"THE JOULE-THOMSON INVERSION CURVES OF RECENT EQUATIONS OF STATE."

By J. Corner.

1. Introduction.

The Joule-Thomson inversion curve has often been used to test equations of state of gases, at temperatures and pressures above the critical values.   The test is rather severe, because the derivatives of the pressure are involved.   It is the purpose of this note to give inversion curves derived from two recent equations of state, one due to Lennard-Jones and Devonshire,[1] and the other to de Boer and Michels.[2]   The first was developed for gases at high pressures and assumes the arrangement of atoms to be similar to those of a solid.   It may be expected to fail below a certain density.   The other equation is an approximation valid at low densities, so that it may be expected to fail above some limiting density.

[1] Lennard-Jones and Devonshire, *Proc. Roy. Soc., A,* 1937, **163,** 53.
[2] de Boer and Michels, *Physica,* 1939, **6,** 97.

Let P, V, T be the pressure, volume, and temperature of a mole of gas ; let R be the gas-constant per mole, and N the number of molecules in a mole. Let H be the total heat of the gas, and C_P its specific heat at constant pressure. The Joule-Thomson coefficient is

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{T\left(\frac{\partial V}{\partial T}\right)_P - V}{C_P},$$

and this is zero when $\qquad T\left(\frac{\partial V}{\partial T}\right)_P - V = 0,$

which is more conveniently written as

$$T\left(\frac{\partial P}{\partial T}\right)_V + V\left(\frac{\partial P}{\partial V}\right)_T = 0 \qquad . \qquad . \quad (1)$$

or as $\qquad V\left(\frac{\partial}{\partial V}\left(\frac{PV}{RT}\right)\right)_T + T\left(\frac{\partial}{\partial T}\left(\frac{PV}{RT}\right)\right)_V = 0. \qquad . \qquad . \quad (2)$

It is usual to plot the curve with reduced temperature and reduced pressure as variables. In Fig. 1 we show some recent data by small circles ; because of the small scale of the figure we have not attempted to show the origin of each point or the gas used. The data were taken from papers on nitrogen,[3, 5, 4] argon,[6] carbon dioxide,[7] and air,[8] which in the critical region behaves like a pure substance. We have omitted results for helium because classical statistics is assumed in the theories to be discussed.

From van der Waals' equation, the inversion curve is

$$(12\theta + \pi - 81)^2 + 216 \, (4\theta + \pi - 27) = 0 \qquad . \qquad . \quad (3)$$

where θ and π are the reduced temperature and pressure respectively. From Dieterici's equation, the curve is

$$\pi\theta^{s-1} = \{4(s + 1) - \theta^s\} e^{\frac{2s + 3}{s + 1} - 4\theta^{-s}} \qquad . \qquad . \qquad . \quad (4)$$

The curve from (3) as well as that from (4) with $s = 1$ and $1\cdot5$, are plotted in Fig. 1. The Dieterici curve with $s = 1\cdot5$ gives agreement which is fair, but not so good as claimed on the basis of early observations. This is as good an agreement as can be obtained from a Dieterici curve.

It should be pointed out that the part of the inversion curve lying near the origin corresponds to high densities of the fluid. As the density decreases the representative point travels along until it reaches the upper inversion temperature at zero pressure and density. This is useful in interpreting the results of a comparison with experimental data.

2. The Equation of Lennard-Jones and Devonshire.

We assume an intermolecular potential

$$\phi = Ar^{-12} - Br^{-6}$$

[3] Benedict, *J. Amer. Chem. Soc.*, 1937, **59**, 2224, 2233.
[4] Roebuck and Osterberg, *Physic. Rev.*, 1935, **48**, 450.
[5] Deming and Deming, *idid.*, 448.
[6] Roebuck and Osterberg, *ibid.*, 1934, **46**, 785.
[7] Clark and Katz, *Can. J. Research, A*, 1938, **16**, 41.
[8] Roebuck, *Proc. Amer. Acad. Sci.*, 1930, **64**, 287.

where A, B are constants, and r is the distance between the molecular centres. We define

$$\phi_0 = \frac{B^2}{4A}; \quad V_0{}^* = \left(\frac{A}{B}\right)^{\frac{1}{4}} = \sigma^3 = \frac{r_0{}^3}{\sqrt{2}}; \quad V_0 = NV_0{}^*$$

Here ϕ_0 is the greatest depth of the potential trough, attained at $r = r_0$, and σ is the finite distance at which the potential is zero. Lennard-
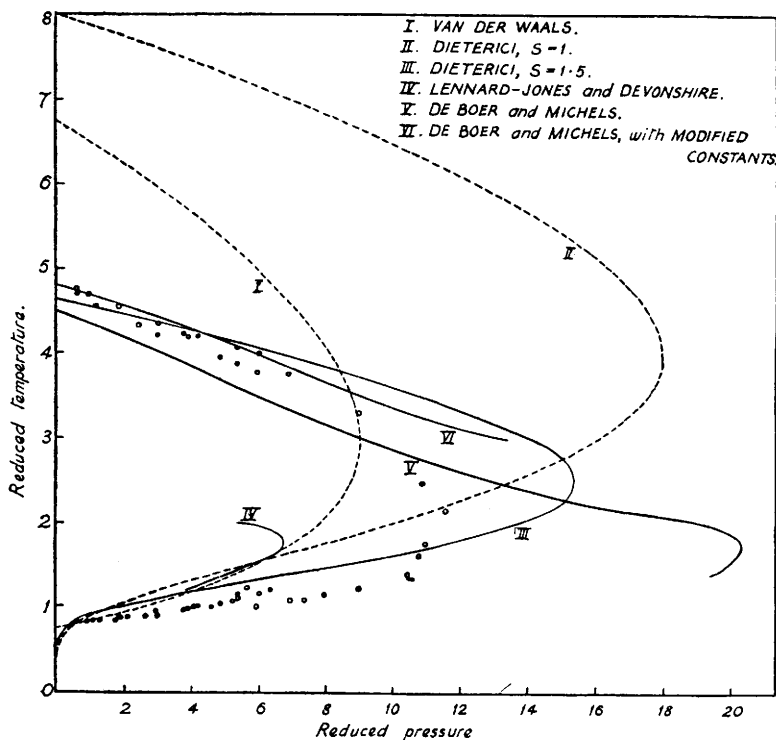

FIG. 1.—Joule-Thomson inversion curves. Circles denote observed points.

Jones and Devonshire have shown that, on certain assumptions which we need not discuss in detail,

$$\frac{PV}{RT} = 1 - \frac{12\phi_0}{kT}\left\{2\cdot4\left(\frac{V_0}{V}\right)^2 - 2\left(\frac{V_0}{V}\right)^4\right\} - \frac{48\phi_0}{kT}\left\{\left(\frac{V_0}{V}\right)^2\frac{g_m}{g} - \left(\frac{V_0}{V}\right)\frac{g_l}{g}\right\},$$

where $\quad g = \int_0^{\frac{1}{2}} 2x^2 \exp.\left[\frac{12\phi_0}{kT}\left\{2\left(\frac{V_0}{V}\right)m(x^2) - \left(\frac{V_0}{V}\right)^4 l(x^2)\right\}\right]dx,$

and $\quad g_l = \int_0^{\frac{1}{2}} 2x^2 l(x^2).\exp.\left[\frac{12\phi_0}{kT}\left\{2\left(\frac{V_0}{V}\right)^2 m(x^2) - \left(\frac{V_0}{V}\right)^4 l(x^2)\right\}\right]dx,$

with corresponding definitions of g_m, g_{lm}, etc., and with

$$l(x^2) = \frac{1 + 12x^2 + 25\cdot2x^4 + 12x^6 + x^8}{(1 - x^2)^{10}} - 1,$$

$$m(x^2) = \frac{1 + x^2}{(1 - x^2)^4} - 1.$$

This equation of state gives a critical point at

$$kT_c = 1\cdot33\ \phi_0\ ; \quad V = 1\cdot93\ V_0\ ; \quad \left(\frac{PV}{RT}\right)_c = 0\cdot712.$$

These values differ slightly from those given by Lennard-Jones and Devonshire ; they were found by evaluating derivatives of the pressure at their approximate critical point. The critical temperature appears to be a few per cent. too high ; the volume is 50 per cent. too small, while $\left(\dfrac{PV}{RT}\right)_c$ should be about $0\cdot3$.

Carrying out the differentiations in (2), the equation of the inversion curve is found to be

$$7\cdot2 - 10\left(\frac{V_0}{V}\right)^2 + 12\frac{g_m}{g} - 20\left(\frac{V_0}{V}\right)^2\frac{g_l}{g}$$
$$+ \frac{48\phi_0}{kT}\left[5\left(\frac{V_0}{V}\right)^6\left(\frac{gg_{ll} - g_l^2}{g^2}\right) - 11\left(\frac{V_0}{V}\right)^4\left(\frac{gg_{lm} - g_lg_m}{g^2}\right)\right.$$
$$\left. + 6\left(\frac{V_0}{V}\right)^2\left(\frac{gg_{mm} - g_m^2}{g^2}\right)\right] = 0.$$

For given V/V_0, this equation has been solved by trial, giving the corresponding ϕ_0/kT. V/V_0 ranged from 2 to $1\cdot24$. The theory is not applicable at larger volumes because the temperature is then too high to permit the assumption, essential to the theory, that the integrand in g is negligible at $x = 0\cdot5$. At volumes less than $1\cdot24$, V_0 the inversion points lie in the two-phase region. Fortunately, the most obvious feature of the inversion curve, the upper limit to the pressure, lies within this density range. The limiting pressure found from the theory proves to be about half the experimental value. For higher densities, that is, for volumes up to about $1\cdot6\ V_0$, the agreement is much the same as that of van der Waals' equation ; at lower densities there is no agreement at all. This is the region in which a breakdown of the theory was expected : there is a very large probability that the molecule is near the " wall " of its " cell," so that the approximations of the theory are here very rough.

We may add that the Joule-Thomson coefficient has been calculated at the critical point, and found to be about a third of the correct value.

3. The Equation of de Boer and Michels.

Mayer and Harrison,[9] Born and Fuchs,[10] and Kahn and Uhlenbeck,[11] have given an expansion of the pressure of a gas as a power series in V^{-1}. The first term leads to the equation of a perfect gas, and the second term is the second virial coefficient. de Boer and Michels have found the third term by numerical integration, using the intermolecular potential $\phi = Ar^{-12} - Br^{-6}$. Higher terms would require much more laborious computation, so that it is fortunate that, as we will show, the first three terms give a good approximation to the critical point. de Boer and Michels expressed their results as the neighbour distribution function, which had a resemblance to the observed distribution functions

[9] Mayer and Harrison, *J. Chem. Physics*, 1938, **6**, 87.
[10] Born and Fuchs, *Proc. Roy. Soc.*, A, 1938, **166**, 391.
[11] Kahn and Uhlenbeck, *Physica*, 1938, **5**, 399.

of liquid alkali metals. Unfortunately, there are no observations on dense gases, with which alone a detailed comparison would be legitimate.

We use the same notation as in section 2, with only slight changes from that of de Boer and Michels. Let

$$g^{(2)*}(R) = \frac{3}{R} \int\int r_1 r_2 \left\{ e^{-\frac{4\phi_0}{kT}(r_1^{-12} - r_1^{-6})} - 1 \right\} \left\{ e^{-\frac{4\phi_0}{kT}(r_2^{-12} - r_2^{-6})} - 1 \right\} dr_1 dr_2,$$

with the limits of integration

$$0 \leqslant r_1 \leqslant \infty,$$
$$| r_1 - R | \leqslant r_2 \leqslant r_1 + R.$$

Let $$g(R\sigma) = \exp. \left[-\frac{4\phi_0}{kT}(R^{-12} - R^{-6}) + \frac{2\pi N\sigma^3}{3V} g^{(2)*}(R) \right]$$
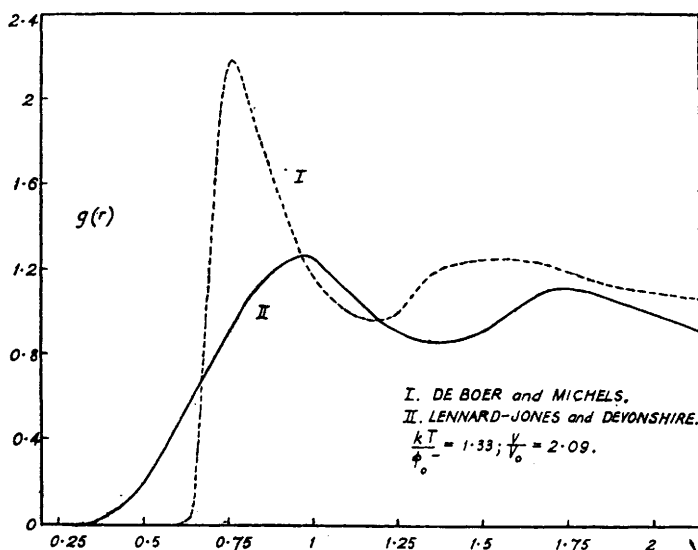
and $r = R\sigma$.

Fig. 2.—Neighbour distribution functions near the critical point. The unit of distance is $2^{\frac{1}{6}}\left(\dfrac{V}{N}\right)^{\frac{1}{3}}$ which is, on the theory of Lennard-Jones and Devonshire, the distance between equilibrium positions of nearest neighbours.

de Boer and Michels have proved that the probability that there will be a molecule at a distance between r and $r + dr$ from any given molecule is $4\pi r^2 g(r)dr$, correct to the term in V^{-1} only. The pressure is given by

$$PV = NkT - \frac{2\pi N^2}{3V} \int_0^\infty r^3 \frac{d\phi}{dr} g(r) dr. \qquad . \qquad . \qquad . \quad (5)$$

Introducing the non-dimensional variable R, and using the relation $N\sigma^3 = V_0$, this equation becomes

$$\frac{PV}{NkT} = 1 - \frac{16\pi V_0}{V} \frac{\phi_0}{kT} \int_0^\infty (R^{-4} - 2R^{-10}) \exp. \left[\frac{4\phi_0}{kT}(R^{-6} - R^{-12}) \right.$$
$$\left. + \frac{2\pi V_0}{3V} g^{(2)*}(R) \right] dR \quad (6)$$

This is correct as far as the V^{-2} term in the expansion of the right-hand side as a power-series in V^{-1}.

The function $g^{(2)*}\left(R, \dfrac{\phi_0}{kT}\right)$ has been tabulated by de Boer and Michels. An example of the resulting distribution function $g(r)$ is given in Fig. 2, together with the corresponding result from the theory of Lennard-Jones and Devonshire.† The temperature and density are near those of the critical point of the latter theory. The marked difference between the distribution functions leads one to expect large differences of pressure. To examine this, the table of $g^{(2)*}(R)$ was subtabulated and extrapolated for a short distance, and the integral in (6) was calculated numerically. Some of the resulting isotherms are plotted in Fig. 3, together with the critical isotherm of the theory of Lennard-Jones and Devonshire, and the isotherm of a perfect gas.
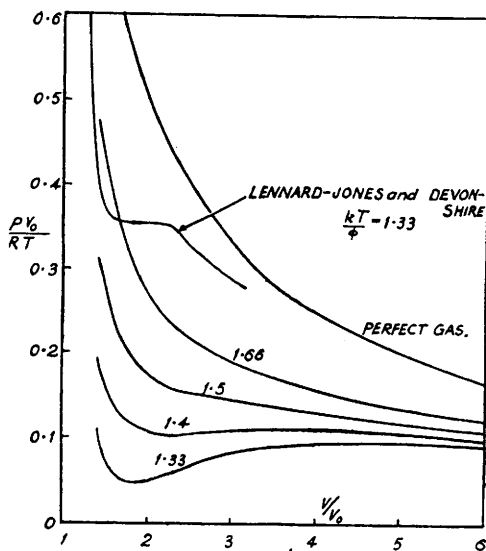

FIG. 3.—Isotherms from the equation of de Boer and Michels. Numbers on the curves are the corresponding values of kT/ϕ_0.

By interpolation, the critical temperature is found to be

$$kT_c = 1\cdot43\ \phi_0 \quad . \qquad . \qquad . \qquad . \qquad . \quad (7)$$

with
$$P_cV_0 = 0\cdot119\ RT_c. \qquad . \qquad . \qquad . \qquad . \quad (8)$$

An accurate value of the critical volume cannot be found from the isotherm. However, the densities of liquid and saturated vapour can be calculated for the temperatures $kT/\phi_0 = 1\cdot4$ and $1\cdot333$; applying the law of the rectilinear diameter, we find

$$V_c = 2\cdot9\ V_0. \qquad . \qquad . \qquad . \qquad . \quad (9)$$

This is consistent with the critical isotherm. It is true that the slope of the "rectilinear diameter" with temperature is larger than the experimental values. From (8) and (9),

$$\left(\frac{PV}{RT}\right)_c = 0\cdot35.$$

Table I shows that these critical constants are in good agreement with experiment. H_2 and He, whose force-constants are known, have

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† The calculation of the latter distribution will be described in a later paper. I wish to thank Dr. A. F. Devonshire and Dr. M. V. Wilkes for their help with the computation of this curve.

been omitted from the table because classical statistics cannot be applied to the translational motion of their molecules at the critical temperature. The critical temperature is about 7 per cent. higher than that from the theory of Lennard-Jones and Devonshire; the change is in the wrong direction. The critical volume and pressure are very different from, and better than, those of the other theory.

TABLE I.

	Ne.	N$_2$.	Ar.
T_c calc. (°K.)	51	137	172
obs.	44	126	150
V_c calc. (c.c./mole)	36	90	70
obs.	44	90	75
$(PV/RT)_c$ calc.	0·35	0·35	0·35
obs.	0·32	0·29	0·29

Applying (2) to the equation of state (5), the inversion curve is determined by

$$\int_0^\infty r^3 \frac{d\phi}{dr}\left[2 - V\frac{\partial}{\partial V} - T\frac{\partial}{\partial T}\right]g(r)dr = 0,$$

that is, by

$$\int_0^\infty r^3 \frac{d\phi}{dr}\left[2 - \frac{\phi}{kT} + \frac{2\pi N\sigma^3}{3V}\left\{g^{(2)*} - T\frac{\partial}{\partial T}g^{(2)*}\right\}\right]$$
$$\exp.\left[-\frac{\phi}{kT} + \frac{2\pi N\sigma^3}{3V}g^{(2)*}\right]dr = 0. \quad (10)$$

The function $\frac{\partial g^{(2)*}}{\partial T}$ can be found by numerical integration but this is too laborious to be considered in a preliminary survey such as this. Instead, the derivative was found from a central difference interpolation formula.   For each R, $g^{(2)*}$ was known for eight unequally spaced values of kT/ϕ_0, so that it was necessary to use divided differences.   Moreover, $g^{(2)*}$ was known to three significant figures only, so that there may be relatively large errors in the derivative.   Fortunately, this occurs only in a sum which is about ten times the value of this doubtful term.

Solution of (10) by trial gives V/V_0 for any chosen value of kT/ϕ_0 The temperature T_I at which the upper part of the inversion curve cuts the temperature axis has been found by Hirschfelder, Ewell, and Roebuck [12] to be

$$kT_I = 6·43\,\phi_0$$

which from (7) is equivalent to

$$T_I = 4·50\,T_c.$$

A lower limit to kT/ϕ_0 is set by the physical meaning of V_0.   The assumed potential leads to a face-centred cubic lattice (Lennard-Jones and Ingham [13]), of molar volume 0·9 V_0, at 0° K.   This is increased a few per cent. by the zero-point energy (Corner [14]).   As we cannot expect

[12] Hirschfelder, Ewell, and Roebuck, *J. Chem. Physics*, 1938, **6**, 205.
[13] Lennard-Jones and Ingham, *Proc. Roy. Soc., A*, 1925, **107**, 636.
[14] Corner, *Trans. Faraday Soc.*, 1939, **35**, 711.

the theory to give good results at densities near that of the solid, the inversion curve need not be followed to temperatures lower than

$$kT = 2\phi_0$$

for which the corresponding volume is already less than V_0.

The result of these calculations is shown in Fig. 1. At low densities the inversion curve is almost straight, and lies a little too low; it continues to pressures which are much too high. The turning point is at a volume of about V_0 and is thus in the region where the theory was expected to fail. Where the curve crosses the experimental points the volume is roughly the critical volume.

The neglected terms in the virial expansion will not affect the calculation of the low-density part of the inversion curve. They will, however, affect the calculated critical constants, and so the reduced co-ordinates of the low-density inversion curve. It seems certain that with a sufficient number of terms and sufficient computation the critical constants would converge to the experimental values. We may therefore use the latter, in terms of ϕ_0 and V_0, though indeed, owing to the small number of reliable force-constants, the numerical factors are still a little uncertain. Assuming $kT_c/\phi_0 = 1\cdot33$ and $P_c = 0\cdot133 \ \phi_0/V_0{}^*$ the inversion curve is shifted upwards (Fig. 1), where it is in excellent agreement with the observed points, at molar volumes down to $5V_0$. At lower volumes the equation of de Boer and Michels may still be useful for calculating less sensitive properties than Joule-Thomson coefficients. It is sufficiently successful to warrant a more accurate computation of the essential function $g^{(2)*}$.

Summary.

The Joule-Thomson inversion curves have been worked out for the equation of state recently given by Lennard-Jones and Devonshire and for that of de Boer and Michels. The former gives results in reasonable agreement with experiment in the region in which it is valid, *viz.*, at high densities, but not at low. The other equation gives fair agreement where it also is most valid, *viz.*, at low densities. Calculations of critical data show that the Lennard-Jones equation gives better critical temperatures, but not so good values for critical volume and pressure as the equation of de Boer and Michels.

The University Chemical Laboratory and Peterhouse,
Cambridge.