

Two-Parameter Equations of State

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Eight new two-parameter equations of state, all of which can be considered as modifications of the van der Waals equation, are proposed and their thermodynamic consequences at subcritical temperatures are investigated using Maxwells' construction. The results are compared with empirical data. The basic idea is to write the equation of state as $[P][V]=RT$, in which the term $[P]$ is taken as $P+f(V,T)$ and the term $[V]$ is taken as the analogous term in some equation of state for hard spheres. The conclusion is that, in the region from the triple point to slightly below the critical point ($0.56 < T/T_{\text{crit}} < 0.95$), an equation of state with $f(V,T)=a/V^2$, and a more elaborate form for $[V]$, such as that obtained from the first five terms in the virial-expansion for the hard sphere gas, represents no significant improvement over van der Waals equation of state. In contrast hereto, modifying $f(V,T)$ to read $aT^{-1/2}(V+3b/2)^{-2}$ or $a(1+a/5bRT)(V+3b/2)^{-2}$ and retaining the van der Waals form of $[V]$ (i.e. $V-b$) produces an equation of state which represents a vast improvement over that of van der Waals, in particular with respect to reproducing the empirically known values for the critical compressibility factor, the molar volume of the gas, and the entropy of evaporation (Troutons' rule).

Although empirical equations of state have been used extensively by many authors, since van der Waals proposed his famous equation, such equations have only recently come into prominence from a theoretical point of view. The recent interest in equations of state of the van der Waals type is due to the papers by Kac, Uhlenbeck and Hemmer,¹ and by Lebowitz and Penrose² which show that, under certain conditions on the intermolecular potential, one might expect a van der Waals-like equation with the Maxwell construction to be an exact equation of state.

It is clear that, from a purely empirical or technical point of view, an equation of state with a larger number of parameters could be more useful

since one can, for a specific substance, make the agreement between the predicted and the experimental values arbitrarily good by simply increasing the number of parameters. The literature on such empirical equations is abundant and we refer to the book by Partington³ for an extensive review of the early work and to the book by Hirschfelder, Curtiss and Bird⁴ for a review of the equations of current interest. From a theoretical point of view, a two-parameter equation is more interesting than a many-parameter equation primarily because it leads to a principle of corresponding states, which is known to hold experimentally for simple substances. Secondly, two parameters is the smallest number possible in an equation which exhibits the characteristics of a phase transition. Thirdly, in view of what was said above, for certain (hypothetical) systems there just may exist an exact two-parameter equation of state.

An equation of state which is used to study phase-transition and two-phase regions should be judged by its ability to reproduce the empirical relationships which hold for the noble gases and some other substances with reasonably low molecular weights. These empirical relationships are

$$z_c = \frac{P_c V_c}{RT_c} = 0.29 \quad (1)$$

$$p_{\text{evap}} = (5.29 - 5.31/t) \quad (2)$$

$$v_{\text{liq}}^{-1} = 1 + \frac{3}{4}(1-t) + \frac{7}{4}(1-t)^{1/3} \quad (3)$$

$$v_{\text{gas}}^{-1} = 1 + \frac{3}{4}(1-t) - \frac{7}{4}(1-t)^{1/3} \quad (4)$$

$$\Delta S_{\text{evap}} = \frac{\Delta S_{\text{evap}}}{R} = \Delta s_0 \left(\frac{1-t}{1-t_0} \right)^{0.38} \frac{t_0}{t} \quad (5)$$

In these equations, small letters denote dimensionless quantities. p, v, t are made dimensionless by dividing P, V , and T by the corresponding critical values, and s is the entropy measured in units of R . A further discussion of eqns. 1–4 can be found, for instance, in the book by Guggenheim,⁵ and, for a discussion of eqn. 5, we refer to textbooks in chemical engineering.⁶ If in eqn. 5 one sets $\Delta s_0 = 10.4$ and $t_0 = 0.65$ (the approximate reduced temperature for the normal boiling point), one obtains Trouton's rule. Any two-parameter equation of state (with a correct mathematical form) will give a numerical value of z_c , the critical compressibility factor (eqn. (1)). Expressions equivalent to those of eqns. 2–4 are obtained using the Maxwell construction, *i.e.* choosing $p_{\text{evap}}(t)$ so that

$$\int_{v_{\text{liq}}}^{v_{\text{gas}}} (p - p_{\text{evap}}) dv = 0$$

where v_{liq} and v_{gas} are the smallest and largest roots in the equation $p(v, t) = p_{\text{evap}}$. By this construction the pressure in the loop is replaced by an average value, and this, of course, corresponds to setting the chemical potential of the liquid equal to that of the vapour. Finally, a relation analogous to that of eqn. 5 is obtained by using the Clapeyron-Clausius equation $p_{\text{evap}}'(t) = \Delta s_{\text{evap}}(v_{\text{gas}} - v_{\text{liq}})^{-1} z_c^{-1}$ or from the expression

$$\Delta s_{\text{evap}} = z_c \int_{v_{\text{liq}}}^{v_{\text{gas}}} (\partial p / \partial t)_v dv \quad (6)$$

in which one inserts $(\partial p / \partial t)_v$ which can be obtained easily from the reduced equation of state.

Comparison of the classical two-parameter equations with empirical data from the condensation region has been carried out earlier by Ree^{7*} who found that van der Waals equation reproduced vapour pressure data quite well, Berthelot's equation reproduced the densities fairly well, and that none of the equations lead to the correct value for the heat of vaporization. In addition to this, it is well known that Dieterici's equation of state, although it is in general a very poor equation, reproduces the empirical value of z_c correctly.

Before describing the modifications of the van der Waals equation which we are going to suggest, we shall very briefly review the statistical mechanical basis of the van der Waals equation.

STATISTICAL MECHANICAL CONSIDERATIONS

A rigorous derivation of the equation of state must start from the partition function; and, for simplicity in the argument, we shall use the canonical ensemble. We then have

$$Q = \frac{1}{N! \Lambda^{3N}} \int \dots \int e^{-U/kT} dq_1 \dots dq_{3N} \quad (7)$$

where $U(q_1, \dots, q_{3N})$ is the potential energy of the gas. From this we easily get

$$P = kT \frac{\partial \ln Q}{\partial V} \quad (8)$$

Using statistical mechanics, three important results have been obtained for the one-dimensional case. First of all, the equation

$$P(L - Nl) = RT \quad (9)$$

which is often called Tonks' equation⁸ is valid exactly for N rods of length l in a one-dimensional box of length L . Secondly, no condensation can occur in a one-dimensional system if the two particle interaction has a finite range.⁹ Thirdly, for a system in which the potential has an infinite range, phase transition is possible even in one-dimensional systems.¹ As mentioned in the introduction, the exact treatment of the third case leads to the van der Waals equation; but this, unfortunately, does not tell much about real gases.

In order to get a simple approximate equation of state from eqn. (7), one must make very crude approximations. If one assumes that the molecules can be treated as hard spheres, *i.e.* if the potential between two molecules is

* Simultaneously with the work of Ree, essentially the same work was carried out by Dr. Dennis Rohan; but it remained unpublished since Ree's paper was submitted first. A laboratory report by Thor A. Bak and Dennis Rohan entitled "Two-parameter Equations of State" is available. We are very much indebted to Dr. Rohan for these preliminary calculations.

zero, except at contact when it rises to infinity, then we have the result that $\exp(-U/kT)$ is 1 except when two or more spheres touch, in which case it vanishes. The volume for which the integrand vanishes is approximately equal to $b = Nv_0$, where v_0 is a volume related to the volume of the molecular sphere; and we therefore have

$$Q = \frac{1}{N!A^{3N}} (V-b)^N \quad (10)$$

which leads to the 3-dimensional Tonks' equation. This equation is only approximately valid even if the molecules actually were hard spheres, since the excluded volume cannot be taken into account in this simple fashion. This is also found experimentally as a dependence of the effective excluded volume on the total volume of the gas. The equation does, however, provide a reasonable interpolation formula between the ideal case and the completely compressed gas, if b is considered as an empirical parameter.

From the form of eqns. 7 and 8 it is seen that, if the intermolecular potential can be split up into a strongly repulsive core and a weakly attractive part, it is likely that the equation of state to a good approximation can be written as

$$[P][V] = RT \quad (11)$$

in which the factor $[P]$ essentially only depends on the attractive forces and the factor $[V]$ only depends on the repulsive forces. If we assume that the potential consists of a hard core and an attractive part with a fairly long range, we can argue that U must be approximately constant outside the region where the hard cores touch each other and equal to

$$U = \frac{1}{2} \frac{N^2}{V} \bar{u} \quad (12)$$

Here u is an average value of the two-body potential ($\bar{u} < 0$), and the factor $\frac{1}{2}$ is inserted to avoid counting the particles twice.

This argument leads to

$$Q = \frac{1}{N!A^{3N}} \exp\left(\frac{N^2\bar{u}}{-2VkT}\right) (V-b)^N \quad (13)$$

and to van der Waals equation with

$$a = \frac{N_{Av}^2 \bar{u}}{2} \quad (14)$$

where N_{Av} is Avogadro's number.

For a potential with finite range, the molecules must primarily interact with other molecules close to it; and the distribution of molecules is not as "random" as it would be with long-range forces, since clustering of molecules now will occur at low temperatures. This means that U should be modified in two ways. When the volume of the gas is very small, the number of particles near a certain particle cannot simply be proportional to N/V ; and, when the temperature is low, the assumed constant value of U is increased. Since the total range of temperatures we shall consider is only within a factor 3 to

4 of the lowest temperature, almost any functional dependance of T will do; and, to get something simple, we set

$$U = U_0 \frac{N^2}{(V + \delta b)T^n} \quad (15)$$

where U_0 is a proportionality factor which absorbs all our approximations, δ a pure number of the order 1, and n a pure number which will also probably be of the order 1.

Another possibility is to set

$$U = U_0 \frac{N^2}{(V + \delta b)} \left(1 + \frac{na/bR}{T} \right) \quad (16)$$

where a/bR has the dimension of a temperature and n is a pure number. In light of what was said above, this is just another approximation formula, intended to work in a rather narrow range.

In accordance with what has been said above, we now suggest the following three $[P]$ terms:

$$P + \frac{a}{V^2} \quad (17)$$

$$P + \frac{a}{T^n(V+b)^2} \quad (18)$$

$$P + \frac{a(1+na/bRT)}{(V+b)^2} \quad (19)$$

These terms can be combined with $[V]$ terms which stem from a more rigorous treatment of the hard sphere gas, as already suggested by Longuet-Higgins and Widom¹² and by Guggenheim.¹³ The most obvious thing to do, perhaps, is to use the virial expansion for a hard sphere gas of which several terms are now known. Using up to the fifth virial coefficient, we get

$$[V] = V \left(1 + \frac{b}{V} + \frac{5}{8} \frac{b^2}{V^2} + 0.2829 \frac{b^3}{V^3} + 0.105 \frac{b^4}{V^4} \right)^{-1} \quad (20)$$

Another possibility would be to use Thiele's solution¹⁰ of the Percus-Yevick equation for hard spheres. This leads to

$$V = (V - b')^3 / (V^2 + Vb' + b'^2) \quad (21)$$

if we use the compressibility equation, which presumably is the more accurate one. A series expansion shows that the parameter b' is related to b by $b' = b/4$. We can now combine either of the $[V]$ factors given by eqns. (10), (20), or (21) with either of the $[P]$ factors given in eqns. (17)–(19). This leads to a total of 9 equations of state of which one is the familiar van der Waals' equation. The equations of state and the numbering of them, which we shall use from now on, is shown in Table 1. It should be remarked, of course, that the equations in which n and δ occur, strictly speaking, are not two-parameter equations. However, once the dimensionless parameters n and δ are given

Table 1. z_{cr} and thermodynamic quantities calculated at $t=0.65$. Table 1 shows the values of z_{cr} , p_{evap} , v_{liq} , v_{gas} , and Δs_{evap} for the 9 possible equations. The numbering of the 9 equations, of which van der Waals equation is 1.1, is shown, as are the values of δ and n .

[P]	[V]	$V-b$	$1+\frac{b}{V}+\frac{5}{8}\left(\frac{b}{V}\right)^2+0.2829\left(\frac{b}{V}\right)^3+0.105\left(\frac{b}{V}\right)^4$	V	$\frac{(V-b)^3}{V^2+Vb+b^2}$						
$P+\frac{a}{V^2}$	z_{cr} p_{evap} v_{liq} v_{gas} Δs_{evap}	1.1	0.375 0.136 0.449 11.2 4.55	1.2	0.356 0.062 0.307 27.9 7.90						
						1.3	0.360 0.075 0.345 22.5 6.93				
								2.3	0.297 0.038 0.223 55.6 9.70		
										2.3	0.297 0.038 0.223 55.6 9.70
$P+\frac{a}{T^m(V+\delta b)^2}$	z_{cr} p_{evap} v_{liq} v_{gas} Δs_{evap}	2.1	0.300 0.041 0.266 43 8.65	2.2	0.297 0.037 0.220 56.8 9.82						
						2.3	0.297 0.038 0.223 55.6 9.70				
								2.3	0.297 0.038 0.223 55.6 9.70		
										2.3	0.297 0.038 0.223 55.6 9.70
$P+\frac{a\left(1+\frac{na}{Rb}\frac{1}{T}\right)}{(V+\delta b)^2}$	z_{cr} p_{evap} v_{liq} v_{gas} Δs_{evap}	3.1	0.300 0.044 0.264 46.2 9.18	3.2	0.302 0.043 0.232 47.8 9.49						
						3.3	0.297 0.042 0.226 41.7 9.56				
								3.3	0.297 0.042 0.226 41.7 9.56		
										3.3	0.297 0.042 0.226 41.7 9.56

numerical values, we are left with two-parameter equations of state for which the theorem of corresponding states holds. The way of fixing n and δ is described in detail in the following section.

THE CALCULATION SCHEME

The calculations involve two steps: 1. The calculation of the coefficients in the reduced equation, and 2. The calculation of the thermodynamic quantities given in eqns. (1)–(5). The first step is trivial in the case of equation 1.1; but, for some of the more complicated equations, it can only be done numerically. In the four-parameter equations, this step also requires that the values of n and δ have been determined beforehand. They were determined in the following way: n and δ were given a series of sets of numerical values. Each set (n, δ) gave us a two-parameter equation of state for which the reduced equation of state and z_c could be calculated. This was done numerically, using a computer program. Using these reduced equations of state and the Maxwell construction, we computed the thermodynamical quantities given in eqn. (2)–(5) at a definite temperature, $t=0.65$, the normal boiling point. This temperature lies in the middle of the temperature interval of interest. The values of n and δ which gave the best agreement between these values and the empirical values, as found from eqns. (1)–(5) inserting t equal to 0.65, were chosen as the final values of n and δ . Since the square of the deviations from the empirical values, considered as a function of n and δ , showed a rather shallow minimum, the final values of n and δ could be taken as round numbers. Final values of n and δ are given in Table 1 together with the thermodynamical quantities (z_c , v_{gas} , v_{liq} , p_{evap} and Δs_{evap}) at $t=0.65$ for all nine equations of state. Table 2 gives, for comparison, the empirical values

Table 2. Average empirical values of the thermodynamic quantities given in eqns. (1)–(5) at $t=0.65$. The temperature, $t=0.65$, is chosen here as in Table 1 because this, roughly speaking, corresponds to the reduced temperature at the normal boiling point.

z_{cr}	0.29
p_{evap}	0.055
v_{liq}	0.4
v_{gas}	50
Δs_{evap}	10.4

of the thermodynamical quantities, also at $t=0.65$. Table 3 gives the reduced equations of state. With n and δ fixed as described, we then calculated the thermodynamical quantities for several temperature values in the range $0.35 \leq t \leq 1$, the spacing between t values being 0.050 in the range from 0.35 to 0.95 and 0.001 in the range from 0.98 to 0.999. The results are given as the curves: $\log_{10} p_{\text{evap}}$ versus t^{-1} (Figs. 1a, b, and c), v_{liq}^{-1} and v_{gas}^{-1} versus t (Figs. 2a, b and c) and finally Δs_{evap} versus t (Figs. 3a, b, and c). Also, the empirical curves are given (heavy lines).

Table 3. The reduced equations of state for the 9 two-parameter equations using the values of n and δ given in Table 1.

1.1	$\left(p + \frac{3}{v^3}\right) \left(v - \frac{1}{3}\right)$	$= \frac{8}{3} \ t$
1.2	$\left(p + 3.9461 \frac{1}{v^2}\right) \frac{v}{1 + 0.53249v^{-1} + 0.17722v^{-2} + 4.2714 \times 10^{-2}v^{-3} + 8.4420 \times 10^{-3}v^{-4}}$	$= 2.8089 \ t$
1.3	$\left(p + 3.8108 \frac{1}{v^2}\right) \frac{1}{v^3 + 0.12867v^{-1} + 1.6555 \times 10^{-2}}$	$= 2.7789 \ t$
2.1	$\left(p + \frac{4.6875}{v^{1/2}(v + 0.2500)^2}\right) (v - 0.16667)$	$= 3.3333 \ t$
2.2	$\left(p + \frac{4.9191}{v^{1/2}(v + 0.24804)^2}\right) \frac{v}{1 + 0.20670v^{-1} + 2.6704 \times 10^{-2}v^{-2} + 2.4985 \times 10^{-3}v^{-3} + 1.9168 \times 10^{-4}v^{-4}}$	$= 3.3639 \ t$
2.3	$\left(p + \frac{4.9357}{v^{1/2}(v + 0.25221)^2}\right) \frac{(v - 5.0442 \times 10^{-2})^3}{v^3 + 5.0442 \times 10^{-2}v + 2.5444 \times 10^{-3}}$	$= 3.3725 \ t$
3.1	$\left(p + 2.4776 \frac{1 + 0.89194 \ t^{-1}}{(v + 0.25000)^2}\right) (v - 0.16667)$	$= 3.3333 \ t$
3.2	$\left(p + 3.0082 \frac{1 + 0.59787t^{-1}}{(v + 0.22766)^2}\right) \frac{v}{1 + 0.22766v^{-1} + 3.2392 \times 10^{-2}v^{-2} + 3.3379 \times 10^{-3}v^{-3} + 2.8204 \times 10^{-4}v^{-4}}$	$= 3.3152 \ t$
3.3	$\left(p + 2.9244 \frac{1 + 0.68767t^{-1}}{(v + 0.25221)^2}\right) \frac{(v - 5.0441 \times 10^{-2})^3}{v^3 + 5.0441 \times 10^{-2}v + 2.5443 \times 10^{-3}}$	$= 3.3724 \ t$

DISCUSSION

We shall first see if we can improve on the van der Waals equation by replacing the factor $V-b$ with the ones given in eqn. (20) or eqn. (21), *i.e.* we compare eqns. 1.1, 1.2, and 1.3.

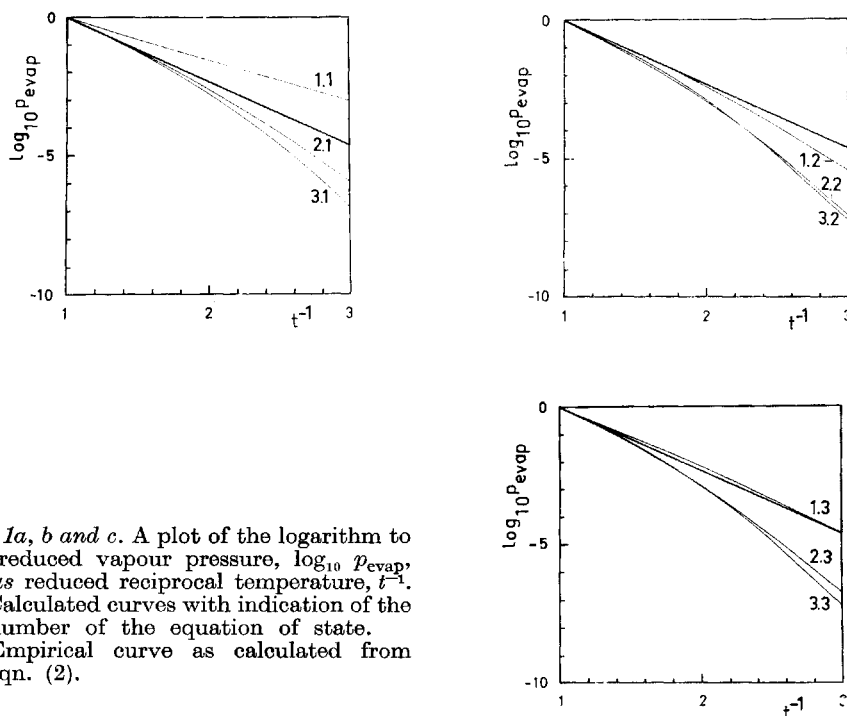


Fig. 1a, b and c. A plot of the logarithm to the reduced vapour pressure, $\log_{10} P_{\text{evap}}$, versus reduced reciprocal temperature, t^{-1} . — Calculated curves with indication of the number of the equation of state. — Empirical curve as calculated from eqn. (2).

The vapour pressure curves given in Fig. 1a, b and c show clearly that there is an improvement especially in the case of eqn. 1.3. Since the vapour pressure predicted by the van der Waals equation is too high as is the liquid volume (Fig. 2a, b, and c), it is perhaps not so surprising that equation 1.3 also represents an improvement with respect to that effect. However, in this case, the improvement results in a value for v_{liq} which is about as much too small as that of van der Waals is too large. The gas volumes (Fig. 2a, b, and c) are considerably improved both by eqn. 1.2 and 1.3 as are the entropies of evaporation (Fig. 3a, b, and c). As can be seen, they are still far too small.

We shall then see what changes we get by altering the $[P]$ term. Roughly speaking, introducing the $[P]$'s from eqns. (18) and (19) in any of the eqns. 1.1, 1.2, and 1.3 give qualitatively the same changes: The vapour pressure and the liquid volume drop, the gas volume increases, and the entropy of evaporation increases. In the near critical region, this represents, in all cases,

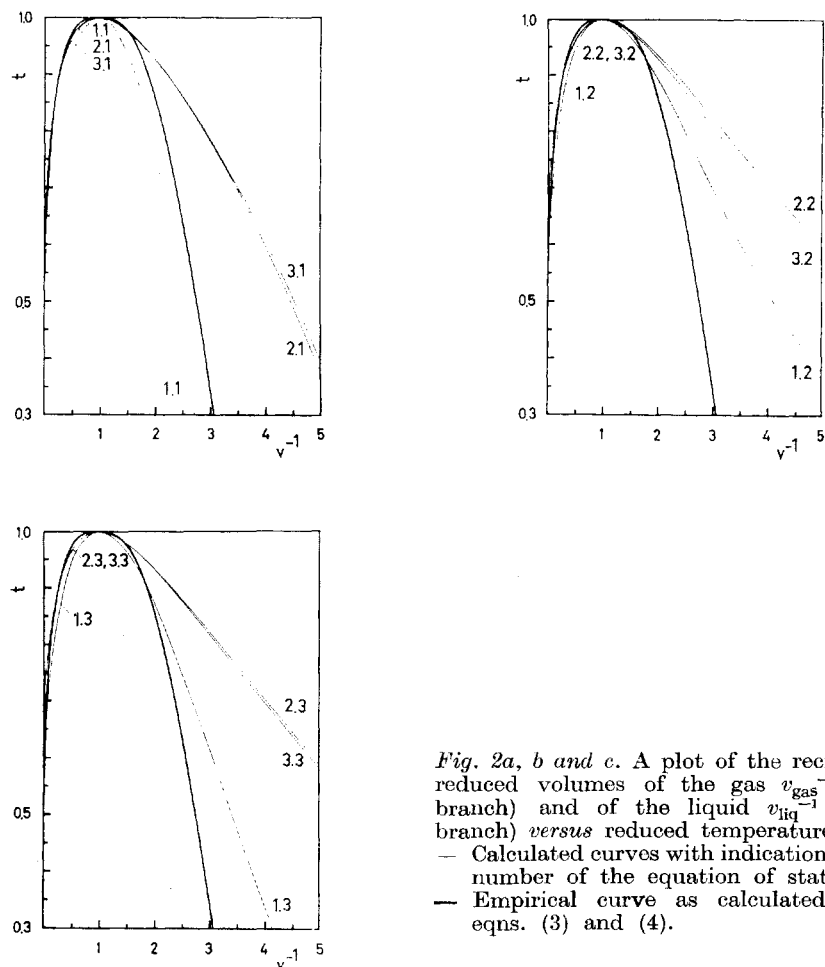


Fig. 2a, b and c. A plot of the reciprocal reduced volumes of the gas v_{gas}^{-1} (left branch) and of the liquid v_{liq}^{-1} (right branch) versus reduced temperature t .
 — Calculated curves with indication of the number of the equation of state.
 — Empirical curve as calculated from eqns. (3) and (4).

improvements; but, at lower temperatures, the effects of modifying the $[P]$ term in this way appear to be too large. At sufficiently low temperatures, therefore, eqns. 1.2 and 1.3 appear to be superior. It should be mentioned that, even if the introduction of the modified $[P]$ terms makes the agreement with the empirical curves significantly better in the region nearest to the critical point, none of the equations of state given here are satisfactory in this region. The reason for this is that for simple liquids it is known that as $(p, v) \rightarrow (1, 1)$ the following asymptotic relationship is valid:¹¹ $1-p \approx |v-1|^5$. In all equations studied here we get the same result as for the van der Waals equation, namely $1-p \approx |v-1|^3$.

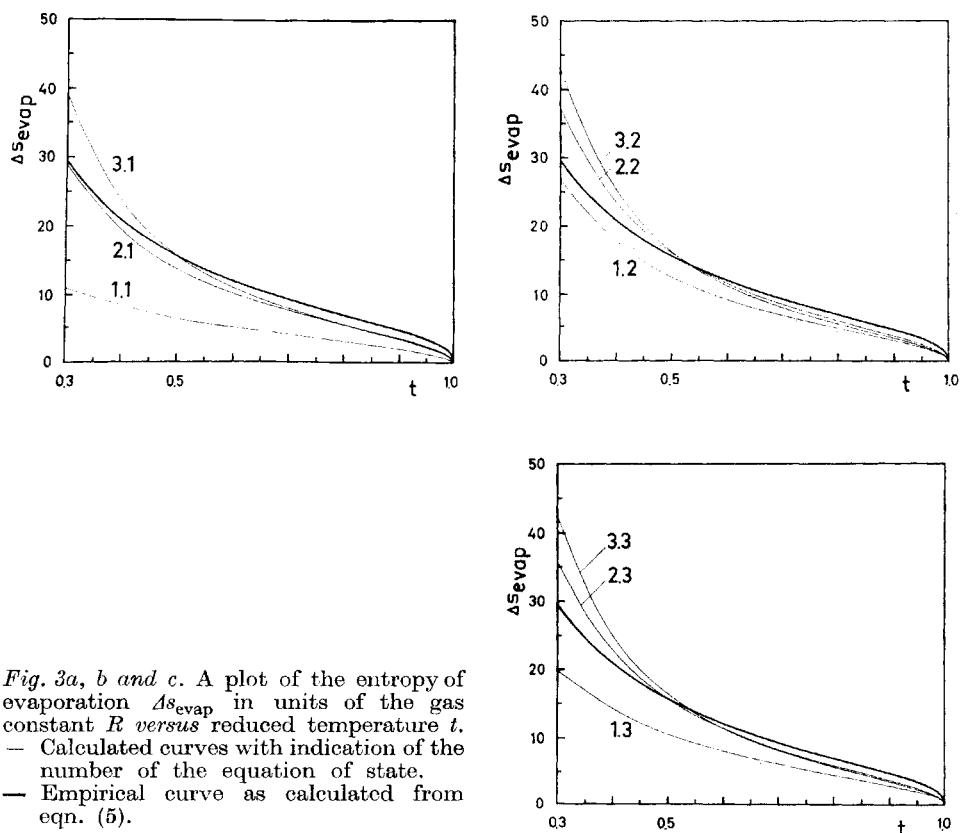


Fig. 3a, b and c. A plot of the entropy of evaporation Δs_{evap} in units of the gas constant R versus reduced temperature t .
 — Calculated curves with indication of the number of the equation of state.
 — Empirical curve as calculated from eqn. (5).

If we limit ourselves to the region $0.95 > t > 0.56$, *i.e.* to temperatures from a little below the critical temperature to about the triple point, we see that the eqns. 2.1 and 3.1 are the best. Table 4 shows the maximum deviation between predicted and average empirical values for these two equations; and, from this, it appears that eqn. 2.1 is slightly better than eqn. 3.1.

Table 4. The maximum deviations between calculated values and empirical averages in the region $0.56 < t < 0.95$, in per cent of the empirical average.

	Equation 2.1	Equation 3.1
z_c	3	3
p_{evap}	35	50
v_{liq}	40	40
v_{gas}	20	10
Δs_{evap}	30	30

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Received October 25, 1968.