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THERMODYNAMICS OF SOLUTIONS X. EQUATION OF STATE
AND VAPOR PRESSURE

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March 1965

Thermodynamics of Solutions X. Equation of State
and Vapor Pressure

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Abstract

A new improvement of the equation of state of Redlich and Kwong is proposed. The new relation can be applied to the liquid state and vapor pressures. It furnishes quite good results down to a reduced temperature of 0.65. The reasonable limiting relations for extreme temperatures or pressures of the original equation are maintained except for the case that both T and P at the same time assume extremely high values. Mean and individual fugacity coefficients are consistently derived from the equation of state without further assumptions or parameters. A flexible computer program provides for convenient use for a variety of problems.

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The practical interest in an equation of state is mainly tied to the calculation of individual fugacity coefficients of mixtures since they are required for the investigation of chemical equilibria and phase equilibria. They can hardly be obtained by any other way but by derivation from an equation of state.

The results obtained by an improvement¹ of the two-parameter equation of Redlich and Kwong² invited further development. The introduction of Pitzer's acentric factor^{3,4} as a third parameter in a "deviation function", added to the old equation for the compressibility factor, proved to be a useful way. But a considerable expansion of the scope and various further improvements appeared to be desirable.

The use of automatic computation has removed almost all holds regarding the complexity of the deviation function, provided that no fourth individual parameter is introduced. It is obvious that each new individual parameter improves the representation of a given set of data and at the same time tends to reduce the ability of a relation to predict the behavior of a substance outside the experimental range. Comparisons^{5,6,15} of the old two-parameter equation with the eight-parameter relation of Benedict, Webb and Rubin confirmed this reasoning much more strongly than it was expected. A fourth parameter will be useful therefore, if at all, only if it has a good theoretical meaning.

Practically the only computational restriction to be imposed on the deviation function is the algebraic integrability with respect to $\log P$, desirable for the calculation of fugacity coefficients. The more important restrictions, those of a general nature, have been discussed before.¹

In the preceding papers the scope was restricted to the gaseous state. The original equation, however, deliberately chosen to be of third degree, offered solutions for the liquid state that were quite reasonable though of course not accurate. Encouraged by these results as well as by the success of Pitzer's tables, we have now extended the program to liquids.

The key to an equation of state encompassing both phases are the vapor pressures, particularly if the attention is concentrated on fugacities. They must be represented reasonably well. Conversely, vapor pressures are an important help in the search for an additional deviation function for the fugacity coefficients of the liquid phase. In particular, the deviation function should quite closely satisfy the definition of the acentric factor

$$W = -1 - \log p_r \quad (1)$$

based on the reduced vapor pressure p_r at the reduced temperature $T_r = 0.7$.

The deviation functions for the gas and the liquid must of course become identical at the critical temperature. In addition, one wishes to refer the fugacity of the liquid to the same standard state as the gas.

The combination of parameters chosen for mixtures differs somewhat from the usual linear and square-root combinations whenever the acentric factors of the components are different. The following empirical combination appears to represent the observed data more closely. It entails some inconvenience in the differentiation of deviation functions with respect to the mole fractions, required in the calculation of individual

fugacity coefficients. The combination rule will be expressed as a definition of the pseudocritical values T_M , P_M and the acentric factor W_M of the mixture. They are given as functions of the mole fractions y_i , the critical constants T_{ci} and P_{ci} , and the acentric factors W_i of the components with the aid of four auxiliary quantities by

$$A = \sum_i y_i T_{ci} / P_{ci} \quad (2)$$

$$B = \sum_i y_i T_{ci}^{1.25} / P_{ci}^{0.5} \quad (3)$$

$$C = \sum_i y_i W_i T_{ci} / P_{ci} \quad (4)$$

$$W_M = C/A \quad (5)$$

$$D = 1 + 0.5 (W_M - \sum_i y_i W_i) \quad (6)$$

$$T_M = (B^2 D / A)^{0.6667} \quad (7)$$

$$P_M = (B D^{1.25} / A^{1.25})^{1.3333} \quad (8)$$

Pitzer's tables provided considerable guidance in the development of suitable deviation functions. The present program goes beyond them by the extension to lower temperatures, by providing reasonable limiting relations for high temperatures or high pressures, and by the consistent computation of individual fugacity coefficients without any further assumption or empirical parameter. The deviation functions fail, however, if both temperature and pressure are simultaneously increased to extreme values. The convenience of automatic computation overbalances the preparatory work of the user even in moderately frequent application.

The Computer Program

The program, written in Fortran II language, can be used advantageously only in a high speed machine. A considerable effort has been made to achieve convenience in input and output as well as highest flexibility, so that one can solve a variety of problems without prescribing computations unnecessary for the specific problem.

The input comprises the three parameters for each substance, a schedule of temperatures and pressures that may be prescribed in a variety of ways, and for mixtures the compositions in mole fractions. As an optional input, P-V-T data can be introduced for comparison with calculated values.

The computation furnishes the compressibility factor, and if desired the fugacity coefficient and the pressure dependent terms of the entropy and enthalpy. For mixtures, in addition, individual fugacity coefficients and fugacities may be obtained. Vapor pressures of pure liquids can be prescribed by a special option; they are computed by an efficient step-by-step approximation.

In complicated integrations such as those of the deviation functions with respect to $\log P$, the computer offers the advantage that the whole operation can be resolved in a series of intermediate steps so that no really involved and lengthy expressions need be written down. Since the arc tan function during integration may change from one range to another, a special subroutine Angle has been added which eliminates its ambiguity.

All integrations and differentiations have been carried out algebraically with the exception of the differentiation of deviation functions

with respect to temperature. Such a differentiation was practically impossible. A numerical differentiation is sufficient if the temperature increment is chosen so low that the function is practically linear, and at the same time so high that the division by the increment does not lead to an intolerable loss of the number of significant figures. This condition can be easily checked by means of the program. The built-in standard increment of 0.1 will probably always be satisfactory for °K or °R. The option provided for other increments should be used if reduced temperatures are introduced.

The solution of the original equation of Redlich and Kwong leads sometimes to unsuitable results, i.e., instable states or negative values. These results are automatically disregarded. The program does not allow computations for negative pressure (tension).

If the computation for a pure substance leads to results for two phases, the comparison of the fugacity coefficients indicates which is stable and which is metastable. No really simple answer can be given regarding the stability of mixed phases. But a special program is under consideration that would furnish the compositions and properties of phases in equilibrium at a given temperature and pressure.

Correctness and Accuracy

It is a disconcerting shortcoming of a complicated computer program that the user can hardly check it completely. To some extent he has to accept it on good faith. Still he can check quite systematically its correctness with little effort by suitable use of the program itself. We have exerted considerable care in developing and extensively performing the following checks.

1. The goodness of fit is of course checked by direct comparison with experimental data. For this purpose the program accepts P-V-T data of any conceivable kind expressed in any dimension and converts them to compressibility factors Z . A few of the results are discussed in the following section.

2. The computation of (mean) fugacity coefficients has been checked by the computation of isothermal sets of Z and numerical integration. The procedure is sensitive enough if carried out with proper care.

3. The correctness of the differentiation with respect to T is checked by printing intermediate quantities with the aid of diagnostic instructions, and by comparing results for entropy and enthalpy with fugacity coefficients computed for a closely spaced set of temperatures. The second procedure is sufficient.

4. A necessary and sufficient check of the computation of the individual fugacity coefficient ϕ_1 and ϕ_2 of a binary mixture is given by their relations with the mean fugacity coefficient ϕ and the mole fractions y_1 and y_2 .

$$\log \phi = y_1 \log \phi_1 + y_2 \log \phi_2 \quad (9)$$

$$d \log \phi / d y_1 = \log (\phi_1 / \phi_2). \quad (10)$$

These checks have been found to be quite efficient in disclosing program errors. They are believed to be practically sufficient.

Results

The vapor pressure comparisons in Table 1 are given for practically the whole range of the acentric factor W . The comparisons of Z in Fig. 1 to 4 and the data in Table 2 are presented for substances with high values of W since good agreement with experimental data has never been a question for low W . For mixtures, examples of components with large differences in W were selected because their representation is in general more difficult.

A satisfactory representation of the lower hydrocarbons can be taken for granted; but even for n -nonane (Fig. 1) the deviations are appreciable only for a very low reduced temperature or for very high reduced pressures. Even for a strongly polar substance such as ammonia (Fig. 2) the discrepancies are large only for low temperatures. The remaining deviations for sulfur dioxide (Fig. 3) are below 0.03 in Z . Although the shape of the deviation curve for the critical isotherm looks strange, the curve for Z itself (Fig. 4) appears to be quite reasonable.

It is especially the combination of the parameters that is being tested in Fig. 4 to 8 and Tables 3 and 4. The phase equilibria in these tables represent a particularly severe test since at the same time the values of Z and the fugacity coefficients of both components are tested for both phases.

These tests will furnish a general impression of the degree of accuracy to be expected in applications. Hydrogen, helium and water are not satisfactorily represented.

Tables 3 and 4 show that the critical locus of mixtures is not well described by the program. A systematic study of critical points, critical

condensation points, and vapor pressures of mixtures may well be a useful step in the future development of an equation of state.

The program has been submitted to SHARE as ES 64, Equation of State 1964.*

This work was done under the auspices of the U.S. Atomic Energy Commission. The authors express their appreciation of the advice extended to them in a part of their computational work by members of the Computation Center of the University of California in Berkeley.

* Until the program is available from SHARE the senior author will be glad to send a copy on request.

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Table 1

Vapor Pressures⁷

	T(°K)	p(atm.)	
		obs.	calc.
Methane (W = 0.013)	113.15	1.129	1.001
	125.15	2.686	2.597
	137.15	5.474	5.488
	149.15	9.906	10.104
	161.15	16.501	16.849
	173.15	25.744	26.121
	185.15	38.382	38.385
Nitrogen (W = 0.034)	81.15	1.526	1.493
	89.15	3.317	3.314
	97.15	6.306	6.353
	105.15	10.844	10.960
	113.15	17.342	17.466
	121.15	26.295	26.133
Carbon Monoxide (W = 0.049)	83.15	1.183	1.155
	95.15	3.686	3.690
	107.15	8.797	8.896
	119.15	17.692	17.881
	127.15	26.413	26.363
Hydrogen Sulfide (W = 0.098)	213.15	1.01	1.04
	253.15	5.38	5.38
	293.15	17.57	17.49
	333.15	42.94	43.10
	353.15	62.55	62.16

Table 1 (Continued)

	T(°K)	p(atm.)	
		obs.	calc.
Ammonia (W = 0.256)	243.15	1.180	1.415
	273.15	4.238	4.355
	303.15	11.512	11.206
	333.15	25.817	25.305
	363.15	50.523	50.644
	373.15	61.780	61.828
Sulfur Dioxide (W = 0.256)	263.15	1.001	1.186
	295.15	3.492	3.547
	327.15	9.272	8.952
	359.15	20.308	19.889
	391.15	39.095	39.010

Table 2

8
Vapor-Liquid Equilibria

	T_r	P_r		obs.	Z calc.	ϕ calc.
Hydrogen Sulfide (W = 0.100)	0.760	0.153	v	0.845	0.872	0.886
			l	.0246	.0251	.884
	.886	.459	v	.689	.713	.778
			l	.0749	.0769	.782
	.959	.766	v	.529	.561	.707
			l	.139	.153	.705
	.988	.919	v	.420	.458	.676
			l	.190	.231	.673
	1.000	1.000	c	.283	.291	.658
Carbon Dioxide (W = 0.225)	0.931	0.608	v	.6233	0.649	0.743
			l	.09692	.101	.740
	.957	.748	v	.5481	.572	.710
			l	.1262	.138	.700
	.981	.888	v	.4575	.476	.680
			l	.1641	.193	.669
	1.000	1.000	c	.2746	.288	.657

Table 3

Compressibility Factor and Fugacities of Methane - n-Pentane⁹(W₁ = 0.013; W₂ = 0.252; v = vapor; l = liquid; c = critical)

T °R	P psi		x ₁	obs.	Z calc.	obs.	f ₁ calc.	obs.	f ₂ calc.
559.68	15.69	v	0.0	.957	.964	0.0	0.0	15.10	15.14
		l	.0	.0050	.0052		.0		15.59
	1000	v	.946	.878	.864	861	861	17.9	19.7
		l	.303	.271	.265		864		13.6
	2000	v	.919	.757	.740	1548	1575	18.1	16.6
		l	.573	.487	.458		880		27.1
	2455	c	.821	.645	.609	1773	1890	20.2	13.9
	679.68	v	.0	.840	.858	0.0	0.0	82.02	83.0
		l	.0	.0301	.0296		.0		80.7
	1000	v	.795	.858	.851	808	804	85.0	92.5
		l	.247	.272	.265		821		82.5
	2081	c	.665	.654	.608	1620	1748	96.4	79.1
779.68	329.16	v	.0	.607	.556	0.0	0.0	238.68	232.6
		l	.0	.110	.103		.0		210.8
	1025	c	.290	.454	.363	.522	660	236.9	208

Table 4

Compressibility Factor and Fugacities of n-Butane - Carbon Dioxide¹⁰(W₁ = 0.201; W₂ = 0.225; v = vapor; l = liquid; c = critical)

T °R	P psi	x ₁	Z		f ₁		f ₂	
			obs.	calc.	obs.	calc.	obs.	calc.
559.68	51.5	v 1.0	0.899	0.915	47.0	47.5	0.0	0.0
		l 1.0	.014	.015		46.7		.0
	300	v .202	.851	.840	40.8	40.2	222.0	220
		l .804	.077	.078		40.1		139
	700	v .100	.675	.643	29.1	24.9	505	505
		l .416	.151	.144		23.5		444
	1095	c .060	.279	.198	12.5	4.6	722	725
	436	v 1.0	.527	.551	303	306	0.0	0.0
		l 1.0	.137	.158		303		.0
	600	v .839	.501	.446	294	294	139	129
		l .927	.195	.201		296		108
	758	c .812	.328	.274	293	283	258	237

Figures

Figure 1. Compressibility Factor Z of n-Nonane⁸
(0-10000 psi).

$$\nabla T_r = 0.523 \text{ (559.68}^\circ\text{R)}$$

$$\odot T_r = 1.059 \text{ (799.68}^\circ\text{R)}$$

Figure 2. Compressibility Factor Z of Ammonia¹¹

$$\nabla T_r = 0.796$$

$$\odot T_r = 0.919$$

$$\triangle T_r = 1.473$$

Figure 3. Deviation DZ of the Compressibility Factor of Sulfur Dioxide¹² (obs. - calc.)

Figure 4. Critical Isotherm of Sulfur Dioxide

Figure 5. Compressibility Factor of Methane - Decane.⁸

Temp.	559.68°R	919.68°R
$y_1 = 0.1$	$\triangleright$	$\diamond$
$y_1 = 0.3$	∇	$\circ$
$y_1 = 0.7$	$\triangle$	$\square$

Figure 6. Compressibility Factor of Methane - Hydrogen Sulfide⁸

Temp.	620°R	740°R calc.
$y_1 = 0.3$	∇	$\triangle$ —
$y_1 = 0.7$	$\circ$	$\square$ - - -

Figure 7. Compressibility Factor of Methane - Carbon Dioxide¹³

Temp.	559.68°R	679.68°R
$y_1 = 0.4055$	$\circ$	
$y_1 = 0.8468$		$\square$

Figure 8. Compressibility Factor of Nitrogen - Ethylene¹⁴

(323.25°K)

$$y_1 = 0.198$$

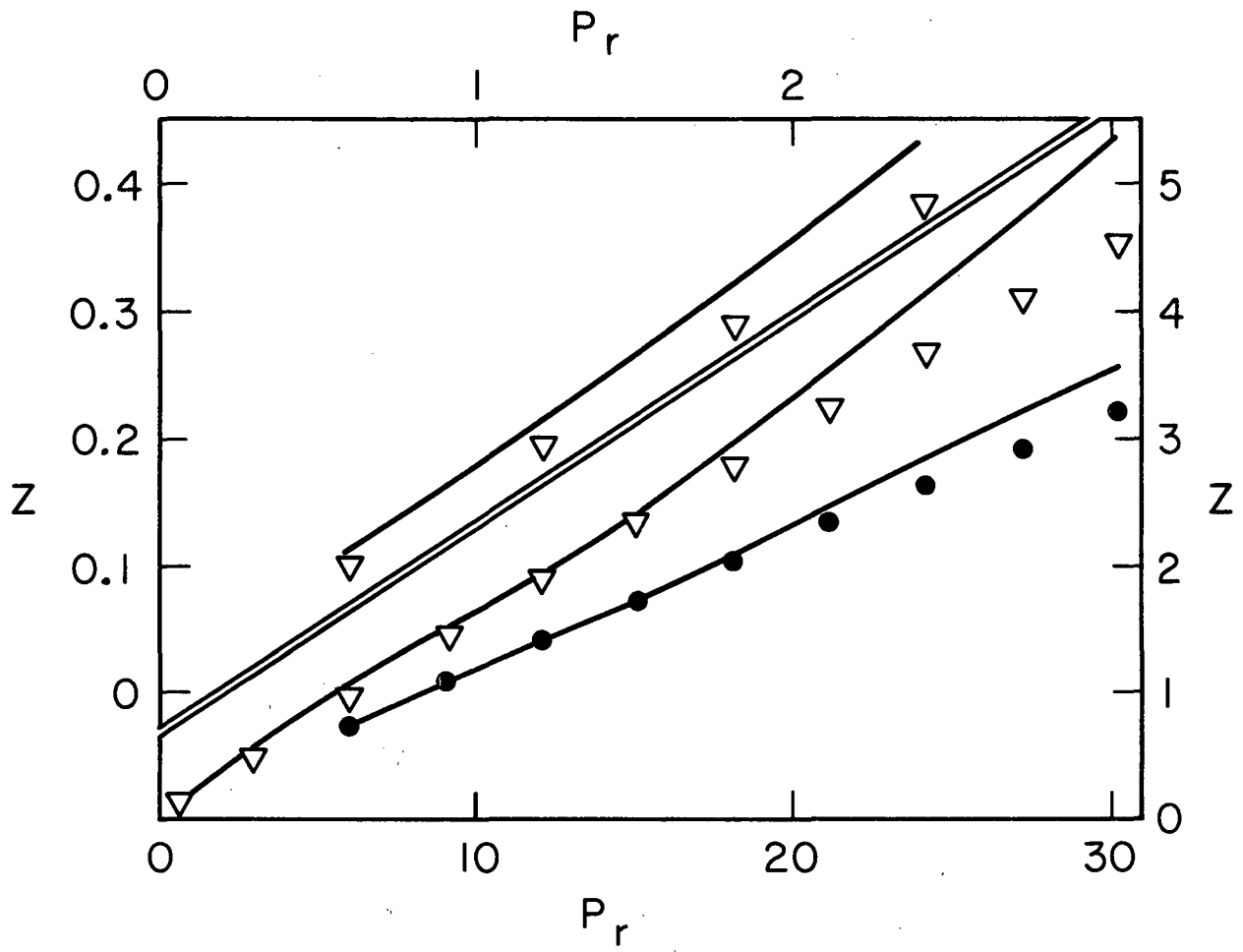


$$y_1 = 0.401$$



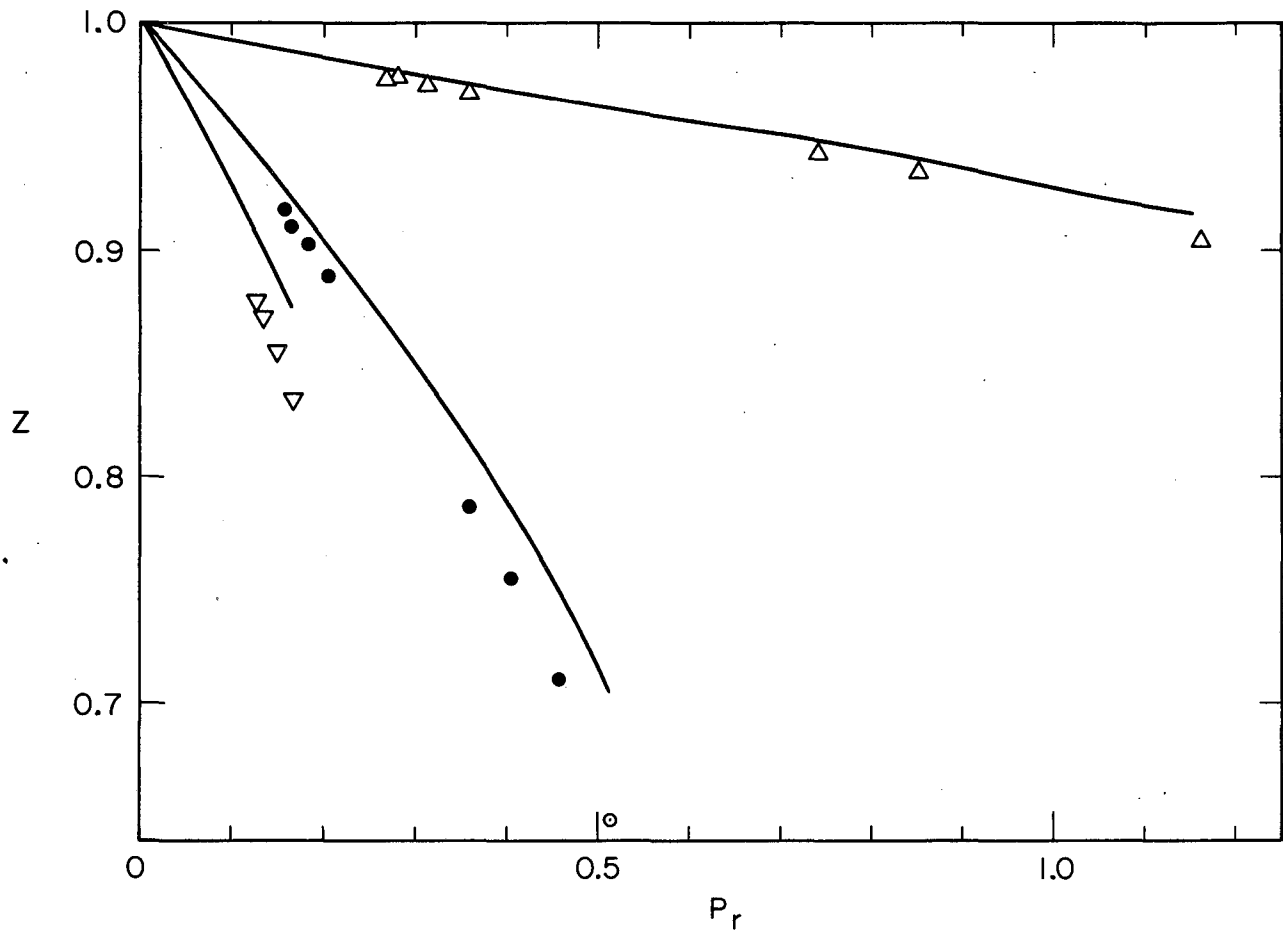
$$y_1 = 0.796$$





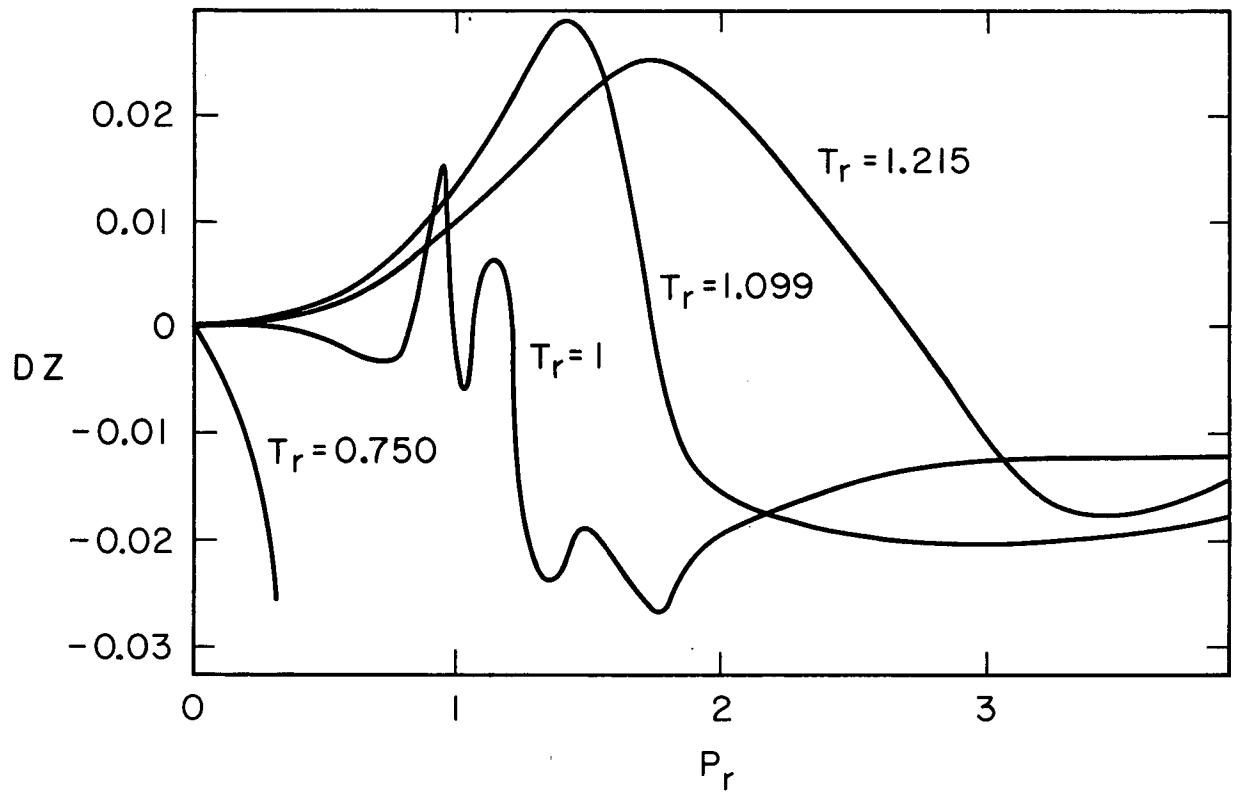
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Fig. 1



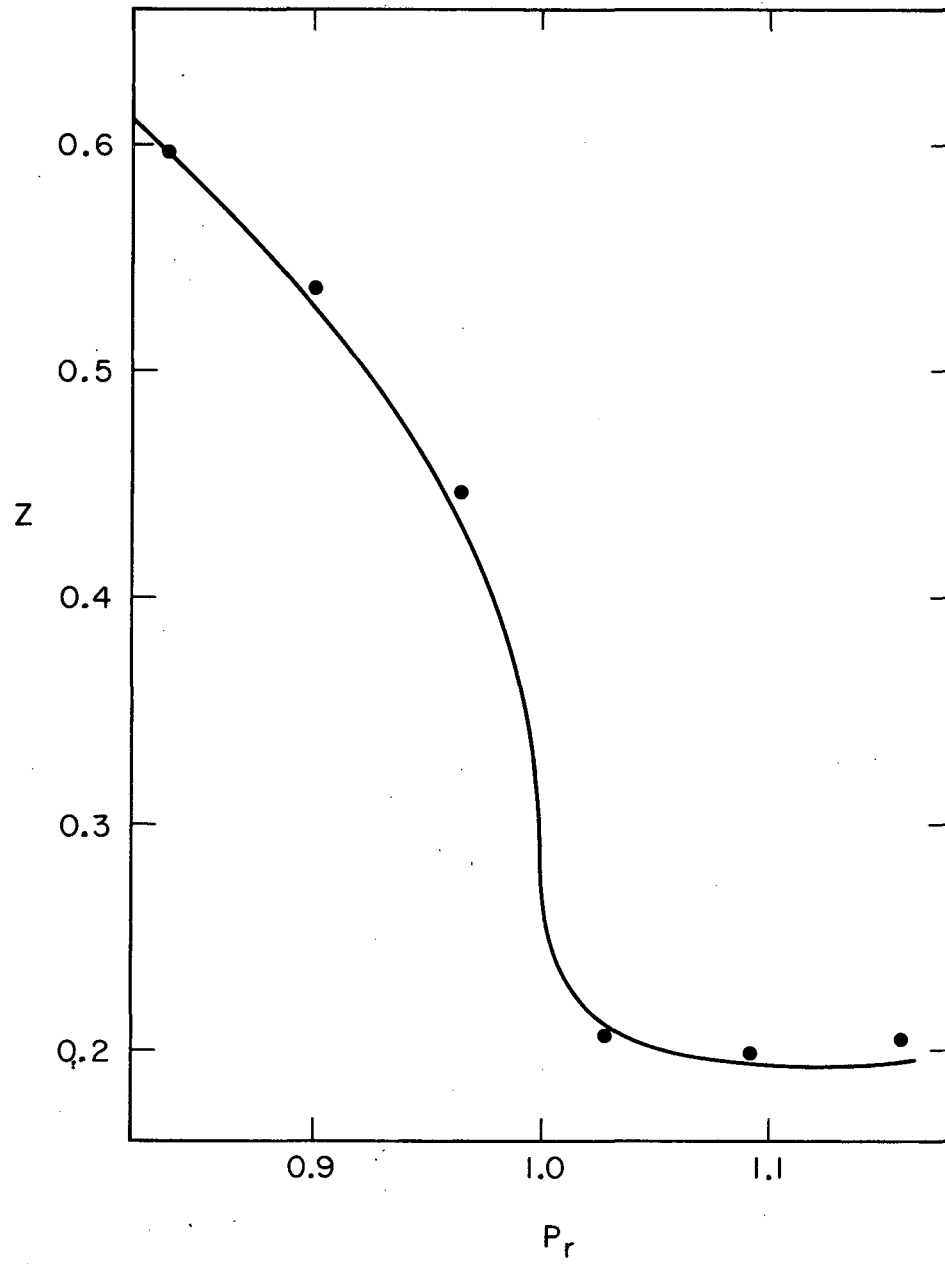
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Fig. 2



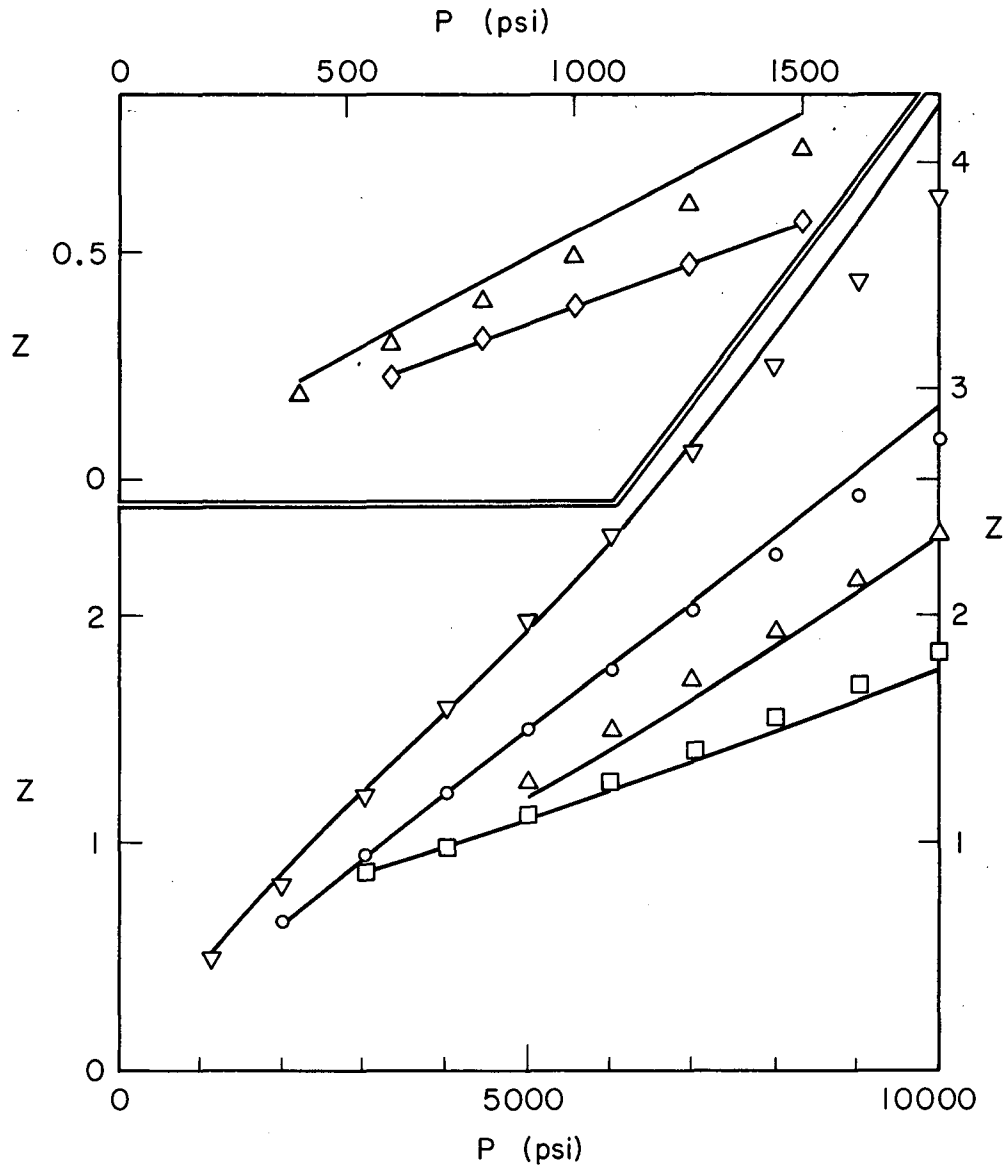
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Fig. 3



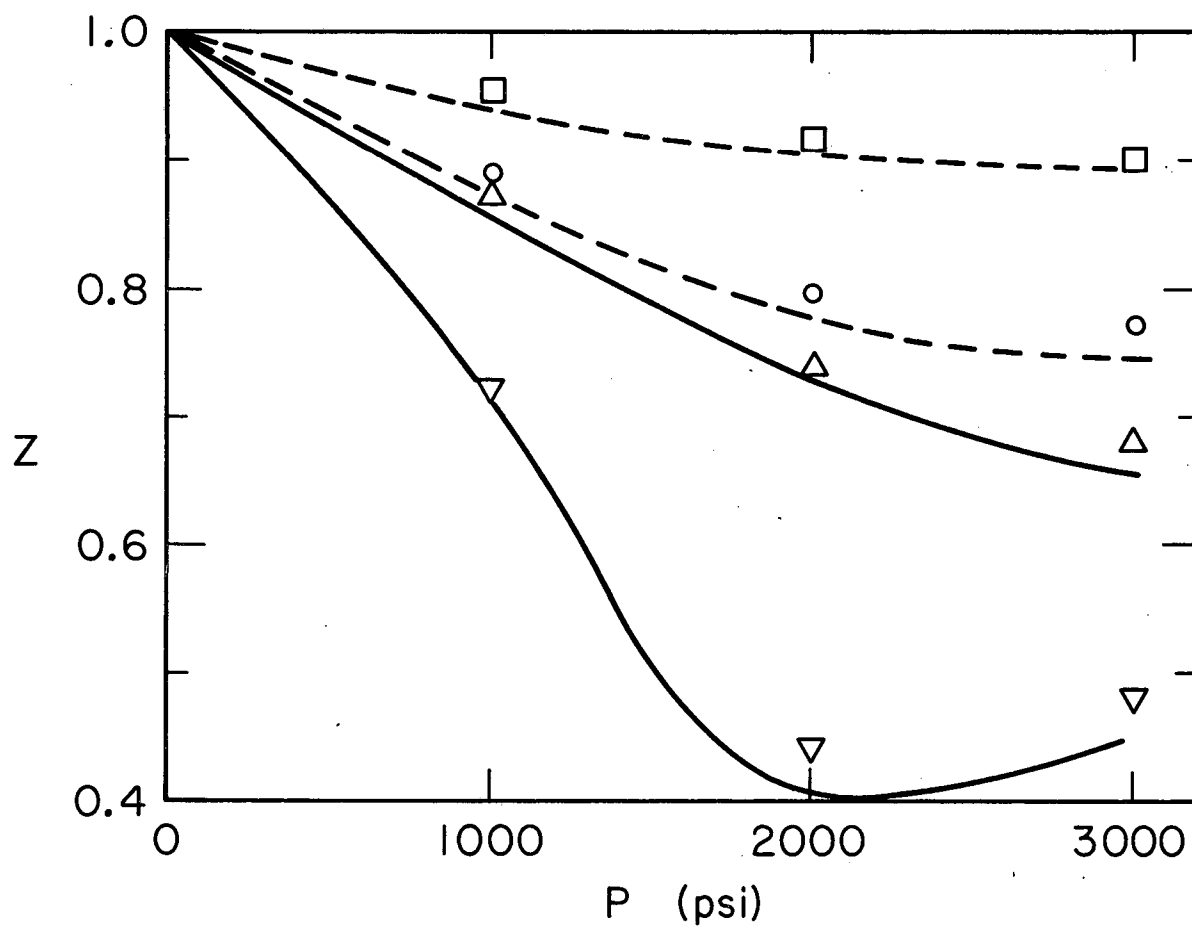
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Fig. 4



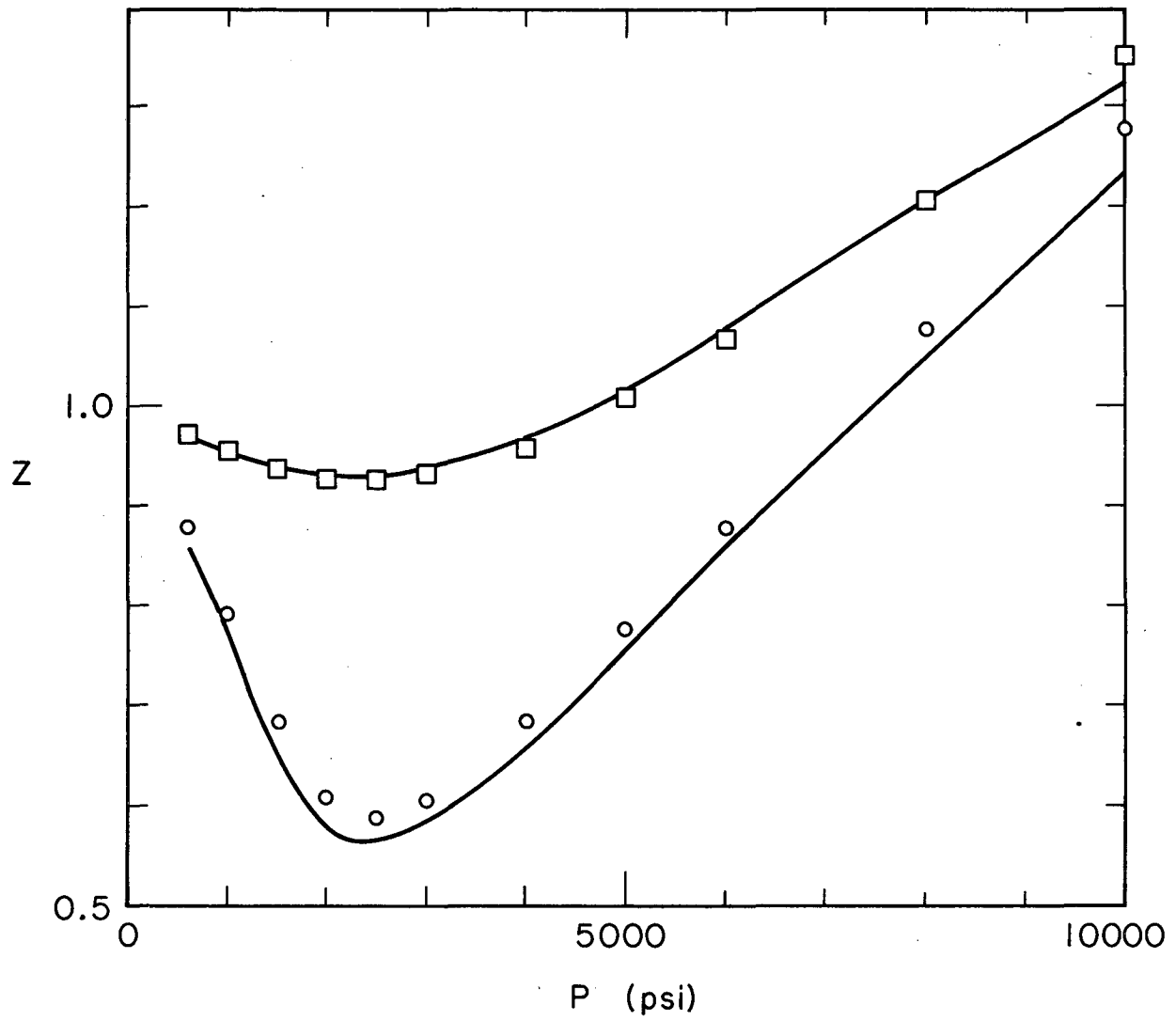
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Fig. 5



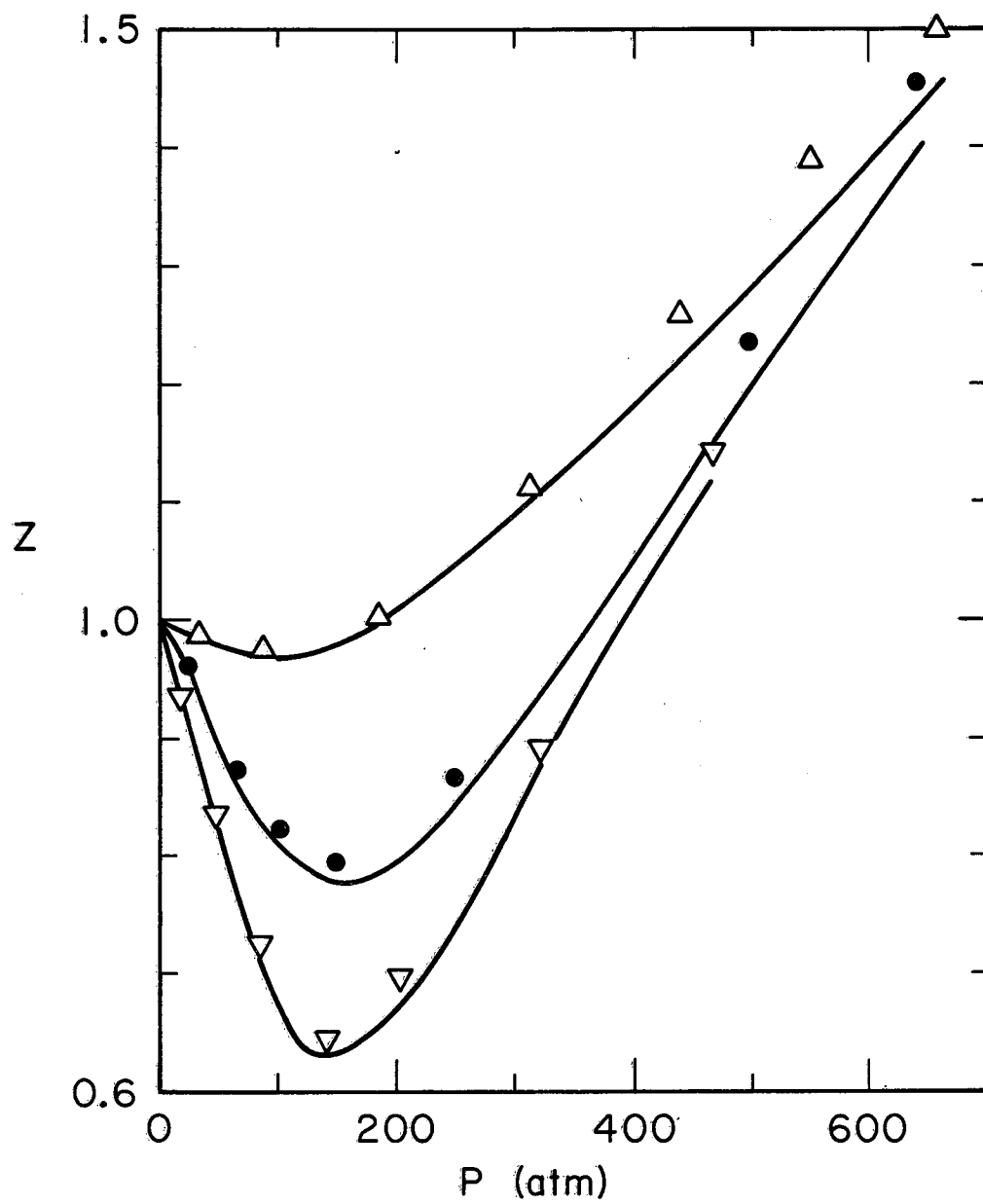
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Fig. 6



MUB-5480

Fig. 7



MUB-5481

Fig. 8

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