In addition to quartz and the compounds $K_2Si_2O_5$ and $KHSi_2O_5$, the following new compounds occur as solid phases: *Potassium disilicate monohydrate*, $K_2Si_2O_5.H_2O$; *potassium metasilicate*, K_2SiO_3; *potassium metasilicate hemihydrate*, $K_2SiO_3.0.5H_2O$; and *potassium metasilicate monohydrate*, $K_2SiO_3.H_2O$.

The data obtained are presented by means of tables, and graphically by means of curves and solid models. Curves are given showing the solubility relations in the binary systems H_2O–K_2SiO_3 and H_2O–$K_2Si_2O_5$ (Fig. 7), the isothermal polybaric saturation curves (Fig. 4), the variation of pressure with SiO_2/K_2O ratio along the isotherms (Fig. 5), the isobaric polythermal saturation curves (Fig. 13), the P-T curves of the various monovariant systems (Fig. 9), and the boundary curves of the different solid phases in the ternary system (Fig. 8). In addition, photographs are given of the solid models showing the variation in the composition of the saturated solutions with temperature, under the corresponding 3-phase pressure (Fig. 11), and the variation of the composition of the saturated solutions with pressure, at the corresponding 3-phase temperatures (Fig. 12).

Brief mention is made of some of the theoretical relations governing the equilibrium in binary and ternary systems containing a volatile component, and a short discussion of the proper application of the term "solubility" is given.

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ON THE DIETERICI EQUATION OF STATE.

BY F. H. MACDOUGALL.

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In a recent article[1] I discussed at some length the Dieterici equation of state, $p = \frac{RT}{v-b} e^{-a/vRT}$ and applied it to a number of substances, among which may be mentioned isopentane, carbon dioxide and hydrogen. Various methods were developed of calculating the values of a and b (two of the "constants" of the equation) below, at, and above the critical temperature; and formulas were deduced connecting the pressure of saturated vapor and the latent heat of vaporization with the densities of liquid and saturated vapor.

In the present paper I desire to bring forward an additional method of calculating a and further to urge strongly the advantages, both theoretical and practical, which the Dieterici equation has over any equation of the van der Waals type.

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[1] THIS JOURNAL, 38, 528–555 (1916).

General Considerations.

It is a simple matter to modify the equation for an ideal gas so as to indicate the effect produced by the intermolecular forces and by the volume of the molecules. One can write $(p + K)(v - b) = RT$, where K is the "cohesive" pressure and b is the volume correction, and this equation is doubtless in a general way perfectly correct, but the exact form of the functions which express the dependence of K and b on the temperature and volume may still be unknown. As is well known, van der Waals assumed that b is an absolute constant and that K is of the form a/v^2, where a is assumed to be a constant. The resulting equation known by the name of van der Waals gives good results only for small pressures and entirely false results when applied to the critical state. For instance, the value of $\frac{RT_c}{p_c v_c}$ deduced from van der Waals' equation is 8/3, while the values experimentally found[1] in a large number of cases are around 3.7.

It may well be that the chief cause of the failure of the van der Waals equation, to be much more than qualitative in its application, is to be sought in the form of the function assumed for the "cohesive" or "internal" pressure. This view will be confirmed if we consider carefully some of the results obtained by Boltzmann in his studies of the kinetic theory of gases.

Let us consider, first of all, a mass of gas, made up of infinitesimal molecules which, however, attract each other, the attraction being appreciable only over extremely small distances. In the interior of the gas, the forces of attraction will, on the average, balance, but in a thin layer at the boundary there will be a resultant force directed towards the interior. Boltzmann has shown that the existence of such a field of force will not affect the distribution of velocities or of kinetic energies, but it will affect the spatial distribution of the molecules, *i. e.*, the density of the gas.[2] A certain amount of work will be done by us if we drag a molecule from the interior of the gas to the wall of the containing vessel. If A represents the work done against the field of force in dragging N molecules to the boundary, where N is the number of molecules in one gram-molecular weight, then the pressure exerted on the wall is given by the following expression:[2]

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

If we introduce now a correction for the volume of the molecules, we obtain $p = \frac{RT}{v - b} e^{-A/RT}$. For low densities[2] at least we may set A proportional to the density or $A = a/v$, finally obtaining in this way the

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[1] Young's "Stoichiometry," 228 (1908).

[2] Jeans, "Dynamical Theory of Gases," 126 (1916).

Dieterici equation of state, $p = \frac{\mathrm{RT}}{v-b}e^{-a/v\mathrm{RT}}$. This then is the correct *form* of the equation of state; the "correction" on account of the "cohesive" pressure is given by an exponential function. As is well known, for low pressures and, therefore, large volumes, the Dieterici equation degenerates into the van der Waals form; for when V is large compared with b and $\frac{a}{\mathrm{RT}}$, we have $p = \frac{\mathrm{RT}}{v-b}\left(1 - \frac{a}{v\mathrm{RT}}\right)$ and this is approximately the same as $p = \frac{\mathrm{RT}}{v-b} - \frac{a}{v^2}$, the van der Waals formula. The van der Waals equation cannot, therefore, be expected to hold at the critical point where v is of the same order of magnitude as b and as a matter of fact, it does not. The Dieterici equation in view of the considerations advanced above, might well be expected to have a much wider range of validity. And if, as I think I have shown to be the case, the Dieterici form is the correct one, the Dieterici equation should hold over any range if we determine a and b as volume and temperature functions. The kinetic theory leads to the conclusion that a and b may be both volume and temperature functions and it will be worth while to determine the nature of these functions, using the Dieterici equation as a basis. To attempt to express the a and b of van der Waals' equation as functions of volume or temperature seems to me clearly a waste of time and effort, since its deduction from the Dieterici equation indicates that its validity is restricted to cases where the volume of a gas is very large compared with the volume of the molecules.

Variations of *a* and *b* with the Volume and Temperature.

Assuming a and b in Dieterici's equation to be independent of the volume, we obtain the following relations at the critical point:

$$v_c = 2b_c;\ \mathrm{T}_c = \frac{a_c}{4\mathrm{R}b_c};\ p_c = \frac{a_c}{4e^2b_c^2};\ \frac{\mathrm{RT}_c}{p_cv_c} = \frac{e^2}{2} = 3.695$$

These results are independent of whether a and b are functions of the temperature or not.

Now the value of the ratio $\frac{\mathrm{RT}_c}{p_cv_c}$ thus obtained is very close to the one that actually holds for a large number of substances. We therefore infer that in the case of these substances, a and b are actually independent of the volume even when the volume is as small as corresponds to the critical point. More accurately stated, the inference is that at the critical point, $\left(\frac{da}{dv}\right)_\mathrm{T}$ and $\left(\frac{db}{dv}\right)_\mathrm{T}$ are very small, if not zero, or they happen to be of such a magnitude that they actually neutralize each other's effect. There is the possibility that at the critical point, a and b may have minimum or maximum values in which case $\left(\frac{da}{dv}\right)_T$ and $\left(\frac{db}{dv}\right)_T$ would be equal to zero. As regards the variation of a and b with the temperature, the general conclusion reached in my previous paper was that b increases as we approach the critical temperature, reaches a maximum and then decreases; a decreases always with rise in temperature.

Work of Bakker on Surface Films.

Any theoretical isotherm on a $p - v$ diagram as given by the equation of state is cut by a line of constant pressure in three points below the critical temperature. If this pressure is that at which the liquid and vapor are in equilibrium, two of the points, corresponding to the volumes v_1 and v_2, represent the volumes of liquid and of saturated vapor, respectively, while the third volume, v_3, is not realizable by the substance in a homogeneous state. In my previous article on this subject, reasons were given for the assumption that this volume v_3 is equal to $2b$ (not $2b_c$). An equivalent assumption is that the density of the substance corresponding to v_3 on the theoretical isotherm is the arithmetic mean of the densities of liquid and saturated vapor. What seems to me to be a confirmation of this view is found in the conclusions reached by Bakker[1] in regard to the average density of the surface layer between liquid and vapor. I became acquainted with the work of Bakker after my paper was published. According to Bakker, the average density of the surface layer is the mean of the densities of liquid and vapor. This result depends, it should be noted, on certain assumptions which may not be strictly correct. Now Bakker points out the analogy between the surface layer and the homogeneous substance in a state corresponding to a point on the theoretical isothermal close to the point we have indicated by v_3. In other words, when liquid and vapor are in equilibrium, we have three specific volumes, namely, those of homogeneous liquid, homogeneous vapor and of transition layer corresponding to the three values on the theoretical isothermal, which we have denoted by v_1, v_2 and v_3, If, then, the average density of the surface layer is equal to that of the homogeneous substance in the unrealizable state corresponding to v_3, Bakker's conclusion is equivalent to the equation: $\frac{2}{v_3} = \frac{1}{v_1} + \frac{1}{v_2}$, and this, on the basis of the Dieterici equation, as shown in my previous paper means that v_3 is equal to $2b$.

Reference List of Equations.

It will be convenient to set down for reference a number of mathematical results taken from my previous paper on this subject.[2]

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[1] *Z. phys. Chem.*, 73, 664 (1910).

[2] THIS JOURNAL, 38, 529, 531, 536, 539, 540 (1916).

The Dieterici equation, $p = \frac{\mathrm{RT}}{v-b} e^{-a/v\mathrm{RT}}$ .... (1)

Relations at critical point, $$\left.\begin{array}{l} v_c = 2b_c;\ \mathrm{T}_c = \frac{a_c}{4\mathrm{R}b_c};\ p_c = \frac{a_c}{4e^2b_c^2} \\ \frac{\mathrm{RT}_c}{p_cv_c} = \frac{e^2}{2} = 3.695 \end{array}\right\} \quad \text{.... (2)}$$

Co-existing phases, $$\left.\begin{array}{l} \frac{1}{v_1} + \frac{1}{v_2} = \frac{2}{v_3} = \frac{1}{b} \\ \frac{v_2 - b}{v_1 - b} = \left(\frac{v_2}{v_1}\right)^2 \end{array}\right\} \quad \text{........................ (3)}$$

Pressure of saturated vapor, $p_s = \frac{\mathrm{RT}}{b} e^{-a/2b\mathrm{RT}}$ .... (4)

Total heat of vaporization,

$$\mathrm{L} = \mathrm{RT} \log_e \frac{v_2 - b}{v_1 - b} = 2\mathrm{RT} \log_e \frac{v_2}{v_1} = \frac{a}{v_1} - \frac{a}{v_2} \quad \text{.......... (5)}$$

$$a_1 = \frac{v_1v_2}{v_2 - v_1} \mathrm{RT} \log_e \frac{v_2 - b}{v_1 - b} = \frac{2v_1v_2}{v_2 - v_1} \mathrm{RT} \log_e \frac{v_2}{v_1} \quad \text{..... (6)}$$

$$a_2 = 2b\mathrm{RT} \log_e \frac{\mathrm{RT}}{pb} \quad \text{.......................... (7)}$$

$$a_3 = v_1\mathrm{RT} \log_e \frac{\mathrm{RT}}{p(v_1 - b)} \quad \text{...................... (8)}$$

$$a_4 = v_2\mathrm{RT} \log_e \frac{\mathrm{RT}}{p(v_2 - b)} \quad \text{...................... (9)}$$

Heat of Vaporization.

It is usually stated that $\frac{a}{v_1} - \frac{a}{v_2}$ measures the internal latent heat of vaporization and this is correct if one uses the original van der Waals equation. For, according to this equation, the total work done in evaporating at constant temperature would be

$$\int_{v_1}^{v_2} \frac{\mathrm{RT}}{v - b} dv = \int_{v_1}^{v_2} \left(p + \frac{a}{v_2}\right) dv = p(v_2 - v_1) + \frac{a}{v_1} - \frac{a}{v_2} = \mathrm{L}.$$

Hence, $\frac{a}{v_1} - \frac{a}{v_2}$ is the internal heat of vaporization. But if we assume the Dieterici equation, we obtain the following results.

Since

$$p_s = \frac{\mathrm{RT}}{v_1 - b} e^{-a/v_1\mathrm{RT}} = \frac{\mathrm{RT}}{v_2 - b} e^{-a/v_2\mathrm{RT}},\ \frac{a}{v_1} - \frac{a}{v_2} = \mathrm{RT} \log_e \frac{v_2 - b}{v_1 - b} = \int_{v_1}^{v_2} \frac{\mathrm{RT}}{v - b} dv = \mathrm{L},$$

and hence, $\frac{a}{v_1} - \frac{a}{v_2}$ measures the total latent heat of vaporization. In applying the van der Waals equation in the above calculations, a is assumed to be independent of the volume and in applying the Dieteric equation, the same assumption is made in the case of b.

As a matter of fact, the values of L, obtained from the equation[1]

$$L = a/v_1 - a/v_2,$$

differ somewhat from those calculated by means of the thermodynamic formula

$$L = (v_2 - v_1)T\frac{dp_s}{dT}.$$

The inference to be drawn from this is that b does vary slightly with the volume when the latter is that of the substance in the liquid state. A study of these deviations might lead to a better knowledge of b as a function of the volume.

New Method of Calculating *a*.

Assuming, however, that the variation of b with changes in volume is negligible, we can deduce an additional method of calculating a and it may be of interest to compare these new values which we shall represent by a_5 with those obtained in my previous paper and represented by a_1, a_2, a_3 and a_4 (see equations numbered 6, 7, 8 and 9 of the present article).

Since $L = (v_2 - v_1)T\frac{dp_s}{dT}$ from thermodynamics, and since we have $L = a\left(\frac{1}{v_1} - \frac{1}{v_2}\right)$, we easily deduce $a_5 = v_1v_2T\frac{dp_s}{dT}$.

I have carried out the calculations for isopentane, using the data as given in my previous paper. The numerical results refer to 1 g. of isopentane, pressures are given in mm. of mercury and volumes in cc. The values of $\frac{dp_s}{dT}$ were obtained by taking three corresponding values of p_s and T, and using the interpolation formula, $\log p = a \log T - \frac{b}{T} + c$. From this, the value of $\frac{dp_s}{dT}$ was calculated for the intermediate pressure and temperature. By repeating this process on different sets of corresponding values of p and T, the values of $\frac{dp_s}{dT}$ from 0° up to the critical temperature were obtained. The values of a_5 found from the equation $a_5 = v_1v_2T\frac{dp_s}{dT}$ are given in the seventh column of Table I and agree very well with those of a_1, a_2, a_3 and a_4. At the critical temperature, the value of a_5 is much lower than that of any of the others. The explanation of this divergence may be due to the fact, pointed out by Mills,[2] that inter-

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[1] THIS JOURNAL, **38**, 542, 544 (1916).

[2] *J. Phys. Chem.*, **9**, 402 (1905).

polation formulas give results for $\frac{dp_s}{dT}$ at the critical point which are considerably too low. In fact, he finds that at the critical point $\frac{dp_s}{dT} = \frac{2R}{v_c}$. This result is in perfect agreement with the Dieterici equation, for if we substitute the value $\frac{2R}{v_c}$ for $\frac{dp_s}{dT}$ in our formula $a = v_1v_2T\frac{dp_s}{dT}$ we obtain for the critical point, $a_c = 2v_cRT_c$, a relation easily deducible from the Dieterici equation.

TABLE I.—ISOPENTANE UNIT MASS = 1G.

$t°$.	dps/dT.	$a_1 \times 10^{-6}$.	$a_2 \times 10^{-6}$.	$a_3 \times 10^{-6}$.	$a_4 \times 10^{-6}$.	$a_5 \times 10^{-6}$.
0	11.17	4.713	4.704	4.708	2.223	4.292
20	21.02	4.583	4.582	4.582	4.450	4.217
40	35.65	4.461	4.466	4.467	4.434	4.175
60	55.67	4.354	4.353	4.354	4.310	4.115
80	81.90	4.248	4.236	4.242	3.987	4.071
100	114.5	4.150	4.120	4.135	3.747	4.006
110	133.9	4.093	4.059	4.075	3.727	3.970
120	155.4	4.036	3.991	4.012	3.650	3.954
130	178.7	3.977	3.922	3.948	3.604	3.894
140	204.2	3.916	3.860	3.881	3.564	3.832
150	232.9	3.850	3.771	3.806	3.512	3.801
160	263.8	3.778	3.690	3.726	3.480	3.725
170	298.4	3.687	3.599	3.633	3.459	3.624
180	335.7	3.579	3.503	3.528	3.436	3.459
187.8 (Critical temperature)	367.7	3.404	3.423	3.423	3.423	3.087

Summary.

In the present paper, it is shown that the Dieterici equation of state is of the correct form and that it degenerates into the equation of van der Waals for a gas under low pressure. The equation of Dieterici might therefore be expected to have a much wider range of validity than one of the van der Waals type.

A new method of calculating a is described and the values so obtained are compared with those calculated by other methods.

MINNEAPOLIS, MINN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN.]

DIFFERENTIAL IODIMETRY IV.—THE ANALYSIS OF PYROLUSITE AND OTHER OXIDIZED MANGANESE ORES.

BY O. L. BARNEBEY AND GEO. M. BISHOP.

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In a previous paper[1] a method has been described for the determination of the available oxygen in precipitated higher oxides of manganese

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[1] THIS JOURNAL, 39, 607 (1917).