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Ernest O. Lawrence Radiation Laboratory

EFFICIENCY OF EQUATIONS OF STATE FOR GASEOUS MIXTURES AT THE CRITICAL LOCUS

I. APPLICATION OF THE EQUATION OF BENEDICT, WEBB, AND RUBIN

II. FURTHER IMPROVEMENTS OF AN EQUATION OF STATE

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UCRL-10650
UC-34 Physics
TID-4500 (19th Ed.)

Research and Development

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

Contract No. W-7405-eng-48

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Frank Jay Ackerman

(M. S. Thesis)

February 1, 1963

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ABSTRACT

The critical state of gaseous mixtures is of practical interest in high-pressure reactions and petroleum engineering. A discussion of the critical state is appropriately based on the equation of state and rigorous thermodynamic relations.

The present investigation compares the eight-parameter equation of state proposed by Benedict, Webb, and Rubin with observed data and a two-parameter equation of Redlich and Kwong. Contrary to expectation, the more elaborate equation furnishes sometimes entirely unreasonable results. This failure is related to the fact that the values of the eight parameters are in general not sufficiently well defined by observations in a limited range of temperature and pressure.

An algebraic equation of state is desirable because it leads shortly to fugacity coefficients, which are the practically important objective in the study of the variables of state. The first part of this thesis illustrates the advantages and shortcomings of the equation of Redlich and Kwong. The improved equation obtained in Part II comes close to the accuracy of Pitzer's tables and at the same time permits an algebraic derivation of fugacity coefficients.

PART I. APPLICATION OF THE EQUATION OF BENEDICT, WEBB, AND RUBIN

A. Introduction

It would be useful to have a reliable method of predicting the critical temperature and pressure of any gas mixture, particularly as a reference point for the purpose of interpolation and correlation. Several methods of estimation using generalized correlations have been proposed.[1,2] A broader basis for an estimation is furnished by a suitable equation of state.

The thermodynamic relations for the derivation of the critical state from an equation of state put the equation to a severe test because first and second derivatives are required, which are always more sensitive to deviations than the original function. Since many equations of state are not considered to be accurate in the critical region, their usefulness in a relation to find the critical state is questionable. Any equation considered must be applicable to mixtures as well as single components.

B. The Critical State

Redlich and Kister used an equation of state[3]

$$P = RT/(V-b) - a/[T^{0.5}V(V+b)],$$

to predict the critical properties of several gas mixtures.[4] Parameters a and b can be expressed in terms of the critical temperature T_C and the critical pressure P_C as

$$a = 0.4278\ R^2 T_C^{2.5}/P_C$$

and

$$b = 0.0867\ RT/P_C\ .$$

Their results were in reasonably fair agreement with experimental results; however, a more accurate prediction would be desirable. A better equation of state should furnish such results.

The eight-constant equation of Benedict, Webb, and Rubin[5] is used over considerable ranges of temperature and pressure to predict the properties of gases and gas mixtures. Benedict found that it described the critical state of pure components with reasonable accuracy for a number of gases within approximately 0.3°C and 0.4 atm of the experimental values.[5] Since Benedict's equation is generally well behaved for pure gases, it was expected that it would also furnish a good representation of the critical state for gas mixtures.

The critical state for a gas mixture is defined by:

$$(\partial\ \ell n\ f/\partial y_1)_{P,T} = 0 \tag{1a}$$

$$(\partial^2\ \ell n\ f/\partial y_1^2)_{PT} = 0\ . \tag{1b}$$

From these two equations one can derive the thermodynamic equations for the critical lines. The two resulting equations are complicated expressions in terms of various partial differential quotients which, in the case considered here, must be solved simultaneously to yield the critical volume and temperature. The critical pressure is then found by substituting back into the equation of state. The equations are unwieldy and the rigorous solution, even with automatic computation methods, would be prohibitively time-consuming.

C. The Limiting Slopes of the Critical Lines

Actually a more elegant solution can be found. The limiting slopes of the critical-pressure line and the critical-temperature line with respect to the composition at the end points of these lines can be rigorously derived. According to Redlich and Kister,[4] we have

$$(dT/dy_1)_c = [(y_1-y_2)(dP/dy_1)^2_{V,T}/RE-(d^2P/dVdy_1)_T]/(d^2P/dTdV)_y \tag{2a}$$

and

$$(dP/dy_1)_c = (dP/dy_1)_{V,T} + (dP/dT)_{V,y}(dT/dy)_c , \tag{2b}$$

where y_1 and y_2 are mole fractions. The use of these relations requires only partial derivatives of the equation of state at the end points of the critical lines, i.e., at the critical points of the pure components.

We use the equation of Benedict, Webb, and Rubin in the form

$$P = RTD + (B_0RT-A_0-C_0/T^2)D^2 + (bRT-a)D^3 + a\alpha D^6 + \frac{CD^3}{T^2}e^{-\gamma D^2} \times (1+\gamma D^2), \tag{3}$$

with

$$D = 1/V.$$

For a mixture, the eight constants are assumed to depend on the constants of the constituent gases according to

$$A_0^{1/2} = \sum_i y_i A_{0_i}^{1/2} ,$$

$$B_0 = \sum_i y_i B_{0_i} ,$$

$$C_0^{1/2} = \sum_i y_i C_{0_i}^{1/2} ,$$

$$a^{1/3} = \sum_i y_i a_i^{1/3} ,$$

$$b^{1/3} = \sum_i y_i b_i^{1/3} ,$$

$$c^{1/3} = \sum_i y_i c_i^{1/3} ,$$

$$\alpha^{1/3} = \sum_i y_i \alpha_i^{1/3} ,$$

and

$$\gamma^{1/2} = \sum_i y_i \gamma_i^{1/2} . \tag{4}$$

The derivatives required by Eqs. (2a) and (2b) are:

$$\left(\frac{dP}{dy_1}\right)_{V,T} = (RT B_0' - A_0' - C_0'/T^2) D^2 + (b'RT - a') D^3 + (a\alpha' + \alpha a')D^6 + [c'(1+\gamma D^2) - C\gamma\gamma' D^4] D^3 e^{-\gamma D^2}/T^2, \tag{5}$$

where

$$A_0' = \frac{dA_0}{dy_1} = 2 (y_1 A_{0_1}^{0.5} + y_2 A_{0_2}^{0.5}) (A_{0_1}^{0.5} - A_{0_2}^{0.5}), \text{ etc.}; \tag{6}$$

$$\left(\frac{d^2P}{dVdy_1}\right) = - D^3 \left\{2 (RT B_0' - A_0' - C_0'/T^2) + 3(b'RT - a') \times D + 6(a\alpha' + a'\alpha)D^4 + De^{-\gamma D^2}\left[C'(3+3\gamma D^2 - 2\gamma^2 D^4) - C\gamma\gamma' D^4(7 - 2\gamma D^2)\right]/T^2\right\}; \tag{7}$$

$$\left(\frac{dP}{dT}\right)_{V,Y} = RD + (B_0 R + 2C_0/T^3)D^2 + bRD^3 - 2CD^3 e^{-\gamma D^2} \times (1+\gamma D^2)/T^3; \tag{8}$$

$$\left(\frac{d^2P}{dTdV}\right)_y = - D^2 \left\{R + 2(B_0 R + 2C_0/T^3) D + 3bRD^2 - 2D^2 e^{-\gamma D^2}\left[3(1+\gamma D^2) + 2\gamma^2 D^4\right]/T^3\right\} . \tag{9}$$

From these equations one can find the value of the slope at the end points ($y_1 = 0$ and $y_1 = 1$) of the critical-temperature and critical-pressure lines.

D. Interpolation

The full critical-pressure and critical-temperature lines can now be approximately determined by means of an interpolation formula. As previously observed by Redlich and Kister,[4] it was found that a logarithmic-hyperbolic interpolation formula gives a reasonable approximation.

For the critical-pressure line, we abbreviate

$$p_1 = \lim_{y_1 \to 1} (dP/dy_1)_c \tag{10}$$

and

$$p_2 = \lim_{y_1 \to 0} (dP/dy_1)_c \, . \tag{11}$$

The interpolation formula is then

$$\ln P = y_1 \ln P_1 + y_2 \ln P_2 + \frac{(\ln P_1 - \ln P_2 - p_2/P_2)(\ln P_1 - \ln P_2 - p_1/P_1) y_1 y_2}{(\ln P_1 - \ln P_2 - p_2/P_2) y_1 - (\ln P_1 - \ln P_2 - p_1/P_1) y_2} \, . \tag{12}$$

If we replace P and p by T and t in Eqs. (10), (11), and (12), we have the formula used to calculate the critical-temperature line.

E. Results

With the available coefficients required in Eqs. (5) to (9), the critical temperatures and pressures as functions of the composition were obtained from Eq. (12) by automatic computation. For a comparison the critical lines were also calculated by means of Redlich and Kwong's equation of state.[3] The equations used are given by Redlich and Kister.[4] Results obtained from the calculations were compared with experimental data for 26 binary mixtures (methane with ethane, propane, n-butane, isobutane, pentane, heptane, decane, and nitrogen; ethane with propane, propene, butane, pentane, heptane, decane, benzene, and nitrogen; propane with butane, n-pentane, isopentane, benzene, and carbon dioxide; propene with 1-butene; butane with carbon dioxide; pentane with heptane and carbon dioxide; and carbon dioxide with sulfur dioxide). These results are presented in the figures.

Several sets of coefficients given by Opfell et al.[6] contain negative values for coefficients to be combined by the square-root formula (see Eq. 4). These sets have not been considered in the following.

F. Discussion and Conclusions

An extensive comparison of the presented results does not reveal a clear advantage of either the equation of Benedict, Webb, and Rubin or that of Redlich and Kwong. This general result can be illustrated by examining some examples.

The critical-temperature line is always very well represented by either equation, Fig. 1 being a typical example. No further discussion of the critical temperature is necessary therefore.

The suitability of either equation, however, varies greatly for the critical-pressure lines of various systems. For many substances various authors have derived different sets of Benedict coefficients (Appendix C). At first we consider only those values of Benedict-Webb-Rubin coefficients that give the best fit. In certain cases the two equations are in good agreement with each other and with experimental data (Figs. 2, 5, 18, and 24). Sometimes the equation of Redlich and Kwong is better (Figs. 6 and 7); more often the better equation is that of Benedict et al. (Figs. 3, 4, 10, 12, 13, 16, 17, 19, 20, 22, and 25). In a few cases neither is very good (Figs. 8, 14, 15, and 26).

Considering now all proposed sets of Benedict coefficients, one finds the overall picture to be quite different. According to Figs. 2, 5, 8, 9, 10, 11, 18, 21, 24, and 26, one set is frequently in good agreement with Redlich and Kwong's equation. The deviations from the experimental data may be small (Figs. 2, 5, 18, and 24) or appreciable (Figs. 8, 9, 10, 11, 21, and 26). In many cases, some set of Benedict coefficients leads to larger deviations than does the equation of Redlich and Kwong (Figs. 2, 3, 4, 6, 7, 8, 12, 13, 17, 18, 21, 23, 24, 25, and 26). The slopes calculated from a few sets of Benedict constants are so far off that the interpolated curves are quite unreasonable (Figs. 13, 17, 18, 21, 25, and 26). These discrepancies are obviously due to entirely wrong values of one or both of the limiting slopes. In view of the thermodynamic connection of these slopes with the equation of state, the error lies with the coefficients, the assumed composition dependence of the coefficients, or both.

Unquestionably the sixteen coefficients of the equation of Benedict et al. for binary mixtures can be chosen so that the critical lines are very well represented. However, the present study shows that the coefficients derived by previous authors from data in different ranges do not always give a good representation of the critical range, and sometimes, indeed, lead to entirely wrong results. A comparison of the two equations as applied to the heat content of gaseous mixtures leads to similar conclusions.[7]

The difficulty of adjusting a set of coefficients to all available data has been pointed out before.[6] The coefficients first derived by Benedict et al. are in general the best (curves A in Figs. 2, 3, 6, 12, and 24).[5] Opfell et al. recommend their coefficients only for the homogeneous region,[8] but their coefficients fit the data for ethane-propane better than the set of Benedict et al. (Fig. 10), though usually the opposite is true (Figs. 3, 6, 12, 13, 17, and 18). The wide variation of curves obtained from different sets of coefficients is illustrated in Figs. 23, 25, and 26.

The cause of the unexpected disadvantage of Benedict's equation in the present attempted application is really deep-seated. It results from the excessive number of coefficients in this equation. Of course, such an equation is supremely capable of being adapted to observations, but it is likely to lead to unreasonable results as soon as the region of observations is left behind.

The conclusion that a crude two-parameter equation is more reliable appears ridiculous at first. Yet there is much less danger of entirely unreasonable results, since the simpler function is necessarily restricted. The lesser adaptability and flexibility is actually an advantage in extending computations beyond the region of direct observation. As a matter of fact, the deviations resulting from the equation of Redlich and Kwong are seldom as high as in Fig. 8 and never unreasonable. They are usually small for two similar components (Figs. 2, 18, and 24).

It may be concluded that the use of the equation of Benedict et al. for the critical properties can be recommended only if a method for the determination of the coefficients is found that is more definite than methods used to now.

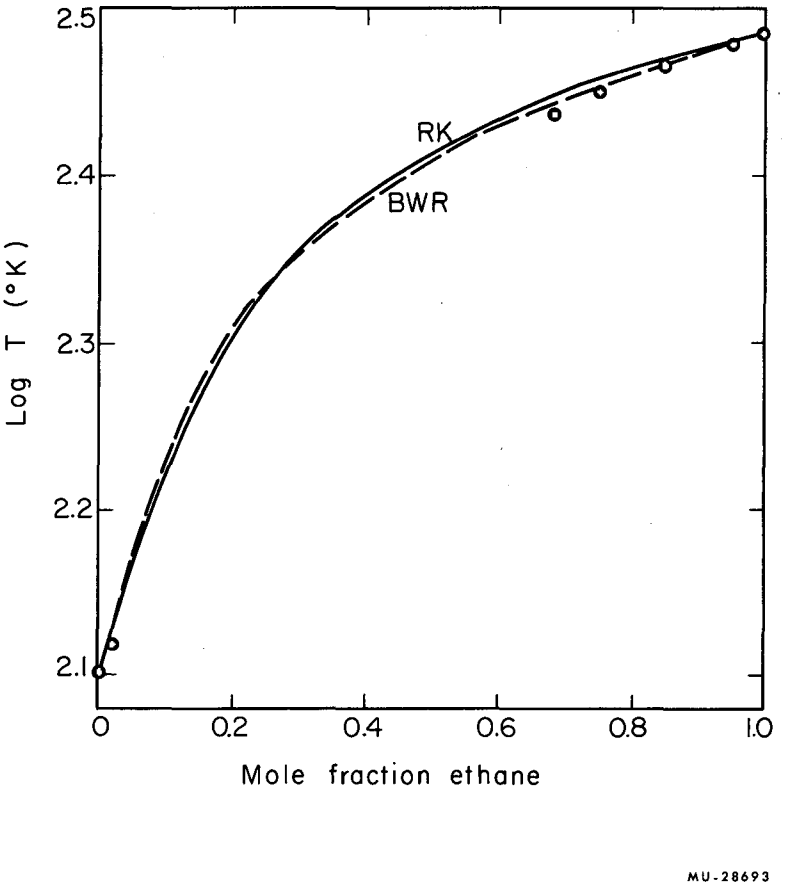

Fig. 1. Critical locus (temperature) of ethane-nitrogen[9] (full line: Redlich and Kwong; broken line: Benedict coeff.[5,10]).

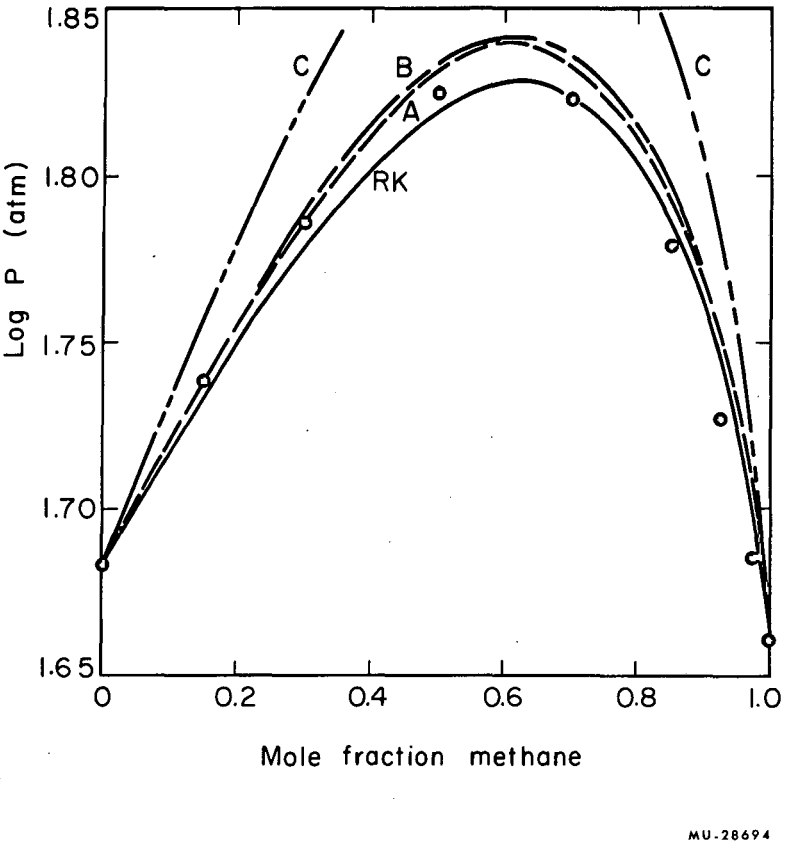

Fig. 2. Critical locus (pressure) of methane-ethane[9] (Benedict coeff. A[5], C[8], B: methane,[5] ethane[11]).

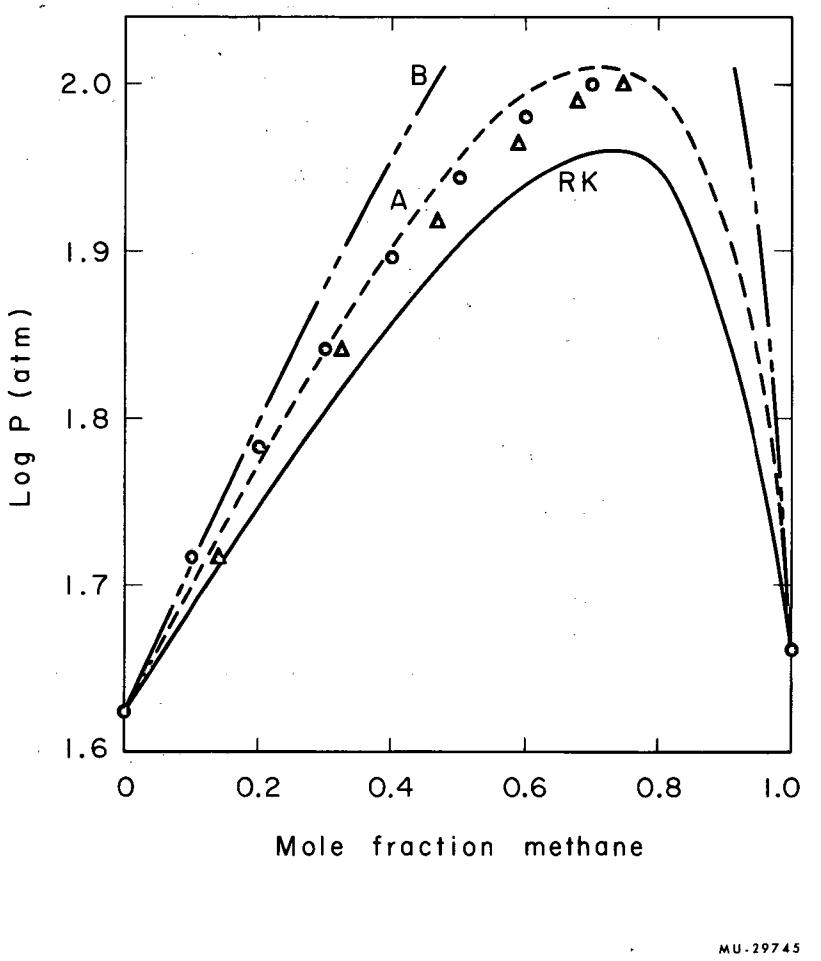

Fig. 3. Critical pressure of methane-propane; Δ[12], O[13] (Benedict coeff. A[5], B[8]).

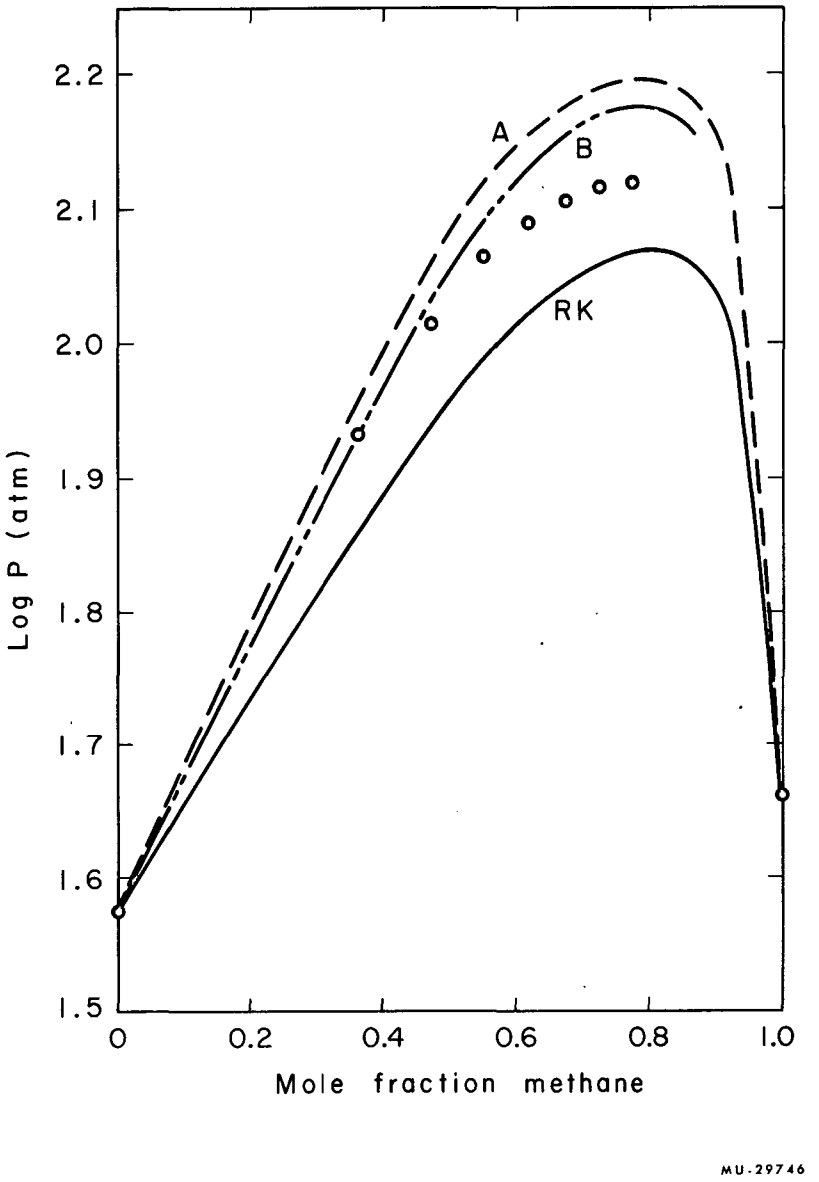

Fig. 4. Critical pressure of methane-butane[14] (Benedict coeff., A[5], B[8]).

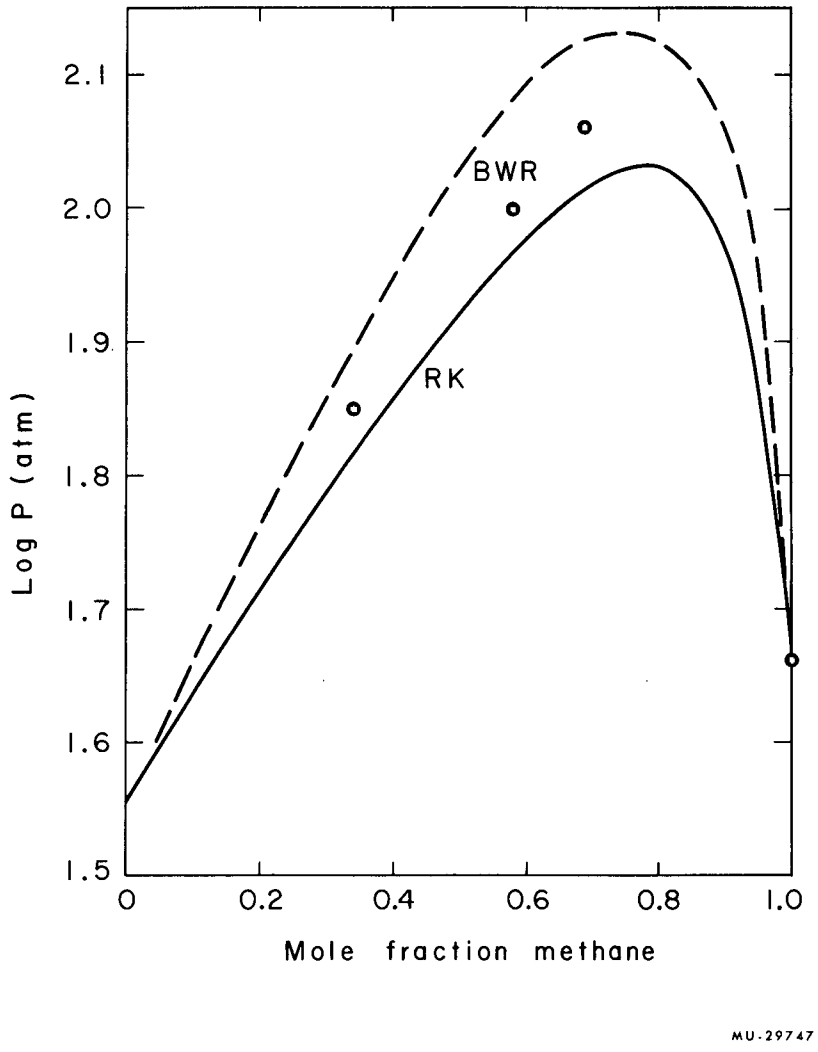

Fig. 5. Critical pressure of methane-isobutane[15] (Benedict coeff.[5]).

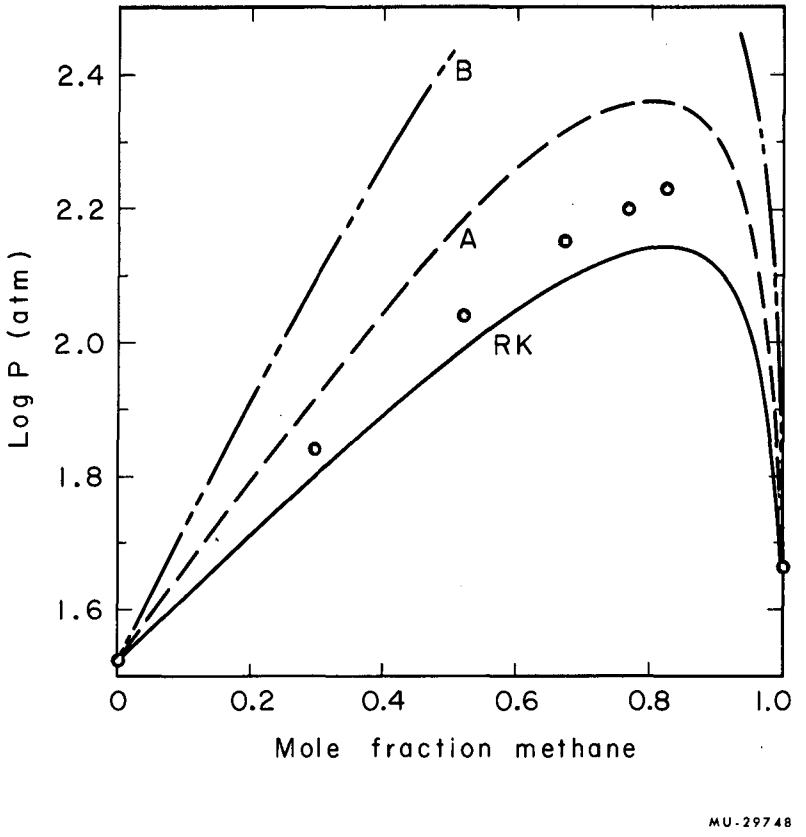

Fig. 6. Critical pressure of methane-pentane[16] (Benedict coeff. A[5], B[8]).

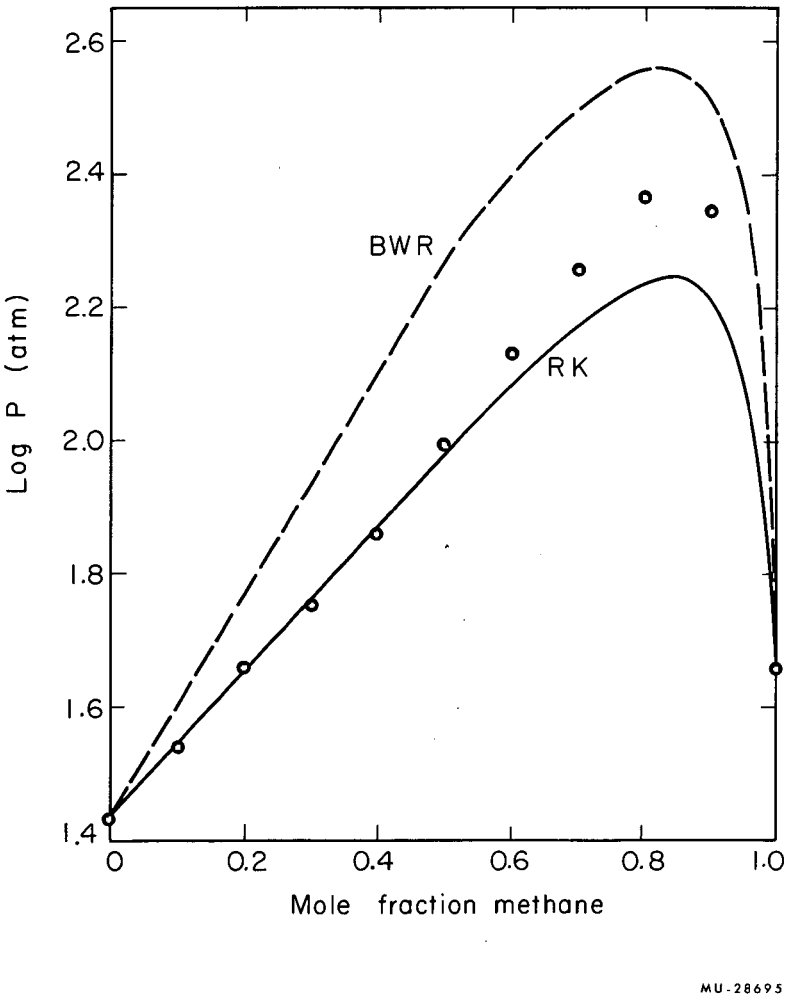

Fig. 7. Critical pressure of methane-heptane[17] (Benedict coeff.[5]).

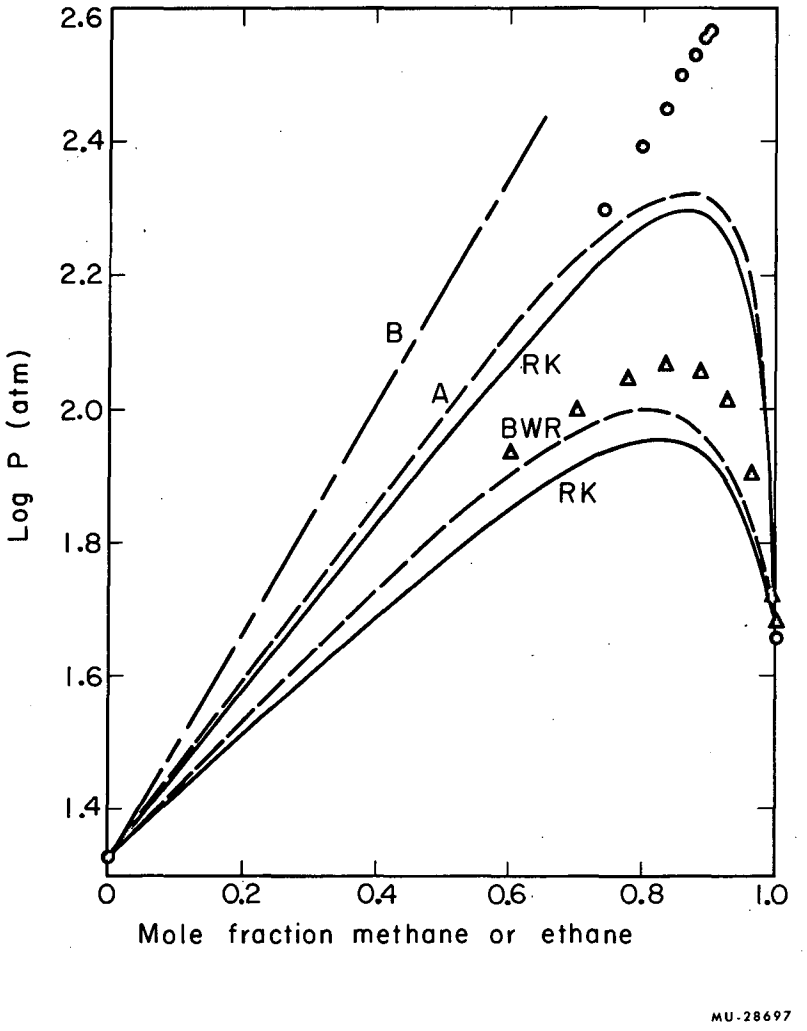

Fig. 8. Critical pressure of methane-decane[18] [Benedict coeff. for methane;[5] decane: A[6] (γ = 0.4) B[6] ($\gamma = \infty$)] and ethane-decane[19] [Benedict coeff. for methane;[5] decane[6] (γ = 0.4)].

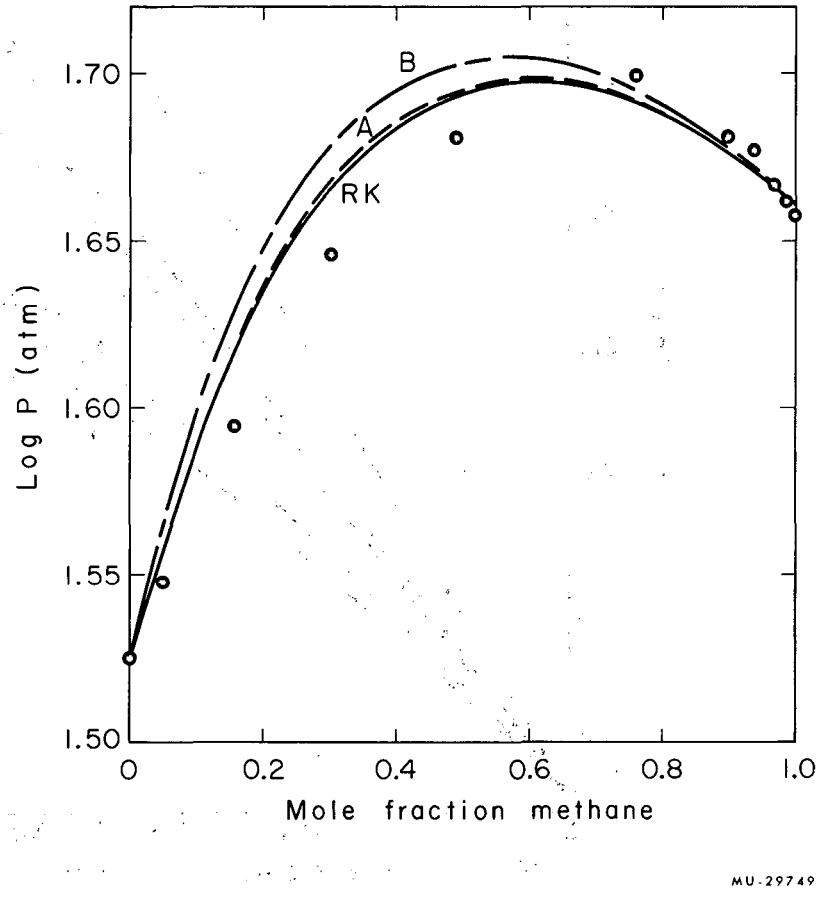

Fig. 9. Critical pressure of methane-nitrogen[20] (Benedict coeff. for methane;[5] for ethane: A[21], B[10]).

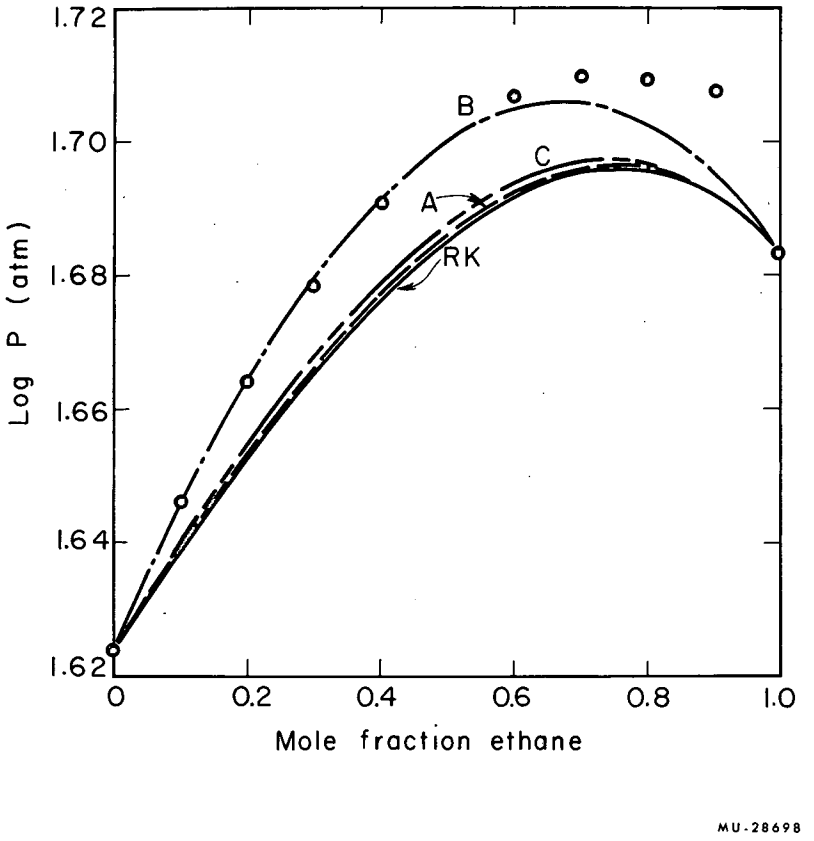

Fig. 10 Critical pressure of ethane-propane[22] (Benedict coeff. A[5], B[8], C: ethane[11], propane[5]).

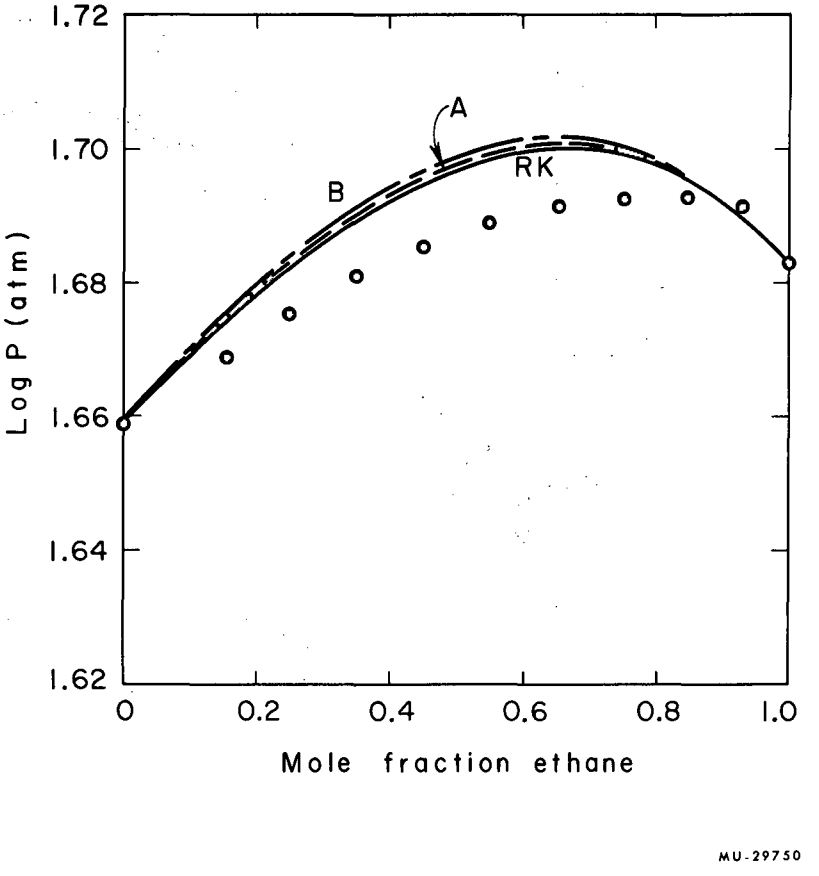

Fig. 11. Critical pressure of ethane-propene[23] (Benedict coeff. A[5], B: ethane[11], propene[5]).

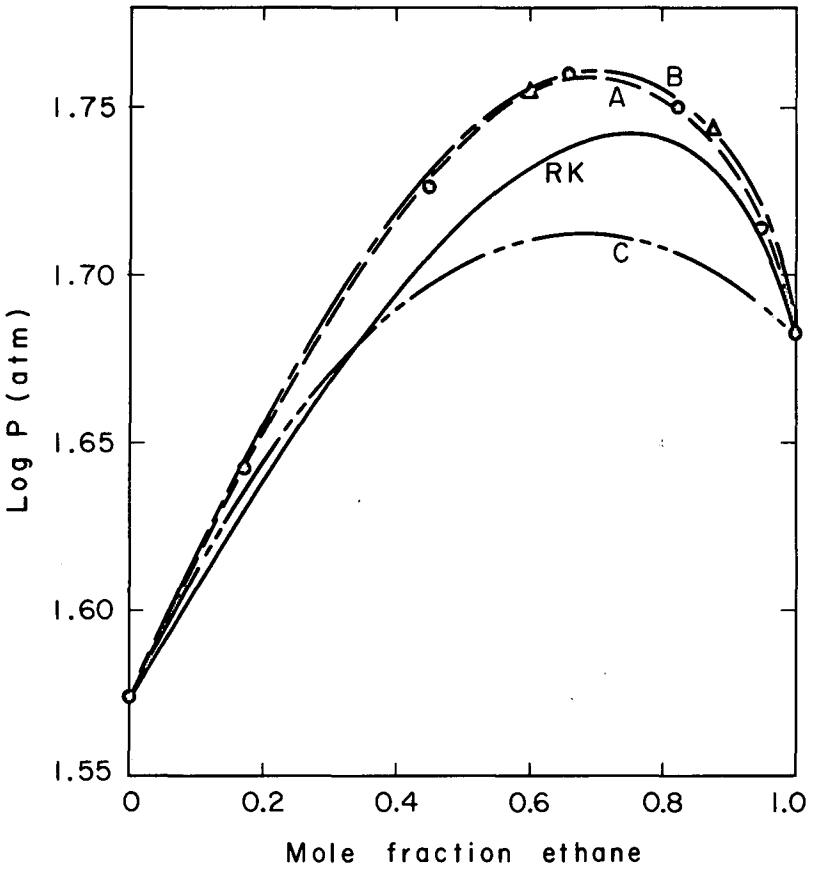

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Fig. 12. Critical pressure of ethane-butane; O[24], Δ[25] (Benedict coeff. A[5], C[8], B: ethane[11], butane[5]).

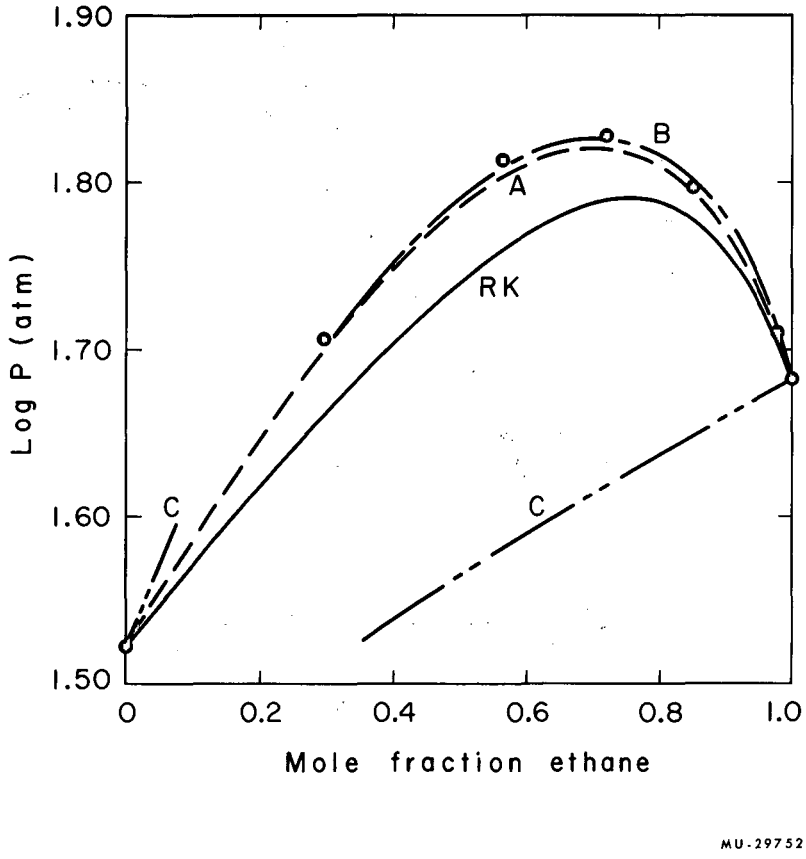

Fig. 13. Critical pressure of ethane-pentane[26] (Benedict coeff. A[5], C[8], B: ethane[11], propene[5]).

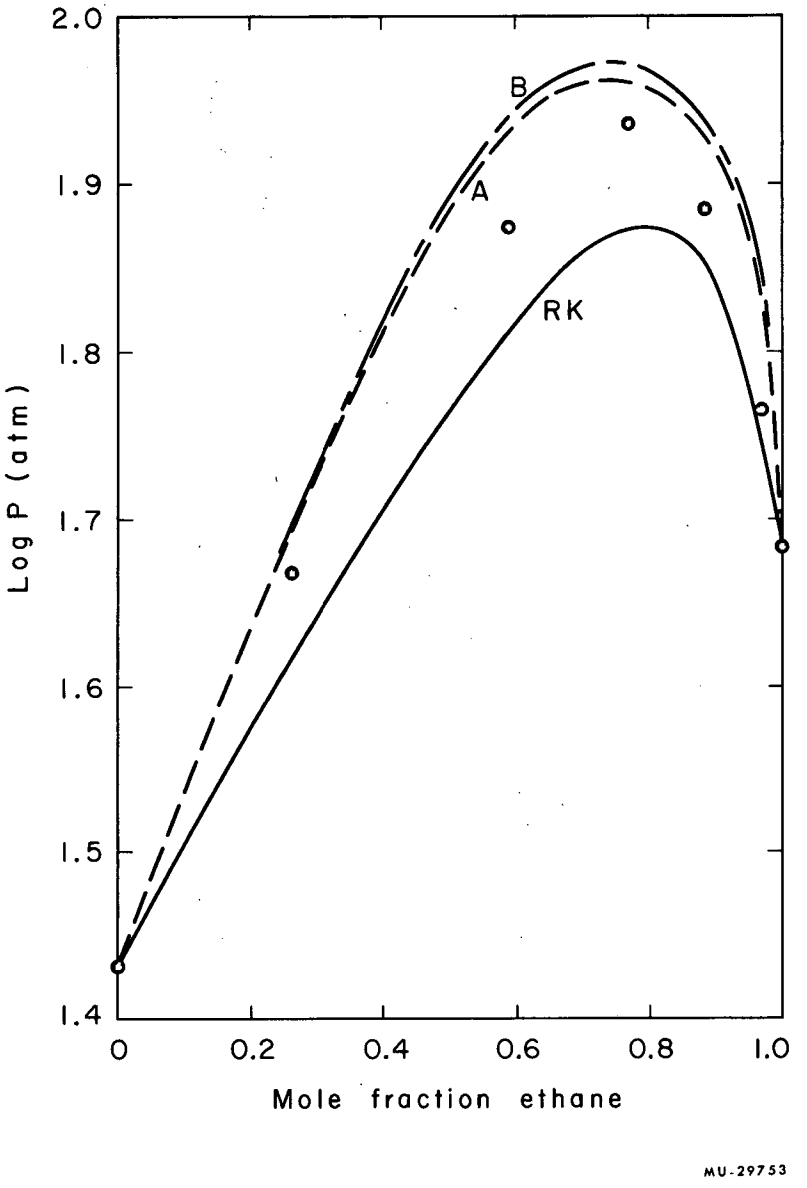

Fig. 14. Critical pressure of ethane-heptane[27] (Benedict coeff. A[5], B: ethane[11], propene[5]).

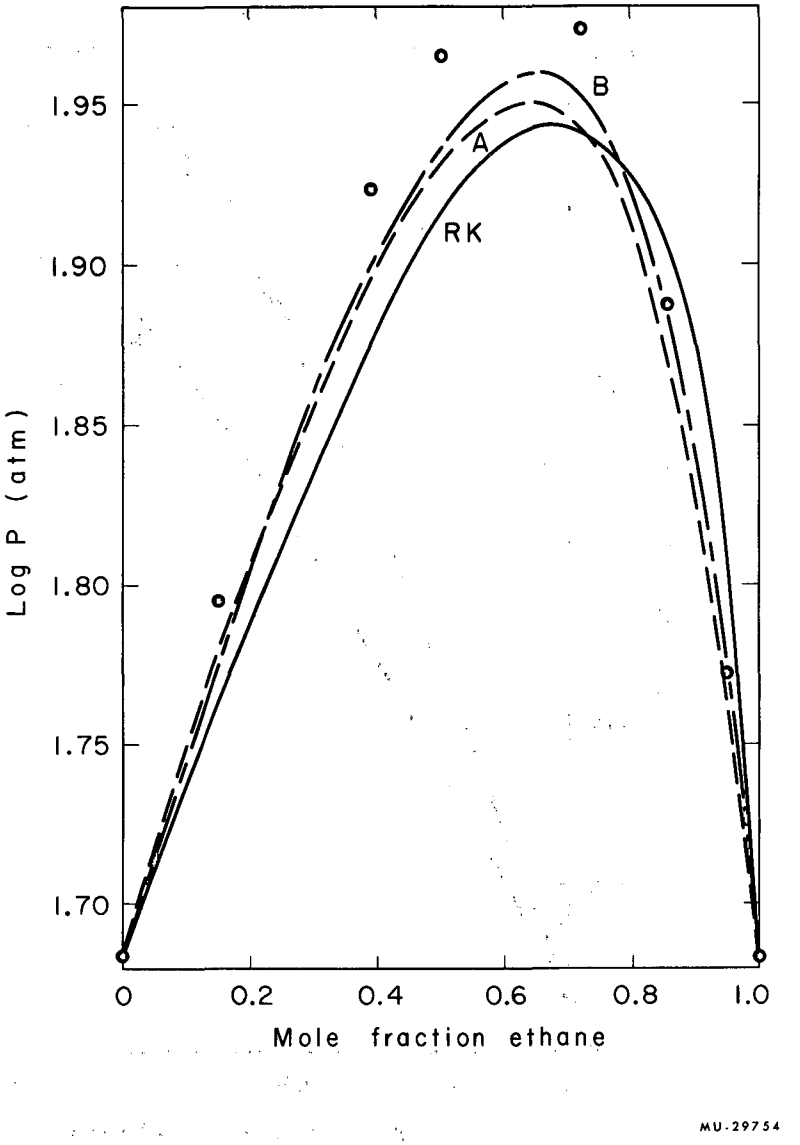

Fig. 15. Critical pressure of ethane-benzene[28] (Benedict coeff. for ethane: A[5], B[11], for benzene[29]).

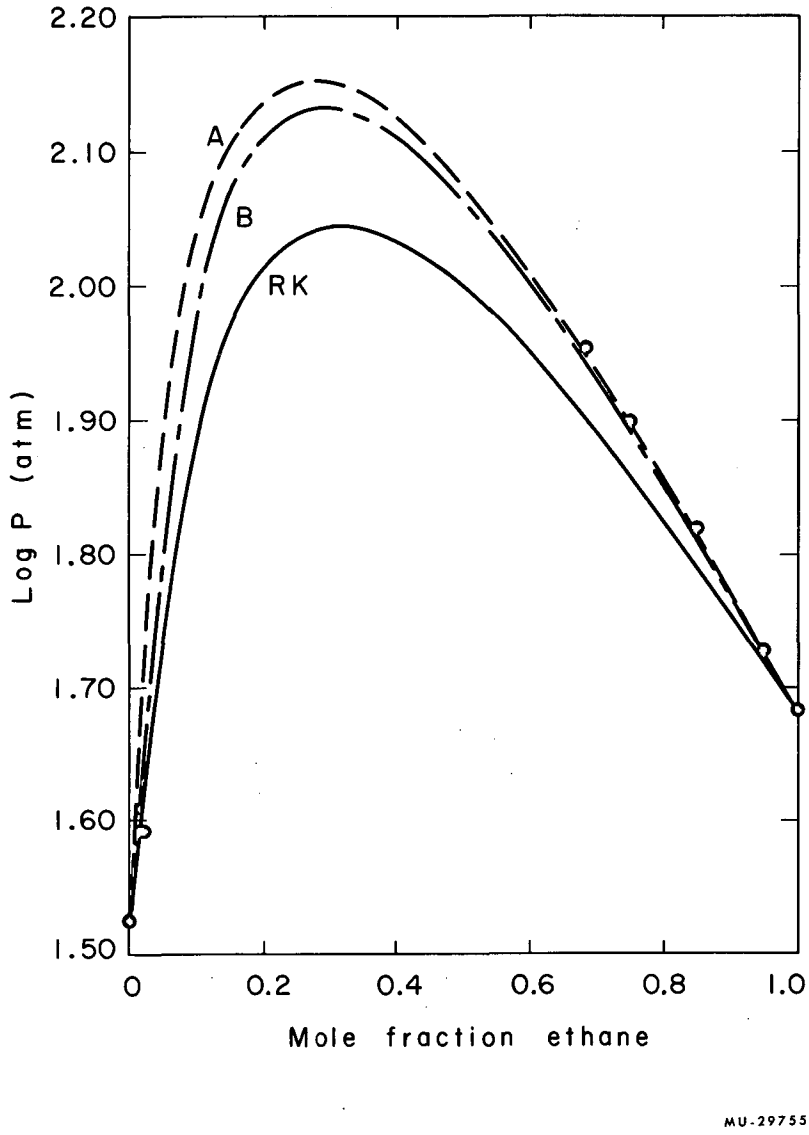

Fig. 16. Critical pressure of ethane-nitrogen[9] (Benedict coeff. for ethane[11]; for nitrogen: A[10], B[21]).

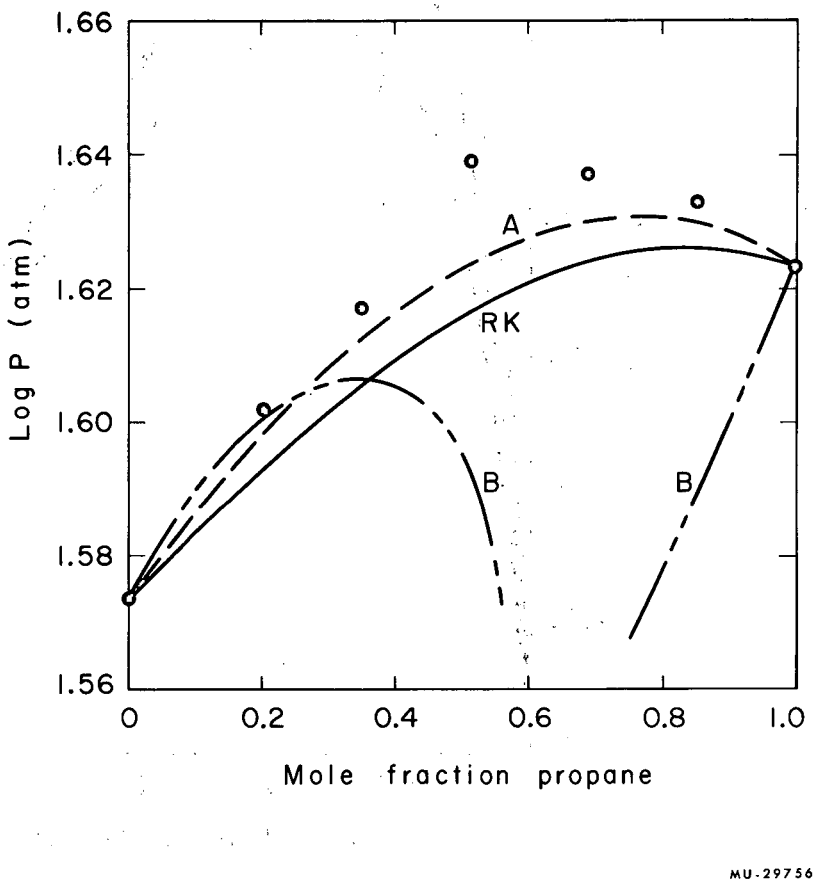

Fig. 17. Critical pressure of propane-butane[30] (Benedict coeff. A[5], B[8]).

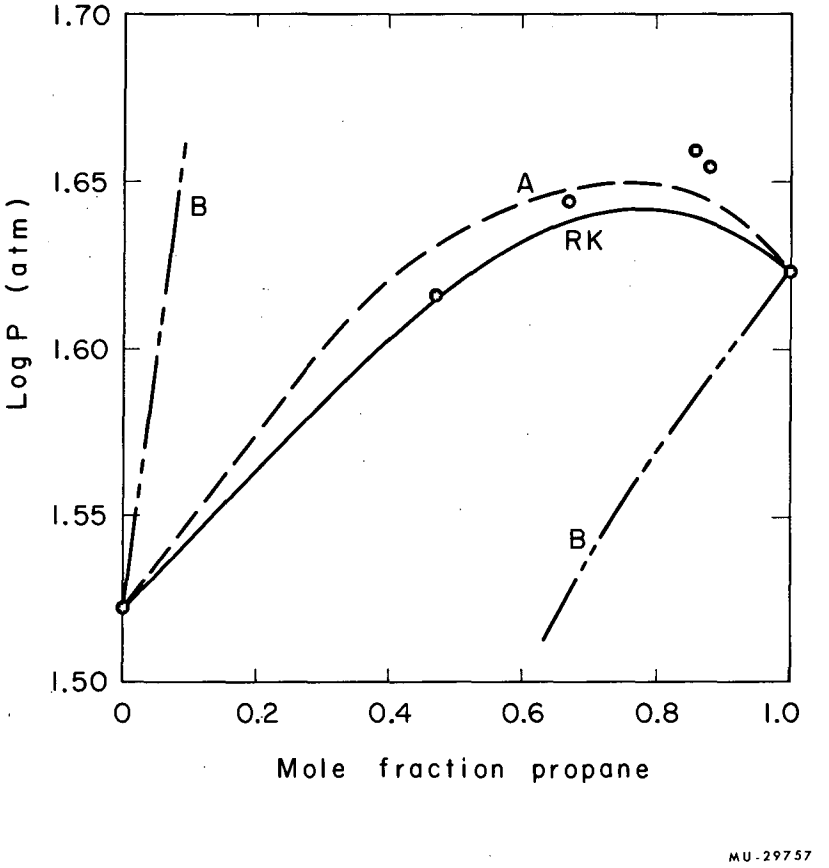

Fig. 18. Critical pressure of propane-pentane[31] (Benedict coeff. A[5], B[8]).

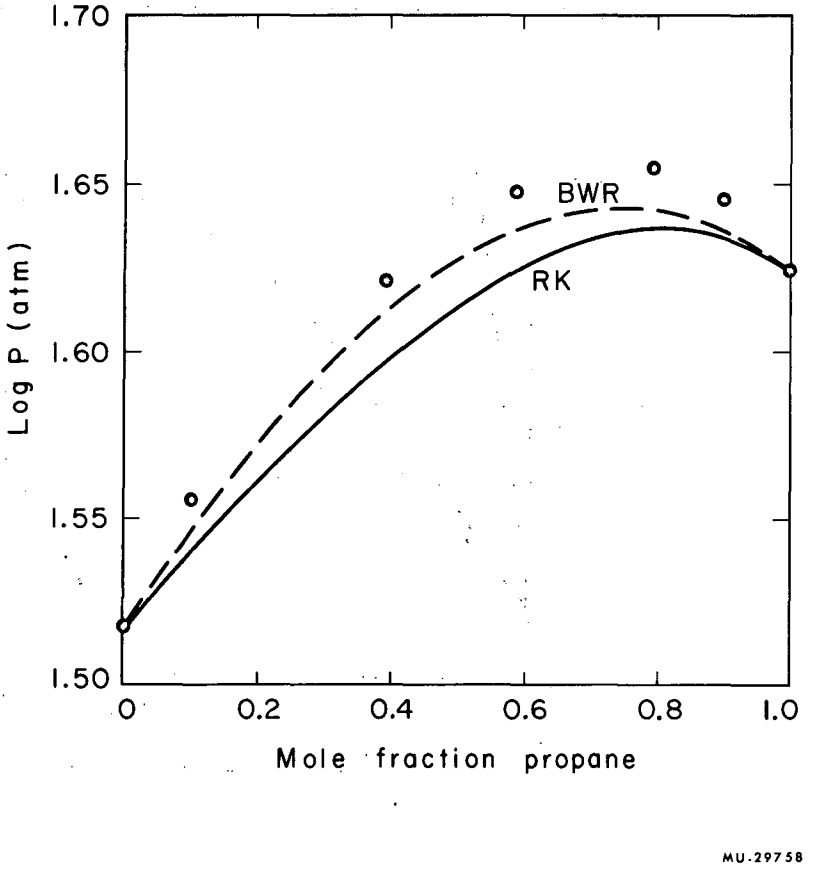

Fig. 19. Critical pressure of propane-isopentane[32] (Benedict coeff. [5]).

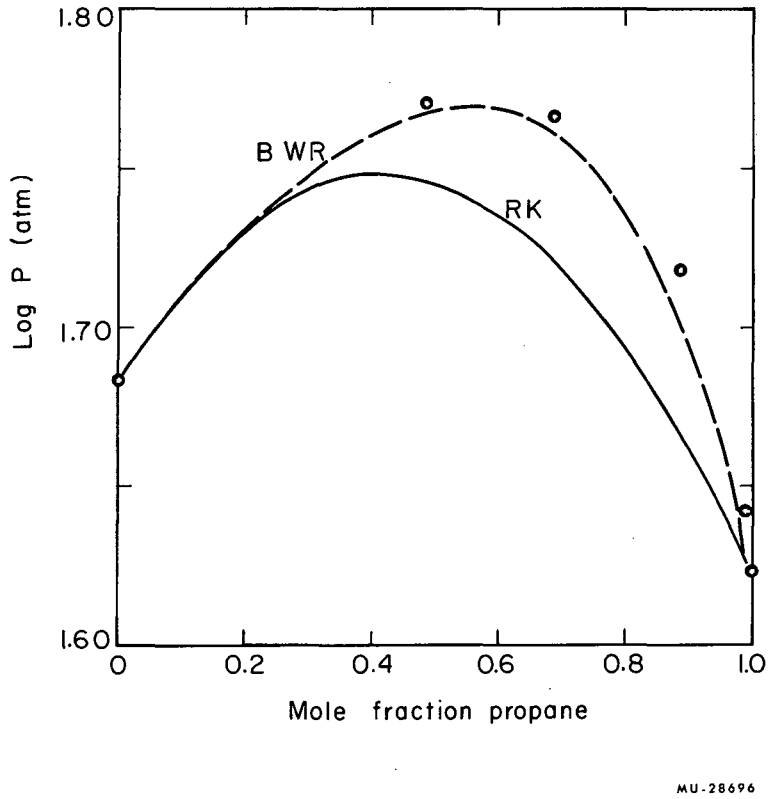

Fig. 20. Critical pressure of propane-benzene[33] (Benedict coeff. for propane[5]; benzene[29]).

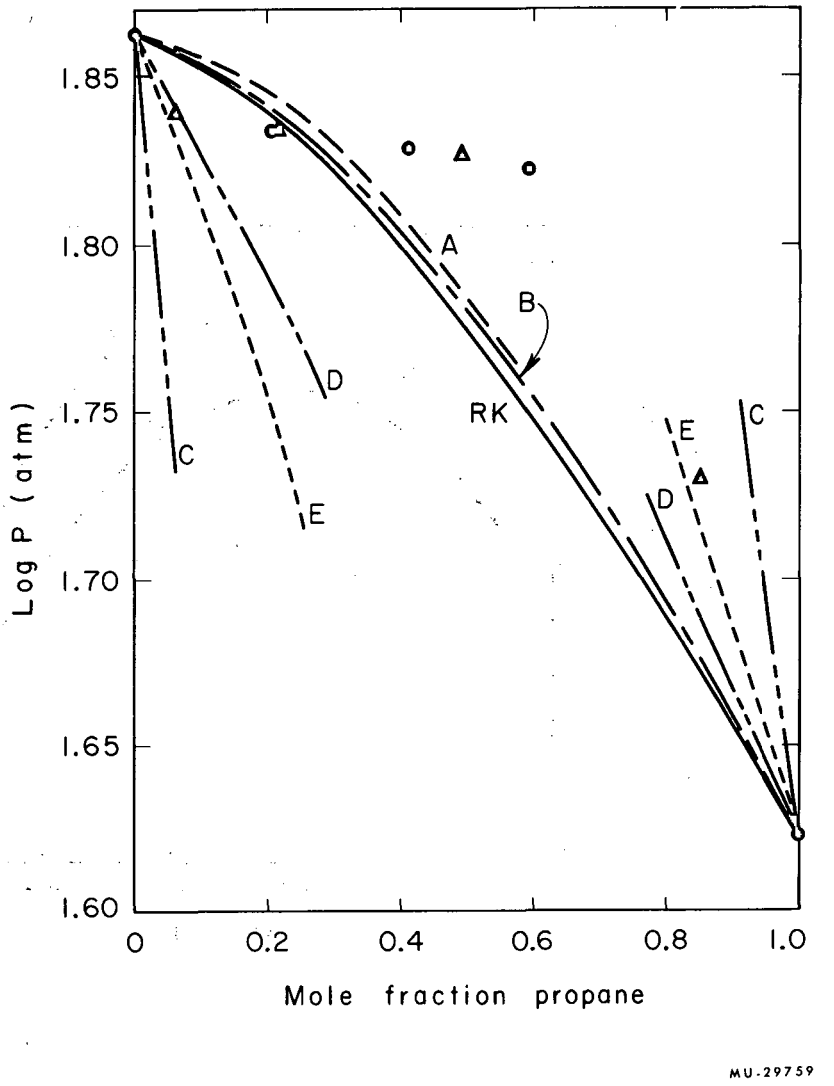

Fig. 21. Critical pressure of propane-carbon dioxide; O[34] Δ[35] [Benedict coeff. for propane[5]; for carbon dioxide: A[36] (set A), B[36] (set B), C[9] (set II), D[11], E[9] (set I)].

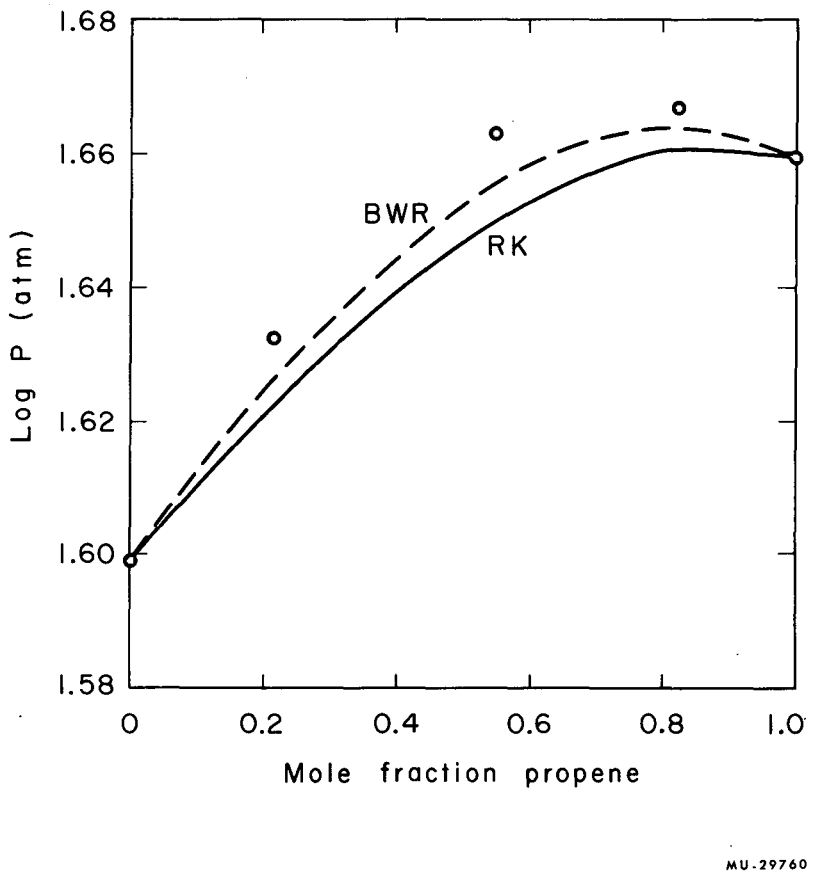

Fig. 22. Critical pressure of propene - 1-butene[37] (Benedict coeff. for propene[5]; 1-butene[38]).

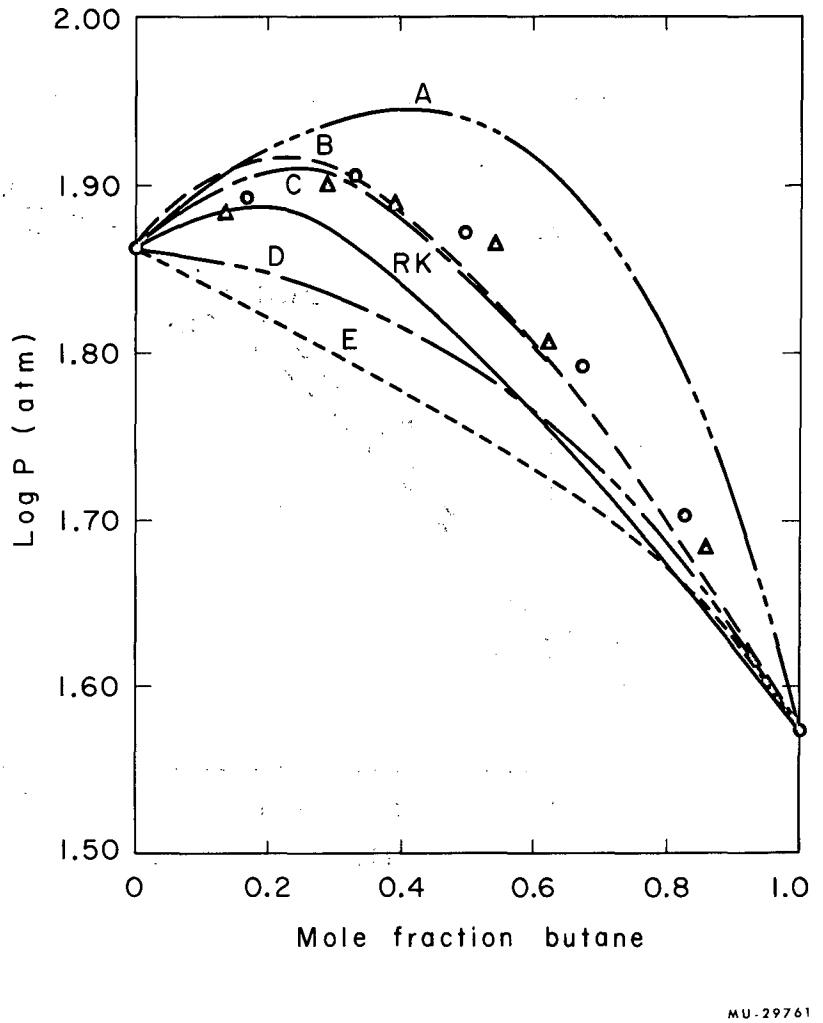

Fig. 23. Critical pressure of butane-carbon dioxide; O[39], Δ[35] [Benedict coeff. for butane[5]; carbon dioxide: A[9] (set II), E[9] (set I), B[36] (set A), C[36] (set B), D[11]].

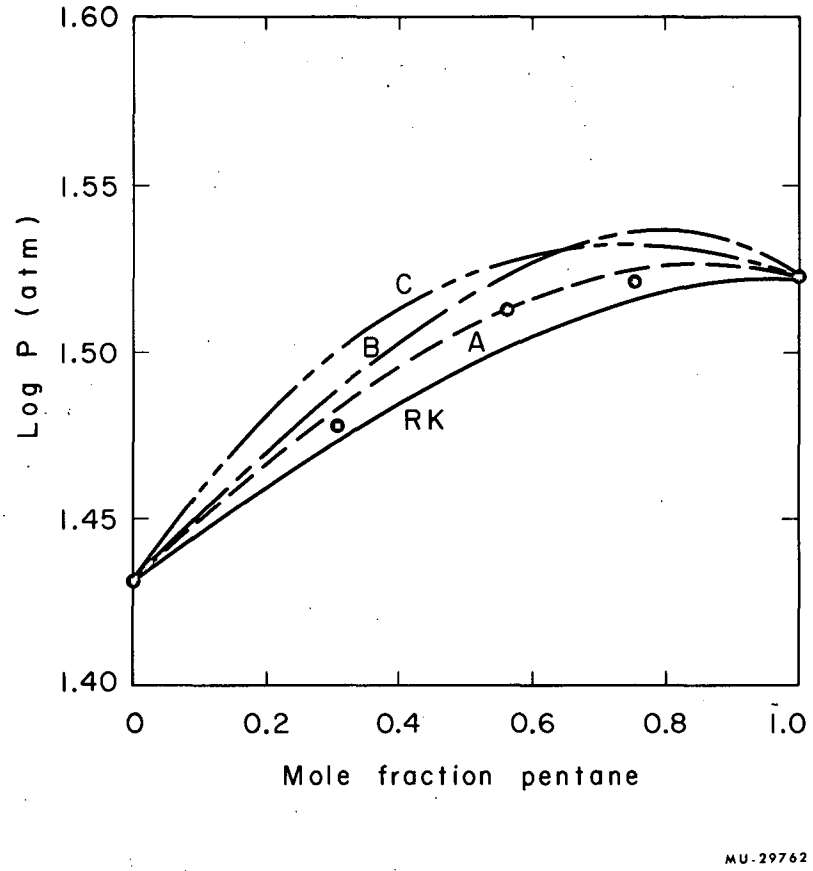

Fig. 24. Critical pressure of pentane-heptane[40] [Benedict coeff. A[5], B[6] ($\gamma = \infty$), C[6] ($\gamma = 0.4$)].

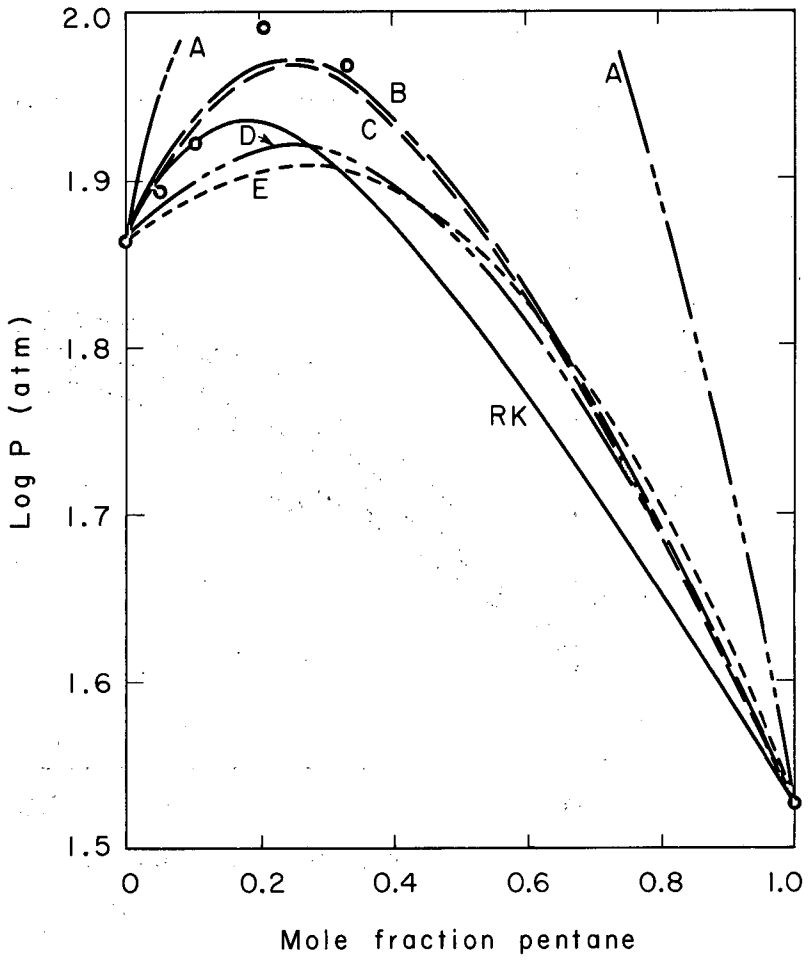

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Fig. 25. Critical pressure of pentane-carbon dioxide[35] [Benedict coeff. for pentane[5]; carbon dioxide: A[9] (set II), B[36] (set B), C[36] (set A), D[11], E[9] (set I)].

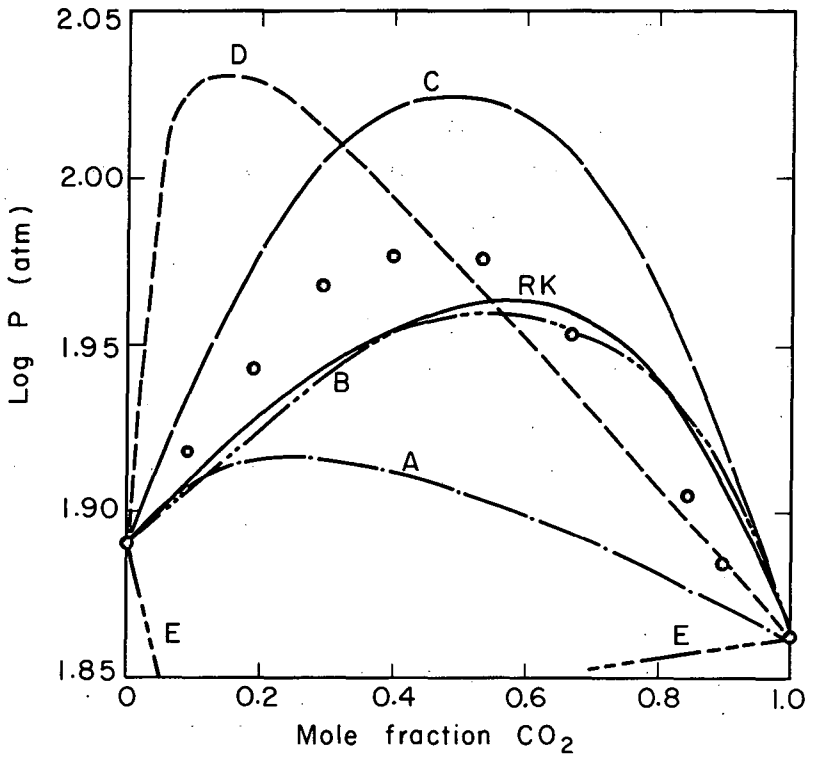

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Fig. 26. Critical pressure of carbon dioxide-sulfur dioxide[41] [Benedict coeff. for CO_2: A[36] (set B), B[11], C[9] (set I), D[9] (set II), E[36] (set A) for SO_2[42]].

G. Appendices

1. Nomenclature

a, b	coefficients in the equation of Redlich and Kwong
D	= 1/V, density (mole/cm^3)
f	fugacity
P	pressure (atm)
p	limiting slope of critical-pressure line
R	universal gas constant, 82.0567 (cm^3-atm/mole-°K)
T	temperature (°K)
t	limiting slope of critical-temperature line
V	volume (cm^3/mole)
y_1, y_2	mole fractions
A_0, B_0, C_0, a, b, c, α, γ	coefficients for the equation of Benedict, Webb, and Rubin. Primed values indicate derivatives with respect to mole fraction, i.e., $B_0' = dB_0/dy$.

Subscripts:

c	critical value: T_c, P_c, etc.
1	component one in the mixture
2	component two in the mixture

2. Critical Data

Gas	T_c (°K)	P_c (atm)	D_c (g-mole/cm^3)
Methane[a]	191.06	45.80	0.010098
Ethane[a]	305.43	48.18	0.006750
Ethylene[b]	282.40	50.50	0.008092
Propane[a]	369.97	42.00	0.004987
Propene[b]	365.00	45.60	0.005537
N-butane[a]	425.17	37.45	0.003922
Isobutane[b]	408.06	36.00	0.003820
1-butene[b]	419.60	39.70	0.004171
N-pentane[b]	469.76	33.30	0.003216
Isopentane[b]	460.96	32.90	0.003243
Heptane[a]	540.17	27.00	0.002345
Decane[a]	619.46	21.19	0.001617
Benzene[b]	561.33	48.30	0.003802
Nitrogen[b]	126.20	33.50	0.011100
Carbon dioxide[b]	304.20	72.90	0.010634
Sulfur dioxide[b]	430.70	77.80	0.008180

[a] F. D. Rossini, Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds (Carnegie Press, Pittsburgh, Pa., 1953).

[b] K. A. Kobe and R. E. Lynn Jr., Chem. Rev. 52, 117 (1953).

3. Constants for the equation of Benedict, Webb, and Rubin

Compound	Ref.	$10^{-6}A_0$	B_0	$10^{-10}C_0$	$10^{-7}a$	$10^{-3}b$	$10^{-12}c$	$10^{-5}\alpha$	$10^{-3}\gamma$
Methane	5	1.85510	42.6012	2.25713	4.94041	3.38023	2.54521	1.24369	6.00034
	8	1.30224	28.4148	3.67305	7.53477	4.03401	3.16369	0.808394	4.67676
Ethane	5	4.15579	62.7742	17.9602	34.5189	11.1226	32.7698	2.43409	11.8006
	8	1.85673	14.8272	27.3592	43.9517	13.3719	33.0952	1.80732	9.74324
	11	4.11722	62.7742	17.9601	34.5188	11.1226	32.0862	2.43409	11.8006
Propane	5	6.87263	97.3157	50.8284	94.7780	22.5013	129.011	6.07226	22.0012
	8	4.22006	34.3795	51.6912	111.156	28.9043	98.4248	3.90012	16.5254
Propene	5	6.11254	85.0671	43.9207	77.4121	18.7069	102.620	4.55734	18.2910
Butane	5	10.0853	124.364	99.2886	188.247	40.0005	316.427	11.0141	34.0019
	8	6.04219	62.7511	126.797	419.697	76.8219	478.828	5.81605	24.9427
	6 γ=0.4	6.80165	0.301654	1.54196	218.927	63.5454	0.0314250	5.42336	26.0051
	6 γ=∞	8.16273	41.0570	1.91682	191.314	56.2399	0	5.98809	0
Isobutane	5	10.2332	137.548	84.9991	193.779	42.4376	286.034	10.7417	34.0019
1-butene	38	9.06051	116.028	92.7332	168.214	34.8175	274.943	9.10966	29.5962
Pentane	5	12.1801	156.755	212.133	407.514	66.8151	824.239	18.1015	47.5027
	8	15.9688	230.362	160.663	337.637	62.6977	593.044	16.2453	40.9216
	6 γ=0.4	9.25552	-5.94723	18.4536	431.567	107.821	122.263	9.00163	38.7006
	6 γ=∞	10.3342	44.5298	11.8308	339.573	89.8510	0	10.1428	0
Isopentane	5	12.7967	160.057	174.642	375.652	66.8157	695.058	17.0014	46.3026
Heptane	5	17.5216	199.011	474.600	1036.57	151.963	2470.21	43.5647	90.0050
	6 γ=0.4	14.8541	-24.7883	102.194	1229.70	250.471	1020.10	20.5443	72.7239
	6 γ=∞	14.2651	46.4063	59.4009	837.491	191.068	0	23.2012	0
Decane	6 γ=0.4	25.2325	-64.5222	388.626	3816.37	646.261	5757.22	57.0791	153.030
	6 γ=∞	19.7449	42.1866	219.930	2317.37	457.418	0	62.7426	0
Benzene	29	6.51013	50.3020	343.016	557.047	76.6343	1176.52	7.00159	29.3016
CO_2	11	2.17261	34.8509	15.2608	17.4735	5.31529	15.1232	0.470039	4.20023
	36 A	2.73755	49.9112	13.8573	13.6823	4.12412	14.9190	0.846689	5.39386
	36 B	2.51617	44.8860	14.7450	13.6823	4.12412	14.9190	0.846690	5.39386
	9 I	1.97575	33.8945	7.78086	17.5020	5.27242	9.78903	0.698624	4.60598
	9 II	2.46616	40.4830	8.41836	63.2033	3.58992	4.09736	0.961331	5.39386
N_2	10	1.05370	40.7437	0.805943	2.51040	2.32782	0.728376	1.27211	5.30028
	21	1.19257	45.8013	0.588940	1.49013	1.98165	0.548110	2.91569	7.50042
SO_2	42	2.12054	26.1827	79.3879	84.4395	14.6542	113.362	0.719604	5.92390

[a]Constants are used with pressure expressed in atmospheres, temperature in °K, and volume in cm^3/gram-mole

PART II. FURTHER IMPROVEMENTS OF AN EQUATION OF STATE

A. Introduction

Numerous attempts have been made to formulate an equation of state for gases. This fact indicates both the need for such a relation and the incomplete success of the attempts described in the literature.

The discussion in Part I illustrates a shortcoming of an otherwise excellent relation: The equation of Benedict, Webb, and Rubin[5] contains so many individual coefficients that it becomes a flexible interpolation aid, but it is not very suitable for predictions beyond the range of the data used for the computation of the coefficients.

On the other hand, a two-parameter equation such as that of Redlich and Kwong does not provide sufficient flexibility.[3] It is necessarily limited by the well-known deviations from the theorem of corresponding states.

A successful compromise is the tables of Pitzer and coworkers.[43, 44, 45] They are based essentially on three individual parameters, and represent the data (with the exception of highly polar substances) with considerable accuracy.

Generalized charts and tables have the important advantage of a potential accuracy higher than that of reasonable algebraic equations;[46] however, they are not very suitable for the most important purpose of an equation of state. Indeed, the practical demand for an equation of state does not stem from a need for representing P-V-T relations themselves. What is really needed is information on fugacity coefficients, particularly those of mixtures. Their derivation from tables is not satisfactory, since numerical integration and still much more numerical differentiation of empirical data severely depresses the accuracy. For these reasons Redlich and Dunlop[47] developed an improvement of the equation of Redlich and Kwong, introducing Pitzer's acentric factor as a third individual coefficient.

In the present attempt an algebraic expression approaching the accuracy of Pitzer's tables is sought. The results of Part I corroborate

the advantage of the choice of the equation of Redlich and Kwong as a starting point. A reasonably good fit in the critical region was thought to be especially desirable, since the equation of Redlich and Kwong leads to large discrepancies in this region, although it is fairly good at much higher pressures.

B. The Deviation Functions

In this work, we represent $z^{(0)}$ of Pitzer's tables by the function Z_{RK} of Redlich and Kwong and a deviation function Z_0 according to

$$z^{(0)} = Z_{RK} + Z_0 , \tag{1}$$

and $z^{(1)}$ of Pitzer's tables by an algebraic function

$$z^{(1)} = Z_1 . \tag{2}$$

Thus the compressibility factor for any gas represented in Pitzer's tables by

$$Z = z^{(0)} + \omega \cdot z^{(1)} \tag{3}$$

is now represented by the algebraic equations

$$Z = Z_{RK} + Z_0 + \omega \cdot Z_1 . \tag{4}$$

Pitzer's acentric factor[44]

$$\omega = \log (P_C/p_S) - 1.00 \tag{5}$$

is computed from the vapor pressure p_S at the reduced temperature $T_r = 0.7$ and the critical pressure P_C.

The form of the functions Z_0 and Z_1 should be such as to preserve the inherent good features of the original equation. These include the boundary conditions (1) $Z \to 1$ as $T_r \to \infty$ and (2) the limiting volume is 0.26 V_C for $P_R \to \infty$. Therefore, the functions Z_0 and Z_1 must disappear for $T \to \infty$ and be finite for $P \to \infty$. For simplicity and ease of handling, it is desired that Z_0 and Z_1 be functions only of the reduced pressure and temperature. Such additional functions do not interfere with the critical conditions

$$\frac{\partial V}{\partial P} = 0; \quad \frac{\partial^2 V}{\partial P^2} = 0 . \tag{6}$$

In addition, the functions should be of a form that can be integrated without serious difficulty. A series expansion for the deviation functions is not suitable because of poor convergence and because the boundary conditions cannot be conveniently satisfied.

With these considerations in mind, functions Z_0 and Z_1 were evolved, first by inspection, and then by trials of the various forms with the aid of a least-squares computer program to determine the coefficients.[48]

C. Results

The functions finally adopted are

$$Z_0 = -A_1 P_r^3 / \left\{1.0 + A_2(T_r - 1.0)^2 + A_3\left[P_r - A_4 - A_5(T_r - 1.0)\right]^4\right\}$$

$$+ \left\{\frac{B_1 P_r \cdot (T_r - B_2 - B_3 P_r + B_4 P_r T_r^2)(1.0 - B_5 P_r + B_6 T_r P_r)}{\left[1.0 + B_7(T_r - B_8 - B_9 P_r - B_{10} P_r T_r)^4\right]}\right\}$$

$$+ B_{11} T_r^3 P_r^3 / (T_r^4 + B_{12} P_r^4)$$

$$Z_1 = \frac{T_r P_r (T_r - 1.0 - 0.049 P_r)(C_1 + C_2 P_r - C_3 T_r P_r + C_4 T_r)}{\left[T_r^4 + C_5 (T_r - C_6 - C_7 P_r + C_8 T_r P_r)^4\right]} \tag{7}$$

The numerical values for the coefficients are given in Table I. Set I was determined by a least-squares computation of the separate functions based on Pitzer's tables. Set II is a least-squares fit to the data of actual gases (232 points for nitrogen,[49, 50] methane,[51, 52] hydrogen sulfide,[53] propane,[54] carbon dioxide,[55, 56] sulfur dioxide,[57] and water[58, 59]). However, Pitzer's tables are based on more extensive experimental material. Therefore we may assume that the coefficients of Set I are more reliable in general application. In the following, the coefficients of Set I are used in all calculations. Table II shows the considerable improvement obtained in the critical region. The improvement in other regions can be seen from Table III which lists deviations from observed compressibility factors for Eq. (7), for Pitzer's tables, and for Dunlop's function. For clarity's sake, deviations smaller than 0.003 are suppressed.

Figures 27-33 compare graphically the deviations of Eq. (7) with those of Pitzer's tables. These values were obtained by means of a computer program of Mr. L. D. Sortland, which interpolates between Pitzer's tabulated data.

Table I. Coefficients for Eq. (7)

A_1	0.035	
A_2	14137.6	
A_3	1397.124	
A_4	1.030	
A_5	13.440	
	Set I	Set II
B_1	0.00260913	0.00476544
B_2	3.19325	5.15397
B_3	1.77486	0.344342
B_4	0.434418	0.422500
B_5	0.144392	0.155967
B_6	0.00704658	0.00648025
B_7	616.830	937.761
B_8	1.00122	0.788177
B_9	0.0112141	0.0423118
B_{10}	0.0495574	0.0436974
B_{11}	0.000442593	0.00050277
B_{12}	0.0602768	0.0559964
C_1	0.825714	0.926890
C_2	0.00736587	0.00691554
C_3	0.00255204	-0.00339345
C_4	0.00115729	0.00115571
C_5	0.101212	0.109996
C_6	2.46596	1.28600
C_7	0.220411	1.03462
C_8	0.0161963	0.0161573

Table II. Results for the critical point

Substance	T_c (°K)	P_c (atm)	ω	Z_c Observed	Z_c Calculated: Pitzer	Redlich-Kwong	Redlich-Dunlop	Present work
N_2	126.3	33.54	0.040	0.292	0.288	0.333	0.339	0.290
CH_4	191.0	45.79	0.013	0.290	0.290	0.333	0.334	0.290
H_2S	373.6	88.87	0.100	0.2833	0.283	0.333	0.315	0.288
C_3H_8	370.0	42.01	0.152	0.2766	0.279	0.333	0.327	0.287
CO_2	304.2	72.80	0.225	0.2746	0.273	0.333	0.323	0.285
SO_2	430.66	77.808	0.2325	0.2697	0.272	0.333	0.314	0.285
H_2O	647.3	218.4	0.348	0.2276	0.263	0.333	0.236	0.283

Table III. Deviations from the observed compressibility factor.
(Deviations below 0.003 are omitted)

NITROGEN

TR	PR	Z(OBS)	ΔZ(EQ 7)	ΔZ(PITZER)	ΔZ(DUNLOP)
1.0000	1.0000	0.2923		0.0043	-0.0491
2.0227	0.3043	0.9933			
2.0227	0.6086	0.9874			
2.0227	1.5216	0.9731			0.0042
2.0227	3.0430	0.9660			0.
2.0227	6.0860	1.0183	-0.0051		-0.0128
2.9027	0.3043	1.0017			
2.9027	0.6086	1.0036			
2.9027	1.5216	1.0105			
2.9027	3.0430	1.0272		-0.0070	
2.9027	6.0860	1.0845	-0.0054	-0.0064	
3.7827	0.3043	1.0044			
3.7827	0.6086	1.0090	0.0030		
3.7827	1.5216	1.0229	0.0067		0.0040
3.7827	3.0430	1.0469	0.0087		0.0055
3.7827	6.0860	1.1022			0.0067
4.6627	0.3043	1.0040			
4.6627	0.6086	1.0094		0.	
4.6627	1.5216	1.0240	0.0065	0.0076	0.0032
4.6627	3.0430	1.0474	0.0088	0.0239	0.0041
4.6627	6.0860	1.0979		0.0292	0.0048
5.5427	0.3043	1.0044		0.0046	
5.5427	0.6086	1.0090			
5.5427	1.5216	1.0231	0.0062	0.0257	
5.5427	3.0430	1.0441	0.0076	0.0784	
5.5427	6.0860	1.0891		0.0916	
0.8346	0.1014	0.9380		0.0068	
0.8346	0.2029	0.8708		0.0118	
0.8346	0.3043	0.7878	-0.0034	0.0038	-0.0064
1.0106	0.1014	0.9670			
1.0106	0.2029	0.9319	0.0034		
1.0106	0.3043	0.8949	0.0049		
1.0106	0.4058	0.8518			
1.0106	0.8118	0.6515	0.0088	0.0054	-0.0035
1.0106	1.2173	0.2425		0.0037	-0.0441
1.0106	1.6230	0.2845	-0.0085		-0.0458
1.0106	2.0288	0.3328	-0.0067		-0.0569
1.2306	0.4058	0.9299	0.0063		0.0055
1.2306	0.8115	0.8526	0.0104		0.0063
1.2306	1.2173	0.7656	0.0082		
1.2306	1.6230	0.6826	0.0067		-0.0108
1.2306	2.0288	0.6155			-0.0241
1.4507	0.4058	0.9600			
1.4507	0.8115	0.9204	0.0034		0.0043
1.4507	1.2173	0.8799		-0.0033	
1.4507	1.6230	0.8459		-0.0038	
1.4507	2.0288	0.8148			-0.0037

Table III. (continued)

METHANE

TR	PR	Z(OBS)	ΔZ(EQ 7)	ΔZ(PITZER)	ΔZ(DUNLOP)
1.0000	1.0000	0.2903			-0.0477
1.6280	0.2970	0.9795			
1.6280	1.4860	0.9072			
1.6280	2.9700	0.8527	-0.0096		-0.0128
1.6280	7.4300	0.9812	-0.0128		-0.0499
1.8020	0.2970	0.9862			
1.8020	1.4860	0.9410		-0.0032	
1.8020	2.9700	0.9108	-0.0062		-0.0072
1.8020	7.4300	1.0120	-0.0099		-0.0353
1.9760	0.2970	0.9913			
1.9760	1.4860	0.9639			
1.9760	2.9700	0.9496			-0.0036
1.9760	7.4300	1.0395	-0.0071	-0.0037	-0.0248
2.1500	0.2970	0.9947			
2.1500	1.4860	0.9788		-0.0039	
2.1500	2.9700	0.9758		-0.0047	
2.1500	7.4300	1.0610	-0.0054	-0.0049	-0.0182
2.3250	0.2970	0.9972			
2.3250	1.4860	0.9908	0.0031	-0.0033	
2.3250	2.9700	0.9949		-0.0051	
2.3250	7.4300	1.0786		-0.0042	-0.0126
2.5000	0.2970	0.9989			
2.5000	1.4860	0.9986	0.0035		
2.5000	2.9700	1.0079			
2.5000	7.4300	1.0916		-0.0031	-0.0089
2.6740	0.2970	1.0002			
2.6740	1.4860	1.0043	0.0037		
2.6740	2.9700	1.0177	0.0040		
2.6740	7.4300	1.1008		-0.0040	-0.0065

Table III. (continued)

HYDROGEN SULFIDE

TR	PR	Z(OBS)	ΔZ(EQ 7)	ΔZ(PITZER)	ΔZ(DUNLOP)
1.0000	1.0000	0.2836	-0.0050		-0.0426
0.7431	0.0766	0.9219	-0.0138	-0.0035	-0.0114
0.8323	0.0766	0.9503	-0.0032	0.0041	
0.8323	0.1531	0.8984	-0.0049	0.0081	-0.0039
0.8323	0.7657	0.1199			0.0129
0.9215	0.0766	0.9650		-0.0036	
0.9215	0.1531	0.9290		-0.0046	
0.9215	0.3829	0.8038			
0.9215	0.7657	0.1265	-0.0075		-0.0069
0.9215	1.5314	0.2378	-0.0036		0.0103
1.0107	0.0766	0.9742			
1.0107	0.1531	0.9500	0.0032		
1.0107	0.3829	0.8633	0.0048		
1.0107	0.7657	0.6775	0.0059	0.0034	
1.0107	1.5314	0.2648	-0.0143		-0.0198
1.0107	3.8290	0.5444			0.0685
1.1000	0.0766	0.9803			
1.1000	0.1531	0.9612			
1.1000	0.3829	0.9004	0.0059		0.0044
1.1000	0.7657	0.7828	0.0103		0.0074
1.1000	1.5314	0.4638		-0.0076	
1.1000	3.8290	0.5606			0.0259
1.1891	0.0766	0.9851			
1.1891	0.1531	0.9705			
1.1891	0.3829	0.9251	0.0049		0.0047
1.1891	0.7657	0.8441	0.0108		0.0098
1.1891	1.5314	0.6561	0.0110	-0.0037	0.0080
1.1891	3.8290	0.5965			

Table III. (continued)

PROPANE

TR	PR	Z(OBS)	ΔZ(EQ 7)	ΔZ(PITZER)	ΔZ(DUNLOP)
1.0000	1.0000	0.2769	-0.0105		-0.0622
0.8400	0.1620	0.8964		0.0117	
0.8400	0.8100	0.1226			0.0083
0.8850	0.1620	0.9143		0.0036	
0.8850	0.3240	0.8068	-0.0071		-0.0064
0.8850	0.8100	0.1240	-0.0046		-0.0065
0.8850	1.6200	0.2503	0.0085	0.0079	-0.0050
0.9300	0.1620	0.9272			
0.9300	0.3240	0.8408			-0.0041
0.9300	0.8100	0.1291	-0.0124		-0.0207
0.9300	1.6200	0.2444	-0.0059		-0.0320
0.9740	0.1620	0.9376			
0.9740	0.3240	0.8665			
0.9740	0.8100	0.5400	-0.0142	-0.0169	-0.0272
0.9740	1.6200	0.2527	-0.0136		-0.0470
0.9740	3.2400	0.4604			-0.0925
1.0200	0.1620	0.9460		-0.0032	
1.0200	0.3240	0.8870			
1.0200	0.8100	0.6606		-0.0039	-0.0114
1.0200	1.6200	0.2751	-0.0164	-0.0034	-0.0592
1.0200	3.2400	0.4678			-0.1003
1.2000	0.1620	0.9683			
1.2000	0.3240	0.9360			
1.2000	0.8100	0.8365	0.0045	-0.0038	
1.2000	1.6200	0.6612	0.0162		-0.0094
1.2000	3.2400	0.5647	-0.0060	-0.0057	-0.0911
1.3800	0.1620	0.9808			
1.3800	0.3240	0.9620			
1.3800	0.8100	0.9065		-0.0059	
1.3800	1.6200	0.8219		-0.0111	-0.0052
1.3800	3.2400	0.7347		0.0037	-0.0454
1.3800	8.1000	1.0051		0.0063	-0.1934

Table III. (continued)

CARBON DIOXIDE

TR	PR	Z(OBS)	ΔZ(EQ 7)	ΔZ(PITZER)	ΔZ(DUNLOP)
1.0000	1.0000	0.2749	-0.0108		-0.0551
1.0400	0.1863	0.9443	0.0035		
1.0400	0.9310	0.6193	-0.0035	-0.0138	-0.0166
1.1310	0.1863	0.9577			
1.1310	0.9310	0.7581	0.0087	-0.0103	-0.0071
1.1310	1.8630	0.4785			-0.0358
1.2410	0.1863	0.9702			
1.2410	0.9310	0.8377		-0.0042	-0.0099
1.2410	1.8630	0.6837	0.0174	-0.0037	-0.0163
1.2410	4.6600	0.6928	0.0043		-0.1125
1.3510	0.1863	0.9793			
1.3510	0.9310	0.8890		-0.0057	-0.0073
1.3510	1.8630	0.7873		-0.0134	-0.0189
1.3510	4.6600	0.7587	-0.0044	0.0056	-0.1047
1.4420	0.1863	0.9843			
1.4420	0.9310	0.9194		-0.0032	-0.0040
1.4420	1.8630	0.8449	-0.0069	-0.0134	-0.0166
1.4420	4.6600	0.8166	-0.0080	0.0063	-0.0881
1.5700	0.1863	0.9886			
1.5700	0.9310	0.9459	-0.0041		-0.0035
1.5700	1.8630	0.8987	-0.0125	-0.0091	-0.0141
1.5700	4.6600	0.8819	-0.0236	-0.0037	-0.0708
1.6790	0.1863	0.9930			
1.6790	0.9310	0.9627	-0.0042		
1.6790	1.8630	0.9307	-0.0138	-0.0079	-0.0111
1.6790	4.6600	0.9249	-0.0386	-0.0087	-0.0592

Table III. (continued)

SULFUR DIOXIDE

TR	PR	Z(OBS)	ΔZ(EQ 7)	ΔZ(PITZER)	ΔZ(DUNLOP)
1.0000	1.0000	0.2700	-0.0156	-0.0035	-0.0592
0.6580	0.0257	0.9532	-0.0173	-0.0039	-0.0053
0.6810	0.0257	0.9608	-0.0123		
0.7040	0.0257	0.9667	-0.0087		
0.7040	0.0514	0.9313	-0.0185	-0.0048	-0.0033
0.7280	0.0257	0.9710	-0.0066		
0.7280	0.0514	0.9407	-0.0135		
0.7280	0.0771	0.9082	-0.0218	-0.0054	-0.0039
0.7500	0.0257	0.9742	-0.0051		
0.7500	0.0514	0.9478	-0.0101		
0.7500	0.0771	0.9206	-0.0151		
0.7500	0.1027	0.8905	-0.0222		-0.0032
0.8670	0.0771	0.9541	-0.0035		
0.8670	0.1543	0.9043	-0.0080		
0.8670	0.2310	0.8495	-0.0140		-0.0044
0.8670	0.3090	0.7843	-0.0248	-0.0054	-0.0117
0.9820	0.0771	0.9702			
0.9820	0.1543	0.9396			
0.9820	0.2310	0.9080			
0.9820	0.3090	0.8743			-0.0031
0.9820	0.3860	0.8387			-0.0041
0.9820	0.4630	0.8001	-0.0037		-0.0059
0.9820	0.5400	0.7588	-0.0045	-0.0034	-0.0075
0.9820	0.6170	0.7133	-0.0054	-0.0047	-0.0096
0.9820	0.6940	0.6608	-0.0078	-0.0041	-0.0133
0.9820	0.7710	0.5983	-0.0116	-0.0073	-0.0184
0.9820	0.8480	0.5119	-0.0223	-0.0224	-0.0304
1.0000	0.2570	0.9036			
1.0000	0.5140	0.7914		-0.0032	-0.0057
1.0000	0.7710	0.6431	-0.0038	-0.0051	-0.0125
1.0000	2.0600	0.3107	-0.0131		-0.0284
1.0000	2.3100	0.3335	-0.0175	-0.0056	-0.0323
1.0000	2.5700	0.3630	-0.0166	-0.0078	-0.0298
1.0000	2.8300	0.3948	-0.0137	-0.0077	-0.0243
1.0000	3.0900	0.4231	-0.0147	-0.0110	-0.0214
1.0000	3.3400	0.4518	-0.0143	-0.0127	-0.0164
1.0000	3.6000	0.4802	-0.0155	-0.0159	-0.0119
1.0000	3.8600	0.5089	-0.0163	-0.0181	-0.0064
1.1000	0.6420	0.8216	0.0048		-0.0055
1.1000	1.2850	0.5912	0.0247		
1.1000	1.9270	0.4000	-0.0143		-0.0545
1.1000	2.5700	0.4188	-0.0209	-0.0067	-0.0793
1.1000	3.2100	0.4713	-0.0213	-0.0169	-0.0890
1.1000	3.8600	0.5349	-0.0185	-0.0170	-0.0901
1.2150	0.6420	0.8841	0.0044		-0.0038
1.2150	1.2850	0.7612	0.0185	0.0044	-0.0035
1.2150	1.9270	0.6461	0.0261		-0.0128
1.2150	2.5700	0.5817	0.0062	-0.0056	-0.0514
1.2150	3.2100	0.5819	-0.0055	-0.0057	-0.0834
1.2150	3.8600	0.6151	-0.0042		-0.1025

Table III. (continued)

WATER

TR	PR	Z(OBS)	ΔZ(EQ 7)	ΔZ(PITZER)	ΔZ(DUNLOP)
1.0000	1.0000	0.2279	-0.0550	-0.0370	-0.0628
0.6000	0.0010	0.9973		0.0331	
0.6000	0.0020	0.9946		0.0317	
0.6000	0.0030	0.9919	-0.0037	0.0302	
0.6000	0.0040	0.9893	-0.0049	0.0289	
0.6000	0.0050	0.9866	-0.0061	0.0274	0.0030
0.6000	0.0060	0.9860	-0.0053	0.0281	0.0057
0.7000	0.0100	0.9857	-0.0045	0.0084	
0.7000	0.0200	0.9715	-0.0088	0.0060	0.0055
0.7000	0.0300	0.9565	-0.0137		0.0077
0.7000	0.0400	0.9402	-0.0198		0.0089
0.8000	0.0400	0.9671	-0.0051	0.0039	0.0052
0.8000	0.0800	0.9312	-0.0122	0.0052	0.0088
0.8000	0.1200	0.8893	-0.0237		0.0083
0.8000	0.1600	0.8393	-0.0419	-0.0115	
0.9000	0.1000	0.9472			0.0048
0.9000	0.2000	0.8858	-0.0095	-0.0042	0.0061
0.9000	0.3000	0.8121	-0.0237	-0.0111	0.
0.9000	0.4000	0.7207	-0.0479	-0.0275	-0.0119
1.0000	0.2000	0.9268			
1.0000	0.4000	0.8407	-0.0041	-0.0048	
1.0000	0.6000	0.7397	-0.0091	-0.0104	
1.0000	0.8000	0.6045	-0.0189	-0.0191	-0.0064
1.1000	0.2000	0.9480			-0.0060
1.1000	0.4000	0.8931			-0.0092
1.1000	0.6000	0.8349		-0.0037	-0.0092
1.1000	0.8000	0.7730	0.0071	-0.0053	-0.0052
1.1000	1.0000	0.7062	0.0148	-0.0040	0.0033
1.1000	1.2000	0.6287	0.0214	-0.0064	0.0123
1.2000	0.2000	0.9599	-0.0046	-0.0042	-0.0106
1.2000	0.4000	0.9224	-0.0043	-0.0043	-0.0156
1.2000	0.6000	0.8853		-0.0040	-0.0173
1.2000	0.8000	0.8478	0.0035	-0.0038	-0.0163
1.2000	1.0000	0.8098	0.0100		-0.0130
1.2000	1.2000	0.7710	0.0171		-0.0081
1.3000	0.2000	0.9665	-0.0091	-0.0084	-0.0144
1.3000	0.4000	0.9399	-0.0102	-0.0090	-0.0203
1.3000	0.6000	0.9158	-0.0080	-0.0075	-0.0224
1.3000	0.8000	0.8929	-0.0037	-0.0058	-0.0220
1.3000	1.0000	0.8704		-0.0035	-0.0201
1.3000	1.2000	0.8482	0.0076		-0.0171

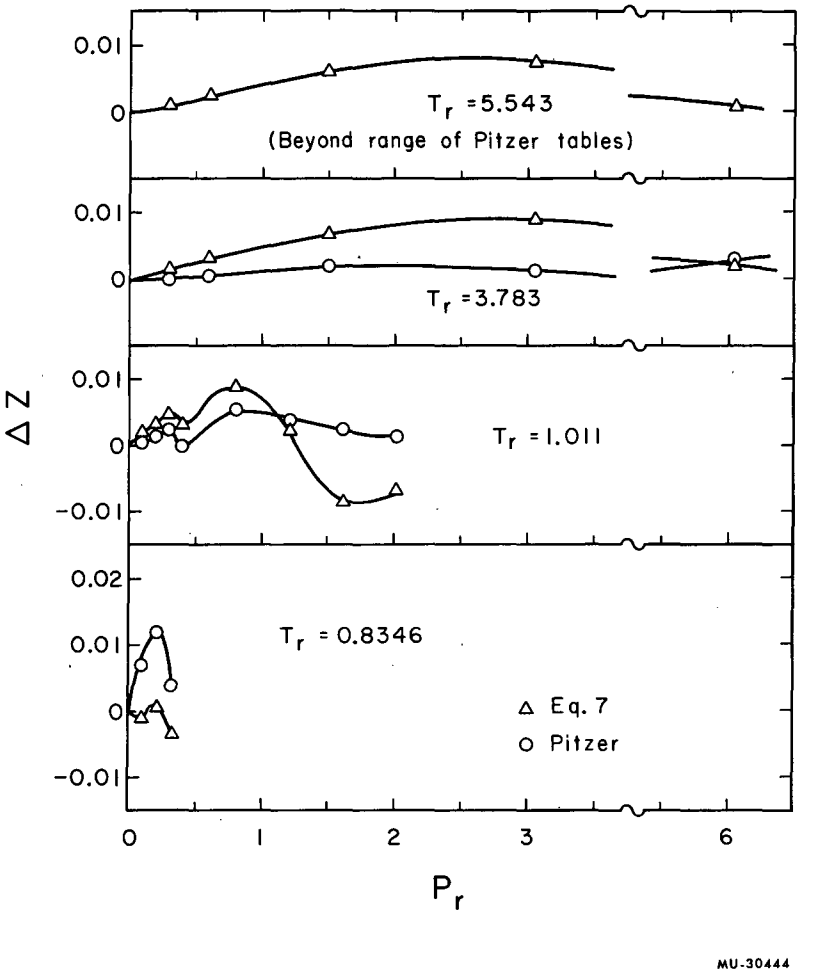

Fig. 27. Deviations from the observed compressibility factor for nitrogen.

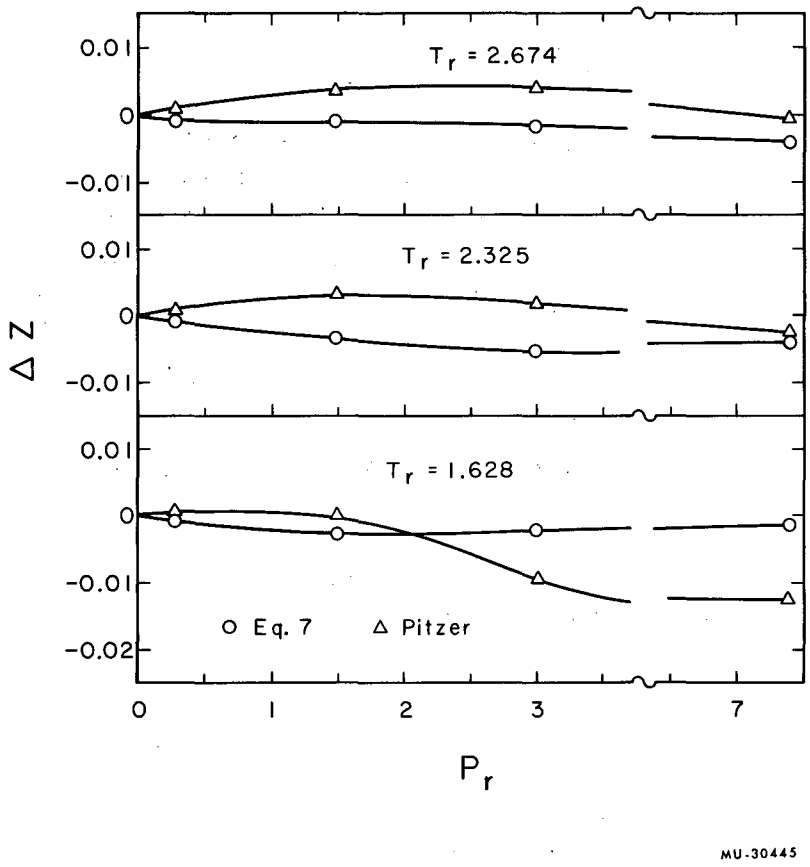

Fig. 28. Diviations from the observed compressibility factor for methane.

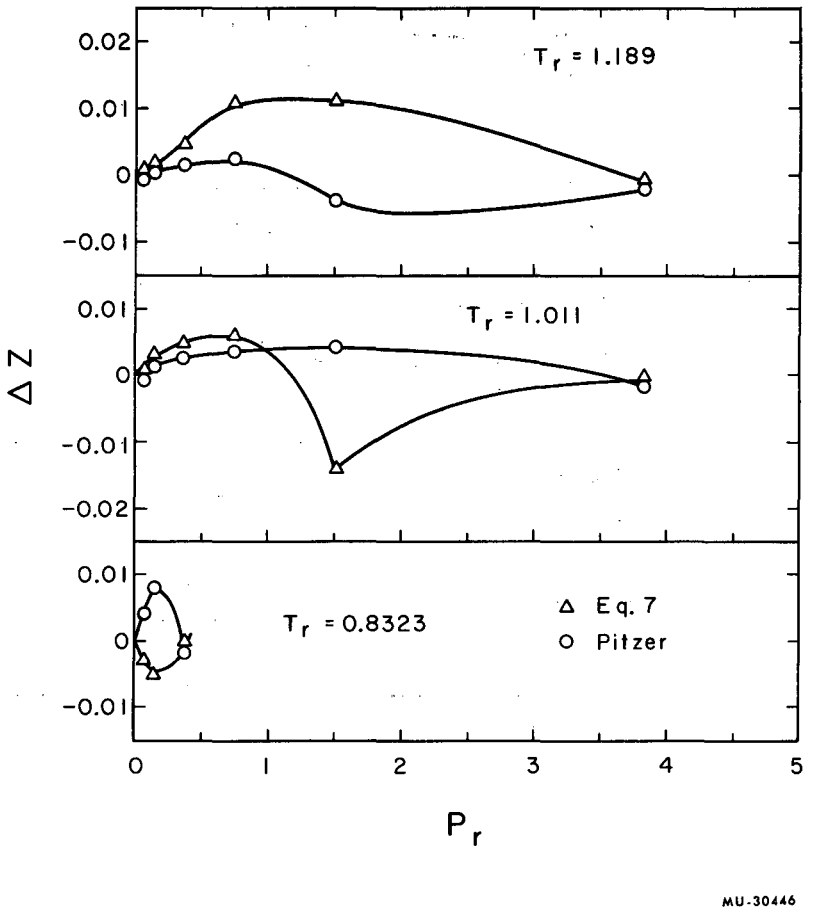

Fig. 29. Deviations from the observed compressibility factor for hydrogen sulfide.

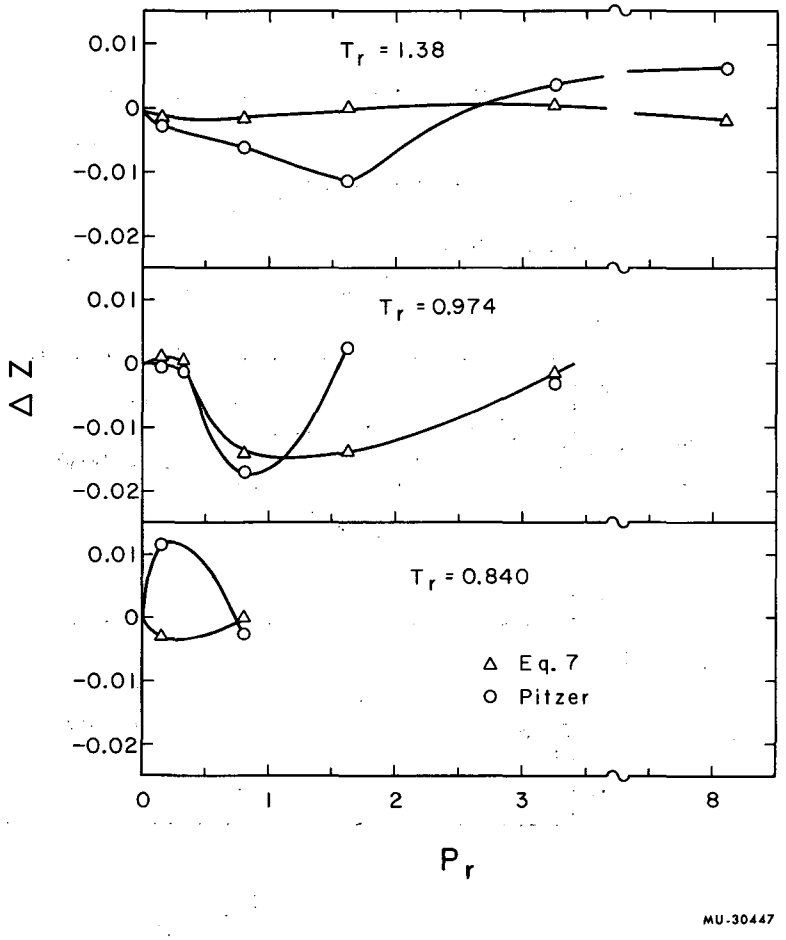

Fig. 30. Deviations from the observed compressibility factor for propane.

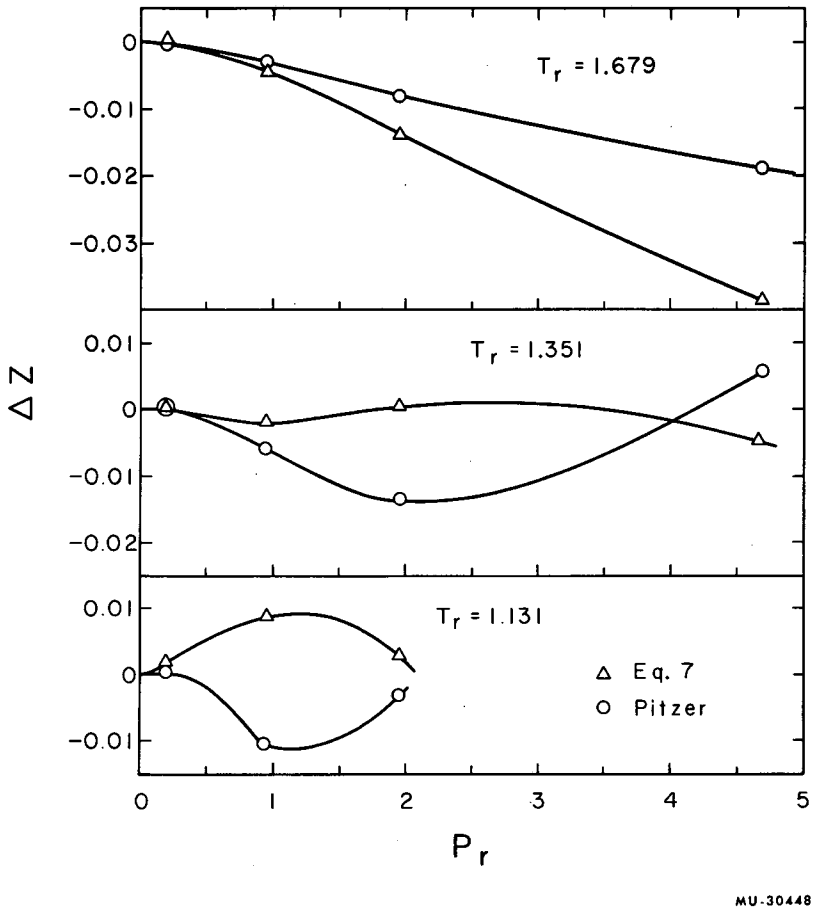

Fig. 31. Deviations from the observed compressibility factor for carbon dioxide.

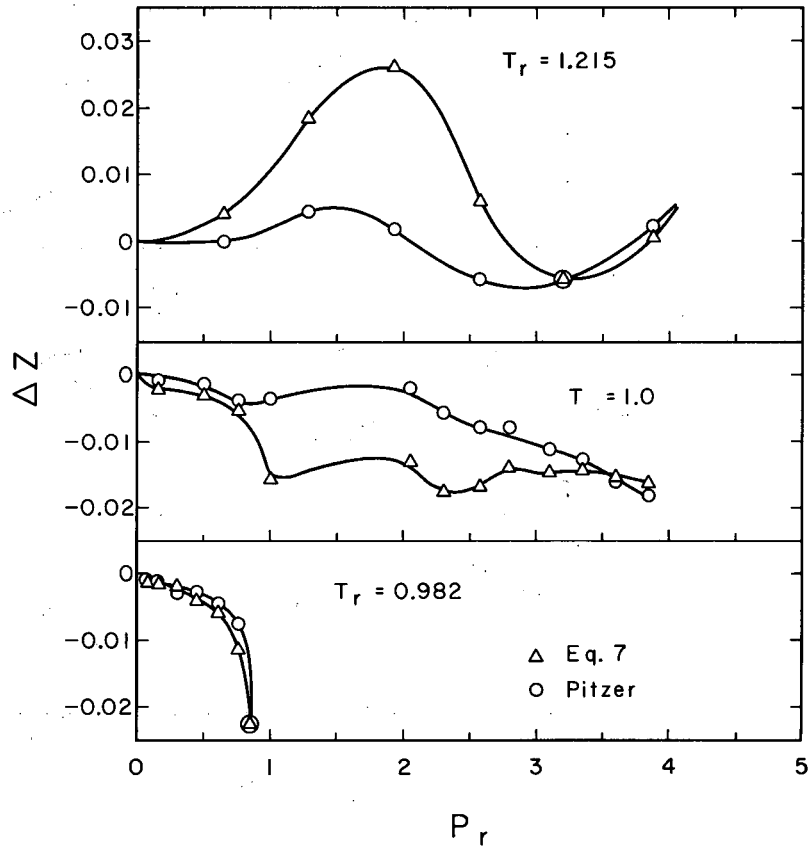

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Fig. 32. Deviations from the observed compressibility factor for sulfur dioxide.

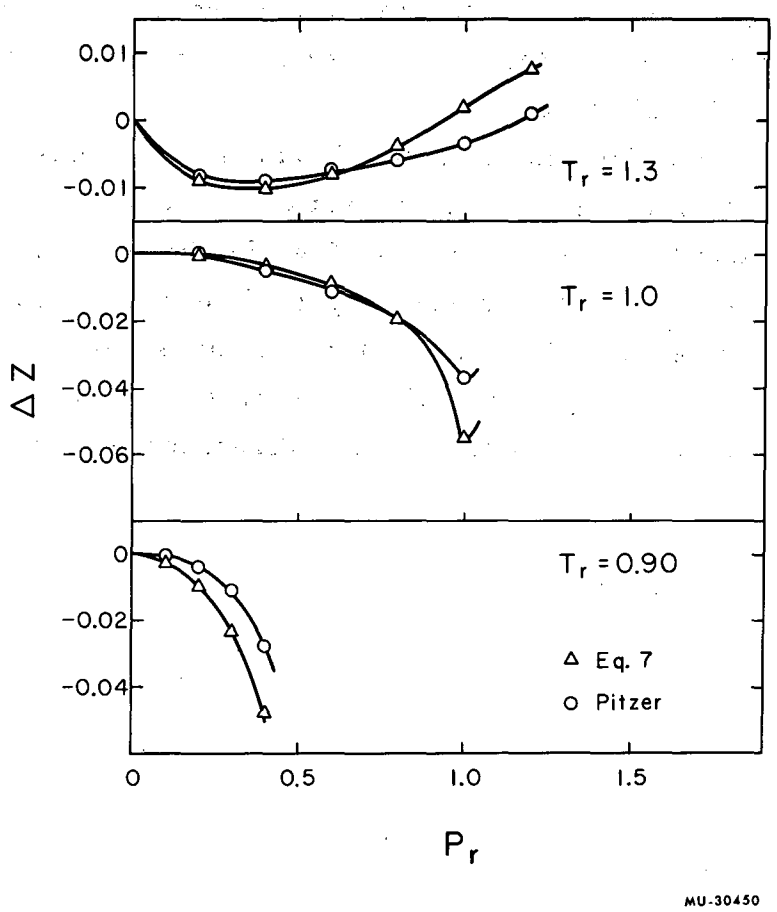

Fig. 33. Deviations from the observed compressibility factor for water.

Considerable improvement over Dunlop, especially in the critical region, is seen in Tables II and III. For water (Table III) Dunlop's values are better. This is to be expected from the manner of choosing the respective functions and the acknowledged poor representation of water by the Pitzer tables. However, even here, Dunlop's values are not significantly better.

The diagrams show that Pitzer's tables give a better representation than Eq. (7). But the algebraic representation comes very close to the results of the tables. As Fig. 27 shows, use of Eq. (7) beyond the range of the tables gives very good results. The data given for nitrogen in Table III at the reduced temperatures 4.6627 and 5.5427 under Z (Pitzer) are extrapolated, since Pitzer's tables do not cover these high temperatures. The results of this direct extrapolation are poor.

D. Appendix: Nomenclature

A, B, C	Constants in the deviation functions
P	Pressure
P_c	Critical pressure
P_r	Reduced pressure
P_s	Vapor pressure at a reduced temperature $T_r = 0.7$
T	Temperature
T_r	Reduced temperature
V	Volume
V_c	Critical volume
Z	PV/RT, the compressibility factor
$z^{(0)}$, $z^{(1)}$	Values from Pitzer's tables
Z_{RK}	Compressibility factor as calculated by using the equation of Redlich and Kwong
Z_0, Z_1	Deviation functions
ω	Pitzer's acentric factor

ACKNOWLEDGMENTS

It gives me great pleasure to express my thanks to Dr. O. Redlich for his guidance. I am grateful to the Bechtel Corporation, San Francisco, for making available a program, written by Mr. L. D. Sortland, for the calculation of compressibility factors based on Pitzer's tables.

To the Computer Center, University of California, I also owe thanks for support and advice.

This work was done under the auspices of the U. S. Atomic Energy Commission.

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