
	a/b	0.2679	0.2662	0.2718	0.2558	0.2878	0.2652
—77°	a	285	302	299	314	375	300
	b	910	942	939	963	1026	938
	a/b	0.3132	0.3202	0.3188	0.3261	0.3655	0.3197
—104°	a	333	360	360	366	396	355
	b	993	1027	1028	1032	1049	1020
	a/b	0.3353	0.3501	0.3500	0.3544	0.3775	0.3480
—147°	a	421	406	421	430	415	419
	b	1120	1089	1120	1144	1110	1118
	a/b	0.3750	0.3729	0.3761	0.3756	0.3739	0.3748
—183°	a	473	486	478	487	604	481
	b	1273	1313	1277	1312	1613	1294
	a/b	0.3716	0.3701	0.3746	0.3710	0.3745	0.3717
—190°	a	490	506	510	531	652	509
	b	1306	1372	1383	1448	1770	1377
	a/b	0.3752	0.3689	0.3685	0.3667	0.3684	0.3696
—205°	a	575	544	567	625	731	578
	b	1621	1506	1572	1760	2045	1615
	a/b	0.3547	0.3615	0.3609	0.3551	0.3575	0.3579

TABLE XI.—HYDROGEN. AVERAGE VALUES OF a, b AND a/b FROM TABLE X.

	0°.	—77°.	—104°.	—147.°.	—183°.	—190°.	—205°.	+ 100° C. (extrapolated).
$a \times 10^6$	225	300	355	419	481	509	578	170?
$b \times 10^6$	847	938	1020	1118	1294	1377	1615	800?
a/b	0.2652	0.3197	0.3480	0.3748	0.3717	0.3696	0.3579	0.2125?

For an ideal gas, we have the relation $p/T = R/v$. For the mass of hydrogen which we are taking as our unit and for a value of v equal to 1/60, the theoretical value of p/T would be 0.21957. An examination of the third column of Table IX will show that somewhere between —147°

and —183°, p/T has its "theoretical" value. By interpolation, we find this temperature to be —171.4°. If we investigate the data for $v = 1/50$, $1/40$, $1/30$ and $1/20$, we obtain the following results for this temperature, *viz.*, —171.4°, —170.3°, —157.5°, —167.0°. Since the results for $v = 1/60$ and $1/50$ are the most accurate, we may accept —171.4° C. as very close to the temperature at which $p/\mathrm{T} = \mathrm{R}/v$. Now, according to the equation of state, for moderate pressures,

$$\frac{p}{\mathrm{T}} = \frac{\mathrm{R}}{v - b} e^{-\frac{a}{v\mathrm{RT}}} = \frac{\mathrm{R}}{v}\left(1 + \frac{b}{v} - \frac{a}{v\mathrm{RT}}\right).$$

Evidently p/T will equal R/v when $b = a/\mathrm{RT}$, or $a/b = \mathrm{RT}$. Since we have found the temperature to be —171.4°, we calculate for this temperature $a/b = \mathrm{RT} = 0.3721$, in excellent agreement with the values of a/b in Table XI. At the temperature —171.4° C. or 101.6° absolute, the pv curve for hydrogen would just fail to have a minimum and would proceed virtually horizontally for several atmospheres. At this temperature, the behavior of hydrogen under moderate pressures would be given very accurately by Boyle's law.

Joule-Thomson Effect for Hydrogen.—The values we have obtained for a and b, at least at 0° and 100° C., are confirmed if we consider their relation to the Joule-Thomson effect. According to the experiments of Joule,[1] the value of $\Delta\mathrm{T}/\Delta p$ of Equation 34, at 6.8° C. is —0.030, and at 90.1° C. is —0.044. We can use at 6.8° C. the values of a and b for 0° C. Their values near 100° C. will be less and a rough extrapolation gives us for 100° C., $a = 0.000170$, and $b = 0.000800$. Using our values of a and b in Equation 34, the calculated value of $\Delta\mathrm{T}/\Delta p$ at 6.8° C. would be —0.032, and at 90.1° C. —0.043, in good agreement with the observed values. The negative lowering means, of course, an elevation of temperature.

Whether there shall be a rise or a fall in temperature in the Joule-Thomson experiment depends on whether $(2a/\mathrm{RT} - b)$ is negative or positive. For most gases at ordinary temperatures b is less than $2a/\mathrm{RT}$ and we have a fall in temperature. In the case of hydrogen at ordinary temperatures $(2a/\mathrm{RT} - b)$ is negative and we have a rise in temperature. At a sufficiently low temperature the sign should be reversed. The inversion temperature for hydrogen has been found by Olszewski[2] to be —80.5° C. or 192.5° abs. At this temperature, then, we should have $(2a/\mathrm{RT} - b) = 0$. Now using the values given in Table XI, at —77° C., $(2a/\mathrm{RT} - b) = -0.000102$ and at —104° C. $(2a/\mathrm{RT} - b) = +0.000128$. Accordingly, at about —89° C. or 184° abs. $(2a/\mathrm{RT} - b)$ would be zero. We therefore calculate the inversion temperature to be 184° instead of 192.5°

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[1] Landolt-Börnstein's *Tabellen*, 1912, p. 786.

[2] *Bull. acad. Cracovie*, 1901, p. 453; quoted in Young's "Stoichiometry," p. 236.

abs. as observed by Olszewski. This investigator later observed in the case of nitrogen and oxygen that the inversion temperature depends on the initial pressure. Equation 34 in its most rigorous form would also show that this must be the case. In any event, the fair agreement of our value with that observed by Olszewski is another confirmation of the approximate correctness of the values we have obtained for a and b.

We are now in a better position to consider the assumption we have made that in the equation

$$\left[\frac{dp}{dT}\right]_v = \frac{p}{T}\left[1 + \frac{a}{vRT} + \frac{T}{v-b}\frac{db}{dT} - \frac{1}{vR}\frac{da}{dT}\right]$$

we may suppose $\frac{T}{v-b}\frac{db}{dT} - \frac{1}{vR}\frac{da}{dT}$ to be negligible with respect to a/vRT. All our values from —205° to 0° C. have been calculated on this assumption, in applying Equation 7. The assumption seems to have been justified by the following facts: (1) The values we have obtained at —183° and —190° (cf. Table XI) agree well with those calculated from the minimum values of pv (cf. Tables VI and VII). (2) When the values of a and b from Table XI are used in the equation $p = \frac{RT}{v-b}e^{-\frac{a}{vRT}}$, the experimental results of Witkowski are reproduced with great accuracy (cf. Table VIII). (3) At 0° C., our values of a and b agree well with the value of $(b - a/RT)$ or $(b - a)$ deduced from Witkowski's empirical equation. (4) Our values of a and b at 0° C. and 100° C. lead us to an estimate of the Joule-Thomson effect in good agreement with experiment. (5) Our calculation of the inversion temperature agrees passably well with Olszewski's observation. (6) At 0° C. the value of $(b - a/RT)$, or in this case $(b - a)$, is determined with some degree of precision by Witkowski's work to be close to 0.000620. All our experience with isopentane, carbon dioxide and other substances not considered in this paper goes to show that a always decreases with rise of temperature. Since at the critical temperature and around —183° C., $(b - a)$ is much greater than 0.000620, the value of b must decrease with rise of temperature to 0° C. Since a and b decrease together, the terms $\frac{T}{v-b}\frac{db}{dT}$ and $-\frac{1}{vR}\frac{da}{dT}$ will tend to neutralize each other; and the preceding statements go to show that this neutralization is fairly complete.

These considerations seem to justify the assumption I have made and to render the values of a and b which I have obtained worthy of some degree of confidence. That b decreases with rise of temperature, at least above —183° C., is a result in harmony with the views expressed by T. W. Richards[1] in regard to the compressibility of atoms. He shows that

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[1] THIS JOURNAL, **36**, 617 (1914); **37**, 2417 (1915).

the value of b for helium (assuming that a is negligible) decreases from 0° C. to 100° C., and explains the decrease as due to the increasing collision-pressure with increase of temperature. Whatever be the explanation, we have found that the same thing is true of b for hydrogen, its value at 0° C. being about 60% of that at the critical temperature.

Our calculations for helium are also in harmony with those of T. W. Richards. According to Kamerlingh Onnes,[1] the critical temperature for helium is 5.25° abs. and the critical pressure 1718 millimeters, or 2.261 atmospheres. From these data we obtain $a = 0.000089$ and $b = 0.001151$, where the unit quantity of helium occupies one cubic centimeter under standard conditions. Evidently the value of a is very small and at ordinary temperatures one is probably justified in considering a/RT negligible with reference to b. If we take 4 g. of helium as our unit mass, the value of b at 5.25° abs. is 25.6 cc. At 0° C. and at 100° C. Richards finds $(b - a/\mathrm{RT})$ or in this case, very approximately, b, equal to 12 cc. and 10.4 cc., respectively. The value of b at 0° C. is thus less than half what it is calculated to be at 5.25° absolute.

In the case of hydrogen, however, the value of a/RT is not negligible with respect to b and for this reason fairly accurate values of both must be determined before one can say whether b decreases or not with the temperature. Thus Richards finds an increase in $(b - a/\mathrm{RT})$ for hydrogen as one goes from 0° C. to 100° C. In spite of this fact, we have found that both a and b decrease in this interval. Richards, of course, fully understood that this might be the case, if the value of a were sufficiently large.

Richards has also expressed the view that b does not differ very much from the volume of the liquefied gas. Our results are so far in agreement with this, that we have found b at temperatures considerably below the critical temperature to be but slightly smaller than the volume of the liquid, as is apparent from the equation $1/b = 1/v_1 + 1/v_2$.

So far we have not particularly concerned ourselves with the question as to whether a and b in addition to being temperature, are also volume functions. The critical state is determined mathematically by the condition that $(dp/dv)_\mathrm{T}$ and $(d^2p/dv^2)_\mathrm{T}$ shall both be zero. Assuming a and b to be independent of the volume has led to results in conformity with experience; for example, to the result that the critical density is 3.695 times as great as the density would be for an "ideal" gas at the critical temperature and pressure. I have therefore felt myself justified in inferring that a and b are essentially independent of the volume within the limits of pressure considered in this paper. It is only right to state, however, that when very great pressures are considered, it seems

[1] *C. A.*, 7, 2327 (1913).

necessary, as a result of some calculations I have made, to assume that *b* under these circumstances suffers a diminution in volume. This question I have, however, not investigated thoroughly, partly owing to the lack of available, accurate data.

As a result of the investigation set forth in this paper, I consider that the following statements are justified: The Dieterici equation of state has a sounder theoretical basis than that of van der Waals. It reproduces the behavior of a gas, not only at low pressures, but also at the critical point and even at much higher pressures. Although, perhaps, not so simple an expression as van der Waals's, many of the deductions from it are characterized by great simplicity and elegance. It has of course the great advantage over the van der Waals equation that it reproduces the critical state accurately, whereas the latter, as is well known, does not. It seems to me, therefore, that we ought to abandon the van der Waals equation, except as a qualitative interpretation of the facts, and adopt the Dieterici equation of state as the only one which has both a sufficiently sound theoretical foundation and a sufficiently accurate correspondence with the facts.

Summary.

In the present paper I have discussed the Dieterici equation of state, $p = \frac{RT}{v - b} e^{-\frac{a}{vRT}}$ in some detail and have indicated in a number of ways how accurately it reproduces the experimental results.

Various methods are developed for calculating the values of *a* and *b* below, at, and above the critical temperature.

A formula is deduced for calculating the pressure of saturated vapor from the densities of the liquid and vapor.

A formula is deduced for calculating the latent heat of vaporization from the densities of liquid and saturated vapor.

Isopentane, carbon dioxide and hydrogen are studied in some detail. In the case of isopentane, *a* decreases and *b* increases from 0° C. up to the critical temperature. The same is true of carbon dioxide. Above the critical temperature, in the case of carbon dioxide, *a* continues to decrease, while *b* remains fairly constant up to 200° C. In the case of hydrogen, *a* decreases from the critical temperature up to ordinary temperatures, while *b* does the same, from —183° C. at least.

In the case of hydrogen, its inversion temperature is calculated, and also the temperature at which it "obeys" Boyle's law for moderate pressures. The latter temperature was calculated to be —171.4° C.

Combining the law of Cailletet and Mathias with a result obtained by Young for a number of substances, it is shown that the density of a substance at the absolute zero is four times the critical density.

Our conclusions in regard to the variation of *b* with the temperature are shown to be in harmony with some of the views of T. W. Richards in regard to the compressibility of atoms.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY. No. 259.]

THE PROPERTIES OF MIXED LIQUIDS. I. SULFURIC ACID-WATER MIXTURES.

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This paper is the first report upon a somewhat extended series of investigations, started some two years ago, upon the drop weights, or surface tensions, of pure liquids, at many temperatures, and their relationship to the values of that property in their binary or other admixtures in various proportions, at those temperatures. The main object of the work is to provide such a further, perhaps more consistent, set of experimental data that eventually it may perhaps be possible to find the cause of the mutual effects of liquids upon one another; which, although absent in some cases, are great, and yet of widely differing magnitude, in others.

For some binary liquid mixtures it is known that the so-called *law of mixtures* holds more or less rigidly, *i. e.*, the value of a certain physical property of the mixture is equal to the sum of the values of that property for the pure constituents under like conditions, each multiplied by the ratio of its weight in the mixture, to the total weight of the system. Or, expressed as an equation, $P_{\text{Mixt.}} = xP_a + (1 - x)P_b$, where the terms P represent the values of the property considered, and x is the weight of the constituent a, when the total weight of the mixture is regarded as unity. In all cases of this sort it is generally assumed, apparently with reason, (1) that no chemical reaction has taken place between the constituents, and (2) that the previous molecular state of each constituent in the pure condition still persists in their mixture.

The great mass of binary liquid mixtures, however, not only fails to follow this law, but shows a variation from it which depends solely upon the constituents selected, and upon the proportions in which they are mixed. From the fact that following the law of mixtures is regarded as indicating that a system is free from any chemical interaction between its constituents, and that the molecular states of its constituents are unaltered as a result of the mixing, it is natural to assume that a system which does not follow this law is one in which either a chemical reaction has taken place, or in which the constituents have undergone a molecular change, of the nature of a breaking down of a previous polymerization of one or both of the individuals, for example.

Many investigators, ignoring the second possible cause of change,