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AN IMPROVED EQUATION OF STATE

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May 1969

Abstract

Repeatedly attempts have been made in the last twenty years to improve the equation of state of Redlich and Kwong by introduction of a third parameter. A new improvement systematically attacks the principal shortcoming of the old equation, namely, its failure near the critical point.

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The general problem of an equation of state suitable for practical applications has been repeatedly discussed. Various authors (Joffe and Zudkevich, 1961. Wilson, 1966. Chueh and Prausnitz, 1967, 1968; and others) applied and modified the equation of Redlich and Kwong (1949). The two main problems have always been to make the equation more flexible by introduction of a third parameter, and to obtain an improved representation of the neighborhood of the critical point. At the same time, the good behavior of the old equation at high pressures and at high temperatures was to be conserved. Any new equation should also be cubic in the volume, at least in its principal terms.

In two previous attempts (Redlich and Dunlop, 1963; Redlich, et. al., 1965), the improvement was achieved by adding a function of temperature and pressure to the compressibility factor Z_k computed by the old equation. Stringent conditions for this function could be formulated and the simplest suitable function resulted from a rather cumbersome comparison with observed data. The disadvantage was the complicated nature of the additional functions although they contained only a single individual parameter in addition to the critical temperature and pressure. It is difficult to ascertain the "reasonable" behavior of a complicated function in the whole range of the two independent variables and the three individual parameters. The purely technical difficulties in the extension of such an equation to mixtures and the derivation of fugacity coefficients are considerable.

Pure Substances

In numerous, fairly systematic attempts to modify the old equation directly rather than by additional terms we were entirely unsuccessful. Finally, the two main problems were solved in the following manner. As the third parameter the critical compressibility factor Z_c has been chosen since the improvement in the region around the critical point is a primary objective. At the same time the critical relations

$$(dP/dV)_c = 0; \qquad (d^2P/dV^2)_c = 0 \tag{1}$$

should furnish as simple relations as the old equation for expressing the other two parameters by T_c and P_c. These conditions can be satisfied by introduction of two functions L and G of the reduced temperature and volume into the old equation. The improved equation

$$P = RT(1-L)/(V-b) - a(1-G)/[T^{0.5}V(V+b)] \tag{2}$$

satisfies the requirements if at the critical point

$$L = 1 - 3Z_c; \qquad (dL/dV)_T = 0; \qquad (d^2L/dV^2)_T = 0 \tag{3}$$

$$G = 0; \qquad (dG/dV)_T = 0; \qquad (d^2G/dV^2)_T = 0 \quad . \tag{4}$$

These conditions in turn can be satisfied if L and G depend on V only through the intermediate variable

$$s = 3V_c/V - 3(V_c/V)^2 + (V_c/V)^3 \quad . \tag{5}$$

Various other conditions must be observed: Both L and G must disappear at high temperature, they must be finite at high pressure, and they must not interfere with the existence of a second virial coefficient (linear dependence of Z on P at low pressures is required at any temperature).

All these conditions are satisfied, and considerable flexibility is obtained by the functions

$$L = (c_3+s-c_3s)c_1 \log(1+c_2s) \tag{6}$$

$$G = c_4\log[1+c_5s^2(s-1)^2] \quad . \tag{7}$$

The coefficient c_3 is chosen

$$c_3 = 1 \text{ for } s \geq 1 \quad . \tag{8}$$

The correct value Z_c for the critical compressibility factor is obtained with

$$c_2 = \exp[2.303(1-3Z_c)/c_1] - 1 \; . \tag{9}$$

The coefficients c_1 to c_5 are functions of the temperature. A satisfactory representation of experimental data and of the tables of Pitzer and his coworkers was obtained with the following values:

$$c_1 = 0.1/[1+2.06(T_r-1)] \tag{10}$$

$$c_3 = 1.43/T_r^{1.5} - 1.32 \text{ (for } s \leq 1) \tag{11}$$

$$c_4 = 0.95[1.21+2.74(T_r-1)]/(1+0.1T_r)^2 \tag{12}$$

$$c_5 = 0.085[1.21+4.34(T_r-1)]/(1+0.1T_r)^2 \quad . \tag{13}$$

With

$$A = Z_c^2P_r/(0.25992106T_r^{2.5}) \tag{14}$$

$$B = 0.25992106Z_cP_r/T_r \tag{15}$$

one can represent eqn. (2) in the standard form

$$Z_M^3 - Z_M^2(1-L) + Z_M[A(1-G) - B(1-L) - B^2] - AB(1-G) = 0 \quad . \tag{16}$$

All coefficients are given by eqns. (6) to (15). The equation is solved for Z_M by a trial and error procedure. One may start with $L = 0$ and $G = 0$. A better starting point is the solution Z_K of the equation of Redlich and Kwong. One introduces the first approximation for Z into eqn. (5) by means of

$$V_c/V = P_rZ_c/(T_rZ) \quad , \tag{17}$$

computes L and G, recalculates the coefficients of (16), and obtains a second approximation by solving the cubic equation again. The straightforward procedure leads often to a periodic repetition of a set of divergent numbers. This is avoided by "damping" the approximation, i.e., choosing for Z in (17) a value between the last and the last-but-one result.

Above the critical temperature the results were unsatisfactory, worse than the results of Redlich and Kwong. We mixed the results calculating $c_{12}Z_M + (1-c_{12})Z_K$, using a "mixing factor"

$$c_{12} = 1 - \exp[-0.05/(T_r - 1)] \quad (\text{for } T_r \geq 1.02) \tag{18}$$

$$c_{12} = 1 \quad (\text{for } T_r < 1.02) \ . \tag{19}$$

This improvement was not yet satisfactory. So we added the deviation function

$$Z_D = P_r(T_r - 1)[(3.281 - 11.1Z_c)(T_r^3 - 2.6T_r + 2.6) + \{(4.36 - 15Z_c)T_r - 6.70 + 21.3Z_c\}P_r^{0.5}]/(T_r^6 + 0.4P_r^2) \tag{20}$$

$$(\text{for } T_r \geq 1.02);$$

$$Z_D = 0 \quad (\text{for } T_r < 1.02) \ . \tag{21}$$

The final representation is now given by

$$Z = c_{12}Z_M + (1 - c_{12})Z_K + Z_D \ . \tag{22}$$

Fugacity Coefficients

The computation of the fugacity coefficient by

$$\ell n\emptyset = \int_0^P (Z-1)dP/P \tag{23}$$

can be carried out algebraically except for a small term involving L and G. This term must be integrated numerically. The computation therefore has been arranged for equal intervals in P (further subdivided for the integration) on arbitrarily chosen isothermals.

The calculation can be carried out separately for the three terms of (22) so that

$$\ell n\emptyset = c_{12}\ell n\emptyset_M + (1-c_{12})\ell n\emptyset_K + \ell n\emptyset_D \quad . \tag{24}$$

The second term is given by Redlich and Kwong as

$$\ell n\emptyset_K = Z_K - 1 - \ell n(Z_K - B_k P_r) - (A_k/B_k)\ell n(1 + B_k P_r/Z_K) \tag{25}$$

with

$$A_k = 0.6540/T_r^{1.25} \; ; \; B_k = 0.0867/T_r \quad . \tag{26}$$

For the computation of $\emptyset_M$ we introduce two small quantities ϵ and η by defining

Table I. Ethane (data by Sage and Lacey).

T_r	P_r	Z			ϕ			H/RT	
		R.K.	present calc.	obs.	R.K.	present calc.	obs.	present calc.	obs.
1.017	2.80	.452	.404	.4251	.353	.332	.343	-4.179	-3.824
	5.59	.773	.745	.7565	.267	.244	.255	-4.069	-3.906
	8.39	1.072	1.072	1.0714	.257	.234	.245	-3.964	-3.820
	11.18	1.360	1.386	1.3688	.273	.250	.261	-3.848	-3.674
	13.98	1.638	1.688	1.6530	.305	.281	.292	-3.670	-3.507
1.344	2.80	.698	.693	.7010	.690	.701	.704	-1.479	-1.452
	5.59	.819	.807	.8114	.573	.579	.582	-2.066	-2.080
	8.39	1.024	1.012	1.0298	.553	.556	.561	-2.175	-2.186
	11.18	1.235	1.226	1.2576	.574	.575	.585	-2.148	-2.165
	13.98	1.444	1.439	1.4799	.618	.618	.634	-2.056	-2.093
1.671	2.80	.874	.885	.8937	.852	.877	.878	-0.688	-0.712
	5.59	.914	.928	.9334	.784	.813	.818	-1.124	-1.131
	8.39	1.043	1.052	1.0658	.774	.808	.816	-1.301	-1.296
	11.18	1.196	1.202	1.2332	.800	.837	.850	-1.351	-1.326
	13.98	1.355	1.359	1.4050	.850	.890	.912	-1.334	-1.307

Table II. Sulfur Dioxide (Data by Kang).

T_r	P_r	Z			∅		
		R.K.	present calc.	obs.	R.K.	present calc.	obs.
1.000	.964	.476	.449	.4473	.679	.668	.67
	1.928	.340	.278	.2869	.416	.388	.40
	2.892	.459	.394	.4020	.325	.296	.31
	3.856	.575	.508	.5086	.283	.253	.26
1.215	.964	.803	.809	.8231	.826	.852	.84
	1.928	.614	.601	.6461	.677	.697	.70
	2.892	.584	.568	.5760	.573	.586	.60
	3.856	.643	.620	.6148	.512	.521	.53

$$Z_M = Z_M/(Z_M-BP_r) - AP_r/(Z_M+BP_r) + \epsilon$$

$$\ell n\phi_M = Z_M - 1 - \ell n(Z_M-BP_r) - (A/B)\ell n(1+BP_r/Z_M) + \eta \quad . \tag{27}$$

Differentiating the last equation, we obtain in view of (23) an expression containing $d\eta/dP_r$ for

$$d\ell n\phi_M/dP_r = (Z_M-1)/P_r \quad . \tag{28}$$

Using (16), one finally arrives at

$$\eta = \int_0^{P_r} (\epsilon Z_M/P_r)d(P_r/Z) \tag{29}$$

with

$$\epsilon = AG/(Z_M+B) - Z_M L/(Z_M-B) \quad . \tag{30}$$

This minor term is computed by numerical integration.

For the integration of the last term in (24)

$$\ell n\phi_D = \int_0^{P_r} (Z_D/P_r)dP_r \quad , \tag{31}$$

with Z_D given by (20), we introduce the abbreviations

$$w = (0.40P_r^2/T_r^6)^{0.25} \tag{32}$$

$$E_A = (3.281-11.10Z_M)(T_r^3-2.6T_r+2.6)(T_r-1)/(0.632456T_r^3) \tag{33}$$

$$E_B = (3.281-11.10Z_M)[(4.36-15.0Z_M)T_r-6.70+21.3Z_M](T_r-1)/T_r^6 \tag{34}$$

$$E_w = 0.17677[\ell n(1-w\sqrt{2}+w^2) - \ell n(1+w\sqrt{2}+w^2)$$

$$+ 2\tan^{-1}(w\sqrt{2}/[1-w^2])] \quad . \tag{35}$$

The result is

$$\ell n \phi_D = E_A \tan^{-1}(w^2) + 2E_B E_w T_r^{4.5}/0.40^{0.75} \quad . \tag{36}$$

With increasing pressure, w runs from 0 to 1 and higher so that the argument of $\tan^{-1}$ in (35) runs from 0 to $+\infty$ and then from $-\infty$ to 0. The $\tan^{-1}$ function is continuous but one has to add π to the fundamental value given by the computer in (35) whenever $w > 1$. The argument of $\tan^{-1}$ in (36) is always in the fundamental range.

The results are illustrated by Tables I and II. Ethane is quite well represented by the equation of Redlich and Kwong; the present equation hardly offers any improvement. But the new results are conspicuously better for sulfur dioxide.

Mixtures

The application of an equation of state to mixtures requires a "combination of parameters", i.e., a rule for computing the parameters A and B of eqns. (14) and (15) for a mixture. There appears to be a general consensus that the best rule (linearity for $A^{0.5}$ and B) is not good enough. In order to allow the introduction of a better combination, we define for a mixture with the mole fractions y_i the interaction coefficients λ_{ij} by

$$A = (\sum_i y_i A_i^{0.5} + \sum_{ij} y_i y_j \lambda_{ij})^2 \quad . \tag{37}$$

If data are available, the best values of the coefficients λ_{ij} can be found, with the aid of the computer program for the equation of state, by a trial and error procedure. If not, the best guess usually will be $\lambda_{ij}=0$.

The critical compressibility factor Z_c is always assumed to be linear in the mole fractions.

Equations (14) and (15) define now the pseudocritical values T_c and P_c of the mixture.

The further calculation does not differ from the procedure for a pure substance, except that ϕ is now the mean fugacity coefficient, defined by the individual fugacity coefficients ϕ_i as

$$\log \phi = \Sigma y_i \log \phi_i \quad . \tag{38}$$

The values of the ϕ_i are obtained (cf. Redlich 1965) according to

$$\log \phi_i = \log \phi + \partial \log \phi / \partial y_i - \sum_a y_a \partial \log \phi / \partial y_a \quad . \tag{39}$$

In the differentiation all mole fractions except the differentiation variable are kept constant. The computation is carried out numerically.

Numerical differentiation of $\ln \phi$ with respect to the temperature leads to the molal heat content and entropy.

The example shown in Table III illustrates the improvement for the mixture containing 0.1 mole n-butane and 0.9 mole carbon dioxide. The mixture containing 0.9 mole n-butane is about equally well represented by both equations.

The computer programs ES68Z (for pure substances, not including fugacity coefficients) and ES68M (for pure substances and mixtures, including fugacity coefficients) are described in detail in our Report, Lawrence Radiation Laboratory UCRL-19011 (1969).

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Table III. N-Butane(1) - Carbon Dioxide(2).
(Compressibility Factor Z. Data by Sage and Lacey)

T	P	$y_1 = 0.1$			$y_1 = 0.9$		
°R	psia	R.K.	present calc.	obs.	R.K.	present calc.	obs.
559.68	2000	.358	.304	.325	.550	.487	.510
	4000	.617	.564	.580	1.048	.933	.989
	6000	.860	.814	.821	1.523	1.352	1.448
	8000	1.091	1.055	1.051	1.982	1.752	1.891
	10000	1.315	1.288	1.272	2.432	2.137	2.324
919.68	2000	.875	.898	.912	.632	.615	.627
	4000	.859	.888	.906	.911	.887	.895
	6000	.933	.960	.973	1.206	1.185	1.199
	8000	1.042	1.063	1.079	1.494	1.478	1.493
	10000	1.163	1.178	1.199	1.775	1.764	1.782

Literature Cited

Chueh, P. L., and J. M. Prausnitz, AIChE Journ. 13, 896, 1099 (1967); Ind. Eng. Chem. Fundamentals, 6, 492 (1967).

Chueh, P. L., and J. M. Prausnitz, Ind. Eng. Chem. 60, No. 3, 34 (1968).

Joffe, J., and D. Zudkevich, Ind. Eng. Chem. Fundamentals, 5, 455 (1966).

Kang, T. L., Hirth, L. J., Kobe, K. A., and J. J. McKetta, J. Chem. Eng. Data, 6, 220 (1961).

Redlich, O., et al. Ind. Eng. Chem. Fundamentals 4, 396 (1965).

Redlich, O., and A. K. Dunlop, Chem. Eng. Progr., Symp. Ser. 59, No. 44, 95 (1963).

Redlich, O., and J. N. S. Kwong, Chem. Rev. 44, 233 (1949).

Sage, B. H., and W. N. Lacey, "Thermodynamic Properties of the Lighter Paraffin Hydrocarbons" New York, American Petroleum Institute (1950).

Sage, B. H., and W. N. Lacey, "Some Properties of the Lighter Hydrocarbons", New York, American Petroleum Institute (1955).

Wilson, G. M., Cryogenic Eng. 9, 168 (1964). 11, 392 (1966).