

## On the Equation of State for Gases

R. J. Tykodi, and Edward P. Hummel

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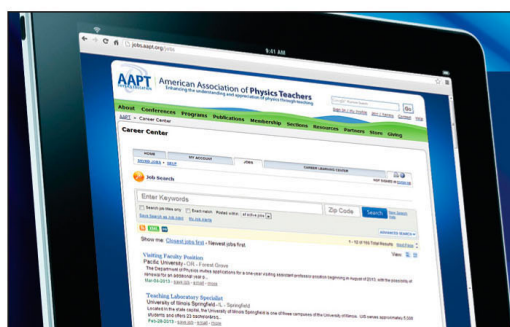
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# On the Equation of State for Gases

R. J. TYKODI  
EDWARD P. HUMMEL

Department of Chemistry  
Southeastern Massachusetts University  
North Dartmouth, Massachusetts 02747

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*The general thermodynamic structure of equations of state is discussed. It is pointed out that empirical equations of state always involve a double set of assumptions. A recipe for producing thermodynamically consistent empirical equations of state is presented and is illustrated in the step-by-step production of yet another equation of state.*

The problem of finding a sufficiently accurate approximation to the equation of state for a gas for the purposes in hand is still very much with us<sup>1,2</sup>; the art of empirical equation of state construction is still a necessary art.<sup>2</sup> In this paper we wish to point out some elementary thermodynamic relations that, in our opinion, have not been adequately exploited in the practice of empirical equation of state construction.

The thermodynamic bases of all equations of state are the relations

$$(\partial U/\partial V)_T = T(\partial P/\partial T)_V - P, \quad (1)$$

$$-(\partial H/\partial P)_T = T(\partial V/\partial T)_P - V, \quad (2)$$

$$[P + (\partial U/\partial V)_T][V - (\partial H/\partial P)_T] = T(C_P - C_V), \quad (3)$$

where we are referring all extensive quantities ( $V$ ,  $U$ ,  $H$ , etc.) to a 1 mole basis. Equation (3) is a simple combination of Eqs. (1) and (2). Note

that if we had exact expressions for the internal energy  $U = U(T, V)$  and the enthalpy  $H = H(T, P)$  we could recover from these two expressions the exact equation of state via Eq. (3).

We shall now manipulate Eqs. (1) and (2) so as to produce more convenient expressions. Note that

$$T^{-2}(\partial U/\partial V)_T = [\partial(P/T)/\partial T]_V \quad (4)$$

and

$$-T^{-2}(\partial H/\partial P)_T = [\partial(V/T)/\partial T]_P; \quad (5)$$

we can, consequently, integrate Eqs. (4) and (5) to obtain (with some rearrangement—see the Appendix) the relations

$$[P + \xi(T, V)]\phi(V) = RT, \quad (6)$$

$$[V - \chi(T, P)]\psi(P) = RT, \quad (7)$$

where

$$\xi(T, V) \equiv -T \int T^{-2}(\partial U/\partial V)_T dT \quad (\text{integration at const. } V), \quad (8)$$

$$\chi(T, P) \equiv -T \int T^{-2}(\partial H/\partial P)_T dT \quad (\text{integration at const. } P), \quad (9)$$

and  $\phi(V)$  and  $\psi(P)$  are arbitrary functions of the indicated arguments.

In the remainder of the paper we shall limit ourselves to the discussion of pressure-explicit equations of state:  $P = P(T, V)$ . If a pressure-explicit equation is to be consistent with the laws of thermodynamics, it must be expressible in the form of Eq. (6). If we had exact expressions for  $U = U(T, V)$  and  $\phi(V)$ , we could recover from them the exact equation of state via Eq. (6).

If we wanted an equation of state that was valid all the way down to 0°K (we normally do not require this much), the third law of thermodynamics in the form

$$0 = \lim_{T \rightarrow 0} (\partial S/\partial V)_T = \lim_{T \rightarrow 0} (\partial P/\partial T)_V \quad (10)$$

would supply us with a relationship between the functions  $\phi(V)$  and  $\xi(T, V)$ :

$$R/\phi(V) = \lim_{T \rightarrow 0} (\partial \xi / \partial T)_V. \quad (11)$$

We shall ignore the constraint imposed by Eq. (11); we are thus limiting ourselves to temperatures in excess of a few degrees Kelvin (this restriction will prove uncomfortable only in the cases of  $^3\text{He}$  and  $^4\text{He}$ ). With this understanding, then, we may treat the functions  $\phi(V)$  and  $\xi(T, V)$  as independent of one another, and we see that approximate equations of state involve (from the thermodynamic point of view) two distinct assumptions—one for  $U = U(T, V)$  [or for  $\xi = \xi(T, V)$ ] and another for  $\phi(V)$ .

### PATTERNS

The choices  $U = U^0(T)$  and  $\phi(V) = V$  lead to the ideal gas equation  $PV = RT$ , whereas the choices  $U = U^0(T) - aV^{-1}$  and  $\phi(V) = V - b$  lead to the van der Waals equation  $(P + aV^{-2})(V - b) = RT$ . The results of the many studies, both experimental and theoretical, on the equation of state for gases since the time of van der Waals indicate that

$$\phi(V) = V + \dots$$

and

$$U = U^0(T) + A(T)V^{-1} + \dots; \quad (12)$$

the leading terms in the series expansions for  $\phi(V)$  and  $U(T, V)$  are well known, and much research has taken the form of extending the expansions in Eq. (12),

$$\phi(V) = V + \sum_{i=0}^m b_i V^{-i}$$

and

$$U = U^0(T) + \sum_{i=1}^n A_i(T)V^{-i}, \quad (13)$$

either by adding on terms or by using expressions developable into infinite series in terms of reciprocal volumes.

Efforts to improve upon the van der Waals equation have led to equations such as the

Beattie-Bridgeman<sup>1,3,4</sup>

$$PV = [RT(1 - \epsilon)(V + B)/V] - A/V, \quad (14)$$

where  $A = A_0(1 - aV^{-1})$ ,  $B = B_0(1 - bV^{-1})$ , and  $\epsilon = c/V T^3$ , and the Hirschfelder-Buehler-McGee-Sutton<sup>4</sup>

$$[P + (c_1 + c_2 T^{-1})V^{-2} + (c_3 T - c_4 T^{-1})V^{-3}] \\ \times (V - b_1 + b_2 V^{-1}) = RT. \quad (15)$$

Equation (15) is clearly of the form of Eq. (6). Equation (14) can be rearranged into the form of Eq. (6) with  $\phi(V) = V/(1 + B_0 V^{-1} - b B_0 V^{-2})$  and

$$\xi = \frac{A_0 + R c T^{-2}}{V^2} - \frac{a A_0 - R B_0 c T^{-2}}{V^3} - \frac{R B_0 b c T^{-2}}{V^4}. \quad (16)$$

Equation (14) contains five adjustable constants and Eq. (15) contains six.

Surprisingly good results have been obtained with equations as simple as the Redlich-Kwong,<sup>1,2</sup>

$$\{P + [a/T^{1/2}V(V + b)]\}(V - b) = RT, \quad (17)$$

and the Wohl,<sup>3</sup>

$$\{P + [a/TV(V - b)] - (c/T^{4/3}V^3)\}(V - b) = RT. \quad (18)$$

All the equations of state that we have looked at thus far are consistent with the thermodynamic requirements of Eq. (6); each equation represents a different choice for the functions  $\xi(T, V)$  and  $\phi(V)$ . Consider now the Dieterici equation<sup>1,3</sup>

$$P(V - b) = RT \exp(-a/VT^n). \quad (19)$$

Upon trying to cast Eq. (19) into the form of Eq. (6), we find that  $\xi = -P$ . It is thus not possible to make the Dieterici equation conform to the thermodynamic requirements of Eq. (6). In spite of occasional laudatory remarks to the contrary,<sup>5</sup> then, the Dieterici equation is an invalid equation of state; and, indeed, it performs rather poorly when put to the test.<sup>1,3,4</sup>

The trouble with the Dieterici equation, of course, is that the cohesive energy effect is introduced via a multiplicative factor rather than by means of an additive term; any equation that treats a (temperature-dependent) cohesive energy effect in such a manner will fail to meet the requirements of Eq. (6).

If we use Eq. (6) to screen empirical equations of state, we find that although it passes an infinite number of such equations it does occasionally reject one as of unsuitable form.

### EQUATION OF STATE ARTISTRY

The gist of our message is simply this: Since we know a good deal about the expected behavior of the functions  $\phi(V)$  and  $U(T, V)$  [Eqs. (12) and (13)], let us, in constructing empirical equations of state, make reasonable guesses as to the functional forms of  $\phi(V)$  and  $U(T, V)$  and then let us parlay our guesses into a finished equation of state via Eq. (6). We here give an example of how such a program might be put into effect.

We know that the internal energy of a gas at a given temperature is very nearly a linear function of the density at low to moderate densities.<sup>3,4</sup> We guess, then, that an internal energy function of the form

$$U = U^0(T) - [\alpha(T)/(V + \alpha)] + [\beta(T)/(V + \beta)] \quad (20)$$

will fit the data over a rather wide range of densities. Equation (20) leads to an expression for  $\xi(T, V)$  which we may write in the following form:

$$\xi(T, V) = [RTA(T)/(V + \alpha)^2] - [RTB(T)/(V + \beta)^2]. \quad (21)$$

If we now couple Eq. (21) with the simple choice  $\phi(V) = V$ , we get as a new equation of state the relation

$$\{P + [RTA(T)/(V + \alpha)^2] - [RTB(T)/(V + \beta)^2]\} V = RT. \quad (22)$$

Equation (22) can be expressed in virial form in

the following way:

$$\frac{PV}{RT} = 1 + \frac{B-A}{V} - \frac{2(\beta B - \alpha A)}{V^2} + \frac{3(\beta^2 B - \alpha^2 A)}{V^3} - \frac{4(\beta^3 B - \alpha^3 A)}{V^4} + \dots \quad (23)$$

Finally, if (guided by experimental studies of the second virial coefficient) we set  $A(T) = a/RT$  and  $B(T) = b \exp(-cT)$ , we end up with a five constant ( $\alpha, \beta, a, b, c$ ) equation of state which has temperature-dependent virial coefficients of approximately the right form<sup>2-4</sup>:

$$\{P + [a/(V + \alpha)^2] - [RTb \exp(-cT)/(V + \beta)^2]\} \times V = RT. \quad (24)$$

### CONCLUSION

We have shown that from the thermodynamic point of view the construction of empirical equations of state always involves two independent assumptions: we need assumptions for  $U(T, V)$  and  $\phi(V)$  or  $H(T, P)$  and  $\psi(P)$ . In the case of pressure-explicit equations of state we showed that Eq. (6) was the basic form for all thermodynamically consistent equations; we also showed by this test that the Dieterici equation was an invalid equation of state. As an illustrative exercise, we constructed a new equation of state. Although we have not tested our new equation extensively, we feel about it as Fortinbras felt about Hamlet<sup>6</sup>:

For he was likely, had he been put on,  
To have prov'd most royal.

### APPENDIX

We here fill in the missing steps in the derivation of Eq. (6) and comment on some additional points. Upon integrating Eq. (4),

$$[\partial(P/T)/\partial T]_V = T^{-2}(\partial U/\partial V)_T,$$

at constant  $V$ , we get

$$P/T = \int T^{-2}(\partial U/\partial V)_T dT + Rf(V), \quad (25)$$

where we have set the function of integration equal

to  $Rf(V)$ . Rearranging the terms of Eq. (25), we have

$$P - T \int T^{-2} (\partial U / \partial V)_T dT = RTf(V). \quad (26)$$

So, setting  $\xi(T, V) \equiv -T \int T^{-2} (\partial U / \partial V)_T dT$  and  $\phi(V) \equiv 1/f(V)$ , we arrive at Eq. (6). Equation (7) is derived in a similar fashion.

Writing Eq. (26) as

$$P + \xi(T, V) = RTf(V), \quad (27)$$

we note that the isothermal requirement

$$\lim_{V \rightarrow \infty} PV/RT = 1 \quad (28)$$

can be satisfied by requiring that

$$\lim_{V \rightarrow \infty} Vf(V) = 1$$

and

$$\lim_{V \rightarrow \infty} V\xi(T, V) = 0 \quad (29)$$

under isothermal conditions. Equation (29) is our

justification for expecting that

$$f(V) = V^{-1} + \dots,$$

$$\xi(T, V) = A^*(T)V^{-2} + \dots. \quad (30)$$

We wish now to display the virial equation of state in the form of Eq. (6). Let us write the virial equation as

$$P = RTV^{-1} + \sum_{i=2}^{\infty} RTC_i V^{-i}, \quad (31)$$

where  $C_i$  is the  $i$ th virial coefficient. Let  $C_i' \equiv dC_i/dT$ , then we find that

$$1/\phi(V) = V^{-1} + \sum_{i=2}^{\infty} V^{-i} (C_i - \int C_i' dT), \quad (32)$$

$$\xi(T, V) = - \sum_{i=2}^{\infty} RTV^{-i} \int C_i' dT. \quad (33)$$

Thus we see that any constant terms in the  $C_i$  enter into the  $\phi(V)$  function, whereas temperature-dependent terms enter into  $\xi(T, V)$ .

<sup>1</sup> K. K. Shah and G. Thodos, *Ind. Eng. Chem.* **57**, No. 3, 30 (1965).

<sup>2</sup> J. J. Martin, *Ind. Eng. Chem.* **59**, No. 12, 34 (1967).

<sup>3</sup> F. H. Crawford, *Heat, Thermodynamics, and Statistical Physics* (Harcourt, Brace and World, New York, 1963), Chap. 3, 12.

<sup>4</sup> E. F. Obert, *Concepts of Thermodynamics* (McGraw-Hill, New York, 1960), Chap. 10.

<sup>5</sup> R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge U. P., Cambridge, 1939), p. 275.

<sup>6</sup> W. Shakespeare, *Hamlet*, Act V, Scene ii, lines 400-401.