A GENERAL FORM OF AN EQUATION OF STATE

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It is shown that all the equations of state are simplified versions of the general equation of state, $P\Omega(V - \mu) = RT$. Ω, the term responsible for the attractive forces, is a function of volume and temperature. μ, the term responsible for the repulsive forces, is also a function of volume and temperature. A detailed analysis of a large number of experimental $P-V-T$ data reveals that the Ω *vs* P function and the μ *vs* P function, at a constant temperature, go through a maximum. These maxima must be predicted by all physically consistent equations of state.

Too much has already been said and written about equations of state and then P–V–T behavior of gases in general[1-11]. With the Redlich–Kwong equatio-of state and all its modifications, the accuracy of predicting the volumetric and thermodynamic behavior of gases by means of semiempirical equations of state has culminated, and, in our opinion, no time should be spent anymore in trying to derive more accurate semiempirical equations of state. The significance of the here presented equation of state is neither in its derivation not in its application. The advantage of this equation lies in the fact that it seems to represent a general form of an equation of state.

Equation of State

By using classical mechanics and probability theory, we have derived a semiempirical equation of state of the form

$$P\Omega(V - \mu) = RT,\qquad(1)$$

where Ω accounts for the attractive forces and μ accounts for the repulsive forces in the gas. Both Ω and μ are functions of volume and temperature. Eq. (1) seems to represent a general form of an equation of state. It is possible to convert all the equations of state into the form given by Eq. (1). We have converted over thirty equations, including the 9-parameter Benedict–Webb–Rubin equation of state into this form.

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For equations of state of the van der Waals type, the Ω-function is given by

$$\Omega = 1 + \sum_{s=1}^{\infty} \left[C_s \frac{a}{RT^i} \frac{1}{\left(1 + \dfrac{b}{V}\right) j} \frac{1}{V} \left(1 - \frac{b}{V}\right)^k \right]^s . \tag{2}$$

For all these equations $\mu \equiv b$. Next we show the values of C_s, i, j, k, and s for the van der Waals equation. This equation can be written in the form

$$P(V - b) \frac{1}{1 - \dfrac{a}{RTV}\left(1 - \dfrac{b}{V}\right)} = RT . \tag{3}$$

Obviously for the van der Waals equation

$$\Omega = \frac{1}{1 - \dfrac{a}{RTV}\left(1 - \dfrac{b}{V}\right)} . \tag{4}$$

For comparison of Eq. (4) with Eq. (1), we expand Eq. (4) into a power series, to obtain

$$\Omega = 1 + \frac{a}{RTV}\left(1 - \frac{b}{V}\right) + \left(\frac{a}{RTV}\right)^2 \left(1 - \frac{b}{V}\right)^2 +$$
$$+ \ldots = 1 + \sum_{s=1}^{\infty} \left[\frac{a}{RT} \frac{1}{V}\left(1 - \frac{b}{V}\right) \right]^s . \tag{5}$$

Thus, for the van der Waals equation of state $i = 1$, $j = 0$, $k = 1$, and $C_s = 1$. In a similar way we obtain for the Berthelot equation of state $i = 2$, $j = 0$, $k = 1$, and $C_s = 1$. For the Dieterici equation of state $i = 1$, $j = 1$, $k = 0$, and $C_s = 1/s!$. For the Redlich–Kwong equation of state $i = 3/2$, $j = 1$, $k = 1$, and $C_s = 1$.

From known values of constant a and b, we can evaluate Ω for various gases from the different equations of state. However, such Ω-values are useless. They are not more accurate than the equations of state from which these values are obtained.

We have developed a method for obtaining Ω-values and μ-values from direct experimental P–V–T data. Using a perturbed Taylor series, we derived the following two expressions:

$$\Omega \simeq \sum_{n=1}^{\infty} (-1)^{n-1} \frac{d^n(RT/P)}{dV^n} \frac{(V - b)^{n-1}}{n!} \tag{6}$$

and

$$\mu \simeq \sum_{n=1}^{\infty} (-1)^{n-1} \frac{d^n(PV)}{dP^n} \frac{P^{n-1}}{n!} . \tag{7}$$

Exact evaluation of these summations is practically impossible. Ignoring all the terms, except the first ones, in both summations, Eqs (6) and (7) assume the forms

TABLE I

Ω and μ values for carbon monoxide in a wide range of pressures at 298·15 K and 373·15 K

P_{exp} atm	V_{exp} dm^3 mol^{-1}	z	Ω	μ dm^3 mol^{-1}	P_{calc} atm
		$T = 298\cdot15$ K			
351·892	0·08263	1·18846	1·2582	0·02746	352
389·192	0·07740	1·23126	1·2600	0·02751	
507·162	0·06631	1·37461			
543·693	0·06392	1·42046	1·3391	0·03046	
685·970	0·05709	1·60081	1·3687[a]	0·03106[a]	687
781·361	0·05392	1·72217	1·3654	0·03096	
982·535	0·04920	1·97571	1·3177	0·03016	
1 415·982	0·04327	2·50456	1·2411	0·02915	
1 556·286	0·04198	2·67033	1·2272	0·02891	
1 867·917	0·03969	3·03064	1·1304	0·02807	
2 040·496	0·03868	3·22594	1·0665	0·02738	2 030
2 271·037	0·03751	3·48179			
3 222·242	0·03412	4·49331			
		$T = 373\cdot15$ K			
490·639	0·08263	1·32482	1·1596	0·02888	491
530·693	0·07860	1·36312			
690·611	0·06734	1·51978	1·1890	0·03017	
925·104	0·05798	1·75287	1·1903	0·03019	926
1 083·773	0·05392		1·1956[a]	0·03029[a]	
1 087·321	0·05385	1·9133	1·1835	0·03004	
1 297·081	0·04996	2·11780	1·1552	0·02950	
1 587·903	0·046165	2·39556	1·1229	0·02895	
1 816·357	0·04395	2·60882	1·0774	0·02828	
2 072·516	0·04198	2·84312	1·0284	0·02759	
2 454·128	0·03969	3·18344			
2 534·514	0·03929	3·25408	0·9758	0·02686	2 525
2 940·708	0·03751	3·60457			

[a] Maximum values.

$$\Omega \simeq \left[\frac{\partial(RT/P)}{\partial P}\right]_T = \left[\frac{\partial(V/z)}{\partial V}\right]_T \tag{8}$$

and

$$\mu \simeq \left[\frac{\partial(PV)}{\partial P}\right]_T = \left[\frac{\partial(RT/\Omega)}{\partial P}\right]_T + \left[\frac{\partial(Pb)}{\partial P}\right]_T . \tag{9}$$

Obviously, Eqs (8) and (9) provide approximate values only. We estimate the errors in both Ω and μ due to the approximation to be less than 5%.

We evaluated Ω-values and μ-values for a large variety of gases in a wide range of pressures and temperatures. These values prove without any doubt that the Ω vs P function and the μ vs P function, at constant temperature, must have an extreme — a maximum. Surprisingly, the maxima on both curves appear, within the limits of accuracy of the evaluation, at the same pressures. With increasing temperature, the maxima on both curves are lowered and shifted toward higher pressures.

This is clearly shown for CO at 25°C and 100°C in Table I (ref.[12]). The data in the last column 'of Table I represent the pressures evaluated from the approximate values of Ω listed in the same table.

The relatively good agreement between the calculated and the experimentally observed pressures prove that in spite of the approximation involved in the derivation of Eqs (8) and (9) they still provide reasonable results for Ω and μ.

The maximum on the Ω vs P function does not come as a surprise. The Ω-function is responsible for the deviation of a gas from ideal behavior due to its attractive forces. At very low and very high pressures, these deviations must be very small. Hence,

$$\lim_{\substack{P\to 0 \\ P\to\infty}} \Omega = 1 . \tag{10}$$

Ω can never be less than one (ideal behavior). Consequently, for each gas there is a pressure for each temperature (except of very high temperatures) at which the deviation from ideal behavior due to the attractive forces reaches a maximum and the condition

$$\left(\frac{\partial\Omega}{\partial P}\right)_T = 0 \tag{11}$$

is met. An interesting conclusion indeed.

As we stated previously, the maximum on the Ω vs P curve and the μ vs P curve is lowered and shifted toward higher pressures with increasing temperature. Thus, at very high temperatures there should be no maximum on either curve. Both Ω and μ-values should become independent of pressure at high temperatures. $\Omega = 1$

and $\mu = b$. For lacking high temperature P-V-T data, we were unable to prove this conclusion for carbon monoxide. We turned, therefore, our attention to hydrogen at 373·15 K. The critical temperature of hydrogen is only 33·2 K and 373·15 K can be considered as a relatively high temperature for hydrogen $\left(T_{\mathrm{r}} = T/T_{\mathrm{c}} \approx 12\right)$. From the experimental P-V-T data[13,14] we evaluated by the method of least squares the V/z vs volume function for hydrogen:

$$\frac{V}{z} = \frac{RT}{P} = 1 \cdot 0011 V - 0 \cdot 01583 \,,$$

where z is the compressibility factor. The slope of this expression is according to Eq. (8) equal to Ω. Thus, for hydrogen at 373·15 K, we have

$$\left[\frac{\partial(V/z)}{\partial V}\right]_{\mathrm{T}} = \left[\frac{\partial(RT/P)}{\partial V}\right]_{\mathrm{T}} = \Omega = 1 \cdot 0011 \,,$$

which means that hydrogen at high temperatures exhibits practically no deviation from ideal behavior due to attractive forces. In spite of its very small molecular mass (quantum effect), hydrogen is a relatively simple gas and its simple P-V-T behavior at large temperatures does not come as a surprise — it is well established. The calculations performed with other gases, however, indicate that, at high temperatures, all gases might exhibit behaviour similar to that of hydrogen.

The μ-function is responsible for the deviation of a gas from ideal behavior due to the repulsive forces. The high pressure limit

$$\lim_{P \to \infty} \mu = b \tag{12}$$

is expected, however, the initial increase of μ with pressure is unexpected and we are unable to give a reasonable explanation for this behavior.

The presence of an extreme (maximum) on the Ω vs P function may serve as a test for physical consistency of equations of state. Equations of state that are unable to predict the maximum cannot be considered as physically consistent. The may provide excellent agreement with experiment in a certain pressure and temperature range, but, depending on the physical and chemical nature of the gas they must break down at some pressure. We have applied the consistency test to about thirty equations of state. Six of them failed to meet the maximum consistency test. Next, we present two such equations of state:

$a)$ The Dieterici equation[1,2]

$$Pe^{a/VRT}(V - b) = RT \quad \text{and}$$

b) The Foulkes equation of state[15], written here in the form

$$P \exp\left[\left(\frac{a}{T^{n+1}}\right) P\right]\left[V - c \exp\left(\frac{a}{T^{n+1}} - b\right)\right] = RT. \qquad (13)$$

It is obvious that the Ω-function predicted by the Dieterici equation is of the form

$$\Omega = e^{a/VRT} \qquad (14)$$

and the Ω- function predicted by the Foulkes equation is

$$\Omega = e^{aP/T^{n+1}} . \qquad (15)$$

Eqs (14) and (15) require that

$$\lim_{P \to \infty} \Omega = \infty . \qquad (16)$$

For the Dieterici equation

$$\mu = b \qquad (17)$$

and for the Foulkes equation

$$\lim_{P \to \infty} \mu = \infty \qquad (18)$$

if $(a/T^{n+1} - b) > 0$ and

$$\lim_{P \to \infty} \mu = 0 \qquad (19)$$

if $(a/T^{n+1} - b) < 0$.

Eqs (16), (17), (18), and (19) clearly demonstrate that the Dieterici equation of state and the Foulkes equation of state do not obey the maximum consistency test and are physically inconsistent. This is true in spite of the fact that the Dieterici equation of state predicts accurate values for the critical compressibility factor: $z_c = 0.271$.

Analysis of a large number of experimental P–V–T data suggest that the Ω-function and μ-function are of the form

$$\Omega = e^{F(V)\Phi(T)} \qquad (20)$$

and

$$\mu = b \, e^{F(V)\Psi(T)} . \qquad (21)$$

The $F(V)$ function seems to be the same for both Ω and μ. We have not been able to derive as yet theoretical expressions for $F(V)$, $\phi(T)$, and $\psi(T)$. Work in this direction continues in our laboratory.

LIST OF SYMBOLS

a, b constants in an equation of state
C_s constant
P pressure
R ideal gas constant
T absolute temperature
T_c critical temperature
T_r reduced temperature
V volume
z_c critical compressibility factor
Ω temperature and volume dependent function
μ temperature and volume dependent function

Superscripts

i. j, k, s   constants characteristic of an equation of state

REFERENCES

1. Chao K. C., Robinson R. L.: *Equations of State in Engineering and Research*, Advan. Chem. Ser. 182. Amer. Chem. Soc., Washington, D. C. 1976.
2. Chao K. C., Greenkorn R. A.: *Thermodynamics of Fluids*. Marcel Dekker, New York 1975.
3. Chueh P. L., Prausnitz J. M.: AIChE J. *13*, 896 (1967).
4. Chueh P. L., Prausnitz J. M.: Ind. Eng. Chem., Fundam. *6*, 492 (1967).
5. Chueh P. L., Prausnitz J. M.: Ind. Chem. *60*, No 3, 34 (1968).
6. Joffe J., Zudkevitch D.: Ind. Eng. Chem., Fundam. *5*, 455 (1966).
7. Joffe J.: Chem. Eng. Progr. *45*, 160 (1949).
8. Ott J. B., Goates J. R., Hall H. T.: J. Chem. Educ. *48*, 515 (1971).
9. Peng D. Y., Robinson D. B.: Ind. Eng. Chem., Fundam. *15*, 59 (1976).
10. Redlich O., Ngo V. B. T.: Ind. Eng. Chem., Fundam. *9*, 287 (1970).
11. Shah K. K., Thodos G.: Ind. Eng. Chem. *57*, No 3, 30 (1965).
12. Michels A., Lupton J. M., Wassenaar T., De Graff W.: Physica (Utrecht) *18*, 121 (1952).
13. Michels A., Goudeket M.: Physica (Utrecht) *8*, 347 (1941).
14. Michels A., Goudeket M.: Physica (Utrecht) *8*, 353 (1941).
15. Foulkes P.: Physica (Utrecht) *17*, 943 (1951).