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Victoria B. T. Ngo
(M. S. Thesis)

December 1968

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Berkeley, California

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CALCULATION METHODS IN CHEMICAL THERMODYNAMICS

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December 1968

Abstract

A new modification of the equation of state of Redlich and Kwong has been developed and tested. Like earlier modifications it introduces only a third parameter and satisfies the limiting conditions for high temperatures and high pressures discussed before. It is essentially of the third order in the volume, i.e., deviations from the third order are introduced only through minor terms. An attempt has been made to arrive at a more elegant and compact form than presented by earlier modifications. This objective is believed to be realized to some extent by the present equation of state. Its practical use however is still restricted to automatic computation.

The representation of observed P-V-T data is in general very satisfactory. Some deviations occur at reduced temperatures between 1.1 and 1.4 in various pressure ranges for highly polar substances and for molecules with long chains. The deviations also increase below reduced temperature 0.8. No attempt has been made to apply the equation to anomalous substances such as water.

The extension to the calculations of fugacity coefficients and to multicomponent mixtures is planned.

The program, called ES68Z is described in the Appendix. Instructions for its use are given and the results of test computations are presented.

Principles of the calculation methods in chemical thermodynamics, except for the equation of state, have been developed by Lewis and Randall before 1923. Details required for the most efficient performance have been discussed and illustrated in the present work. The examples given are the ammonia synthesis, the representation of explosion limits in the ternary system water-hydrogen peroxide-acetic acid, and a model for the calculation of the equilibrium conditions of simultaneous reactions. This model serves as an illustration of methods used in automatic computation.

1. Introduction

Various tables of standard free energies and of activity coefficients are available as aids to calculations in chemical thermodynamics. Less satisfactory is the available information of fugacity coefficients. As a matter of fact, fugacity coefficients are practically never measured directly; they are derived from an equation of state. Such an equation could be defined in every single case in a purely empirical manner. But the advantage and the promise of a general relation, containing only few individual parameters, are so great that one would hesitate to do without it. Yet the problem of a technically useful equation of state does not appear to be finally solved, in spite of numerous attempts. A new modification of the two-parameter equation of Redlich and Kwong has been considered to be promising. Its development is outlined in the second chapter; the corresponding computer program ES68Z is described in detail in the Appendix.

The practical methods of using available thermodynamic data have been given little attention. Examples are of course described in many textbooks. In a technique like that of chemical thermodynamic calculations the emphasis will always lie on concrete examples. But there is a number of rules which can greatly enhance the efficiency, speed and reliability of calculations. It is useful to describe them in general terms and to show their applications in a few concrete examples. This is done in the third chapter.

2. An Improved Equation of State

21. The Problem of the Equation of State

A considerable part of the applications of chemical thermodynamics rests directly or indirectly on an equation of state. Fugacities of pure gases and of components of gaseous mixtures are practically always derived from an equation of state. Our knowledge of the free energy of liquids is to a large extent based on information of the fugacities of gases and therefore indirectly derived from an equation of state.

This situation explains the large number of proposed relations. Molecular theory has been useful in the validity range of the second and third virial coefficients. Beyond this range it has been of little help in obtaining quantitative information.

For practical purposes, especially in chemical technology, a relation is needed that can be applied to mixtures and that leads to fugacity coefficients of the components in a rigorous manner. Since the fugacity coefficients are the actual objective the strict realization of the thermodynamic connection between the equation of state and the fugacity coefficients is important. Practically we never measure fugacity coefficients; the derivation therefore must be reliable.

22. Advantages and Shortcomings of Older Equations

The great value of the equation of state of van der Waals lies in the derivation of the properties of imperfect gases from molecular theory and in the description of the critical point. The equation is qualitatively correct in this and other respects, for instance, in the conclusion that the volume of a gas is finite at infinite pressure. The

representation of the critical phenomena results from the fact that the equation is of third order.

Strangely enough, later authors have given up some of the great advantages of van der Waals. The equations proposed by Wohl (1914) and by Beattie and Bridgeman (1927) are of higher order. The relations proposed by Beattie and Bridgeman as well as the famous equation of Benedict, Webb, and Rubin (1940) result in the volume zero for high pressure. Moreover these equations contain too many empirical parameters. An excess number of parameters is not only undesirable because of the large number of empirical data required; it is detrimental because the coefficients cannot be unambiguously obtained even from a large number of data.

The tables proposed by Riedel (1954) and by Pitzer and his co-workers (1955) have the advantages of an unambiguous and reasonably accurate representation in a fairly large range. The tables show that three individual parameters are sufficient for all substances with the exception of associating substances such substances as water or alcohols, and hydrogen and helium. The disadvantages of the tabular representations are the inconvenience of double interpolations (with respect to temperature and pressure), and above all, the unsatisfactory connection with fugacity coefficients by numerical integration and differentiation.

23. Objectives

The preceding discussion indicates the objectives one would wish to attain: representation by an equation of essentially third order, containing three individual parameters. The limiting volume at high pressure should be 0.26 times the critical volume, as amply demonstrated by observed data. At the limit of low pressures or high temperatures

the perfect gas equation should be approached. The equation need not be strictly of third order. But the main terms should satisfy this condition; there may be minor correction terms in addition to the main terms. A fair representation of the critical point and the critical conditions is required.

Some of these objectives have been attained by the equation of Redlich and Kwong (1949). No relation however containing only two individual parameters can be flexible enough to give a satisfactory representation. This fact is sufficiently demonstrated by the failure of the two-parameter theorem of corresponding states. Moreover this equation leads to a critical compressibility factor $Z_c = 0.333$, higher than the observed value for any substance. For most substances Z_c has values between 0.25 and 0.29.

Several authors attempted to improve the equation of Redlich and Kwong replacing the two parameters by temperature dependent empirical functions. Redlich and Dunlop (1963) and Redlich, Ackerman, Gunn, Jacobson and Lau (1965) proposed computer programs containing deviation functions which depended on Pitzer's acentric factors. The disadvantage of these deviation functions was their complicated form. Although numerous attempts have shown in the last twenty years that no improvement can be attained by simple means, a more elegant solution of the problem was desirable.

The call of the problem lies in the critical point. The equation should furnish the correct value of the critical compressibility factor, which is introduced as the third parameter. The following section therefore investigates the critical isotherm. Later various corrections are introduced for several regions of the P-T field.

24. The Critical Isotherm

In the equation of Redlich and Kwong the compressibility factor Z is represented as

$$Z = PV/RT = 1/(1-h) - (A'^2/B')h/(1+h) \quad (2.1)$$

by means of the auxiliary variable

$$h = B'P/Z \quad (2.2)$$

and the two parameters

$$A'^2 = 0.4278/(P_c T_r^{2.5}) \quad (2.3)$$

$$B' = 0.0867/(P_c T_r) . \quad (2.4)$$

Since the reduced temperature is given by

$$T_r = T/T_c \quad (2.5)$$

the parameters can be computed from the critical values T_c and P_c .

For the following discussion it will be convenient to redefine the parameters

$$A = Z_c^2 P_r / (0.26 T_r^{2.5}) \quad (2.6)$$

$$B = 0.26 Z_c P_r / T_r . \quad (2.7)$$

The figure 0.26 is an abbreviation for 0.25992106 which follows from the solution of Eq. (2.1) for the critical point. It represents the ratio of the limiting volume at high pressure to the critical volume. If we introduce $Z_c = 0.3333$ the relation between the new and old parameters is

$$A = A'^2 P \quad (2.8)$$

$$B = B' P .$$

Introducing the new parameters into Eqs. (2.1) and (2.2) one obtains

$$Z = Z/(Z-B) - A/(Z+B) \quad (2.10)$$

or, in the standard form,

$$Z^3 - Z^2 + Z(A-B-B^2) - AB = 0 \quad (2.11)$$

The second and third critical conditions furnish the values (Eq. 2.6) and (Eq. 2.7) for A and B; the value $Z_c = 0.3333$ is then obtained from Eq. (2.11).

The problem is now to modify Eq. (2.11) in such a manner that the second and third critical conditions are maintained and the individual value Z_c for the critical compressibility factor is obtained. At first it looks as if there were infinite numbers of modifications which may satisfy these requirements. But the additional conditions discussed in Section 23 restrict the choice quite severely. The most general modification appears to be given by the functions $L(s)$ and $G(s)$ of the intermediate variable s that is a function of the reduced density

$$D_r = V_c/V \quad (2.12)$$

The functions L and G must satisfy at the critical point the following conditions:

$$L = 1-3Z_c; \quad (dL/dV)_T = 0; \quad d^2L/dV^2 = 0 \quad (2.13)$$

$$G = 0; \quad (dG/dV)_T = 0; \quad d^2G/dV^2 = 0 \quad (2.14)$$

These functions are used for a generalization of Eq. (2.10) in the form

$$Z = Z(1-L)/(Z-B) - A(1-G)/(Z+B) \quad (2.15)$$

leading to the standard form

$$Z^3 - Z^2(1-L) + Z[A(1-G) - B(1-L) - B^2] - AB(1-G) = 0 \quad (2.16)$$

The condition (Eq. 2.13) can be satisfied if one chooses

$$s = 3D_r - 3D_r^2 + D_r^3 \quad (2.17)$$

since at the critical point

$$s = 1; \quad ds/d(D_r) = 0; \quad d^2s/d(D_r)^2 = 0. \quad (2.18)$$

Five coefficients c_1 to c_5 were introduced into L and G in order to satisfy the observed data. With

$$c_2 = \exp[2.303(1-3Z_c)/c_1] - 1 \quad (2.19)$$

a satisfactory representation was obtained by

$$L(s) = (c_3 + s - c_3 s) c_1 \log(1 + c_2 s) \quad (2.20)$$

$$G(s) = c_4 \log[1 + c_5 s^2 (s-1)^2] \quad (2.21)$$

The coefficient c_3 is chosen

$$c_3 = 1 \text{ for } s \geq 1 \quad (2.22)$$

The other coefficients are given in (2.23) to (2.25).

The continuity of L and its first two derivatives is maintained because of Eq. (2.18).

The introduction of the second and third critical conditions into Eq. (2.16) leads back, in view of Eqs. (2.13) and (2.14), to the relations (2.6) and (2.7) for A and B. In addition the solution of Eq. (2.16) for the critical point leads to any value Z_c introduced as the third parameter.

Figure 1 shows the satisfactory agreement of an equation of the type (Eq. 2.16) with the results for the acentric factors 0.0 and 0.5, obtained by Pitzer and his coworkers through smoothing experimental data.

25. Temperature Dependence

The functions L and G introduced in the preceding section endow the modified equation with a considerable flexibility through the

coefficients c_1 to c_5 of Eqs. (2.19) to (2.21). Any of these coefficients may be functions of the temperature. Pitzer's tables were used as a primary experimental basis for finding the best values of these functions. The approach of the perfect gas equation ensures the validity at high temperatures. Increasing deviations may be expected below a reduced temperature $T_r = 0.8$, which is the lower limit of Pitzer's tables.

The coefficients c_1 , c_4 , and c_5 in Eqs. (2.19) and (2.21) have been represented by:

$$c_1 = c_6/[1+c_7(Tr-1)] \quad (2.23)$$

$$c_4 = c_8[1.21+c_9(Tr-1)]/(1+0.1Tr)^2 \quad (2.24)$$

$$c_5 = c_{10}[1.21+c_{11}(Tr-1)]/(1+0.1Tr)^2 \quad (2.25)$$

These three coefficients are defined in such a way that they meet the restrictions imposed in Section 23. As can be seen, at the critical temperature the terms with the coefficients c_7 , c_9 and c_{11} become zero. The best numerical values for the coefficients c_6 to c_{11} were found to be

$$c_1 = 0.1/[1+2.06(Tr-1)] \quad (2.26)$$

$$c_4 = 0.95[1.21+2.74(Tr-1)]/(1+0.1Tr)^2 \quad (2.27)$$

$$c_5 = 0.085[1.21+4.34(Tr-1)]/(1+0.1Tr)^2 \quad (2.28)$$

The coefficient c_3 could be represented by

$$c_3 = 1.43/Tr^{1.5} - 1.32 \quad (2.29)$$

Equation (2.16) proved to be satisfactory only within the region $0.8 < Tr \leq 1.0$. An inspection of Eqs. (2.25) and (2.28) shows that the computation becomes meaningless for $T_r < 0.721$ since c_5 may assume a

negative value. Improvement for higher temperatures was achieved by gradual approach of the original equation of Redlich and Kwong. For this purpose a mixing factor

$$\begin{aligned} c_{12} &= 1 - \exp[-0.05/(T_r-1)] & (T_r \geq 1) \\ c_{12} &= 1 & (T_r \leq 1) \end{aligned} \quad (2.30)$$

was introduced.

If we denote by Z_K the result of Redlich and Kwong, and by Z_M the root of the modified equation (2.16), the mixed compressibility factor is given by

$$Z = c_{12}Z_M + (1-c_{12})Z_K \quad (2.31)$$

Even so, appreciable deviations from observed values were still found at supercritical temperatures. The addition of a deviation function was found to be necessary. The expression

$$Z_D = \frac{\text{Pr}(T_r-1)[(3.281-11.1Z_c)(T_r^3-2.6(T_r-1)) + \{(4.36-15Z_c)T_r-6.70+21.3Z_c\} \text{Pr}^{0.5}]}{[T_r^6+0.4\text{Pr}^2]} \quad (2.32)$$

$$Z_D = 0 \quad (T_r \leq 1)$$

was found to give the best representation. The final form of the equation is now

$$Z = c_{12}Z_M + (1-c_{12})Z_K + Z_D \quad (2.33)$$

The results described in this section and the preceding one constitute the basis of the Computer Program ES68Z. This program and all tests carried out are described in detail in the Appendix.

26. Comparison with Observed Data

In Fig. 1 the good fit of the critical isotherm was shown on the basis of the data given by Pitzer and his co-workers for substances with the acentric factors 0.0 and 0.5, i.e., with critical compressibility factors of 0.291 and 0.251. Figures 2 to 4 show the agreement for the reduced temperatures 0.8, 1.2 and 4.0. The most serious discrepancy occurs at low pressures and $Tr = 1.2$ and an acentric factor of 0.5 (which is actually beyond the range of Pitzer's tables). For lower values of the acentric factor one can reasonably expect smaller deviations. Aside from this region near the critical point, the agreement is quite satisfactory.

Results for liquid n-nonane at the reduced temperatures 0.747 and 0.859 are shown in Fig. 5. For the higher temperatures the deviations are moderate even at a reduced pressure as high as 30 far beyond the range of Pitzer's tables. Also at the lower temperatures the deviations are small up to $Pr = 10$. But the equation cannot be relied upon below $Tr = 0.8$.

One sees immediately from the diagram of the critical isotherm of sulfur dioxide (Fig. 6) that a curve of this kind is difficult to represent algebraically. Actually the deviations of the calculated values from the observed curve are small. At the reduced temperature $Tr = 1.215$ and the reduced pressure $Pr = 1.928$ the deviation in Z amounts to 0.045. This is the region in which the largest deviations from Pitzer's tables for an acentric factor 0.5 have been found. On the whole, the result is quite satisfactory for a substance as strongly polar as sulfur dioxide.

Ammonia (Fig. 7), another strong polar substance is well represented. The deviations in Z do not exceed 0.024 at a reduced temperature 1.475, i.e., 326°C. This is in the technically interesting temperature region.

Detailed data for a comparison of observed and calculated values of Z are shown in the Appendix for substances discussed in this section and for benzene, 1-butene, hydrogen sulfide, carbon dioxide, helium, xenon, hydrogen, nitrogen and oxygen. The results are similar to those discussed. On the whole, they are considered to be satisfactory.

3. Examples of Thermodynamic Calculations

31. General Rules

Sixty years have passed since Caratheodory made the last major contribution to fundamental thermodynamics, and G. N. Lewis to its practical applications. Numerous attempts in both fields have produced little progress in fundamental thermodynamics, but thermodynamic calculations in chemical engineering problems have been steadily and vigorously developed. Even so, there is still a wide field opened for improvement in the efficiency of thermodynamic calculations. Efficient methods are of particular value in the design of routine calculations in the chemical plant and laboratory; they are useful also in the design of computer programs.

A series of computations of the same kind, e.g., computation of equilibrium conversions under varying conditions, is advantageously carried out in a table. No part of the computation is performed on a separate sheet. One line of the table is assigned to each single step carried out directly or by slide rule or by desk calculator.

Each single computation problem (e.g., set of conversion conditions) is assigned one column. This choice is almost always preferable to assigning one line to each problem and one column to each operation.

The reason for this choice is the easier performance of an operation based on data that are aligned in a column rather than in a horizontal line. The opposite choice may be preferable in a rare exceptional case such as a numerical integration.

Computation is best carried out line by line. Speed and reliability are increased by immediately repeating the same operation. There is a good chance of detecting an error by casually inspecting similar intermediate results written in one line. The same advantage is obtained in the inspection of the final results. It will often be useful to observe directly the response of the results to a change in conditions.

In graphical representation a distinction should be made between diagrams for computing and illustrations. The scales in diagrams of the first kind should be chosen so that experimental errors are noticeable. Otherwise the graphical representation leads to a loss of accuracy. If this condition cannot be reasonably satisfied, one plots a deviation function, i.e., the difference between the observed values and a simple crude approximation function (linear or parabolic function). The computation is then carried out partly numerically and partly graphically.

In illustrations this rule will usually be disregarded. Here the objective is to give information of the functional relation at the first glance. A few rules are obvious: the curves should fill essentially the whole available space and the slope of the major part should be roughly 45° or 135° .

The usefulness of all these rules is best shown by a few examples like those following.

32. Ammonia Synthesis

The objective of a thermodynamic examination of the synthesis of ammonia is to calculate the equilibrium yield of ammonia, as it is influenced by pressure, temperature, and the presence of argon.

The ammonia synthesis is based on the equilibrium reaction



The thermodynamic equilibrium constant for this reaction can be calculated from

$$\ln K = -\Delta G^\circ / RT. \quad (3.2)$$

The standard free energy change ΔG° for the reaction must first be determined. These free energy changes at different temperatures may either be read directly from thermodynamic tables or calculated from thermodynamic equations as a function of temperature. In our case, the ΔG° is calculated in the following manner.

In the compilation of Wicks and Block (1963) we find

$$\Delta C_p = -6.0 + 4.32 \times 10^{-3} T - 0.55 \times 10^{-5} T^{-2}. \quad (3.3)$$

Since

$$\Delta C_p = (\partial \Delta H / \partial T)_p \quad (3.4)$$

we have

$$\Delta H = -6T + 2.16 \times 10^{-3} T^2 + 0.55 \times 10^{-5} T^{-1} + c_1. \quad (3.5)$$

The integration constant c_1 is found by substituting a known value of ΔH at a given temperature. In this case, we use the value of -11400 cal/gmole for ΔH° at 298.15°K. Solving for c_1 we have $c_1 = -9628$. The relation

$$\partial(\Delta G^\circ / T) / \partial T = -\Delta H^\circ / T^2 \quad (3.6)$$

furnishes

$$\Delta G^\circ/T = 6 \ln T - 2.16 \times 10^{-3} T + 0.27 \times 10^5 T^{-2} - 9628/T + c_2. \quad (3.7)$$

To find the integration constant c_2 , we substitute $\Delta G^\circ = -4000$ cal/gmole at $T = 298.15^\circ\text{K}$ into the equation, and c_2 is found to be -14.93 . Rearranging, we obtain

$$\Delta G^\circ = 6T \ln T - 2.16 \times 10^{-3} T^2 + 0.27 \times 10^5 T^{-1} - 9628 - 14.93T. \quad (3.8)$$

We then proceed to solve for K at any desired temperature from Eq. (3.2), as shown in Table 1, which presents the first, simple example of applying the rules of the preceding section.

Table 1. Ammonia Synthesis.

$T^\circ\text{K}$	623.15	773.15
$\log T$	2.7946	2.888
$A = 6 \cdot 2.303 \log T$	38.62	39.91
$B = 2.16 \times 10^{-3} T$	1.346	1.670
$C = 0.27 \times 10^5 / T^2$	0.043	0.045
$D = 9628/T$	15.45	12.45
$E = A - B + C - D - 14.93$	6.937	10.905
$\log K = -E/2.303 \cdot 1.987$	-1.5160	-2.3831
K	0.03048	0.00414

In Table 2 the values of $\log K$ at various temperatures for the ammonia synthesis are shown as calculated from equations of Wicks and Block, and Harrison and Kobe (1953).

Usually one introduces the reactants in the stoichiometric ratio of $1\text{N}_2:3\text{H}_2$ so that the residue can be recycled without a special make up. If argon is present, it is enriched in the residue; the result is a lower conversion such that some of the residue must be rejected. Calculations of the conversion to ammonia at equilibrium are made both for the absence and the presence of 10 mole % argon in the feed stream.

Table 2. Equilibrium Constants.

T(°K)	Wicks & Block	Harrison & Kobe
	Eq. (3.8)	
	log K_W	log K_H
298.15	2.921	
400	0.8171	
500	- .4661	-0.52178
600	-1.351	-1.39940
700	-2.003	-2.04342
800	-2.504	-2.53646

Table 3 gives a summary of the following terms expressed as a function of α , the mole fraction of argon in feed and c , the fraction of feed converted to ammonia at equilibrium:

n_i° = number of moles i in the feed initially

n_i = number of moles i in equilibrium

n = total number of moles of components in the equilibrium mixture

y_i = mole fraction of any component in the equilibrium mixture.

The partial molal free energy of any component in a mixture, \bar{G}_i , is the sum of the partial molal free energy of the gas when it behaves ideally, \bar{G}_i^{id} , and the excess partial molal free energy, \bar{G}_i^E .

$$\bar{G}_i = \bar{G}_i^{id} + \bar{G}_i^E \quad (3.9)$$

It should be noted that \bar{G}_i^E is a correction factor for the deviation from ideality, and at the same time a function of fugacity coefficient ϕ . \bar{G}_i^{id} and \bar{G}_i^E are expressed as

$$\bar{G}_i^{id} = G_i^{\circ} + RT \ln y_i \quad (3.10)$$

$$\bar{G}_i^E = RT \ln \phi_i \quad (3.11)$$

Table 3. Composition.

	0.5N ₂	+	1.5H ₂	=	NH ₃	+	Ar
i	(1)		(2)		(3)		(4)
n _i ^o	0.5(1-α)		1.5(1-α)		0		2α
n _i	0.5(1-α)(1-c)		1.5(1-α)(1-c)		c(1-α)	2α'	n = 2 - 2α - αc
y _i	$\frac{0.5(1-\alpha)(1-c)}{2-c+\alpha c}$		$\frac{1.5(1-\alpha)(1-c)}{2-c+\alpha c}$		$\frac{c(1-\alpha)}{2-c+\alpha c}$		

The free energy change for any reaction is given as

$$\Delta G = \sum n_i \bar{G}_i. \quad (3.12)$$

Substituting Eqs. (3.9), (3.10) and (3.11) into Eq. (3.12), we have,

$$\Delta G = \Delta G^\circ + nRT \ln P + RT \sum n_i \ln y_i + RT \sum n_i \ln \phi_i. \quad (3.13)$$

Since at equilibrium,

$$\Delta G = 0$$

one obtains

$$-\Delta G^\circ = RT [\ln P^n + \sum n_i \ln (y_i \phi_i)] \quad (3.14)$$

or

$$-\frac{\Delta G^\circ}{RT} = \ln \left[\frac{y_3}{P y_1^{0.5} y_2^{1.5}} \cdot \frac{\phi_3}{\phi_1^{0.5} \phi_2^{1.5}} \right] \quad (3.15)$$

Equating Eq. (3.2) to Eq. (3.15), we obtain,

$$\ln K = \ln \left[\frac{1}{P} \cdot \frac{y_3}{y_1^{0.5} y_2^{1.5}} \cdot \frac{\phi_3}{\phi_1^{0.5} \phi_2^{1.5}} \right] \quad (3.16)$$

Denoting the second and third quantities on the right hand side of the equation as Y and Φ respectively, and simplifying, we have

$$K = Y\Phi/P \quad (3.17)$$

Since

$$Y = \frac{y_3}{y_1^{0.5} y_2^{1.5}} \quad (3.18)$$

and

$$y_2 = 3y_1 \quad (3.19)$$

substituting Eq. (3.19) and the y_i 's in Table 3 into Eq. (3.18) we have

$$Y = \frac{1}{3^{1.5}} \cdot \frac{c(2-c+\alpha c)}{0.5^2(1-\alpha)(1-c)^2} \quad (3.20)$$

From Eqs. (3.17) and (3.20) we obtain

$$K = \frac{1}{3^{1.5}(.25)} \cdot \frac{c(2-c+\alpha c)}{(1-\alpha)(1-c)^2} \cdot \frac{\Phi}{P} \quad (3.21)$$

Simplifying and rearranging, we have a quadratic equation:

$$(1.3PK + \Phi)(1-\alpha)c^2 - 2[1.3PK(1-\alpha) + \Phi]c + 1.3PK(1-\alpha) = 0 \quad (3.22)$$

Solving for c,

$$c = \frac{[1.3PK(1-\alpha) + \Phi] \pm \sqrt{[1.3PK(1-\alpha) + \Phi]^2 - [1.3PK(1-\alpha)]^2(1.3PK+\Phi)}}{(1-\alpha)(1.3PK+\Phi)} \quad (3.23)$$

From Table 3,

$$y_3 = \frac{c(1-\alpha)}{2-c+\alpha c} \quad (3.24)$$

From Eqs. (3.23) and (3.24), one can compute the mole fraction y_3 of ammonia at equilibrium at a given temperature and pressure.

Since the fugacity coefficient Φ is dependent on temperature, pressure and composition of the gases, it is necessary to find first the values of Φ at each specified condition before going into the actual calculations for c.

From the fugacity coefficients obtained from an equation of state (Redlich et al. 1965), we can calculate Φ for different compositions. Values of Φ at a specified temperature and pressure are then plotted against y_3 in Figs. 8 and 9. The result obtained by Hougen, Watson and Ragatz (1954) and that by Dodge (1944) are also shown in the figures. Since y_3 is not known beforehand, one has to repeat the calculation after a first trial.

Table 4 shows an example of tabular computation of y_3 at 773.15°K and 300 atm from Eqs. (3.23) and (3.24), with $\alpha = 0.0$ and $\alpha = 0.1$. We first assume a value of y_3 , indicated by parenthesis in Table 4, obtain numerical values of K and Φ from Table 1 and Fig. 9, substituting into Eq. (3.23), we find the value for c . From Eq. (3.24), we in turn solve for y_3 . If the assumed and the calculated values of y_3 do not agree, a second trial is made using the first calculated y_3 as assumed. In the present case, two trials are sufficient to obtain good results.

The simplicity of tabular computation will be evident by comparison with any other way of solving Eqs. (3.23) and (3.24). The steps indicated in Table 4 are the same as those to be used in a computer program.

The effects of the process variables on the ammonia conversion c (Eq. 3.23) are shown in Tables 5 and 6. Table 6 gives the conversion of ammonia in the equilibrium mixture at 300 atm and 773.15°K. Columns 3, 4 and 5 give respectively the conversion as calculated by the Lewis rule, by the virial equation and by the equation of Redlich and Kwong. These figures have been given by Sortland and Prausnitz (1965). Column 6 is obtained from the experimental data given by Curtis (1932). The fugacity rule of Lewis and Randall leads to a serious discrepancy. The other results agree fairly well with each other and also with the observed values of Curtis.

Table 4. Equilibrium Calculation.

T(°K)	773.15			
K	0.00414			
P(atm)	300			
α	0		0.10	
A = (1- α)	1		0.90	
B = 1.3PK	1.615		1.615	
D = A·B	1.615		1.454	
Iteration	1	2	1	2
y_3	(0.3)	0.249	(0.3)	0.204
ϕ	0.9116	0.91	0.9116	0.91
-b = D + ϕ	2.527	2.525	2.366	2.364
b^2	6.386	6.376	5.598	5.589
E = B + ϕ	2.527	2.525	2.527	2.525
$4ac = DAE$	4.081	4.078	3.307	3.305
$b^2 - 4ac = r^2$	2.305	2.298	2.291	2.284
r	1.519	1.516	1.513	1.51
-b - r	1.008	1.009	0.853	0.854
$2a = AE$	2.527	2.525	2.274	2.273
$C = (-b-r)/2a$	0.399	0.400	0.375	0.376
CA	0.399	0.400	0.338	0.338
$C\alpha$	0	0	0.034	0.034
$2 - c + C\alpha = s$	1.601	1.60	1.659	1.659
$y_3 = CA/s$	0.249	0.250	0.204	0.204

Table 5. Ammonia Conversion.

T(°K)	P(atm)	c, Mole % NH ₃		
		0% Ar		10% Ar
		Observed	Calculated	Calculated
623.15	200	52.4	53.7	43.0
	500	-	74.8	57.5
773.15	200	19.5	18.8	15.2
	500	37.2	34.8	28.0

Table 6. Calculated Conversions.

T(°K)	P(atm)	c, Mole % NH ₃					
		0% Ar				10% Ar	
		Lewis	Virial	Redlich Kwong	Curtis	Present result	Present result
773.15	300	22.75	25.93	25.15	26.44	25.00	20.40

Since the combination of hydrogen and nitrogen to form ammonia is accompanied by a decrease in volume, it is apparent from the general principle underlying any equilibria that an increase in pressure will favor the forward direction, and thus a higher ammonia content. From Table 5, the percentage of ammonia at equilibrium at 632.15°K decreases from 74.8 to 53.7% when the pressure drops from 500 to 200 atm.

The effect of temperature is also very marked. Since the ammonia synthesis is exothermic, the reaction is favored at lower temperatures. As can be seen from Table 5, at a pressure of 500 atm, the ammonia content rises from 34.8% at 773.15°K to 74.8% at 623.15°K.

The presence of an inert gas such as argon in the system affects the equilibrium yield of ammonia to a great extent. The effect can be seen from the data shown in Tables 5 and 6.

The ammonia conversion in equilibrium with a 3:1 mixture of hydrogen and nitrogen gases is dependent on several variables which one has to take into careful consideration in order to obtain the highest possible conversion.

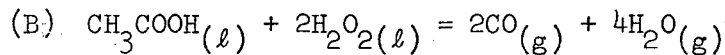
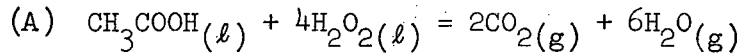
33. A Phase Diagram for Explosion Limits

Any reaction, not taking place near equilibrium is accompanied by a decrease of free energy. The sign of the calculated virtual change provides a means to find out whether or not a given reaction is spontaneous under specified conditions. In order for an explosion to occur, there must be a sizable decrease in free energy. In general, the greater the decrease of the free energy change, the more violent may be the explosion. The violence of an explosion may be particularly great if the decrease of enthalpy is large.

Explosion hazard has become a serious problem in the handling of organic solutions of hydrogen peroxide. It is of interest to investigate the possibility of detonation of the mixtures and the characteristics of the system within the explosion limits.

Tables of the free energy are used in the calculations of ΔG° and ΔH° for a given change. The data used have been obtained from Table A-7 in "Thermodynamics" by Lewis - Randall - Pitzer - Brewer (1961). The function $-(G^\circ - H^\circ)/T$ will be called q . The symbol q_0 is used if the enthalpy refers to 0°K as a standard state, and q_{298} is used for a standard state at 298°K . To convert q_0 to q_{298} , we add $(\Delta H_{298}^\circ - \Delta H_0^\circ)/T$ with ΔH denoting the

value for the formation from the elements. All calculations are made for a temperature of 298°K. As a somewhat involved example of explosion danger the ternary system acetic acid-hydrogen peroxide-water will be examined. Five changes, chemical or physical, are anticipated to occur within this system. They will be called simple reactions:



To determine the possibility of an explosion of this system from the values of ΔG and ΔH , the first step is to compute ΔG° and ΔH° of each of these reactions. It is obvious that the reactions proceed from liquid reactants to gaseous products. Hence various conversions are necessary in the computation. The symbol (') refers to the gaseous state. An asterisk * will be used to indicate that a summation is to be carried out for the values of the liquid reactants and gaseous product.

From the tables we obtain the values q_0' for the gaseous substances and therefore the values of $G^\circ' - H_0^\circ'$. They are converted (Table 7) for the liquid reactants to the quantities $G^\circ - H_0^\circ$ by means of the vapor pressures p° (atm) according to

$$G^\circ = G^\circ' + RT \ln p^\circ. \quad (3.25)$$

Then we obtain (Table 8) $\Delta G^{\circ*}$ for the reaction from the pure liquids to the pure gases by

$$\Delta G^{\circ*} = \Delta(G^\circ - H_0^\circ) + \Delta H_0^\circ' \quad (3.26)$$

In other words, using $G^{\circ} - H_{\text{O}}^{\circ}$ for the liquids, one finds the desired ΔG° by using the enthalpy change for the purely gaseous reaction.

The enthalpy change ΔH_{298}^* for the reaction from liquids to gases must be computed separately (Table 8).

Vapor pressures are taken from the literature, and heats of vaporization computed from the equation of Clausius and Clapeyron.

Pure substances under consideration are characterized by the subscripts 1 to 6. The numbers 7 to 17 are used to indicate mixtures in the ternary phase diagram.

Various auxiliary quantities are assembled in Table 7. The vapor pressures for water and acetic acid have been taken from Perry's Handbook, that of hydrogen peroxide from Maass and Hiebert (1924). In this and the following tables the symbol \uparrow is used to indicate the quantity given in the preceding line. The symbol $\uparrow\uparrow$ is used for the quantity in the line before.

The standard enthalpy of formation ($\Delta H_{\text{O}}^{\circ}$ or ΔH_{298}° of Pitzer and Brewer) will be called H_{O}^f or H_{298}^f in the following section.

Variations in the composition of a mixture will result in different combinations of the simple reactions in the system. Hence the values of ΔG and ΔH of a system of this kind depend greatly on its composition. The explosive reaction is represented as a composite of the simple reactions (A) to (E). We denote by a, b...e the numbers of moles converted according to the reaction equations (A), (B)...(E). Since we start from a mixture (liquid, mole fractions $x_1, x_2 \dots$) and obtain a mixture (gaseous, mole fractions $y_1, y_2 \dots$), we have to include the composition dependent parts of the free energy. Since they are small in any case, we assume that the relations for perfect solutions and perfect gas mixtures furnish

Table 7. Auxiliary Quantities.

	CH ₃ COOH (g, l)	H ₂ O (g, l)	CO ₂ (g)	H ₂ O (g, l)	CO (g)	O ₂ (g)
i	(1)	(2)	(3)	(4)	(5)	(6)
q _o '	56.50	46.95	43.56	37.17	40.25	42.06
G ^o ' - H _o ^o '	-16845	-13998	-12987	-11082	-12001	-12540
P ^o (mmHg)	33.18	2.1		23.756		
760/P ^o	22.905	361.90		31.992		
-log ↑	-1.360	-2.559		-1.505		
2.3RT·↑	-1855	-3491		-2053		
G ^o ' - H _o ^o ' + ↑	-18700	-17489		-13135		
H ₂₉₈ ^{f'}	-103800	-32530	-94052	-57798	-26416	0
H _o '	-100500	-31040	-93969	-57107	-27202	0

a sufficient approximation. Thus we obtain

$$\begin{aligned} \Delta G = & a\Delta G_a^{o*} + b\Delta G_b^{o*} + c\Delta G_c^{o*} + \dots \\ & + y_1^{RT} \ln y_1 + y_2^{RT} \ln y_2 + \dots \\ & - x_1^{RT} \ln x_1 - x_2^{RT} \ln x_2 - \dots \end{aligned} \quad (3.27)$$

$$\Delta H = a\Delta H_a^{o*} + b\Delta H_b^{o*} + c\Delta H_c^{o*} + d\Delta H_d^{o*} + e\Delta H_e^{o*} \quad (3.28)$$

The computation will be based on one mole of acetic acid

$$n_1 = 1 \quad (3.29)$$

Because of $x_1 + x_2 + x_4 = 1$ (3.30)

we have

$$n_2 = x_2/x_1 \quad (3.31)$$

$$n_4 = x_4/x_1 \quad (3.32)$$

Table 8. Standard Values.

	$\text{CH}_3\text{COOH}(\ell)$	$+ 4\text{H}_2\text{O}_2(\ell)$	$= 2\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g})$	Δ
i	(1)	(2)	(3)	(4)
n_i	-1	-4	+2	+6
$G^{\circ} - H^{\circ}_O$			-12987	-11082
$n_i \uparrow$			-25974	-66492
$G^{\circ} - H^{\circ}_O$	-18700	-17489		
$n_i \uparrow$	+18700	+69956		-3810
H^f_O	-100500	-31040	-93969	-57107
$n_i \uparrow$	+100500	+124160	-187938	-342642
$\Delta G^{\circ*}$				-309805
H^f_{298}	-103800	-32530	-94052	-57798
$n_i \uparrow$	+103800	+130120	-188104	-346788
H_{vap}	+3625	+11678		
$n_i \uparrow$	-3625	-46712		-50337
$\Delta H^{\circ*}_{298}$				-250635

In the range

$$n_2 > 4n_1 \quad (3.33)$$

$$x_2/x_1 > 4 \quad (3.34)$$

$$x_2 > 4x_1 \quad (3.35)$$

The reactions participate according to

$$a = n_1 = 1 \quad (3.36)$$

$$b = 0 \quad (3.37)$$

$$c = n_2 - 4n_1 = x_2/x_1 - 4 \quad (3.38)$$

$$d = n_4 = x_4/x_1 \quad (3.39)$$

For

$$n_2 = 4n_1 \quad (3.40)$$

$$x_2 = 4x_1 \quad (3.41)$$

one obtains

$$a = 1 \quad (3.42)$$

$$b = 0 \quad (3.43)$$

$$c = 0 \quad (3.44)$$

$$d = x_4/x_1 \quad (3.45)$$

In the range

$$n_2 < 4n_1 \quad (3.46)$$

$$x_2/x_1 < 4 \quad (3.47)$$

$$x_2 < 4x_1 \quad (3.48)$$

We have

$$4a + 2b = n_2 = x_2/x_1 \quad (3.49)$$

$$a + b = n_1 = 1 . \quad (3.50)$$

Solving these equations we obtain

$$a = x_2/(2x_1) - 1 \quad (3.51)$$

$$b = 2 - x_2/(2x_1) . \quad (3.52)$$

In addition we have

$$c = 0 \quad (3.53)$$

$$d = x_4/x_1 . \quad (3.54)$$

These relations are needed to determine the amounts of gaseous products. They are given (in numbers of moles) by

$$n_1' = e \quad (3.55)$$

$$n_3' = 2a \quad (3.56)$$

$$n_4' = 6a + 4b + c + d \quad (3.57)$$

$$n_5' = 2b \quad (3.58)$$

$$n_6' = 0.5c \quad (3.59)$$

$$n' = 8a + 6b + 1.5c + d + e . \quad (3.60)$$

The amounts of the liquid reactants are

$$n_1 = a + b + e \quad (3.61)$$

$$n_2 = 4a + 2b + c \quad (3.62)$$

$$n_4 = d \quad (3.63)$$

$$n = 5a + 3b + c + d + e . \quad (3.64)$$

The various steps in the computations of ΔG and ΔH of some of the mixtures are tabulated in Table 9.

Table 9. Free Energy and Enthalpy.

x_1	0.2	0.1	0.083	0.333	0.167	0
x_2	0.8	0.4	0.333	0.667	0.333	0
x_4	0	0.5	0.584	0	0.5	1
a	1	1	1	0	0	0
b	0	0	0	1	1	0
c	0	0	0	0	0	0
d	0	5	7	0	3	1
e	0	0	0	0	0	0
n_3'	2	2	2	0	0	0
n_4'	6	11	13	4	7	1
n_5'	0	0	0	2	2	0
n_6'	0	0	0	0	0	0
n'	8	13	15	6	9	1
y_3	0.25	0.154	0.133	0	0	0
y_4	0.75	0.846	0.867	0.667	0.778	0
y_5	0	0	0	0.333	0.222	0
y_6	0	0	0	0	0	1
$n_3' \log y_3$	-1.204	-1.624	-1.752	0	0	0
$n_4' \log y_4$	-0.750	-0.803	-0.806	-0.704	-0.763	0
$n_5' \log y_5$	0	0	0	-0.956	-1.308	0
$n_6' \log y_6$	0	0	0	0	0	0
$\sum n_i' \log y_i$	-1.954	-2.427	-2.558	-1.660	-2.071	0
$M = 2.3 \text{ RT.}\uparrow$	-2666	-3311	-3490	-2265	-2826	0

Table 9. (continued)

n_1	1	1	1	1	1	0
n_2	4	4	4	2	2	0
n_4	0	5	7	0	3	1
$n_1 \log x_1$	-0.699	-1	-1.081	-0.478	-0.777	0
$n_2 \log x_2$	-0.388	-1.592	-1.912	-0.352	-0.956	0
$n_4 \log x_4$	0	-1.505	-1.638	0	-0.903	0
$\Sigma n_i \log x_i$	-1.087	-4.097	-4.631	-0.830	-2.636	0
$N = 2.3RT \cdot \uparrow$	-1483	-5590	-6318	-1132	-3596	0
$a\Delta G_a^{0*}$	-309730	-309730	-309730	0	0	0
$b\Delta G_b^{0*}$	0	0	0	-134904	-134904	0
$c\Delta G_c^{0*}$	0	0	0	0	0	0
$d\Delta G_d^{0*}$	0	10265	+14371	0	+6159	2053
ΔG^0	-309730	-299465	-295359	+134904	-128745	2053
$\Delta G = \uparrow +M-N$	-310913	-297186	-292531	-136037	-127975	2053
$a\Delta H_a^{0*}$	-250635	-250635	-250635	0	0	0
$b\Delta H_b^{0*}$	0	0	0	-88183	-88183	0
$c\Delta H_c^{0*}$	0	0	0	0	0	0
$d\Delta H_d^{0*}$	0	+52600	+73640	0	+31560	10520
ΔH	-250635	-198035	-176995	-88183	-56623	10520

The units of ΔH and ΔG are expressed in calories/g-mole. Converting to 1 kg, and denoting the molal weights by M_1, M_2, \dots , we obtain

$$g = \Delta G / (n_1 M_1 + n_2 M_2 + n_4 M_4) \text{ kcal/kg} \quad (3.65)$$

$$h = \Delta H / (n_1 M_1 + n_2 M_2 + n_4 M_4) \text{ kcal/kg} \quad (3.66)$$

The calculation procedure is shown in Table 10.

Table 10. Free Energy and Enthalpy per kg.

Point No.	16	15	14	17	18	4
x_1	0.2	0.1	0.083	0.333	0.167	0
x_2	0.8	0.4	0.333	0.667	0.333	0
x_4	0	0.5	0.584	0	0.5	1
$M_1 n_1 = 60.05 n_1$	60.05	60.05	60.05	60.05	60.05	0
$M_2 n_2 = 34.02 n_2$	136.08	136.08	136.08	68.04	68.04	0
$M_4 n_4 = 18.02 n_4$	0	90.1	126.14	0	54.06	18.02
$\Sigma n_i M_i$	196.13	286.23	322.27	128.09	182.15	18.02
$1/\uparrow$.0051	.0035	.0031	.0078	.0055	.0555
$g = \uparrow \cdot \Delta G$	-1586	-1037	-907	-1063	-703	+114
$h = \uparrow \uparrow \cdot \Delta H$	-1278	-691	-549	-689	-311	+584

These mixtures are represented by straight lines from points 16 to 4 and from 17 to 4. These lines are the most critical ones since acetic acid and hydrogen peroxide are present in the stoichiometric ratios for the reactions (A) and (B). For interpolation, g and h are cross plotted in Figs. 10 and 11.

From the curves in Figs. 10 and 11 we can find the compositions of mixtures for which g and h equal 0, -300, -600, -900, -1200 and -1500

kcal/kg, respectively. These data are then plotted in triangular coordinates at constant g and constant h . Figures 12 and 13 are the ultimate goals of the calculation. Cusps are to be expected in these contour lines where they cross the lines 16-4 and 17-4 because the nature of the chemical reactions involved changes there. Smooth interpolation is appropriate elsewhere.

The most interesting contour lines are those for $g = 0$ and $h = 0$. All mixtures containing less H_2O_2 than indicated by the line $g = 0$ are perfectly safe. Actually one will not expect any detonation for H_2O_2 concentrations lower than those of the line $h = 0$. But for higher H_2O_2 concentrations the danger is obvious. As a matter of fact, very serious explosions of mixtures high in H_2O_2 and low in H_2O have taken place.

Phase diagrams of the kind presented in Figs. 12 and 13 furnish direct information on hazards in industrial operations.

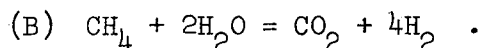
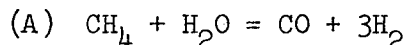
34. A Model for Automatic Computation of Equilibrium Conditions

In thermodynamic calculations, attention has been focused to a great extent on a single chemical reaction with a given set of reactants. In practice one is frequently apt to be concerned with two or more reactions occurring simultaneously. The equilibrium is then characterized by a minimum of the total free energy with respect to all virtually possible changes. One can easily carry out the computation when there is only a single reaction to be considered. Difficulties are encountered if this method is extended to several simultaneous equilibria. Numerical mathematical procedures have been developed for such purposes. The use of electronic computers is of great importance.

For instructive purposes, we shall examine a simple example. Only two simultaneous reactions will be considered, namely, those between

methane and steam at a temperature of 1000°K and under atmospheric pressure.

The two reactions, designated by A and B are



Generally, in more complicated problems one has to resort to trial-and-error methods in order to find the minimum of the free energy. Even the highly sophisticated method of steepest descent is based on trial and error. The working of such procedures will be illustrated by a primitive calculation. The free energy will be computed for points in a two-dimensional network, then for points in a more closely meshed network in the neighborhood of the lowest point, and so on.

Instead of the free energy we shall use the more convenient Massieu's function

$$Q = G/(2.3RT). \quad (3.67)$$

The data have been taken from the Thermodynamics of Lewis, Randall, Pitzer and Brewer.

The total Gibbs free energy G for these gaseous mixtures, which are assumed to be perfect, is

$$G = \sum_i n_i (G_i^0 + RT \ln y_i) . \quad (3.68)$$

so that

$$Q = Q^0 + \sum_i n_i \log y_i$$

with

$$Q^0 = \sum_i n_i G_i^0 / (2.3RT). \quad (3.69)$$

We take as the initial mixture of the reactants 1 mole of methane and 2 moles of steam. The substances present in the system at equilibrium, CH_4 , H_2O , CO , H_2 and CO_2 , are numbered as 1, 2, 3, 4 and 5

respectively. Hence, at equilibrium, we have for the conversions a and b by the reactions A and B, respectively,

$$n_1 = 1 - a - b \quad (3.70)$$

$$n_2 = 2 - a - 2b \quad (3.71)$$

$$n_3 = a \quad (3.72)$$

$$n_4 = 3a + 4b \quad (3.73)$$

$$n_5 = b \quad (3.74)$$

Since n_1 cannot be negative, $a + b$ cannot be greater than 1.

Tables 11 and 12 show the calculations of the standard changes $\Delta G^\circ/T$ with $T = 1000^\circ\text{K}$ for the reactions A and B

Table 11. Standard Free Energy Change (A).

	CH ₄	+	H ₂ O	=	CO	+	3H ₂	Δ
i	(1)		(2)		(3)		(4)	
n_i	-1		-1		1		3	
$-(G^\circ - H^\circ)/T$	47.65		47.01		48.77		32.74	
$n_i \uparrow = -\Delta(G^\circ - H^\circ)/T$	-47.65		-47.01		48.77		98.22	52.33
H°_f	-15990		-57107		-27202		0	
$n_i \uparrow = \Delta H^\circ_f$	15990		57107		-27202		0	
$\Delta H^\circ_f/T$	15.99		57.107		-27.202		0	45.895
$\Delta G^\circ/T = \uparrow + \Delta(G^\circ - H^\circ)/T$								-6.435

To determine the minimum Q, we assign values to a and b under the condition $a + b \leq 1$. For the first approximation, we calculate Q at $a = 0$ while b increases from 0 to 1.0 at an interval of 0.2; then we proceed with $a = 0.2$, and b = 0 to 0.8; then $a = 0.4$ etc.

Table 12. Standard Free Energy Change (B).

	CH ₄	+ 2H ₂ O	= CO ₂	+ 4H ₂	Δ
i	(1)	(2)	(5)	(4)	
n _i	-1	-2	1	4	
-(G ^o -H ^o)/T	47.65	47.01	54.11	32.74	
n _i ↑ = -Δ(G ^o -H ^o)/T	-47.65	-94.02	54.11	130.96	43.40
H _o ^f	-15990	57107	-93969	0	
n _i ↑ = ΔH _o ^f	15990	114214	-93969	0	
ΔH _o ^f /T	15.99	114.214	-93.969	0	36.235
ΔG ^o /T = ↑ + Δ(G ^o -H ^o)/T					-7.165

A few sample calculations of Q are shown in Table 13. The results of the first step are presented in Figs. 14 to 16. They reveal that a minimum is somewhere in the neighborhood of $a = 0.8$ and $b = 0.2$.

In the next step several points are chosen in intervals of 0.02 in a and b (Fig. 17). The interval for a is reduced to 0.01 in the third step. The diagram shows that the minimum is close to $a = 0.71$ and $b = 0.24$. The final determination is made with the aid of crossplots. Figure 18 shows Q as a function of b for $a = 0.71$, and Fig. 19 gives Q as a function of a for $b = 0.24$. A reasonable interpolation based on Figs. 17 to 19 furnishes the final result

$$a = 0.711; \quad b = 0.246; \quad q = -3.6359 \quad (3.75)$$

It is seen that this crude method gives a quite definite and accurate result. The price paid for it is high. Although Table 13 shows that the computation of each point in the chosen arrangement can be performed quickly and with a low risk of error, it is the number of points required

Table 13. Calculation of Q.

a	0.4	0.6	0.8
b	0.2	0.2	0.2
$n_1=1-a-b$	0.4	0.2	0
$n_2=2-a-2b$	1.2	1.0	0.8
$n_3=a$	0.4	0.6	0.8
$n_4=3a+4b$	2.0	2.6	3.2
$n_5=b$	0.2	0.2	0.2
$\Sigma n_i=n$	4.2	4.6	5.0
y_1	0.095	0.044	0
y_2	0.286	0.217	0.16
y_3	0.095	0.130	0.16
y_4	0.476	0.565	0.64
y_5	0.048	0.044	0.04
$\log y_1$	-1.022	-1.357	∞
$\log y_2$	-0.544	-0.664	-0.796
$\log y_3$	-1.022	-0.886	-0.796
$\log y_4$	-0.322	-0.248	-0.194
$\log y_5$	-1.319	-1.357	-1.398
$n_1 \log y_1$	-0.409	-0.271	0
$n_2 \log y_2$	-0.653	-0.664	-0.637
$n_3 \log y_3$	-0.409	-0.532	-0.637
$n_4 \log y_4$	-0.644	-0.645	-0.621
$n_5 \log y_5$	-0.264	-0.271	-0.280
$\Sigma n_i \log y_i$	-2.379	-2.383	-2.175
$a(\Delta G_a^0/T)$	-2.574	-3.861	-5.148
$b(\Delta G_b^0/T)$	-1.433	-1.433	-1.433
$\Sigma(\Delta G^0/T)$	-4.007	-5.294	-6.581
$Q^0=\uparrow/2.3R$	-0.876	-1.157	-1.438
$Q = \uparrow + \Sigma n_i \log y_i$	-3.255	-3.540	-3.613

that makes the computational burden heavy. But the method can be advantageously used in a simple computer program. Of course, the complication increases rapidly with the number of simultaneous reactions under consideration. More elaborate procedures of finding the minimum of the total

free energy will often be considerably more efficient. But the inherent danger of the existence of several relative minima increases with the number of reactions. There may be a point where plain mapping rather than a high sophisticated procedure leads to the most reliable results.

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References

- Bartlett, E. P., J. Am. Chem. Soc. 49, 694 (1927).
- Beattie, J. A., Bridgeman, O. C., J. Am. Chem. Soc. 49, 1665 (1927).
- Beattie, J. A., Lawrence, C. K., J. Am. Chem. Soc. 52, 10 (1930).
- Beattie, J. A., et. al., J. Chem. Phys. 19, 1219 (1951).
- Benedict, M., Webb, G. B., Rubin, L. C., J. Chem. Phys. 8, 334 (1940).
- Curtis, H. A., Fixed Nitrogen (The Chemical Catalog Company, New York 1932).
- Dodge, B. F., Chemical Engineering Thermodynamics (McGraw Hill 1944).
- Harrison, R. H., Kobe, K. A., Chem. Eng. Progr. 49, 349 (1953).
- Hougen, O. A., Watson, K. M., Ragatz, R. A., Chemical Process Principles, Part II (John Wileys and Sons, Inc., New York 1954).
- International Critical Tables (McGraw Hill, New York 1926-30).
- Kang, T. L., et. al., Chem. Eng. Data 6, 220 (1961).
- Landolt-Boernstein, Tabellen, 5th ed. (Springer, Berlin, 1930, 1935).
- Lewis, G. N., Randall, M., Pitzer, K. A., Brewer, L., Thermodynamics (McGraw Hill, New York 1961).
- Maass, O., Hiebert, P. G., J. Am. Chem. Soc. 46, 2693 (1924).
- Michels, A., Physica 20, 1209 (1954).
- Redlich, O., Kwong, J. S., Chem. Revs. 44, 233 (1949).
- Redlich, O., Dunlop, A. K., Chem. Eng. Progr. Symp. Ser. 50, 95 (1963).
- Redlich, O. et. al., Ind. Eng. Chem. Fundamentals, 4, 369 (1965).
- Riedel, L., Chemie-Ing.-Tech. 26, 83, 259, 679 (1954).
- Rossini, F. D., et. al., Selected Values of Properties of Hydrocarbons (National Bureau of Standards, Washington 1947).
- Sage, B. H., Lacey, W. N., Lighter Hydrocarbons, Hydrogen Sulfide, and Carbon Dioxide (American Petroleum Institute, New York 1955).
- Selected Values of Properties of Hydrocarbons and Related Compounds (American Petroleum Institute 1966).
- Smith, L. B., Taylor, R. S., J. Am. Chem. Soc. 45 (1923).

Sortland, L. D., Prausnitz, J. M., Chem. Eng. Science 20, 847 (1965).

White, D., et. al., J. Am. Chem. Soc. 72, 3565 (1950).

Wicks, C. E., Block, F. E., Thermodynamic Properties of 65 Elements
(United States Government Printing Office, Washington 1963).

Wohl, A. Z., Physik. Chem. 87, 1 (1914).

4. Appendix

The Program ES68Z

4.1. General Scope

The program ES68Z - Equation of State 1968 - can be used for the computation of the compressibility factor $Z = PV/RT$ for pure substances. It is based on the equation of state by Redlich and Kwong, modified by the addition of a third individual parameter.

The program ES68Z is written in Fortran IV. It consists of the main program ES68Z and the subroutine VIETA.

The main program ES68Z can be divided into four major parts: (1) Input and Preparation, (2) Main Cycle, (3) Approximation Cycle, and (4) Results.

The data cards to be introduced are: (1) the Title Card which states the title of the problem. The integer KCL controls intermediate quantities to be printed out. MCL is used to indicate the kind of experimental data to be read in. The experimental data may be given as compressibility factors Z; if PV, volume or density are given, the program converts the data to Z. WOM (molar weight of the substance) is punched on the Title Card when the observed data are expressed in mass or volume units instead of molar units. (2) Experimental Data are given as Z, or PV, volume or density. A blank card follows the last data card. (3) the Substance Card gives the name of the substance, the critical temperature (TC), pressure (PC) and compressibility factor (ZC). The last quantity LAA controls the number of approximation cycles desired. (4) the Temperature-Pressure Schedule Cards allow a variety of prescriptions for different sets of temperatures and pressures. The T-schedule provides for sets consisting of a starting temperature TL and an arbitrary number of higher temperatures $TL + DT$, $TL + 2DT$, $TL + 3DT$, at equal intervals. The

P-schedule may follow one of the three schemes: (a) starting pressure PL and any number of higher pressures $PL + DP$, $PL + 2DP$, $PL + 3DP$, at equal intervals, (b) starting pressure PL and any number of pressures of the amounts $2PL$, $5PL$, $10 PL$, etc., (c) starting pressure PL plus any number of additional pressures read in on cards following the Schedule Card. Several sets of T-P schedules may be put in provided the total number of points (product of NOT and NOP) does not exceed 500. Any positive value for KS in the schedule card means that another schedule card follows. The last schedule card carries $KS = 0$. Calculation for a new substance can be prescribed simply by adding a new complete set starting with the Title Card and so on. A card containing $KCL = -1$ will terminate the computation.

The data are to be given in arbitrary but consistent absolute units throughout, e.g., all temperatures in $^{\circ}K$ or $^{\circ}R$, and pressures in atm, psia, etc. The output is given in the same units.

The program can also be used for computations starting from the reduced variables T_r and P_r . In this case, both T_c and P_c are set at 1 and T_r and P_r are introduced wherever T and P are prescribed.

The subroutine used in this program is VIETA-MODIFICATION 4 to solve the general cubic equation. This is a modified version of a SHARE routine. The solution gives any of the three cases: two equal roots (MTYPE=0), two complex roots (MTYPE=1) and three real roots (MTYPE=-1).

42. Outline of the Program

The first part (addresses 101 to 199) takes care of the input and assigns a point number ME to every experimental value ZE and the corresponding values of T_r and P_r as prescribed in the T-P schedule.

In the Main Cycle (addresses 201 to 299) the computation of ZE is carried out if ZE is given by data for density, volume or PV. The results of the equation of Redlich and Kwong and several coefficients of the modified cubic equation are computed.

In the Approximation Cycle (addresses 301 to 399) the coefficients A(2), A(3), A(4) of the modified cubic equation are computed. The subroutine VIETA furnishes the first results, which are fed-back. The final result is mixed with the result of Redlich and Kwong if $T_r > 1$. In this case also the deviation function DC is computed and added.

The last part (addresses 401 to 499) takes care of the main output and of the return to a new problem.

In the following the symbols used in the text and in the program are coordinated.

Symbols in Program	Symbols in Text	Equations in Text
AC	A	2.6, 2.8, 2.10, 2.11
AK	A' ²	2.1, 2.3
BC	B	2.7, 2.9, 2.10, 2.11
BK	B'	2.1, 2.2, 2.4
D	Dr	2.17', 2.18
DC	Z _D	2.32
GG	G	2.14, 2.15, 2.16, 2.21
GL	L	2.13, 2.15, 2.16, 2.20
PA	P	
PRR	P _r	
QZ	C ₁₂	2.30, 2.31, 2.33
TK	T	

TRR	T_r	
TT	T_r^3	2.32
U	C_5	2.21, 2.25, 2.28
UF	C_{10}	2.25
UG	C_{11}	2.25
V	C_4	2.21, 2.24, 2.27
VF	C_8	2.24
VG	C_9	2.24
W	C_1	2.19, 2.20, 2.23, 2.26
WA	C_2	2.19, 2.20
WB	C_3	2.20, 2.22, 2.29
WF	C_6	2.23
WG	C_7	2.23
ZF	Z	2.33
ZFK	Z_K	2.31, 2.33
ZG	Z	2.31
ZGG	Z_M	2.31, 2.33

43. Input

1. Title Card

Column

2-37 Title of the problem.

38-39 KCL = Print intermediate quantities: 0 no print
9 print
-1 termination

40-41 MCL: Experimental data
If MCL = 0: no data;
MCL > 0: data.

If MCL = 1, data are given as Z, but
if MCL > 1, data are given as PV,
or volume or density.

- 42-43 NPC: Reserved for punch control (not included in the program).
- 44-53(4 dec.) WOM: molar weight (if required for the computation of experimental Z).
- 54-63(4 dec.) ECL: not used in this program.

The following list shows the values of MCL and WOM to be used when the set of experimental data is given as PV, or volume or density; WOM = 0 when the data are given as Z.

	<u>Units</u>		<u>MCL</u>	<u>WOM</u>
for P	for T	for volume or density		
atm	°K	amagat	2	0
atm	°K	cm ³ /g	23	MW
atm	°K	g/cm ³	21	MW
atm	°K	lit/mole	23	0
atm	°K	moles/lit	21	0
mmHg	°K	lit/mole	3	0
psia	°R	cu ft/lb	33	MW
psia	°R	lb/cu ft	31	MW
psia	°R	cu ft/lb-mole	33	0
psia	°R	lb-mole/cu ft	31	0

2. Experimental Data (only if MCL ≥ 1)

Insert any number of cards up to 499.

Column

- 2-10(4 dec.) ZE: Experimental value of Z or PV or volume or density. No card with ZE = 0 is allowed.

The last card is followed by a blank card.

3. Substance Card

Column

2-24 Name of the substance.
25-36(6 dec.) TC: critical temperature in any absolute units.
37-48(6 dec.) PC: critical pressure in any absolute units.
49-60(6 dec.) ZC: critical compressibility factor.
61-62 LAA: number of approximation cycles;
if LAA = 0, computer sets LAA = 40
if LAA > 0, computer sets number of approximation
cycles LA = LAA + 10.

4. T-P Schedule Cards

Column

3-4 KS: control
KS > 0 indicates that the schedule card is to be
followed by another one, while
KS = 0 means that the schedule card is the last in
the set.
5-6 NOT: number of temperatures to be introduced.
7-8 NOP: number of pressures to be introduced.
9-20(6 dec.) TL: lowest temperature to be introduced, in the same
unit as TC.
21-32(6 dec.) DT: temperature increment in the same unit as TC.
33-44(6 dec.) PL: lowest pressure to be introduced, in the same
unit as PC.
45-56(6 dec.) DP = -1: pressure schedule is PL, 2PL, 5PL, 10 PL,
etc. for NOP pressures.
DP = 0: schedule is given by PL and the following
NOP-1 additional pressure cards.
DP > 0: pressure increment for NOP pressures in the
same unit as PL.

5. Additional Pressure Cards

NOP - 1 cards (only if DP = 0).

6. A complete set of data cards starting with the Title Card may be put in for a new problem. A new count of points (up to 499) starts. A card containing KCL = -1 in col. 38-39 terminates the calculation.

44. Diagnostic Options

A diagnostic option KCL is provided at the end of the approximation cycle. If KCL = 9 several intermediate quantities will be printed out. (Format 20).

The first three columns contain the number ME of the point and the reduced values T_r and P_r . Then follows QZ, the mixing factor (C_{12}) for supercritical temperatures. The value ZFK obtained by the equation of Redlich and Kwong is given, then the experimental value ZE. The following column contains the value ZGG obtained by the solution of the third order equation modified by the functions L and G. The value ZG is obtained by mixing ZFK and ZGG as prescribed by QZ. The next column contains the final value ZF for the first phase obtained from ZG by addition of the deviation function DC (following column). The last column contains the numerator UP of DC.

45. Output

The first line of the output reproduces the Title Card. It is followed by the Substance Card and the T-P Schedule Cards.

If the solution of the modified cubic equation is not obtained within 0.0004 (in Z) after IAA approximation cycles, the computer prints (Format 17) the number ME of the point, the number JA of the approximation cycle, the phase distribution MTYPE of VIETA (-1 three phases, 0 critical, 1 a single phase), the factors of the cubic equation (input for VIETA), and its roots (output of VIETA).

The main output is arranged in tables for each set of temperatures and pressures. Each table starts with the following heading:

ME Number of the point for each problem.
TK Absolute temperature in °K or °R.
PA Absolute pressure in atm, psia, etc.
TR Reduced temperature.
PR Reduced pressure.
ZFK Z obtained according to Redlich and Kwong.
ZE Z observed.
ZF Z calculated.
DF Difference between ZE and ZF.

The printout for the first phase of any point may be followed by a line for a second phase.

ZSK Z for the second phase computed by the equation of Redlich and Kwong.
ZE Z observed.
ZS Z for the second phase computed by the present modified equation.
DS Difference between ZE and ZS.

If the final results from the computations do not converge within the tolerance of 0.0004 or due to some other reasons, the computer prints some number between 9.0 and 9.9.

The following is a list of the numbers which may appear in the main output rather than the actual results obtained from the calculation.

<u>Number</u>	<u>Quantity</u>	<u>Reason</u>
9.0	ZF, ZS	LA cycles do not satisfy the tolerance of 0.0004.

<u>Number</u>	<u>Quantity</u>	<u>Reason</u>
9.1	ZF, ZS	$ZFK \leq 0$.
9.2	ZF, ZS	ZC (as given in the input) > 0.333.
9.3	ZF, ZS	$T_r < 0.721$.
9.5	ZSK	only one phase is obtained from the equation of Redlich and Kwong.
9.9	ZS	The final calculation leads to a single phase.

At the critical point (and very close to it) the subroutine VIETA is insufficient. In this case inaccurate results are printed, not indicated by a printout of 9.0 or higher.

46. Phases

Since the present modified equation of state is of third order, it may furnish one or three real solutions for Z. If the equation furnishes three real solutions, the computer prints out the highest root of Z as the value for the gaseous phase and the lowest root as that for the liquid phase.

The present program does not give an indication of which of the phases is stable. This decision can be made only after the computation of the fugacity coefficients (The calculated fugacity coefficient is higher for the metastable phase).

47. Convergence

The computation of Z from the modified cubic equation is carried out by a step-by-step approximation with a damped feedback. The calculation stops either after sufficiently converging to the result or after completing a prescribed number of cycles LA without converging. The number of approximation cycles set without special instruction is 50.

More cycles can be prescribed if desired. The computer prints out the intermediate quantities for the last 10 cycles. As mentioned in Section 44, the computer does not print out the results in the main output if they do not converge except due to insufficient approximation of the VIETA feature; the number 9.0 is printed out instead.

To start the cycle, the Z value obtained from the original equation of state by Redlich and Kwong is used for the first approximation.

Oscillations of the results are suppressed by feeding back into the computation the sum of the last result multiplied by QIN, and the last-but-one result multiplied by (1-QIN). The damping factor (1-QIN) of the feedback (influence of the last-but-one result) is increased if the last two changes of the result go into opposite directions, it is decreased if the steps go into the same direction.

48. Program and Examples

In the following the complete program ES68Z as of 13 September, 1968 is reproduced.

Calculation examples are given for

Pitzer's Tables for acentric factor 0.0

0.5

Benzene (Sage and Lacey, 1955)

1-Butene (Sage and Lacey, 1955)

n-Nonane (Sage and Lacey, 1955)

Sulfur dioxide (Kang, 1961)

Hydrogen sulfide (Sage and Lacey, 1955)

Ammonia (Beattie and Lawrence, 1930)

Carbon dioxide (Sage and Lacey, 1955)

Helium (Landolt and Boernstein)

Xenon (Beattie, 1951)

Hydrogen (Landolt and Boernstein; Bartlett, 1927)

Nitrogen (Smith, 1923; Bartlett, 1927)

Oxygen (Michels, 1954)

The critical constants T_c , P_c and Z_c for each substance are either obtained from the quoted source of the data or from "International Critical Tables (1926-1930) or "Selected Values of Properties of Hydrocarbons and Related Compounds."

The arrangement of the output tables has been discussed in Section 45. References A, B, or C have been added to some of the output lines at the right hand side. They represent the following comments.

A. The result of this line refers to a metastable phase. Usually, though not always, the stable phase is presented in the preceding line (gas) or in the following line (liquid).

B. The calculated results for Z_c in Pitzer's Tables are 0.288 and 0.313 although the values 0.291 and 0.251 have been prescribed in the input. The subroutine VIETA cannot strictly handle the critical point. The error appears to be magnified by insufficiency of the approximation procedure. It is advisable to replace any output by a proper comment if both T_r and P_r are between 0.995 and 1.005. This has been avoided in the program so that the effect is demonstrated.

C. The input data result in $T_r < 0.721$, excluded according to Section 25.

```

PROGRAM ES68Z(INPUT,OUTPUT)
CES68 EQUATION OF STATE 1968 13 SEPT 1968
DIMENSION TI(6),SUB(4),A(4),F(4),ZE(500),P(500),TR(500),PR(500),
ZZFK(500),ZSK(500),ZF(500),ZS(500),ZG(500),X(3),Y(3),ZA(500),
ZZGG(500)
11 FORMAT (1X,6A6,3I2,2F10.4)
12 FORMAT (///)
13 FORMAT (1X,F9.4)
14 FORMAT (1X,A5,3A6,3F12.6,I2)
15 FORMAT (2X,3I2,4F12.6)
16 FORMAT (19X,F12.6)
17 FORMAT (1X,3I3,7H 1ST ,9F9.4)
18 FORMAT (1X,I3,2F10.4,3(F9.3,F7.3))
19 FORMAT (20X,2(F9.3,F7.3))
20 FORMAT (1X,I3,9F6.3,F12.4)
21 FORMAT (72H NO T P TR PR ZK ZFX
2P ZCALC DIFF//)

```

```

C
C INPUT AND PREPARATION
READ 11,(TI(M),M=1,6),KCL,MCL,MPC,WOM,ECL
101 PRINT 12
PRINT 11,(TI(M),M=1,6),KCL,MCL,MPC,WOM,ECL
IF (MCL-1) 102,103,103
102 MZ=0
GO TO 104
103 ME=1
105 READ 13,ZE(ME)
IF (ZE(ME)) 101,106,131
131 ME=ME+1
GO TO 105
106 MZ=ME-1
IF (MCL-2) 104,107,108
107 MVD=0
GO TO 104
108 RP=0.016037
IF (WOM) 132,132,133
132 WOM=1.0
133 CONTINUE
MVD=-1
IF (MCL-21) 104,109,109
109 MVD=22-MCL
IF (WOM-1.0) 110,110,111
110 RP=12.1871
GO TO 112
111 RP=0.0121871
112 IF (MCL-31) 104,113,113
113 RP=0.093184
MVD=32-MCL
114 CONTINUE
READ 14,(SUB(M),M=1,4),TC,PC,ZC,LAA
PRINT 14,(SUB(M),M=1,4),TC,PC,ZC,LAA
PRINT 12
AA=ZC*ZC/.25992106
BA=.25992106*ZC
K=1
MX=0
114 READ 15,KS,NOT,NOP,TL,DT,PL,DP
PRINT 15,KS,NOT,NOP,TL,DT,PL,DP
P(1)=PL
JP=2
IF (DP) 115,116,117

```

```
115 P(JP)=P(JP-1)*2.0
    JP=JP+1
    IF (JP-NOP) 116,118,119
118 P(JP)=P(JP-1)*2.5
    JP=JP+1
    IF (JP-NOP) 120,120,119
120 P(JP)=P(JP-1)*2.0
    JP=JP+1
    IF (JP-NOP) 115,115,119
121 READ 16,P(JP)
    PRINT 16,P(JP)
    JP=JP+1
116 IF (JP-NOP) 121,121,119
117 P(JP)=P(JP-1)+DP
    JP=JP+1
    IF (JP-NOP) 117,117,119
119 CONTINUE
    DO 122 JT=1,NOT
    HT=FLOAT(JT)-1.0
    DO 123 JQ=1,NOP
    ME=MX+(JT-1)*NOP+JQ
    TR(ME)=(TL+HT*DT)/TC
    PR(ME)=P(JQ)/PC
123 CONTINUE
122 CONTINUE
    MX=MX+NOT*NOP
    IF (KS) 124,124,125
125 K=K+1
    GO TO 114
124 IF (LAA) 126,126,127
126 LAA=4.0
127 LA=LAA+1.0
    IF (MZ=MX) 128,129,129
128 ML=MZ+1
    DO 130 ME=ML,MX
130 ZE(ME)=0.0
129 CONTINUE
    A(1)=1.0
    E(1)=1.0
    E(2)=-1.0
    PRINT 12
C
C M-IN CYCLE
    DO 201 ME=1,MAX
    TRR=TR(ME)
    TRS=SQRT(TRR)
    TU=TRR-1.0
    PRR=PR(ME)
    IF (NCL-2) 202,203,204
203 ZE(ME)=ZE(ME)*273.15/(TRR*TC)
    GO TO 202
204 IF (MVD) 205,203,206
206 ZE(ME)=1.0/ZE(ME)
205 ZF(ME)=RR*W04*ZE(ME)*PRR*PC/(TRR*TC)
202 CONTINUE
    QIN=1.0
    IF (TRR-1.02) 209,209,210
210 UZ=1.0-EXP(-0.05/TU)
209 CONTINUE
C
R AND K
A=0.4274*PRR/(TRR*TRR*TRS)
B=0.08667*PRR/TRR
```

```
E(3)=AK-BK*(1.0+BK)
E(4)=-AK*BK
CALL VIETA(E,Y,MI)
ZFK(ME)=Y(1)
IF (MI) 211,211,212
211 ZSK(ME)=Y(3)
GO TO 213
212 ZSK(ME)=9.5
213 CONTINUE
AC=AA*PRR/(TRR*TRR*TRS)
BC=BA*PRR/TRR
DEN=(1.0+0.1*TRR)*(1.0+0.1*TRR)
W=0.1/(1.0+2.06*TRR)
V=1.15*(1.0+2.26*TRR)/DEN
U=0.103*(1.0+3.59*TRR)/DEN
WA=EXP(2.3:259*(1.0-3.0*ZC)/W)-1.0
ZA(1)=Y(1)
```

C
C

```
APPROXIMATION CYCLE
DO 301 JA=1,LA
IF (ZA(JA)) 302,302,303
302 ZF(ME)=9.1
ZS(ME)=9.1
GO TO 201
303 D=PRR*ZC/(TRR*ZA(JA))
S=D*(3.0-U*(3.0-D))
GLL=1.0+W*A*S
IF (GLL) 304,304,305
304 ZF(ME)=9.2
ZS(ME)=9.2
GO TO 201
305 GL=**ALOG10(GLL)
IF (S-1.0) 306,307,307
306 WB=1.43/(TRR*TRS)-1.32
GL=GL*(WB+(1.0-WB)*S)
307 GLG=1.0+U*S*S*(S-1.0)*(S-1.0)
IF (GLG) 308,308,309
308 ZF(ME)=9.3
ZS(ME)=9.3
GO TO 201
309 GG=V*AL(GLG)
A(2)=GL-1.0
A(3)=AC*(1.0-GG)-BC*(1.0-GL+BC)
A(4)=-AC*BC*(1.0-GG)
CALL VIETA(A,X,MIYPE)
IF (JA-LAA) 312,312,313
313 PRINT 17,ME,JA,MIYPE,(A(N),N=2,4),(X(N),N=1,3)
312 ZG(ME)=X(1)
IF (ABS(ZG(ME)-ZA(JA))-0.0004) 314,325,325
325 IF (0A-10) 315,315,321
321 DIS=(X(1)-ZA(JA))*(ZA(JA)-ZA(JA-1))
IF (DIS) 322,322,323
322 QIN=0.9*QIN
GO TO 315
323 QIN=QIN/0.9
IF (QIN-1.0) 315,315,324
324 QIN=1.0
315 ZA(JA+1)=QIN*ZG(ME)+(1.0-QIN)*ZA(JA)
301 CONTINUE
ZF(ME)=9.0
ZS(ME)=9.0
GO TO 201
```

```
314 ZGG(ME)=ZG(ME)
      IF (TRR-1.02) 313,310,311
311 ZG(ME)=ZFK(ME)+GZ*(ZGG(ME)-ZFK(ME))
310 CONTINUE
      IF (MTYPE) 316,317,317
317 ZS(ME)=9.9
      GO TO 318
316 ZS(ME)=X(3)
      DC=0.0
318 IF (TRR-1.02) 319,320,320
320 TT=TRR*TRR*TRR
      UP=(3.281-11.16*ZC)*(TT-2.6*TU*((4.36-15.0*ZC)*TRR-6.70+21.3*ZC)*
      2*SQRT(PRR))
      DC=UP*TU*PPR/(TT*TT+0.4*PPR*PPR)
319 ZF(ME)=ZG(ME)+DC
      IF (KCL-9) 201,326,201
326 PRINT 20,ME,TRR,PPR,GZ,ZFK(ME),ZE(ME),ZGG(ME),ZG(ME),ZF(ME),DC,UP
201 CONTINUE
C
C RESULTS
PRINT 12
PRINT 21
DO 401 ME=1,MX
  DF=0.0
  DS=0.0
  TK=TR(ME)*TC
  PA=PR(ME)*PC
  IF (ZF(ME)-9.0) 402,403,403
402 DF=ZE(ME)-ZF(ME)
403 PRINT 18,ME,TK,PA,TR(ME),PR(ME),ZFK(ME),ZE(ME),ZF(ME),DF
  IF (ZS(ME)) 401,401,406
406 IF (ZS(ME)-9.0) 405,401,401
405 DS=ZE(ME)-ZS(ME)
  PRINT 19,ZSK(ME),ZE(ME),ZS(ME),DS
401 CONTINUE
  READ 11,(TI(M),M=1,6),KCL,MCL,MPC,WOM,ECL
  IF (KCL) 99,101,101
99 STOP
END
```

C

```
.....
.....
SUBROUTINE VIETA (A, Y, MTYPE)
CV4 SOLUTION OF THE GENERAL CUBIC EQUATION
C A(1)*Y**3+A(2)*Y**2+A(3)*Y+A(4)=0
C WITHOUT CUBERTF, ASINF, ACOSF, FOR GENERAL USE
.....
DIMENSION A(4), B(3), Y(3)
B(1) = A(2)/A(1)
B1OV3 = B(1)/3.0
B(2) = A(3)/A(1)
B(3) = A(4)/A(1)
ALF = B(2) - B(1)*B1OV3
BET = 2.0*B1OV3**3 - B(2)*B1OV3 + B(3)
BETOV2 = BET/2.0
ALFOV3 = ALF/3.0
CUAOV3 = ALFOV3**3
SQBOV2 = BETOV2**2
DEL = SQBOV2 + CUAOV3
IF (DEL) 40,20,30
.....
C
C MTYPE=0 TWO REAL ROOTS
.....
20 MTYPE = 0
GAM = SQRTF(-ALFOV3)
IF (BET) 22,22,21
21 Y(1) = -2.0*GAM - B1OV3
Y(2) = GAM - B1OV3
Y(3) = Y(2)
GO TO 50
22 Y(1) = 2.0*GAM - B1OV3
Y(2) = -GAM - B1OV3
Y(3) = Y(2)
GO TO 50
.....
C
C MTYPE=1 TWO COMPLEX ROOTS
.....
30 MTYPE = 1
EPS = SQRTF(DEL)
TAU = -BETOV2
RCU=TAU+EPS
SCU=TAU-EPS
SIR=1.0
SIS=1.0
IF (RCU) 31,32,32
31 SIR=-1.0
32 IF (SCU) 33,34,34
33 SIS=-1.0
34 R=SIR*(SIR*RCU)**0.33333333
S=SIS*(SIS*SCU)**0.33333333
Y(1) = R + S - B1OV3
Y(2) = -(R+S)/2.0 - B1OV3
Y(3) = 0.86602540*(R-S)
GO TO 50
.....
C
C MTYPE=-1 THREE REAL ROOTS
.....
40 MTYPE = -1
QUOT = SQBOV2/CUAOV3
ROOT = SQRTF(-QUOT)
IF (BET) 42,41,41
41 PHI = (1.5707963 + ATANF(ROOT / SQRTF(1.0 - ROOT**2))) / 3.0
GO TO 43
42 PHI = ATANF(SQRTF(1.0 - ROOT**2) / ROOT) / 3.0
43 FACT = 2.0*SQRTF(-ALFOV3)
Y(1) = FACT*COSEF(PHI) - B1OV3
Y(2) = FACT*COSEF(PHI + 2.0943951) - B1OV3
.....
```

```

.....
.....
Y(3) = FACT*COSF(PHI + 4.1887902) - R10V3
.....
C
C
Y(1) HIGHEST ROOT, Y(3) LOWEST ROOT
YA=AMAX1(Y(1),Y(2),Y(3))
YC=AMIN1(Y(1),Y(2),Y(3))
YB=Y(1)+Y(2)+Y(3)-YA-YC
Y(1)=YA
Y(2)=YB
Y(3)=YC
50 RETURN
END
.....
.....

```

```

.....
PITZERS TABLES REDUCED          -0 1-0  -0.      -0.
ACENTRIC 0.0                    1.000000  1.000000  .291000-0
.....

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1 5 5	.800000	.100000	.200000	.400000
1 5 8	.800000	.100000	2.000000	1.000000
1 5 5	1.400000	.400000	.200000	.400000
1 5 8	1.400000	.400000	2.000000	1.000000
1 1 5	4.000000	-0.	.200000	.400000
-0 1 8	4.000000	-0.	2.000000	1.000000

NO	T	P	TR	PR	ZK	ZEXP	ZCALC	DIFF
1	.8000	.2000	.600	.200	.856	.851	.850	.001
2	.8000	.6000	.800	.600	.034	.851	.033	.818 A
3	.8000	1.0000	.600	1.000	.161	.100	.096	.004
4	.8000	1.4000	.600	1.400	.166	.164	.158	.006
5	.8000	1.8000	.800	1.800	.228	.225	.219	.006
6	.9000	.2000	.900	.200	.289	.287	.279	.008
7	.9000	.6000	.900	.600	.901	.904	.898	.006
8	.9000	.6000	.900	.600	.597	.102	.612	-.510 A
9	.9000	1.0000	.900	1.000	.111	.102	.108	-.006
10	.9000	1.4000	.900	1.400	.175	.167	.160	.007
11	.9000	1.8000	.900	1.800	.235	.229	.220	.009
12	1.0000	.2000	1.000	.200	.294	.288	.278	.010
12	1.0000	.6000	1.000	.600	.929	.932	.931	.001
12	1.0000	.6000	1.000	.600	.756	.757	.755	.002

13	1.0000	1.0000	1.000	1.000	.298	.291	.288	.003 6
14	1.0000	1.4000	1.000	1.400	.277	.250	.237	.013
15	1.0000	1.8000	1.000	1.800	.324	.304	.285	.019
16	1.1000	.2000	1.100	.200	.947	.950	.951	-.001
17	1.1000	.6000	1.100	.600	.830	.833	.831	.002
18	1.1000	1.0000	1.100	1.000	.691	.691	.682	.009
19	1.1000	1.4000	1.100	1.400	.521	.512	.498	.014
20	1.1000	1.8000	1.100	1.800	.431	.408	.411	-.003
21	1.2000	.2000	1.200	.200	.960	.963	.964	-.001
22	1.2000	.6000	1.200	.600	.875	.879	.878	.001
23	1.2000	1.0000	1.200	1.000	.785	.788	.783	.005
24	1.2000	1.4000	1.200	1.400	.693	.690	.683	.007
25	1.2000	1.8000	1.200	1.800	.612	.598	.597	.001
26	.8000	2.0000	.800	2.000	.320	.318	.311	.007
27	.8000	3.0000	.800	3.000	.466	.461	.458	.003
28	.8000	4.0000	.800	4.000	.608	.605	.600	.005
29	.8000	5.0000	.800	5.000	.746	.746	.740	.006
30	.8000	6.0000	.800	6.000	.881	.883	.876	.007
31	.8000	7.0000	.800	7.000	1.014	1.017	1.009	.008
32	.8000	8.0000	.800	8.000	1.145	1.150	1.140	.010
33	.8000	9.0000	.800	9.000	1.274	1.280	1.268	.012
34	.9000	2.0000	.900	2.000	.322	.316	.309	.007
35	.9000	3.0000	.900	3.000	.460	.458	.451	.007
36	.9000	4.0000	.900	4.000	.591	.591	.588	.003
37	.9000	5.0000	.900	5.000	.718	.718	.723	-.005
38	.9000	6.0000	.900	6.000	.841	.842	.854	-.012
39	.9000	7.0000	.900	7.000	.962	.966	.983	-.017
40	.9000	8.0000	.900	8.000	1.080	1.089	1.110	-.021
41	.9000	9.0000	.900	9.000	1.197	1.210	1.234	-.024
42	1.0000	2.0000	1.000	2.000	.349	.329	.313	.016
43	1.0000	3.0000	1.000	3.000	.472	.458	.442	.016
44	1.0000	4.0000	1.000	4.000	.592	.582	.570	.012
45	1.0000	5.0000	1.000	5.000	.707	.702	.696	.006
46	1.0000	6.0000	1.000	6.000	.820	.819	.819	-.000
47	1.0000	7.0000	1.000	7.000	.930	.932	.941	-.009
48	1.0000	8.0000	1.000	8.000	1.037	1.048	1.061	-.013
49	1.0000	9.0000	1.000	9.000	1.144	1.166	1.179	-.013
50	1.1000	2.0000	1.100	2.000	.431	.402	.409	-.007
51	1.1000	3.0000	1.100	3.000	.510	.484	.486	-.002
52	1.1000	4.0000	1.100	4.000	.610	.589	.589	-.000
53	1.1000	5.0000	1.100	5.000	.713	.699	.696	.003
54	1.1000	6.0000	1.100	6.000	.814	.810	.802	.008
55	1.1000	7.0000	1.100	7.000	.913	.916	.907	.009
56	1.1000	8.0000	1.100	8.000	1.011	1.019	1.010	.009
57	1.1000	9.0000	1.100	9.000	1.108	1.129	1.112	.017
58	1.2000	2.0000	1.200	2.000	.584	.568	.570	-.002
59	1.2000	3.0000	1.200	3.000	.576	.554	.561	-.007
60	1.2000	4.0000	1.200	4.000	.647	.618	.630	-.012
61	1.2000	5.0000	1.200	5.000	.732	.714	.717	-.003
62	1.2000	6.0000	1.200	6.000	.821	.810	.807	.003
63	1.2000	7.0000	1.200	7.000	.910	.907	.899	.008
64	1.2000	8.0000	1.200	8.000	.998	1.000	.990	.010
65	1.2000	9.0000	1.200	9.000	1.086	1.100	1.081	.019
66	1.4000	.2000	1.400	.200	.976	.977	.980	-.003
67	1.4000	.6000	1.400	.600	.927	.929	.931	-.002
68	1.4000	1.0000	1.400	1.000	.880	.883	.882	.001
69	1.4000	1.4000	1.400	1.400	.836	.838	.835	.003
70	1.4000	1.8000	1.400	1.800	.797	.795	.793	.002
71	1.8000	.2000	1.800	.200	.990	.991	.994	-.003
72	1.8000	.6000	1.800	.600	.972	.974	.977	-.003
73	1.8000	1.0000	1.800	1.000	.955	.958	.960	-.002
74	1.8000	1.4000	1.800	1.400	.941	.944	.945	-.001

75	1.8000	1.8000	1.800	1.800	.928	.931	.933	-.002
76	2.2000	.2000	2.200	.200	.996	.997	1.000	-.003
77	2.2000	.6000	2.200	.600	.989	.990	.994	-.004
78	2.2000	1.0000	2.200	1.000	.983	.984	.989	-.005
79	2.2000	1.4000	2.200	1.400	.979	.980	.985	-.005
80	2.2000	1.8000	2.200	1.800	.976	.977	.982	-.005
81	2.6000	.2000	2.600	.200	.999	1.000	1.002	-.002
82	2.6000	.6000	2.600	.600	.997	1.000	1.002	-.002
83	2.6000	1.0000	2.600	1.000	.996	1.000	1.002	-.002
84	2.6000	1.4000	2.600	1.400	.996	1.000	1.002	-.002
85	2.6000	1.8000	2.600	1.800	.997	1.002	1.004	-.002
86	3.0000	.2000	3.000	.200	1.000	1.001	1.003	-.002
87	3.0000	.6000	3.000	.600	1.001	1.003	1.005	-.002
88	3.0000	1.0000	3.000	1.000	1.003	1.005	1.008	-.003
89	3.0000	1.4000	3.000	1.400	1.005	1.008	1.010	-.002
90	3.0000	1.8000	3.000	1.800	1.008	1.012	1.014	-.002
91	1.4000	2.0000	1.400	2.000	.781	.777	.776	-.001
92	1.4000	3.0000	1.400	3.000	.737	.720	.731	-.011
93	1.4000	4.0000	1.400	4.000	.753	.734	.745	-.011
94	1.4000	5.0000	1.400	5.000	.800	.781	.791	-.010
95	1.4000	6.0000	1.400	6.000	.861	.844	.851	-.007
96	1.4000	7.0000	1.400	7.000	.928	.921	.918	.003
97	1.4000	8.0000	1.400	8.000	.997	.994	.988	.006
98	1.4000	9.0000	1.400	9.000	1.068	1.071	1.060	.011
99	1.8000	2.0000	1.800	2.000	.923	.926	.927	-.001
100	1.8000	3.0000	1.800	3.000	.909	.908	.912	-.004
101	1.8000	4.0000	1.800	4.000	.911	.908	.915	-.007
102	1.8000	5.0000	1.800	5.000	.929	.925	.934	-.009
103	1.8000	6.0000	1.800	6.000	.958	.955	.963	-.008
104	1.8000	7.0000	1.800	7.000	.995	.993	1.000	-.007
105	1.8000	8.0000	1.800	8.000	1.037	1.039	1.042	-.003
106	1.8000	9.0000	1.800	9.000	1.083	1.091	1.087	.004
107	2.2000	2.0000	2.200	2.000	.975	.975	.981	-.006
108	2.2000	3.0000	2.200	3.000	.974	.974	.982	-.006
109	2.2000	4.0000	2.200	4.000	.982	.981	.991	-.010
110	2.2000	5.0000	2.200	5.000	.997	.997	1.007	-.010
111	2.2000	6.0000	2.200	6.000	1.017	1.020	1.030	-.010
112	2.2000	7.0000	2.200	7.000	1.043	1.048	1.058	-.010
113	2.2000	8.0000	2.200	8.000	1.073	1.080	1.088	-.008
114	2.2000	9.0000	2.200	9.000	1.105	1.118	1.122	-.004
115	2.6000	2.0000	2.600	2.000	.998	1.003	1.005	-.002
116	2.6000	3.0000	2.600	3.000	1.004	1.010	1.012	-.002
117	2.6000	4.0000	2.600	4.000	1.015	1.023	1.025	-.002
118	2.6000	5.0000	2.600	5.000	1.029	1.040	1.041	-.001
119	2.6000	6.0000	2.600	6.000	1.047	1.059	1.062	-.003
120	2.6000	7.0000	2.600	7.000	1.068	1.083	1.085	-.002
121	2.6000	8.0000	2.600	8.000	1.092	1.109	1.111	-.002
122	2.6000	9.0000	2.600	9.000	1.118	1.139	1.139	.000
123	3.0000	2.0000	3.000	2.000	1.009	1.014	1.016	-.002
124	3.0000	3.0000	3.000	3.000	1.019	1.028	1.026	.002
125	3.0000	4.0000	3.000	4.000	1.031	1.041	1.040	.001
126	3.0000	5.0000	3.000	5.000	1.045	1.058	1.057	.001
127	3.0000	6.0000	3.000	6.000	1.062	1.077	1.076	.001
128	3.0000	7.0000	3.000	7.000	1.080	1.100	1.097	.003
129	3.0000	8.0000	3.000	8.000	1.101	1.124	1.119	.003
130	3.0000	9.0000	3.000	9.000	1.123	1.150	1.144	.006
131	4.0000	.2000	4.000	.200	1.062	1.003	1.004	-.001
132	4.0000	.6000	4.000	.600	1.005	1.005	1.008	-.003
133	4.0000	1.0000	4.000	1.000	1.009	1.013	1.013	.000
134	4.0000	1.4000	4.000	1.400	1.013	1.017	1.017	-.000
135	4.0000	1.8000	4.000	1.800	1.017	1.022	1.022	.000
136	4.0000	2.0000	4.000	2.000	1.019	1.024	1.024	-.000

137	4.0000	3.0000	4.000	3.000	1.031	1.038	1.037	.001
138	4.0000	4.0000	4.000	4.000	1.043	1.053	1.051	.002
139	4.0000	5.0000	4.000	5.000	1.057	1.068	1.066	.002
140	4.0000	6.0000	4.000	6.000	1.071	1.086	1.082	.004
141	4.0000	7.0000	4.000	7.000	1.087	1.104	1.099	.005
142	4.0000	8.0000	4.000	8.000	1.103	1.124	1.117	.007
143	4.0000	9.0000	4.000	9.000	1.119	1.143	1.135	.008

PITZERS TABLES REDUCED

ACENTRIC n.5

1.000000 -0 1-0 -0. -0.
1.000000 .251000-0

1 5 5	.800000	.100000	.200000	.400000
1 5 8	.800000	.100000	2.000000	1.000000
1 5 5	1.400000	.400000	.200000	.400000
1 5 8	1.400000	.400000	2.000000	1.000000
1 1 5	4.000000	-0.	.200000	.400000
-0 1 8	4.000000	-0.	2.000000	1.000000

NO	T	P	TR	PR	ZK	ZEXP	ZCALC	DIFF
1	.8000	.2000	.800	.200	.856	.803	.809	-.006
2	.8000	.6000	.800	.600	.034	.803	.034	.769A
3	.8500	1.0000	.800	1.000	.166	.129	.135	-.006
4	.8500	1.4000	.800	1.400	.228	.175	.188	-.013
5	.8500	1.8000	.800	1.800	.289	.227	.239	-.012
6	.9000	.2000	.900	.200	.901	.883	.871	.012
7	.9000	.6000	.900	.600	.597	.675	.606	-.531A
8	.9000	1.0000	.900	1.000	.175	.124	.137	-.013
9	.9000	1.4000	.900	1.400	.235	.174	.188	-.014
10	.9000	1.8000	.900	1.800	.294	.223	.239	-.016
11	1.0000	.2000	1.000	.200	.929	.926	.921	.005
12	1.0000	.6000	1.000	.600	.756	.747	.745	.002
13	1.0000	1.0000	1.000	1.000	.298	.251	.313	-.062B
14	1.0000	1.4000	1.000	1.400	.277	.206	.203	.003
15	1.0000	1.8000	1.000	1.800	.324	.246	.244	.002
16	1.1000	.2000	1.100	.200	.947	.951	.957	-.006
17	1.1000	.6000	1.100	.600	.830	.841	.838	.003
18	1.1000	1.0000	1.100	1.000	.691	.719	.683	.036
19	1.1000	1.4000	1.100	1.400	.521	.567	.480	.087
20	1.1000	1.8000	1.100	1.800	.431	.426	.393	.033
21	1.2000	.2000	1.200	.200	.960	.968	.974	-.006
22	1.2000	.6000	1.200	.600	.875	.893	.892	.001
23	1.2000	1.0000	1.200	1.000	.785	.823	.795	.028
24	1.2000	1.4000	1.200	1.400	.693	.755	.687	.068
25	1.2000	1.8000	1.200	1.800	.612	.683	.594	.089
26	.8000	2.0000	.800	2.000	.320	.253	.279	-.026
27	.8000	3.0000	.800	3.000	.466	.371	.405	-.034
28	.8000	4.0000	.800	4.000	.608	.490	.527	-.037
29	.8000	5.0000	.800	5.000	.746	.616	.647	-.031
30	.8000	6.0000	.800	6.000	.881	.738	.763	-.025
31	.8000	7.0000	.800	7.000	1.014	.857	.877	-.020
32	.8000	8.0000	.800	8.000	1.145	.975	.990	-.015

33	.8000	9.0000	.800	9.000	1.274	1.105	1.100	.005
34	.9000	2.0000	.900	2.000	.322	.246	.278	-.032
35	.9000	3.0000	.900	3.000	.460	.368	.400	-.032
36	.9000	4.0000	.900	4.000	.591	.486	.518	-.032
37	.9000	5.0000	.900	5.000	.718	.598	.634	-.036
38	.9000	6.0000	.900	6.000	.841	.707	.747	-.040
39	.9000	7.0000	.900	7.000	.962	.816	.858	-.042
40	.9000	8.0000	.900	8.000	1.080	.929	.967	-.038
41	.9000	9.0000	.900	9.000	1.197	1.035	1.074	-.039
42	1.0000	2.0000	1.000	2.000	.349	.267	.281	-.014
43	1.0000	3.0000	1.000	3.000	.472	.383	.392	-.009
44	1.0000	4.0000	1.000	4.000	.592	.497	.503	-.006
45	1.0000	5.0000	1.000	5.000	.707	.602	.611	-.009
46	1.0000	6.0000	1.000	6.000	.820	.704	.718	-.014
47	1.0000	7.0000	1.000	7.000	.930	.802	.823	-.021
48	1.0000	8.0000	1.000	8.000	1.037	.898	.926	-.028
49	1.0000	9.0000	1.000	9.000	1.144	1.001	1.027	-.026
50	1.1000	2.0000	1.100	2.000	.431	.402	.390	.012
51	1.1000	3.0000	1.100	3.000	.510	.449	.456	-.007
52	1.1000	4.0000	1.100	4.000	.610	.539	.551	-.012
53	1.1000	5.0000	1.100	5.000	.713	.634	.649	-.015
54	1.1000	6.0000	1.100	6.000	.814	.730	.748	-.018
55	1.1000	7.0000	1.100	7.000	.913	.811	.846	-.035
56	1.1000	8.0000	1.100	8.000	1.011	.894	.942	-.048
57	1.1000	9.0000	1.100	9.000	1.118	.989	1.036	-.049
58	1.2000	2.0000	1.200	2.000	.584	.653	.565	.088
59	1.2000	3.0000	1.200	3.000	.576	.589	.549	.040
60	1.2000	4.0000	1.200	4.000	.647	.618	.609	.009
61	1.2000	5.0000	1.200	5.000	.732	.694	.687	.007
62	1.2000	6.0000	1.200	6.000	.821	.770	.772	-.002
63	1.2000	7.0000	1.200	7.000	.910	.847	.858	-.011
64	1.2000	8.0000	1.200	8.000	.998	.920	.945	-.025
65	1.2000	9.0000	1.200	9.000	1.086	1.005	1.031	-.026
66	1.4000	.2000	1.400	.200	.976	.985	.992	-.007
67	1.4000	.6000	1.400	.600	.927	.954	.952	.002
68	1.4000	1.0000	1.400	1.000	.880	.924	.909	.015
69	1.4000	1.4000	1.400	1.400	.836	.903	.865	.038
70	1.4000	1.8000	1.400	1.800	.797	.885	.823	.062
71	1.8000	.2000	1.800	.200	.990	1.000	1.006	-.006
72	1.8000	.6000	1.800	.600	.972	1.001	1.002	-.001
73	1.8000	1.0000	1.800	1.000	.955	1.003	.998	.005
74	1.8000	1.4000	1.800	1.400	.941	.999	.995	.004
75	1.8000	1.8000	1.800	1.800	.928	1.006	.994	.012
76	2.2000	.2000	2.200	.200	.996	1.004	1.011	-.007
77	2.2000	.6000	2.200	.600	.989	1.013	1.018	-.005
78	2.2000	1.0000	2.200	1.000	.983	1.022	1.027	-.005
79	2.2000	1.4000	2.200	1.400	.979	1.033	1.036	-.003
80	2.2000	1.8000	2.200	1.800	.976	1.043	1.046	-.003
81	2.6000	.2000	2.600	.200	.999	1.005	1.012	-.007
82	2.6000	.6000	2.600	.600	.997	1.019	1.023	-.004
83	2.6000	1.0000	2.600	1.000	.996	1.034	1.035	-.001
84	2.6000	1.4000	2.600	1.400	.996	1.048	1.048	-.000
85	2.6000	1.8000	2.600	1.800	.997	1.060	1.062	-.002
86	3.0000	.2000	3.000	.200	1.000	1.006	1.012	-.006
87	3.0000	.6000	3.000	.600	1.001	1.018	1.024	-.006
88	3.0000	1.0000	3.000	1.000	1.003	1.035	1.037	-.002
89	3.0000	1.4000	3.000	1.400	1.005	1.048	1.050	-.002
90	3.0000	1.8000	3.000	1.800	1.008	1.062	1.064	-.002
91	1.4000	2.0000	1.400	2.000	.781	.872	.805	.067
92	1.4000	3.0000	1.400	3.000	.737	.820	.759	.061
93	1.4000	4.0000	1.400	4.000	.753	.809	.768	.041
94	1.4000	5.0000	1.400	5.000	.800	.836	.807	.029

95	1.4000	6.0000	1.400	6.000	.861	.879	.859	.020
96	1.4000	7.0000	1.400	7.000	.928	.941	.919	.022
97	1.4000	8.0000	1.400	8.000	.997	.999	.983	.016
98	1.4000	9.0000	1.400	9.000	1.066	1.066	1.049	.017
99	1.8000	2.0000	1.800	2.000	.923	1.006	.993	.013
100	1.8000	3.0000	1.800	3.000	.909	1.013	1.001	.012
101	1.8000	4.0000	1.800	4.000	.911	1.038	1.023	.015
102	1.8000	5.0000	1.800	5.000	.929	1.070	1.056	.014
103	1.8000	6.0000	1.800	6.000	.958	1.110	1.094	.016
104	1.8000	7.0000	1.800	7.000	.995	1.153	1.135	.018
105	1.8000	8.0000	1.800	8.000	1.037	1.199	1.179	.020
106	1.8000	9.0000	1.800	9.000	1.083	1.241	1.223	.018
107	2.2000	2.0000	2.200	2.000	.975	1.046	1.051	-.005
108	2.2000	3.0000	2.200	3.000	.974	1.077	1.083	-.006
109	2.2000	4.0000	2.200	4.000	.982	1.109	1.121	-.012
110	2.2000	5.0000	2.200	5.000	.997	1.147	1.166	-.019
111	2.2000	6.0000	2.200	6.000	1.017	1.195	1.214	-.019
112	2.2000	7.0000	2.200	7.000	1.043	1.248	1.264	-.016
113	2.2000	8.0000	2.200	8.000	1.073	1.299	1.315	-.016
114	2.2000	9.0000	2.200	9.000	1.105	1.353	1.365	-.012
115	2.6000	2.0000	2.600	2.000	.998	1.066	1.069	-.003
116	2.6000	3.0000	2.600	3.000	1.004	1.107	1.106	.001
117	2.6000	4.0000	2.600	4.000	1.015	1.146	1.148	-.002
118	2.6000	5.0000	2.600	5.000	1.029	1.188	1.194	-.006
119	2.6000	6.0000	2.600	6.000	1.047	1.233	1.244	-.011
120	2.6000	7.0000	2.600	7.000	1.068	1.281	1.295	-.014
121	2.6000	8.0000	2.600	8.000	1.092	1.334	1.348	-.014
122	2.6000	9.0000	2.600	9.000	1.118	1.389	1.401	-.012
123	3.0000	2.0000	3.000	2.000	1.009	1.069	1.072	-.003
124	3.0000	3.0000	3.000	3.000	1.019	1.113	1.109	.004
125	3.0000	4.0000	3.000	4.000	1.031	1.156	1.150	.006
126	3.0000	5.0000	3.000	5.000	1.045	1.198	1.193	.005
127	3.0000	6.0000	3.000	6.000	1.062	1.247	1.239	.008
128	3.0000	7.0000	3.000	7.000	1.080	1.290	1.287	.003
129	3.0000	8.0000	3.000	8.000	1.101	1.349	1.336	.013
130	3.0000	9.0000	3.000	9.000	1.123	1.400	1.386	.014
131	4.0000	.2000	4.000	.200	1.002	1.008	1.010	-.002
132	4.0000	.6000	4.000	.600	1.005	1.015	1.021	-.006
133	4.0000	1.0000	4.000	1.000	1.009	1.033	1.033	.000
134	4.0000	1.4000	4.000	1.400	1.013	1.047	1.045	.002
135	4.0000	1.8000	4.000	1.800	1.017	1.057	1.057	.000
136	4.0000	2.0000	4.000	2.000	1.019	1.064	1.063	.001
137	4.0000	3.0000	4.000	3.000	1.031	1.098	1.095	.003
138	4.0000	4.0000	4.000	4.000	1.043	1.133	1.127	.006
139	4.0000	5.0000	4.000	5.000	1.057	1.168	1.161	.007
140	4.0000	6.0000	4.000	6.000	1.071	1.201	1.196	.005
141	4.0000	7.0000	4.000	7.000	1.087	1.239	1.232	.007
142	4.0000	8.0000	4.000	8.000	1.103	1.279	1.269	.010
143	4.0000	9.0000	4.000	9.000	1.119	1.318	1.307	.011

SAGE AND LACEY ZEXP -0 1-0 -0. -0.
 BENZENE RANKINE PSI 1912.700000 714.000000 .274000-0

1 2 2 559.680000 189.000000 200.000000 400.000000
 1 1 1 919.680000 -0. 600.000000 -0.
 -0 3 4 559.680000 189.000000 1000.000000 -1.000000

NO	T	P	TR	PR	ZK	ZEXP	ZCALC	DIFF
1	559.6000	200.0000	.553	.280	.054	.048	9.300	0. C
2	559.6000	600.0000	.553	.840	.161	.145	9.300	0. C
3	739.6000	200.0000	.730	.280	.685	.642	.679	-.637
					.048	.042	.041	.000
4	739.6000	600.0000	.730	.840	.141	.125	.117	.008
5	919.6000	600.0000	.908	.840	.151	.125	.128	-.002
6	559.6000	1000.0000	.553	1.401	.266	.240	9.300	0. C
7	559.6000	2000.0000	.553	2.801	.527	.477	9.300	0. C
8	559.6000	5000.0000	.553	7.003	1.287	1.170	9.300	0. C
9	559.6000	10000.0000	.553	14.006	2.565	2.286	9.300	0. C
10	739.6000	1000.0000	.730	1.401	.232	.206	.193	.013
11	739.6000	2000.0000	.730	2.801	.451	.406	.378	.028
12	739.6000	5000.0000	.730	7.003	1.066	.980	.902	.078
13	739.6000	10000.0000	.730	14.006	2.024	1.880	1.709	.171
14	919.6000	1000.0000	.908	1.401	.237	.203	.206	-.003
15	919.6000	2000.0000	.908	2.801	.433	.386	.395	-.008
16	919.6000	5000.0000	.908	7.003	.959	.890	.919	-.029
17	919.6000	10000.0000	.908	14.006	1.752	1.660	1.713	-.053

SAGE AND LACEY ZEXP -0 1-0 -0. -0.
 1-RUTENE BANKINE PSIA 756.680000 588.000000 .279000-0

1 3 5 559.680000 120.000000 200.000000 200.000000
 -0 3 9 559.680000 120.000000 2000.000000 1000.000000

NO	T	P	TR	PR	ZK	ZEXP	ZCALC	DIFF
1	559.6000	200.0000	.740	.340	.564	.552	.599	-.546
					.058	.052	.050	.002
2	559.6000	400.0000	.740	.680	.114	1.044	.099	.945
3	559.6000	600.0000	.740	1.020	.176	.156	.148	.008
4	559.6000	800.0000	.740	1.361	.225	.207	.196	.011
5	559.6000	1000.0000	.740	1.701	.279	.257	.243	.014
6	679.6000	200.0000	.898	.340	.818	.812	.811	.001
7	679.6000	400.0000	.898	.680	.123	.106	.467	-.362
					.500	.106	.110	-.004
8	679.6000	600.0000	.898	1.020	.177	.156	.156	.001
9	679.6000	800.0000	.898	1.361	.229	.206	.205	.001
10	679.6000	1000.0000	.898	1.701	.279	.254	.253	.001
11	799.6000	200.0000	1.057	.340	.895	.901	.899	.002
12	799.6000	400.0000	1.057	.680	.772	.778	.770	.008
13	799.6000	600.0000	1.057	1.020	.612	.618	.593	.025
14	799.6000	800.0000	1.057	1.361	.390	.393	.356	.037
15	799.6000	1000.0000	1.057	1.701	.363	.327	.328	-.001
16	559.6000	2000.0000	.740	3.401	.539	.504	.477	.027
17	559.6000	3000.0000	.740	5.102	.769	.745	.700	.045
18	559.6000	4000.0000	.740	6.803	1.031	.980	.915	.065

19	559.6000	5000.0000	.740	8.503	1.267	1.210	1.125	.065
20	559.6000	6000.0000	.740	10.204	1.499	1.434	1.329	.105
21	559.6000	7000.0000	.740	11.905	1.728	1.657	1.529	.120
22	559.6000	8000.0000	.740	13.605	1.953	1.875	1.725	.150
23	559.6000	9000.0000	.740	15.306	2.177	2.092	1.918	.174
24	559.6000	10000.0000	.740	17.007	2.398	2.307	2.107	.200
25	679.6000	2000.0000	.898	3.401	.513	.482	.485	-.003
26	679.6000	3000.0000	.898	5.102	.731	.697	.705	-.008
27	679.6000	4000.0000	.898	6.803	.939	.905	.918	-.013
28	679.6000	5000.0000	.898	8.503	1.140	1.108	1.123	-.015
29	679.6000	6000.0000	.898	10.204	1.337	1.307	1.324	-.017
30	679.6000	7000.0000	.898	11.905	1.529	1.502	1.519	-.017
31	679.6000	8000.0000	.898	13.605	1.719	1.691	1.710	-.019
32	679.6000	9000.0000	.898	15.306	1.907	1.878	1.896	-.018
33	679.6000	10000.0000	.898	17.007	2.092	2.062	2.077	-.015
34	799.6000	2000.0000	1.057	3.401	.534	.511	.495	.016
35	799.6000	3000.0000	1.057	5.102	.719	.700	.685	.015
36	799.6000	4000.0000	1.057	6.803	.898	.884	.871	.013
37	799.6000	5000.0000	1.057	8.503	1.072	1.061	1.053	.008
38	799.6000	6000.0000	1.057	10.204	1.241	1.236	1.230	.006
39	799.6000	7000.0000	1.057	11.905	1.407	1.408	1.404	.004
40	799.6000	8000.0000	1.057	13.605	1.570	1.577	1.574	.003
41	799.6000	9000.0000	1.057	15.306	1.731	1.742	1.742	.000
42	799.6000	10000.0000	1.057	17.007	1.889	1.903	1.906	-.003

SAGE AND LACEY CU FT PER LB MOLE -033-0 -0. -0.
 N-NONANE PANKINE PSIA 1079.210000 332.000000 .254000-0

1 4 5 559.600000 120.000000 200.000000 200.000000
 -0 4 9 559.600000 120.000000 2000.000000 1000.000000

NO	T	P	TR	PR	ZK	ZEXP	ZCALC	DIFF
1	559.6000	200.0000	.523	.602	.120	.097	9.300	0. C
2	559.6000	400.0000	.523	1.205	.238	.193	9.300	0. C
3	559.6000	600.0000	.523	1.807	.356	.290	9.300	0. C
4	559.6000	800.0000	.523	2.410	.473	.386	9.300	0. C
5	559.6000	1000.0000	.523	3.012	.589	.481	9.300	0. C
6	679.6000	200.0000	.635	.602	.107	.086	9.300	0. C
7	679.6000	400.0000	.635	1.205	.212	.172	9.300	0. C
8	679.6000	600.0000	.635	1.807	.315	.257	9.300	0. C
9	679.6000	800.0000	.635	2.410	.417	.342	9.300	0. C
10	679.6000	1000.0000	.635	3.012	.518	.428	9.300	0. C
11	799.6000	200.0000	.747	.602	.101	.081	.078	.002
12	799.6000	400.0000	.747	1.205	.199	.161	.157	.004
13	799.6000	600.0000	.747	1.807	.294	.240	.234	.006
14	799.6000	800.0000	.747	2.410	.387	.318	.310	.008
15	799.6000	1000.0000	.747	3.012	.479	.395	.384	.011
16	919.6000	200.0000	.859	.602	.105	.080	.477	-.397A
					9.500	.080	.087	-.007
17	919.6000	400.0000	.859	1.205	.200	.158	.165	-.007
18	919.6000	600.0000	.859	1.807	.291	.234	.244	-.010
19	919.6000	800.0000	.859	2.410	.378	.309	.320	-.011

20	919.6000	1000.0000	.859	3.012	.462	.382	.395	-.013	
21	559.6000	2000.0000	.523	6.024	1.159	.954	9.300	0.	C
22	559.6000	3000.0000	.523	9.036	1.718	1.419	9.300	0.	C
23	559.6000	4000.0000	.523	12.048	2.267	1.877	9.300	0.	C
24	559.6000	5000.0000	.523	15.060	2.810	2.330	9.300	0.	C
25	559.6000	6000.0000	.523	18.072	3.347	2.778	9.300	0.	C
26	559.6000	7000.0000	.523	21.084	3.880	3.223	9.300	0.	C
27	559.6000	8000.0000	.523	24.096	4.409	3.670	9.300	0.	C
28	559.6000	9000.0000	.523	27.108	4.935	4.112	9.300	0.	C
29	559.6000	10000.0000	.523	30.120	5.459	4.545	9.300	0.	C
30	679.6000	2000.0000	.635	6.024	1.010	.845	9.300	0.	C
31	679.6000	3000.0000	.635	9.036	1.484	1.250	9.300	0.	C
32	679.6000	4000.0000	.635	12.048	1.948	1.651	9.300	0.	C
33	679.6000	5000.0000	.635	15.060	2.404	2.043	9.300	0.	C
34	679.6000	6000.0000	.635	18.072	2.853	2.432	9.300	0.	C
35	679.6000	7000.0000	.635	21.084	3.298	2.817	9.300	0.	C
36	679.6000	8000.0000	.635	24.096	3.739	3.198	9.300	0.	C
37	679.6000	9000.0000	.635	27.108	4.176	3.572	9.300	0.	C
38	679.6000	10000.0000	.635	30.120	4.611	3.938	9.300	0.	C
39	799.6000	2000.0000	.747	6.024	.916	.774	.744	.029	
40	799.6000	3000.0000	.747	9.036	1.332	1.140	1.083	.057	
41	799.6000	4000.0000	.747	12.048	1.735	1.496	1.406	.090	
42	799.6000	5000.0000	.747	15.060	2.129	1.847	1.718	.129	
43	799.6000	6000.0000	.747	18.072	2.516	2.188	2.021	.167	
44	799.6000	7000.0000	.747	21.084	2.899	2.520	2.317	.204	
45	799.6000	8000.0000	.747	24.096	3.277	2.862	2.606	.256	
46	799.6000	9000.0000	.747	27.108	3.652	3.188	2.891	.297	
47	799.6000	10000.0000	.747	30.120	4.025	3.519	3.172	.347	
48	919.6000	2000.0000	.859	6.024	.858	.734	.754	-.020	
49	919.6000	3000.0000	.859	9.036	1.229	1.070	1.091	-.021	
50	919.6000	4000.0000	.859	12.048	1.586	1.394	1.413	-.019	
51	919.6000	5000.0000	.859	15.060	1.934	1.712	1.721	-.009	
52	919.6000	6000.0000	.859	18.072	2.275	2.018	2.018	.001	
53	919.6000	7000.0000	.859	21.084	2.611	2.319	2.305	.014	
54	919.6000	8000.0000	.859	24.096	2.942	2.618	2.584	.034	
55	919.6000	9000.0000	.859	27.108	3.271	2.909	2.855	.054	
56	919.6000	10000.0000	.859	30.120	3.597	3.202	3.121	.081	

KANG CHEM ENG DATA 6 1961 ZEP -0 1-0 -0, -0,
 SULFLF DIC4IDE K PSI 430.65000 77.803000 .269700-0

1 2 3	323.15000	50.00000	2.00000	1.00000
1 2 2	423.15000	7.50000	10.00000	11.00000
1 1 2	373.15000	-0.	14.00000	17.00000
1 1 4	423.15000	-0.	30.00000	17.00000
1 1 3	430.65000	-0.	50.00000	-1.00000
-0 2 4	430.65000	72.50000	75.00000	77.00000

NC	T	P	TR	PR	ZK	ZEP	ZCALC	DIFF
1	323.1500	2.0000	.750	.026	.980	.974	.972	.002
					.004	.974	.004	.970 A
2	323.1500	5.0000	.750	.064	.949	.934	.933	.002
					.011	.934	.011	.924 A
3	323.1500	8.0000	.750	.103	.911	.891	.894	.004
					.011	.891	.015	.874 A
4	373.1500	2.0000	.366	.026	.987	.985	.979	.006
5	373.1500	5.0000	.366	.064	.950	.962	.953	.009
6	373.1500	8.0000	.366	.103	.941	.938	.928	.010
7	423.1500	10.0000	.933	.129	.957	.950	.947	.003
8	423.1500	20.0000	.933	.257	.901	.877	.896	.001
9	430.6500	10.0000	1.000	.129	.951	.953	.952	.001
10	430.6500	20.0000	1.000	.257	.907	.904	.904	-.003
11	373.1500	14.0000	.366	.180	.901	.887	.881	.005

12	23.1500	26.0000	.865	.334	.791	.761	.783	-.022
13	23.1500	30.0000	.983	.386	.841	.839	.841	-.001
14	23.1500	40.0000	.983	.514	.791	.774	.778	-.005
15	23.1500	50.0000	.983	.643	.711	.658	.706	-.038
16	23.1500	60.0000	.983	.771	.621	.600	.615	-.015
17	30.6500	50.0000	1.000	.543	.731	.724	.726	-.002
18	30.6500	100.0000	1.000	1.285	.261	.215	.208	.007
19	30.6500	250.0000	1.000	3.213	.491	.435	.432	.004
20	30.6500	75.0000	1.000	.564	.471	.447	.449	-.002
21	30.6500	150.0000	1.000	1.928	.341	.287	.278	.009
22	30.6500	225.0000	1.000	2.892	.451	.402	.394	.008
23	30.6500	300.0000	1.000	3.856	.571	.509	.508	.000
24	23.1500	75.0000	1.215	.964	.801	.823	.809	.014
25	23.1500	150.0000	1.215	1.928	.611	.646	.601	.045
26	23.1500	225.0000	1.215	2.892	.581	.576	.568	.008
27	23.1500	300.0000	1.215	3.856	.641	.515	.620	-.005

SAGE AND LACEY ZEXP -0 1-0 -0. -0.
HYDROGEN SULFIDE R PSI 671.930000 1306.000000 .263200-0

1 1 7 499.680000 -0. 100.000000 -1.000000
-0 2 7 559.680000 120.000000 100.000000 -1.000000

NO	I	P	TR	PR	ZK	ZEXP	ZCALC	DIFF
1	499.6800	100.0000	.744	.077	.931	.922	.928	-.006
					.011	.922	.012	.910 A
2	499.6800	200.0000	.744	.153	.851	.025	.854	-.829 A
					.021	.025	.024	.000
3	499.6800	500.0000	.744	.383	.051	.061	.477	-.416 A
					.9.591	.061	.056	.005
4	499.6800	1000.0000	.744	.765	.121	.122	.114	.007
5	499.6800	2000.0000	.744	1.531	.251	.240	.225	.015
6	499.6800	5000.0000	.744	3.823	.601	.579	.544	.035
7	499.6800	10000.0000	.744	7.657	1.141	1.114	1.041	.073
8	559.6800	100.0000	.833	.077	.951	.950	.947	.003
9	559.6800	200.0000	.833	.153	.901	.898	.896	.003
					.021	.898	.031	.867 A
10	559.6800	500.0000	.833	.383	.717	.061	.717	-.656 A
					.051	.061	.063	-.002
11	559.6800	1000.0000	.833	.766	.121	.120	.119	.001
12	559.6800	2000.0000	.833	1.531	.241	.224	.233	.001
13	559.6800	5000.0000	.833	3.823	.571	.554	.556	-.003
14	559.6800	10000.0000	.833	7.657	1.071	1.052	1.058	-.006
15	779.6800	100.0000	1.011	.077	.971	.974	.975	-.001
16	779.6800	200.0000	1.011	.153	.941	.948	.949	-.001
17	779.6800	500.0000	1.011	.383	.861	.864	.863	.001
18	779.6800	1000.0000	1.011	.766	.691	.678	.670	.008
19	779.6800	2000.0000	1.011	1.531	.301	.265	.250	.015
20	779.6800	5000.0000	1.011	3.823	.571	.545	.530	.015
21	779.6800	10000.0000	1.011	7.657	.997	.973	.985	-.012
22	799.6800	100.0000	1.190	.077	.981	.985	.988	-.003
23	799.6800	200.0000	1.190	.153	.961	.971	.974	-.003

24	799.6800	5000.0000	1.190	.383	.915	.925	.926	-.001
25	799.6800	1000.0000	1.190	.766	.835	.844	.837	.008
26	799.6800	2000.0000	1.190	1.531	.651	.657	.638	.019
27	799.6800	5000.0000	1.190	3.828	.625	.597	.609	-.012
28	799.6800	10000.0000	1.190	7.657	.961	.946	.953	-.005

BEATIE AND LAWRENCE CC PER GRAM -023-0 17.0210 -0.
 AMMONIA KELVIN AIM 405.550000 111.500000 .242500-0

1	1	1	323.150000	-0.	1.137000	-0.
1	1	1	323.150000	-0.	4.985000	-0.
1	1	1	323.150000	-0.	9.567000	-0.
1	1	1	323.150000	-0.	14.370000	-0.
1	1	1	323.150000	-0.	15.050000	-0.
1	1	1	323.150000	-0.	15.722000	-0.
1	1	1	323.150000	-0.	16.520000	-0.
1	1	1	323.150000	-0.	18.540000	-0.
1	1	1	373.150000	-0.	1.374000	-0.
1	1	1	373.150000	-0.	5.832000	-0.
1	1	1	373.150000	-0.	11.352000	-0.
1	1	1	373.150000	-0.	17.360000	-0.
1	1	1	373.150000	-0.	19.109000	-0.
1	1	1	373.150000	-0.	20.280000	-0.
1	1	1	373.150000	-0.	26.120000	-0.
1	1	1	373.150000	-0.	36.470000	-0.
1	1	1	373.150000	-0.	45.190000	-0.
1	1	1	373.150000	-0.	51.090000	-0.
1	1	1	373.150000	-0.	58.280000	-0.
1	1	1	473.150000	-0.	1.747000	-0.
1	1	1	473.150000	-0.	7.489000	-0.
1	1	1	473.150000	-0.	14.765000	-0.
1	1	1	473.150000	-0.	22.930000	-0.
1	1	1	473.150000	-0.	25.361000	-0.
1	1	1	473.150000	-0.	27.010000	-0.
1	1	1	473.150000	-0.	35.400000	-0.
1	1	1	473.150000	-0.	51.290000	-0.
1	1	1	473.150000	-0.	66.050000	-0.
1	1	1	473.150000	-0.	77.130000	-0.
1	1	1	473.150000	-0.	92.570000	-0.
1	1	1	598.150000	-0.	29.590000	-0.
1	1	1	598.150000	-0.	35.040000	-0.
1	1	1	598.150000	-0.	45.340000	-0.
1	1	1	598.150000	-0.	63.360000	-0.
1	1	1	598.150000	-0.	89.690000	-0.
1	1	1	598.150000	-0.	106.250000	-0.
-0	1	1	598.150000	-0.	130.400000	-0.

NO	T	P	TR	PR	ZK	ZEAP	ZCALC	DIFF
1	323.1500	1.1870	.797	.011	.995	.991	.978	.013
2	323.1500	4.9850	.797	.045	.971	.961	.932	.028
3	323.1500	9.5670	.797	.086	.947	.922	.891	.031
4	323.1500	14.3700	.797	.129	.911	.877	.853	.024

5	223.1500	15.0500	.797	.135	.901	.870	.847	.023
6	223.1500	15.7220	.797	.141	.901	.863	.842	.021
7	223.1500	16.6200	.797	.149	.891	.854	.836	.018
8	223.1500	18.5400	.797	.166	.881	.834	.821	.012
9	273.1500	1.3740	.920	.012	.991	.994	.979	.015
10	273.1500	5.8320	.920	.052	.977	.973	.949	.025
11	273.1500	11.3520	.920	.102	.951	.947	.922	.025
12	273.1500	17.3600	.920	.156	.921	.917	.895	.022
13	273.1500	19.1090	.920	.171	.921	.909	.888	.021
14	273.1500	20.2900	.920	.182	.911	.902	.883	.020
15	273.1500	26.1200	.920	.234	.891	.872	.857	.014
16	273.1500	36.4700	.920	.327	.841	.811	.810	.001
17	273.1500	45.1300	.920	.405	.794	.754	.758	-.014
18	273.1500	51.0900	.920	.458	.761	.710	.737	-.026
19	273.1500	58.2800	.920	.523	.711	.648	.696	-.047
20	473.1500	1.7470	1.167	.015	.991	.996	1.003	-.007
21	473.1500	7.4890	1.167	.067	.981	.986	.996	-.010
22	473.1500	14.7660	1.167	.132	.971	.972	.984	-.013
23	473.1500	22.9300	1.157	.205	.951	.956	.970	-.014
24	473.1500	25.3610	1.167	.227	.951	.951	.965	-.014
25	473.1500	27.0100	1.167	.242	.941	.948	.962	-.014
26	473.1500	35.4000	1.157	.317	.921	.932	.946	-.014
27	473.1500	51.2300	1.157	.460	.891	.900	.913	-.013
28	473.1500	66.0500	1.167	.592	.861	.869	.881	-.011
29	473.1500	77.1300	1.167	.692	.831	.846	.855	-.009
30	473.1500	92.5700	1.167	.830	.801	.812	.816	-.004
31	598.1500	29.5900	1.475	.265	.971	.975	.995	-.019
32	598.1500	35.0400	1.475	.314	.961	.973	.991	-.019
33	598.1500	46.3400	1.475	.416	.951	.965	.985	-.020
34	598.1500	68.3500	1.475	.613	.931	.949	.971	-.022
35	598.1500	85.6900	1.475	.804	.911	.934	.957	-.023
36	598.1500	106.2500	1.475	.953	.901	.922	.945	-.024
37	598.1500	130.4000	1.475	1.170	.881	.905	.929	-.024

SAGE AND LACEY ZEXP -0.1-0 -0. -0.
 CARBON DIOXIDE R PSI 547.430000 1059.870000 .274500-0

1	1	2	499.580000	-0.	200.000000	401.000000
1	4	2	559.680000	120.000000	200.000000	401.000000
1	1	4	499.580000	-0.	1000.000000	-1.000000
-0	4	4	559.680000	120.000000	1000.000000	-1.000000

NC	I	P	TR	PR	ZK	ZEXP	ZCALC	DIFF
1	499.6800	200.0000	.913	.187	.911	.906	.945	-.039
2	499.6800	600.0000	.913	.561	.651	.087	.714	-.627A
3	559.6800	200.0000	1.022	.187	.931	.938	.940	-.002
4	559.6800	600.0000	1.022	.561	.791	.793	.792	.001
5	619.6800	200.0000	1.241	.187	.961	.968	.975	-.006
6	619.6800	600.0000	1.241	.561	.891	.504	.906	-.002
7	739.6800	200.0000	1.461	.187	.981	.983	.989	-.006
8	739.6800	600.0000	1.461	.561	.941	.951	.954	-.003
9	819.6800	200.0000	1.680	.187	.981	.992	.997	-.005

10	119.6900	500.0000	1.580	.551	.951	.976	.979	-.004
11	199.6900	1000.0000	.913	.935	.165	.143	.152	-.009
12	199.6900	2000.0000	.913	1.869	.301	.275	.282	-.007
13	199.6900	5000.0000	.913	4.673	.671	.623	.645	-.022
14	199.6900	10000.0000	.913	9.347	1.221	1.160	1.205	-.044
15	159.5800	1000.0000	1.022	.935	.581	.587	.566	.020
16	159.5800	2000.0000	1.022	1.869	.341	.302	.290	.012
17	159.5800	5000.0000	1.022	4.673	.671	.624	.616	.003
18	159.5800	10000.0000	1.022	9.347	1.171	1.120	1.137	-.017
19	179.6900	1000.0000	1.241	.935	.821	.839	.831	.003
20	179.6900	2000.0000	1.241	1.869	.651	.681	.647	.034
21	179.6900	5000.0000	1.241	4.673	.711	.695	.697	-.002
22	179.6900	10000.0000	1.241	9.347	1.101	1.087	1.087	.000
23	199.5900	1000.0000	1.461	.935	.901	.920	.919	.001
24	199.5900	2000.0000	1.461	1.869	.821	.853	.837	.016
25	199.5900	5000.0000	1.461	4.673	.801	.825	.816	.009
26	199.5900	10000.0000	1.461	9.347	1.091	1.102	1.085	.017
27	119.6900	1000.0000	1.580	.935	.941	.960	.962	-.002
28	119.6900	2000.0000	1.580	1.869	.901	.930	.925	.005
29	119.6900	5000.0000	1.580	4.673	.881	.925	.925	.001
30	119.6900	10000.0000	1.580	9.347	1.091	1.127	1.123	.004

LANDOLT AND BOERNSTEIN AMAGAT -0.2-0 -0. -0.
 HELIUM KELVIN ATM 5.250000 2.260000 .393000-0

1	1	1	293.150000	-0.	27.430000	-0.
1	1	1	293.150000	-0.	48.640000	-0.
1	1	1	293.150000	-0.	63.410000	-0.
1	1	1	169.510000	-0.	21.440000	-0.
1	1	1	169.510000	-0.	49.960000	-0.
1	1	1	71.640000	-0.	20.100000	-0.
1	1	1	48.140000	-0.	55.360000	-0.
1	1	1	17.110000	-0.	22.500000	-0.
1	1	1	4.270000	-0.	.993000	-0.
1	1	1	3.460000	-0.	.570000	-0.
-0	1	1	2.630000	-0.	.364900	-0.

NC	T	P	TR	PR	ZK	ZEXP	ZCALC	DIFF
1	293.1500	27.4300	55.838	12.137	1.019	1.014	1.018	-.005
2	293.1500	48.6400	55.838	21.522	1.033	1.022	1.033	-.010
3	293.1500	63.4100	55.838	26.053	1.043	1.030	1.042	-.013
4	169.5100	21.4400	32.288	9.487	1.025	1.018	1.024	-.006
5	169.5100	49.9600	32.288	22.106	1.058	1.044	1.056	-.012
6	71.6400	20.1000	13.543	8.894	1.052	1.036	1.048	-.013
7	48.1400	55.3600	9.170	24.353	1.207	1.139	1.136	-.047
8	17.1100	22.5000	3.259	9.956	1.144	1.001	1.102	-.101
9	4.2700	.9930	.813	.439	.594	.634	.620	.065

			-71-		.075	.634	.071	.614
10	3.4600	.5700	.659	.252	.044	.845	9.300	0.
11	2.6300	.6648	.501	.029	.932	.893	.931	-.033
					.006	.893	.005	.388

BEATTIE MOLES PER LITER -021-0 -0. -0.
 XENDN KELVIN ATM 289.800000 57.890000 .292600-0

1	1	1	289.800000	-0.	57.780000	-0.
1	1	1	289.800000	-0.	57.880000	-0.
1	1	1	289.800000	-0.	57.910000	-0.
1	1	1	289.800000	-0.	58.020000	-0.
1	1	1	298.150000	-0.	65.970000	-0.
1	1	1	298.150000	-0.	67.320000	-0.
1	1	1	298.150000	-0.	68.600000	-0.
1	1	1	298.150000	-0.	70.380000	-0.
1	1	1	323.150000	-0.	89.320000	-0.
1	1	1	323.150000	-0.	95.580000	-0.
1	1	1	323.150000	-0.	101.590000	-0.
1	1	1	323.150000	-0.	109.390000	-0.
1	1	1	523.150000	-0.	275.570000	-0.
1	1	1	523.150000	-0.	321.390000	-0.
1	1	1	523.150000	-0.	372.920000	-0.
1	1	1	548.150000	-0.	298.510000	-0.
1	1	1	548.150000	-0.	349.190000	-0.
1	1	1	548.150000	-0.	406.150000	-0.
1	1	1	573.150000	-0.	321.160000	-0.
-0	1	1	573.150000	-0.	377.390000	-0.

NC	T	P	TR	PR	ZK	ZEXP	ZCALC	DIFF
1	289.8000	57.7800	1.000	.998	.351	.347	.346	.001
2	289.8000	57.8800	1.000	1.000	.299	.304	.315	-.011
3	289.8000	57.9100	1.000	1.000	.296	.271	.273	-.002
4	289.8000	58.0200	1.000	1.002	.289	.244	.258	-.014
5	298.1500	65.9700	1.029	1.140	.401	.395	.364	.021
6	298.1500	67.3200	1.029	1.163	.370	.344	.334	.010
7	298.1500	68.6000	1.029	1.185	.347	.312	.314	-.002
8	298.1500	70.3800	1.029	1.216	.329	.288	.297	-.009
9	323.1500	89.3200	1.115	1.552	.505	.434	.486	-.002
10	323.1500	95.5800	1.115	1.651	.481	.451	.461	-.011
11	323.1500	101.5900	1.115	1.757	.464	.426	.445	-.010
12	323.1500	109.3900	1.115	1.890	.454	.413	.435	-.002
13	523.1500	275.5700	1.305	4.760	.925	.917	.926	-.000
14	523.1500	321.3900	1.305	5.552	.945	.936	.946	-.010
15	523.1500	372.9200	1.305	6.442	.975	.965	.976	-.010
16	548.1500	298.5100	1.391	5.157	.953	.943	.955	-.002
17	548.1500	349.1900	1.391	6.032	.976	.970	.979	-.009
18	548.1500	406.1500	1.391	7.016	1.009	1.003	1.012	-.009
19	573.1500	321.1600	1.978	5.548	.978	.976	.981	-.006
20	573.1500	377.3900	1.978	6.514	1.004	1.002	1.009	-.007

LANDOLT AND BOERNSTEIN AMAGAT =0 1-C -0. -0.
HYDROGEN KELVIN ATM 33.244000 12.797000 .305000-0

1	1	1	33.240000	-0.	12.963000	-0.		
1	1	1	33.240000	-0.	51.457000	-0.		
1	1	1	36.840000	-0.	17.910000	-0.		
1	1	1	36.840000	-0.	40.635000	-0.		
1	1	1	55.820000	-0.	34.242000	-0.		
1	1	1	55.820000	-0.	56.525000	-0.		
1	1	2	203.150000	-0.	200.000000	400.000000		
1	1	4	273.150000	-0.	100.000000	300.000000		
1	1	2	372.400000	-0.	400.000000	300.000000		
1	1	2	473.400000	-0.	300.000000	300.000000		
-C	1	3	572.900000	-0.	200.000000	400.000000		

NC	T	P	TR	PR	ZK	ZEXP	ZCALC	DIFF
1	33.2400	12.9630	1.000	1.013	.272	.357	.258	.099
2	33.2400	51.4570	1.000	4.021	.594	.604	.609	-.005
3	36.8400	17.9100	1.108	1.400	.542	.495	.524	-.029
4	36.8400	40.6350	1.138	3.175	.531	.500	.514	-.014
5	55.8200	34.2420	1.679	2.676	.878	.829	.859	-.030
6	55.8200	56.5250	1.679	4.417	.883	.804	.859	-.055
7	203.1500	200.0000	6.111	15.629	1.180	1.162	1.145	.017
8	203.1500	600.0000	6.111	46.886	1.609	1.554	1.511	.044
9	273.1500	1000.0000	6.111	78.143	2.056	1.943	1.901	.042
10	273.1500	100.0000	8.217	7.914	1.069	1.070	1.058	.011
11	273.1500	400.0000	8.217	31.257	1.293	1.284	1.257	.027
12	273.1500	700.0000	8.217	54.700	1.541	1.505	1.471	.035
13	273.1500	1000.0000	8.217	78.143	1.789	1.721	1.689	.032
14	372.4000	400.0000	11.232	31.257	1.224	1.218	1.201	.017
15	372.4000	700.0000	11.232	54.700	1.492	1.375	1.361	.014
16	372.4000	1000.0000	11.232	78.143	1.582	1.536	1.524	.012
17	473.4000	300.0000	14.240	23.443	1.134	1.129	1.122	.007
18	473.4000	600.0000	14.240	46.886	1.272	1.256	1.250	.007
19	473.4000	900.0000	14.240	70.329	1.413	1.391	1.380	.001
20	572.9000	200.0000	17.233	15.629	1.074	1.073	1.059	.004
21	572.9000	600.0000	17.233	46.886	1.227	1.211	1.211	.000
22	572.9000	1000.0000	17.233	78.143	1.382	1.342	1.356	-.015

BARTLETT AND BEATTIE GRAMS PER CC =021-C 2.0160 -0.
HYDROGEN & KELVIN ATM 33.244000 12.797000 .303500-0

1	1	2	273.150000	-0.	100.000000	200.000000		
-C	1	2	273.150000	-0.	600.000000	400.000000		

NC	T	P	TR	PR	ZK	ZEXP	ZCALC	DIFF
1	273.1500	100.0000	8.217	7.814	1.069	1.071	1.060	.011
2	273.1500	300.0000	8.217	23.443	1.219	1.205	1.193	.012
3	273.1500	600.0000	8.217	46.886	1.459	1.424	1.408	.016
4	273.1500	1000.0000	8.217	78.143	1.789	1.713	1.705	.009

BEATTIE AND SMITH CC PER GRAM -023-0 28.0140 -0.
 NITROGEN KELVIN ATM 126.020000 33.490000 .291700-0

1	1	1	323.120000	-0.	106.130000	-0.		
1	1	1	323.120000	-0.	138.263000	-0.		
1	1	1	323.120000	-0.	200.153000	-0.		
1	1	1	373.150000	-0.	125.564000	-0.		
1	1	1	373.150000	-0.	164.401000	-0.		
1	1	1	373.150000	-0.	240.052000	-0.		
1	1	1	473.150000	-0.	163.911000	-0.		
1	1	1	473.150000	-0.	216.132000	-0.		
-C	1	1	473.150000	-0.	319.534000	-0.		

NC	T	P	TR	PR	ZK	ZEXP	ZCALC	DIFF
1	323.1200	106.1300	2.564	3.159	1.004	1.009	1.010	-.001
2	323.1200	138.2630	2.564	4.128	1.014	1.023	1.022	.000
3	323.1200	200.1530	2.564	5.977	1.045	1.057	1.056	.001
4	373.1500	125.5640	2.961	3.749	1.026	1.034	1.034	.000
5	373.1500	164.4010	2.961	4.909	1.043	1.053	1.052	.001
6	373.1500	240.0520	2.961	7.158	1.083	1.098	1.097	.001
7	473.1500	163.9110	3.755	4.894	1.054	1.054	1.052	.002
8	473.1500	216.1320	3.755	6.454	1.078	1.092	1.088	.004
9	473.1500	319.5340	3.755	9.541	1.131	1.153	1.146	.006

BARTLETT AND BEATTIE GRAM PER CC -021-0 28.0140 -0.
 NITROGEN KELVIN ATM 126.020000 33.490000 .291700-0

1	1	2	273.150000	-0.	50.000000	50.000000		
-C	1	5	273.150000	-0.	200.000000	200.000000		

NC	T	P	TR	PR	ZK	ZEXP	ZCALC	DIFF
1	273.1500	50.0000	2.168	1.493	.976	.983	.981	.002
2	273.1500	100.0000	2.168	2.936	.971	.983	.976	.007
3	273.1500	200.0000	2.168	5.972	1.013	1.032	1.023	.009

4	273.1500	400.0000	2.158	11.944	1.213	1.253	1.226	.027
5	273.1500	600.0000	2.158	17.915	1.457	1.520	1.471	.049
6	273.1500	800.0000	2.158	23.838	1.710	1.797	1.725	.073
7	273.1500	1000.0000	2.158	29.860	1.965	2.065	1.979	.085

MICHEL'S	AMAGAT	-0.2-0	-0.	-0.
OXYGEN	KELVIN ATM	154.330000	49.713000	.292100-0

1	1	1	273.150000	-0.	22.429000	-0.
1	1	1	273.150000	-0.	40.014400	-0.
1	1	1	273.150000	-0.	66.464500	-0.
1	1	1	273.150000	-0.	80.703600	-0.
1	1	1	273.150000	-0.	98.417400	-0.
1	1	1	273.150000	-0.	119.466000	-0.
1	1	1	298.150000	-0.	24.619600	-0.
1	1	1	298.150000	-0.	44.140100	-0.
1	1	1	298.150000	-0.	73.370300	-0.
1	1	1	298.150000	-0.	90.048600	-0.
1	1	1	298.150000	-0.	110.353700	-0.
1	1	1	298.150000	-0.	134.776700	-0.
1	1	1	323.150000	-0.	26.812300	-0.
1	1	1	323.150000	-0.	48.256700	-0.
1	1	1	323.150000	-0.	81.262300	-0.
-C	1	1	323.150000	-0.	99.401200	-0.
					122.320800	-0.

NC	T	P	TR	PR	ZK	ZEXP	ZCALC	DIFF
1	273.1500	22.4290	1.770	.451	.977	.980	.981	-.001
2	273.1500	40.0144	1.770	.805	.960	.965	.964	.000
3	273.1500	66.4646	1.770	1.337	.938	.944	.942	.003
4	273.1500	80.7036	1.770	1.623	.928	.935	.931	.004
5	273.1500	98.4174	1.770	1.930	.918	.925	.920	.005
6	273.1500	119.4660	1.770	2.403	.908	.915	.910	.005
7	298.1500	24.6196	1.932	.495	.982	.986	.987	-.001
8	298.1500	44.1401	1.932	.889	.970	.975	.975	.000
9	298.1500	73.3703	1.932	1.486	.955	.961	.959	.002
10	298.1500	90.0486	1.932	1.911	.949	.956	.952	.003
11	298.1500	110.3537	1.932	2.220	.942	.950	.946	.004
12	298.1500	134.7767	1.932	2.711	.933	.946	.941	.005
13	323.1500	26.8123	2.094	.539	.987	.990	.991	-.001
14	323.1500	48.2567	2.094	.971	.979	.983	.983	.000
15	323.1500	81.2623	2.094	1.635	.969	.976	.973	.003
16	323.1500	99.4012	2.094	2.000	.965	.973	.969	.004
17	323.1500	122.3208	2.094	2.461	.962	.972	.967	.005

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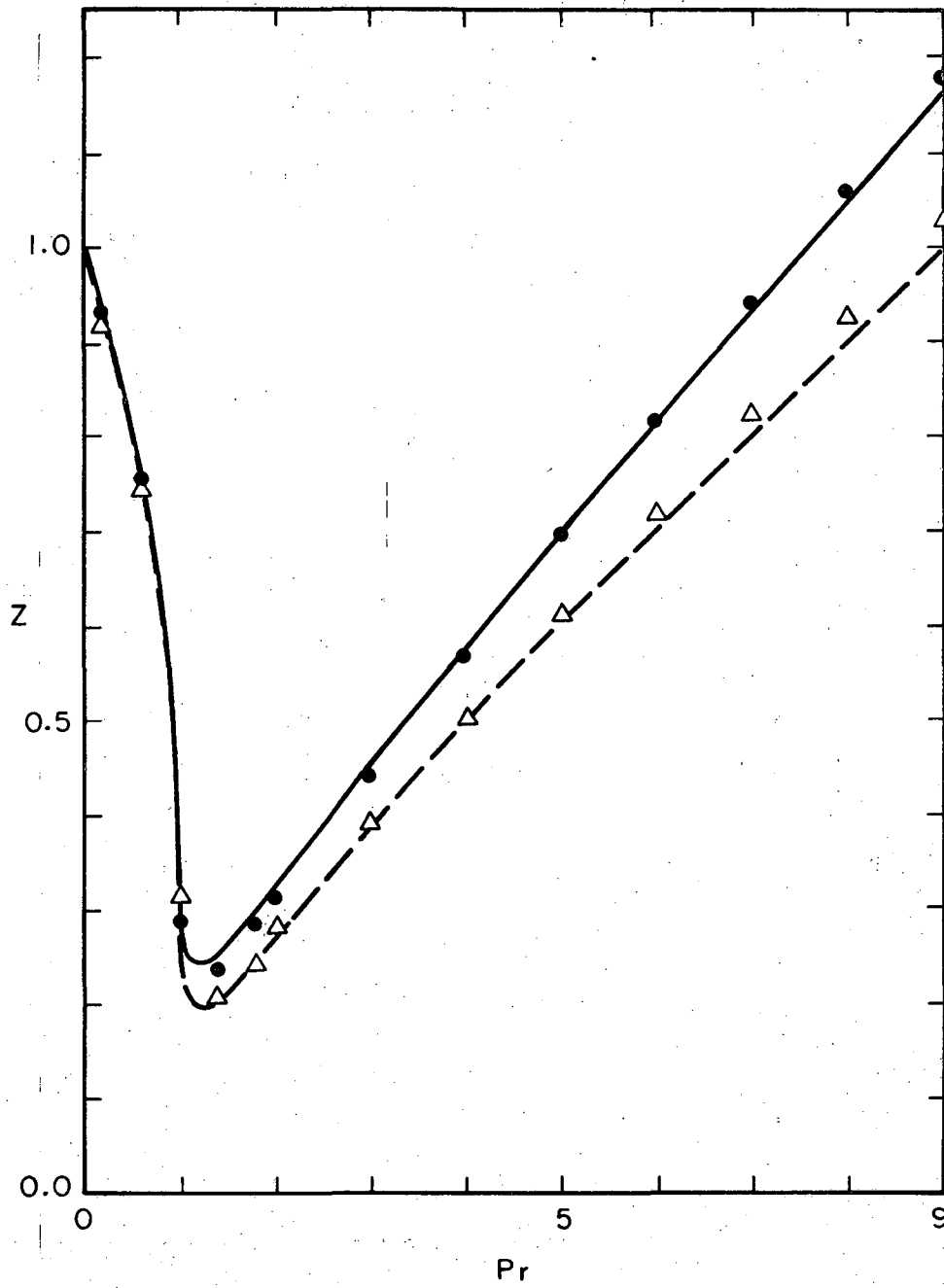
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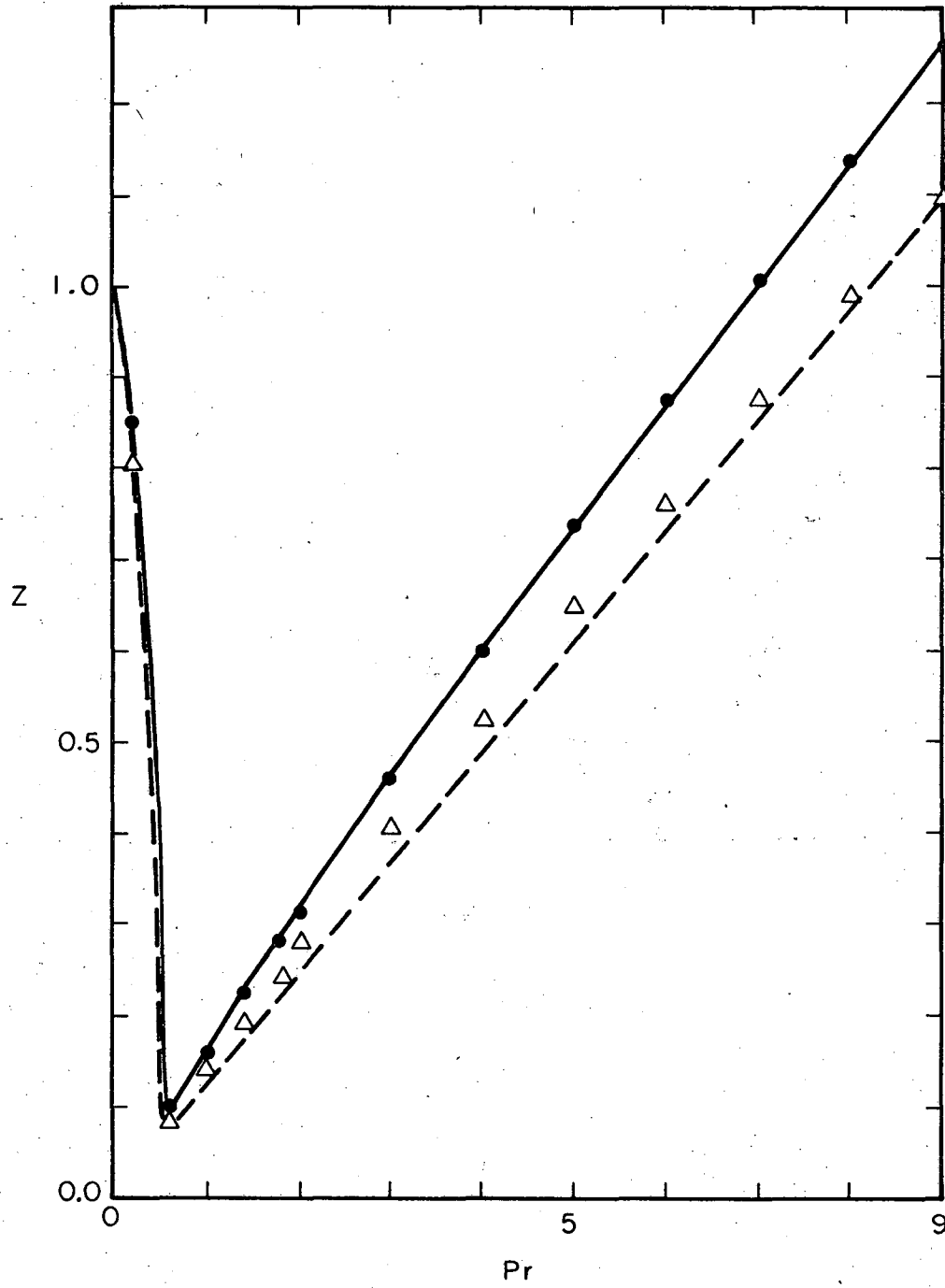
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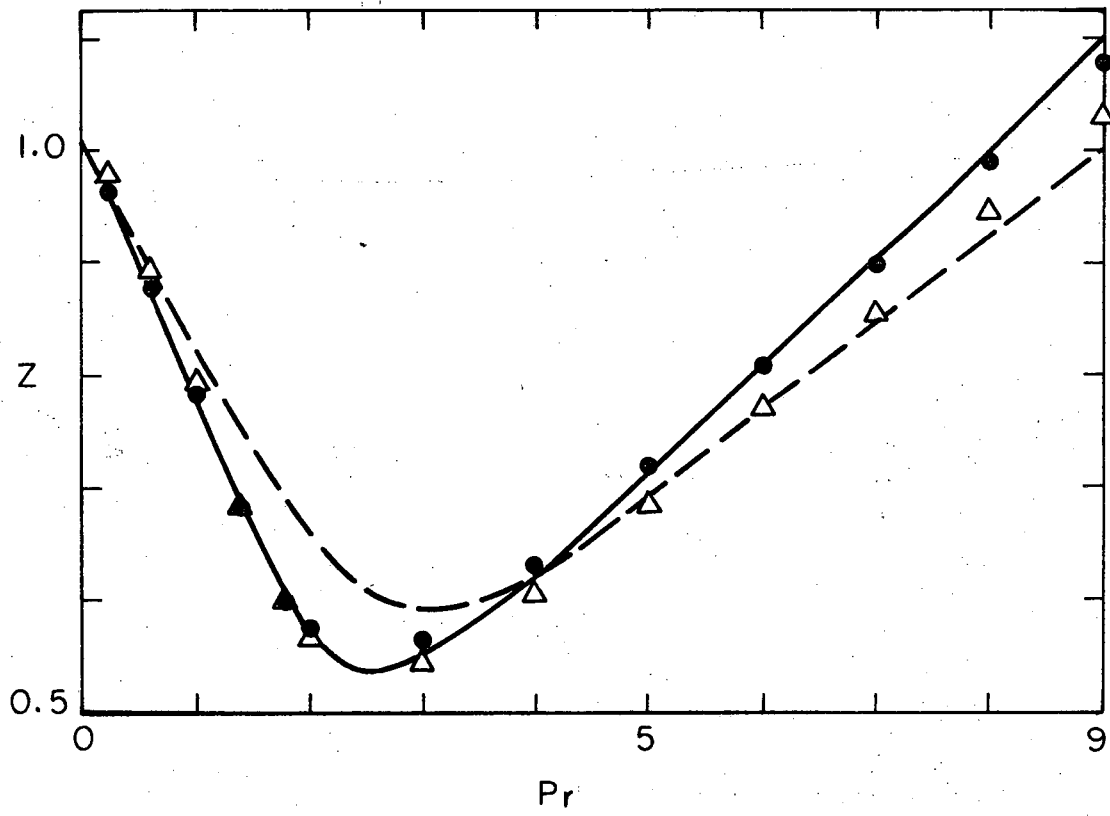
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Fig. 1



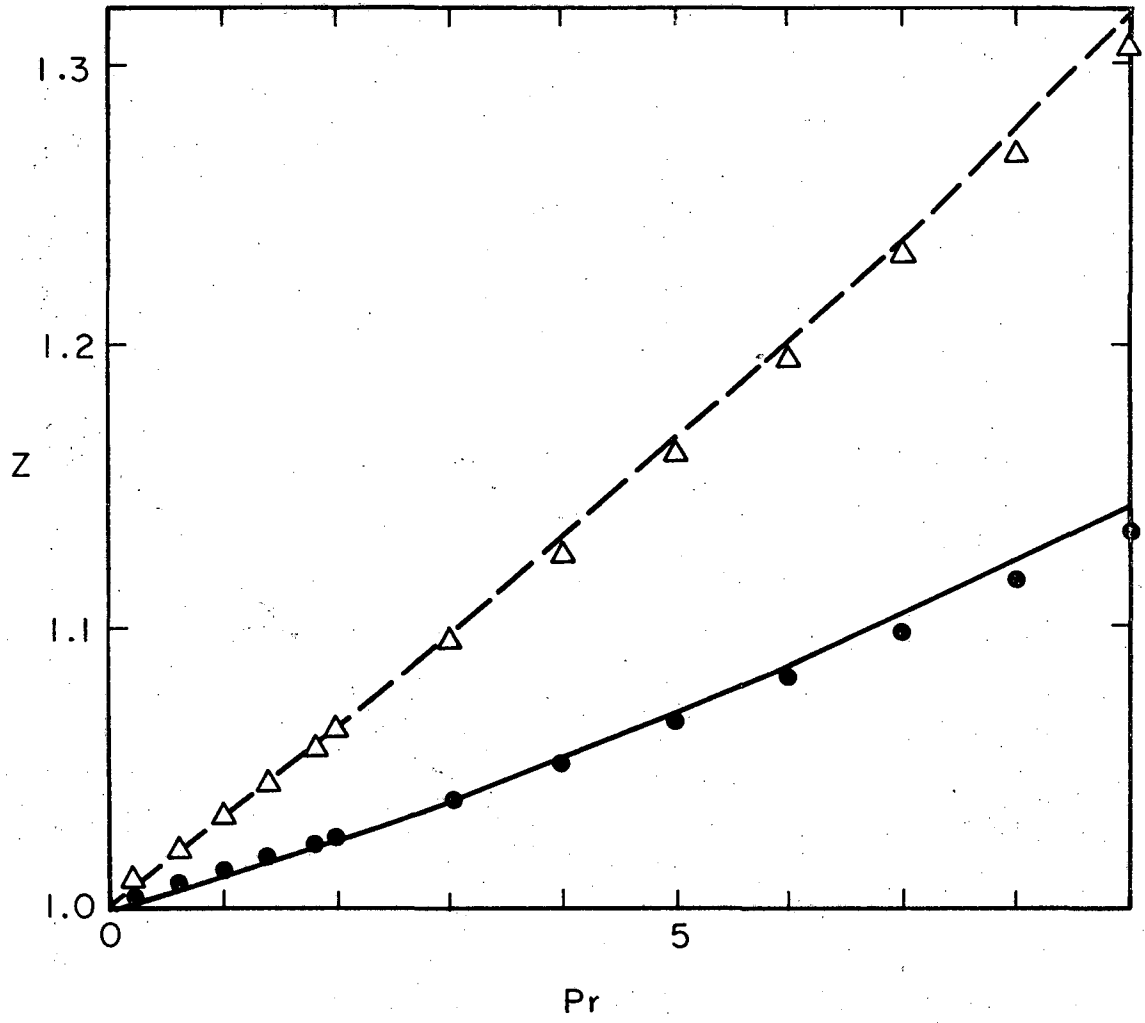
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Fig. 2



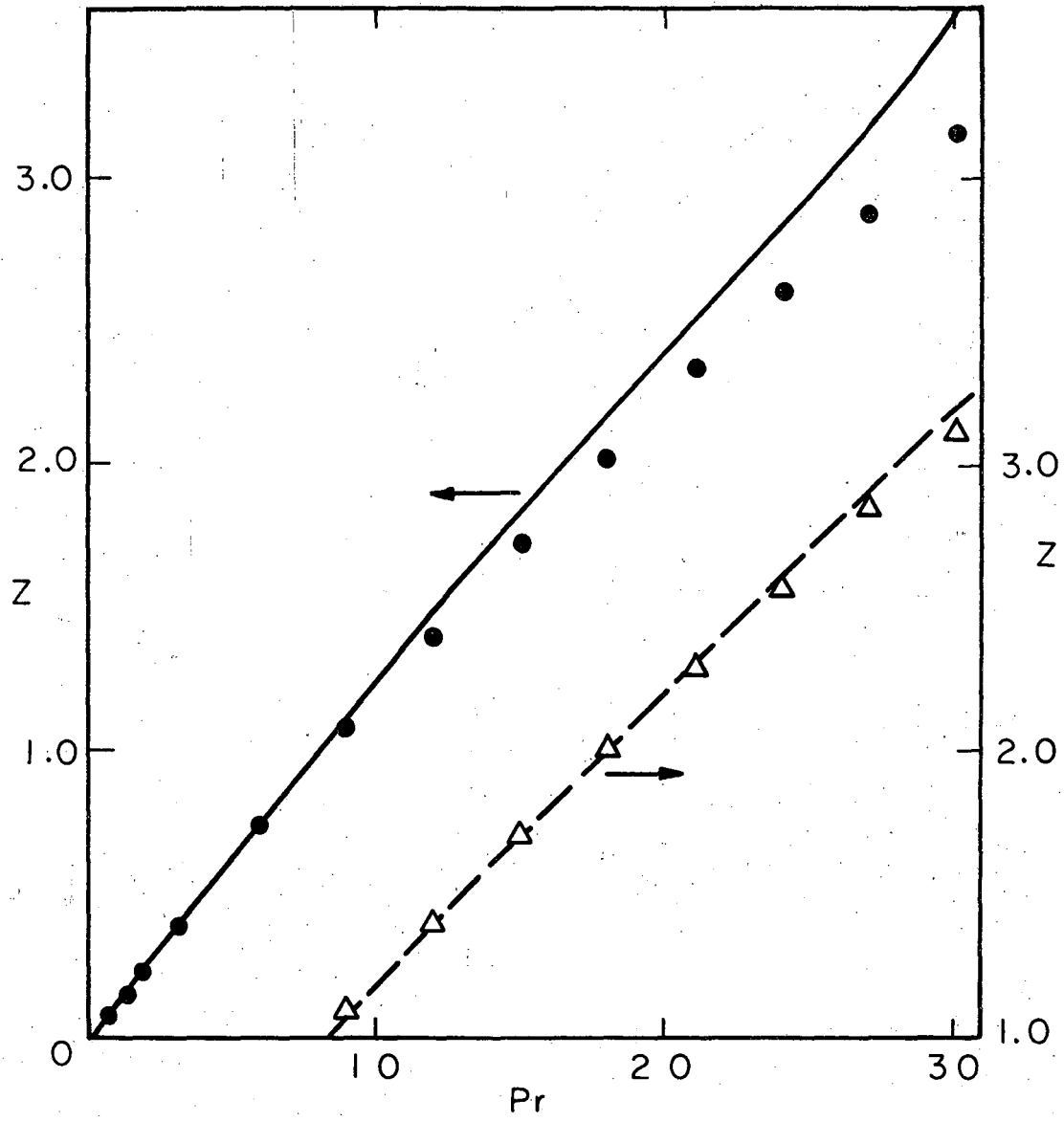
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Fig. 3



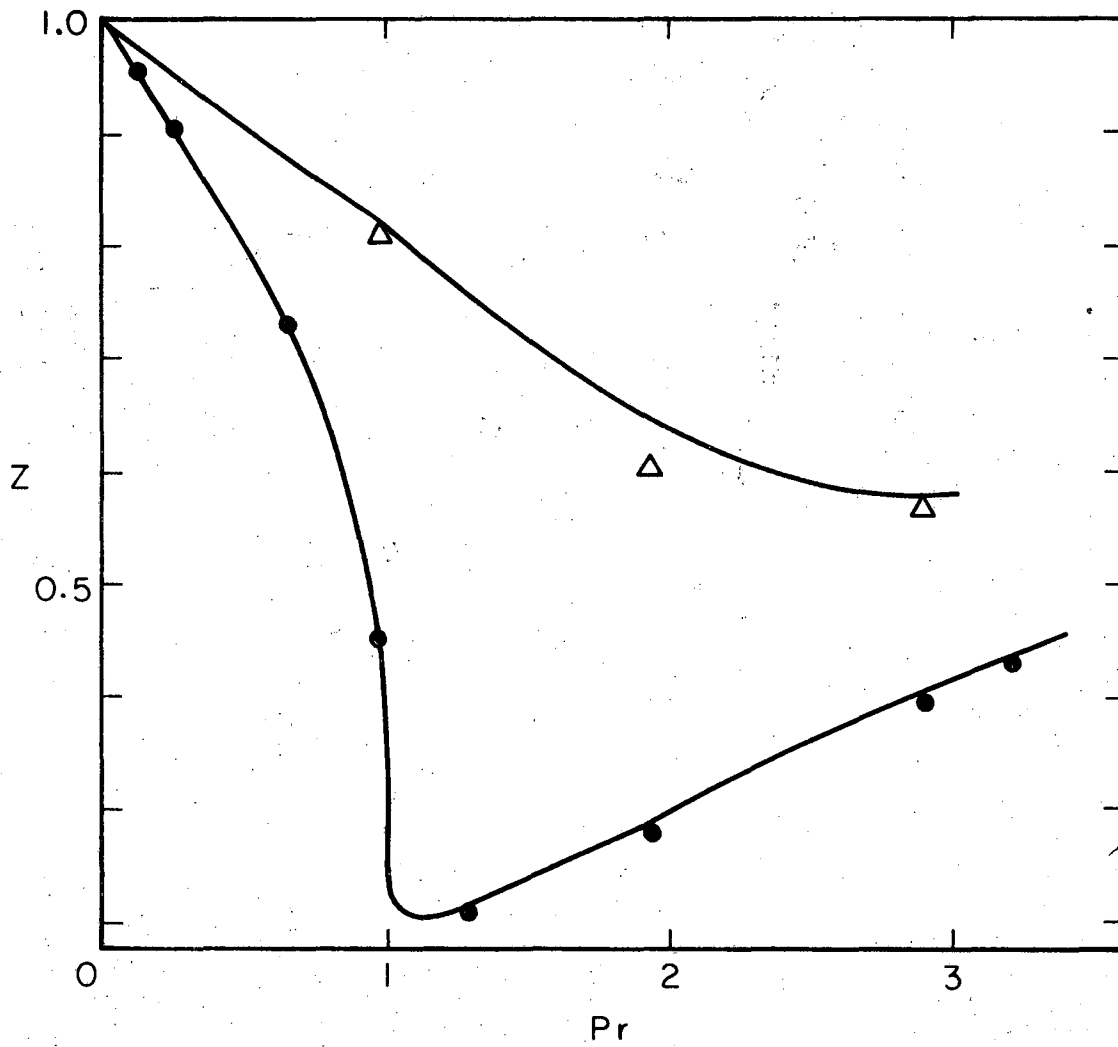
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Fig. 4



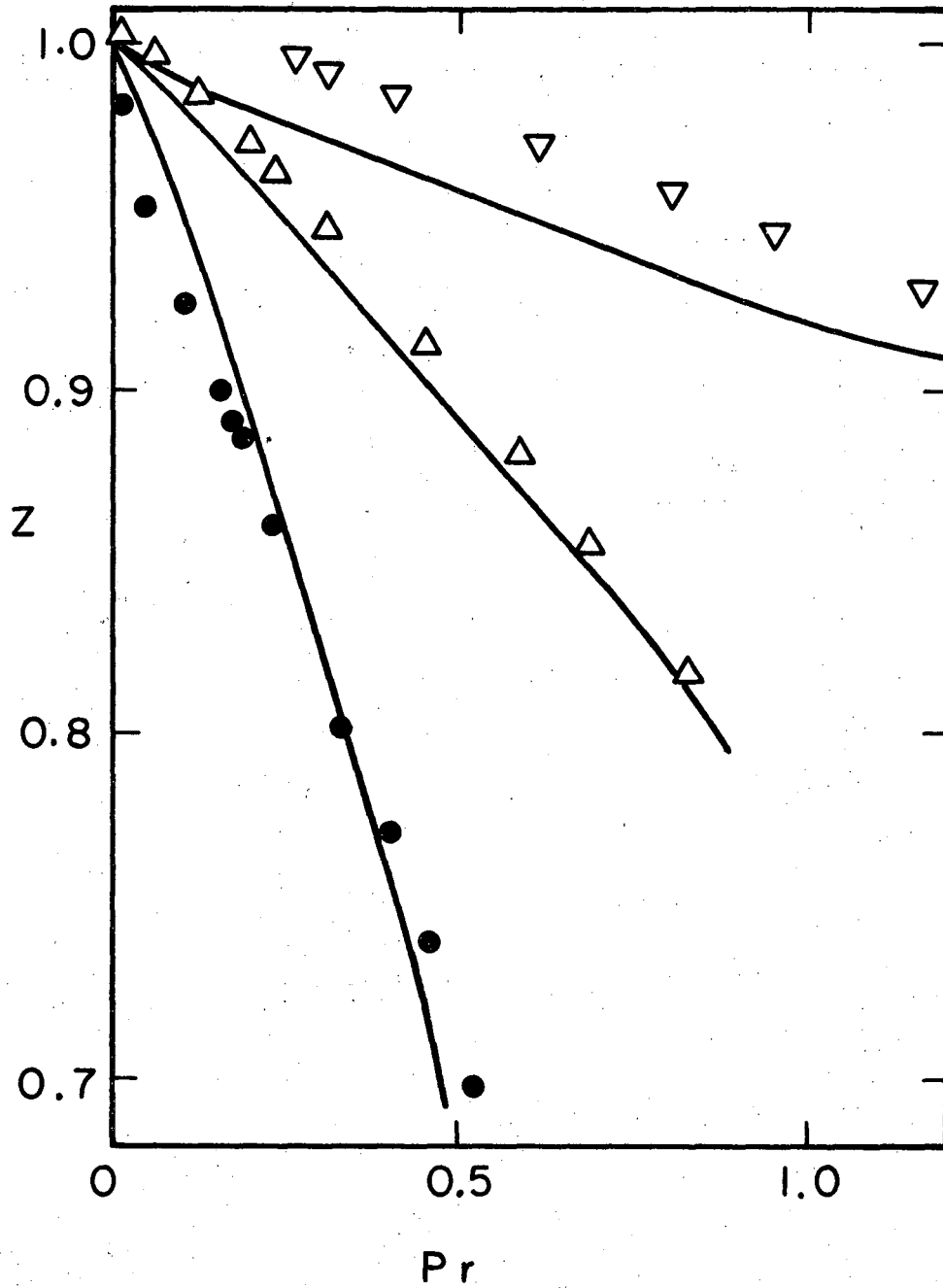
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Fig. 5



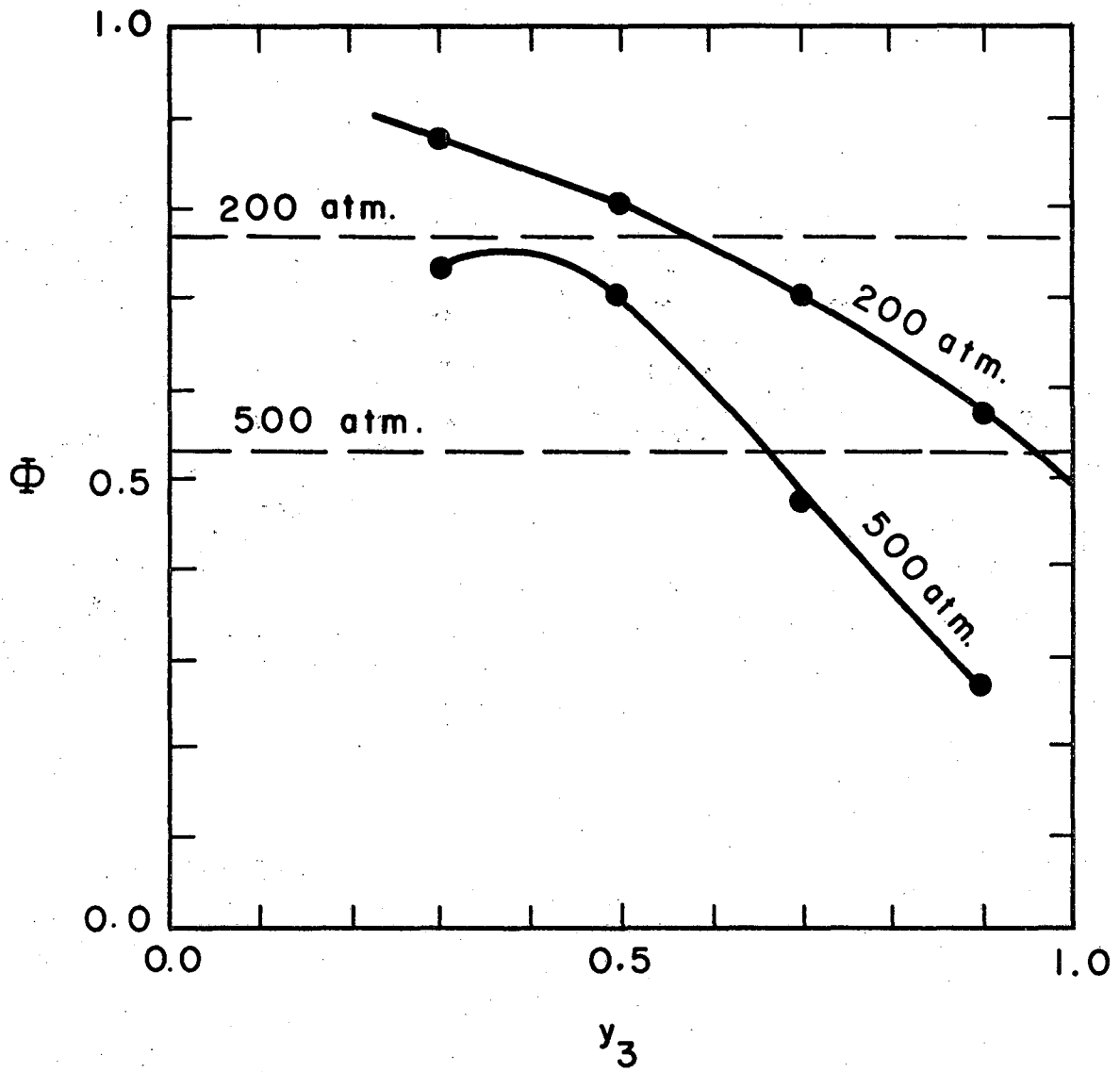
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Fig. 6



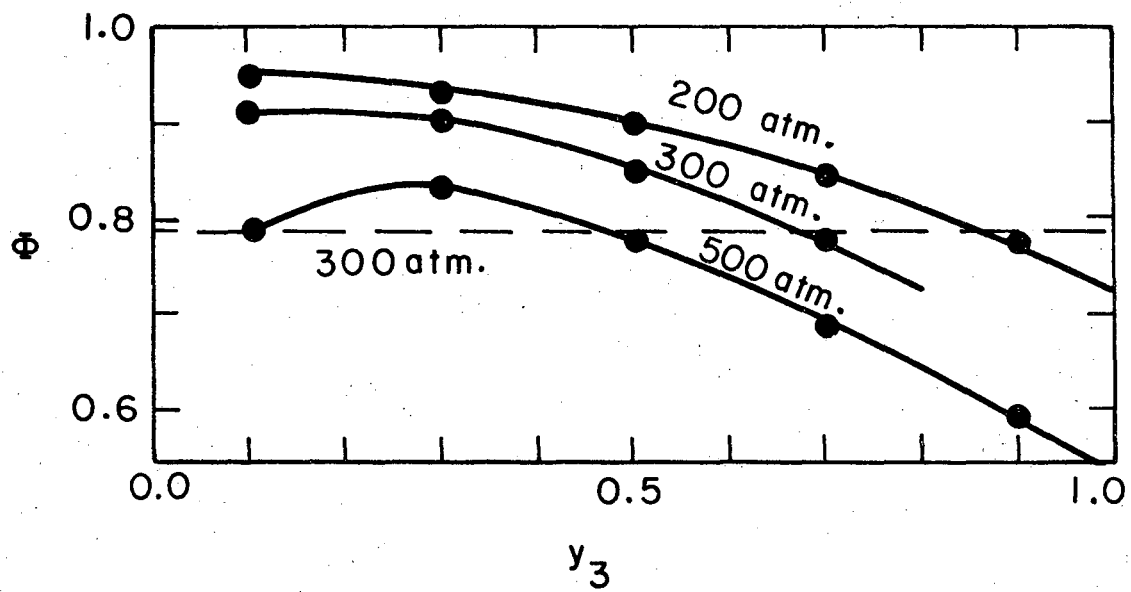
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Fig. 7



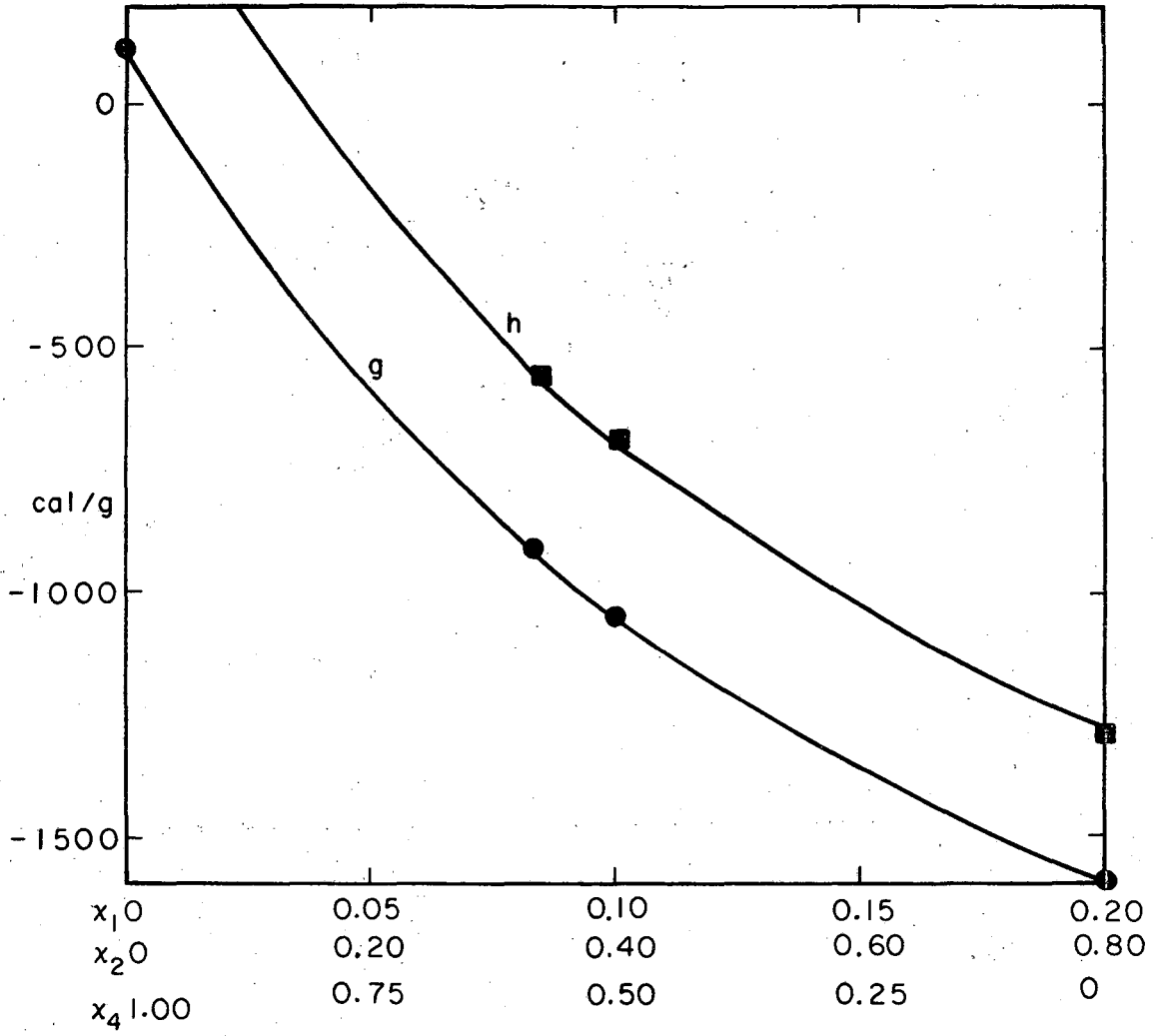
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Fig. 8



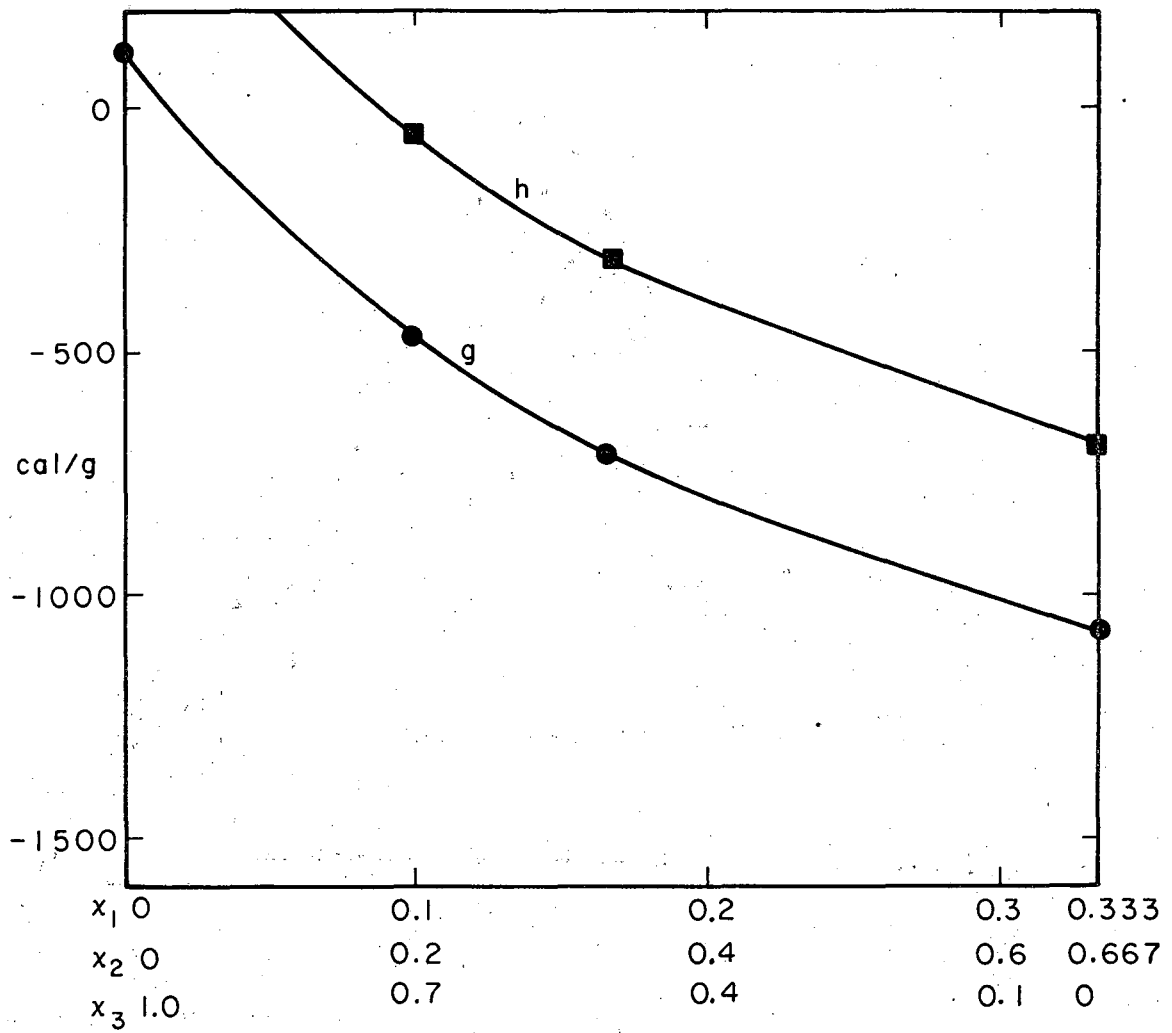
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Fig. 9



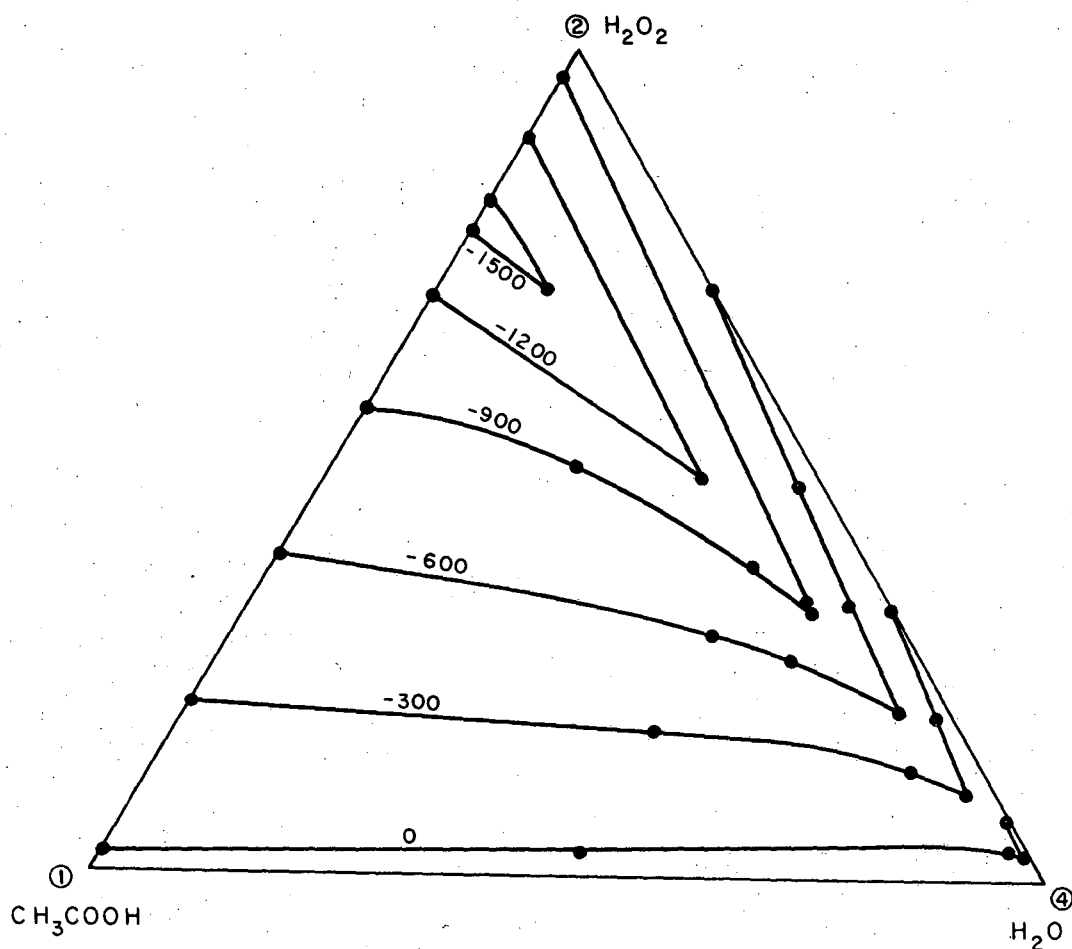
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Fig. 10



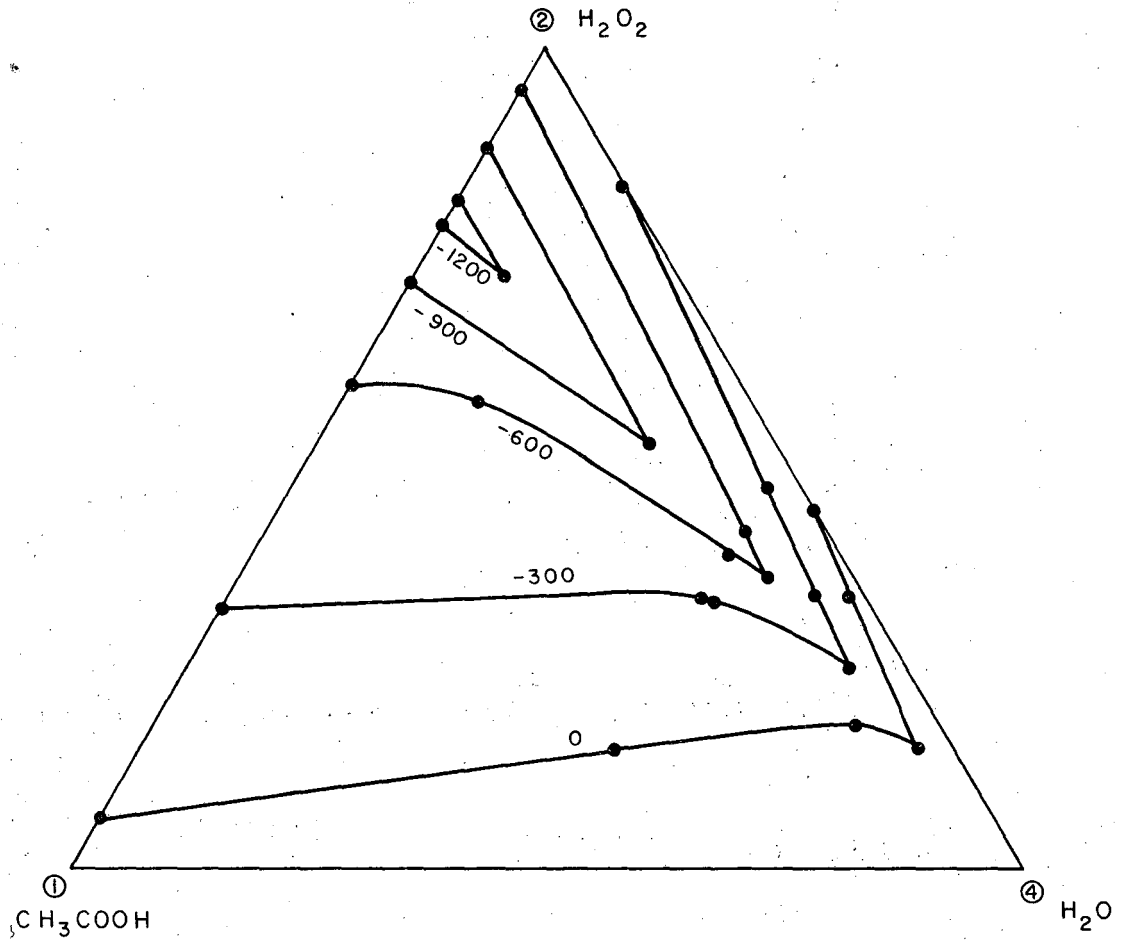
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Fig. 11



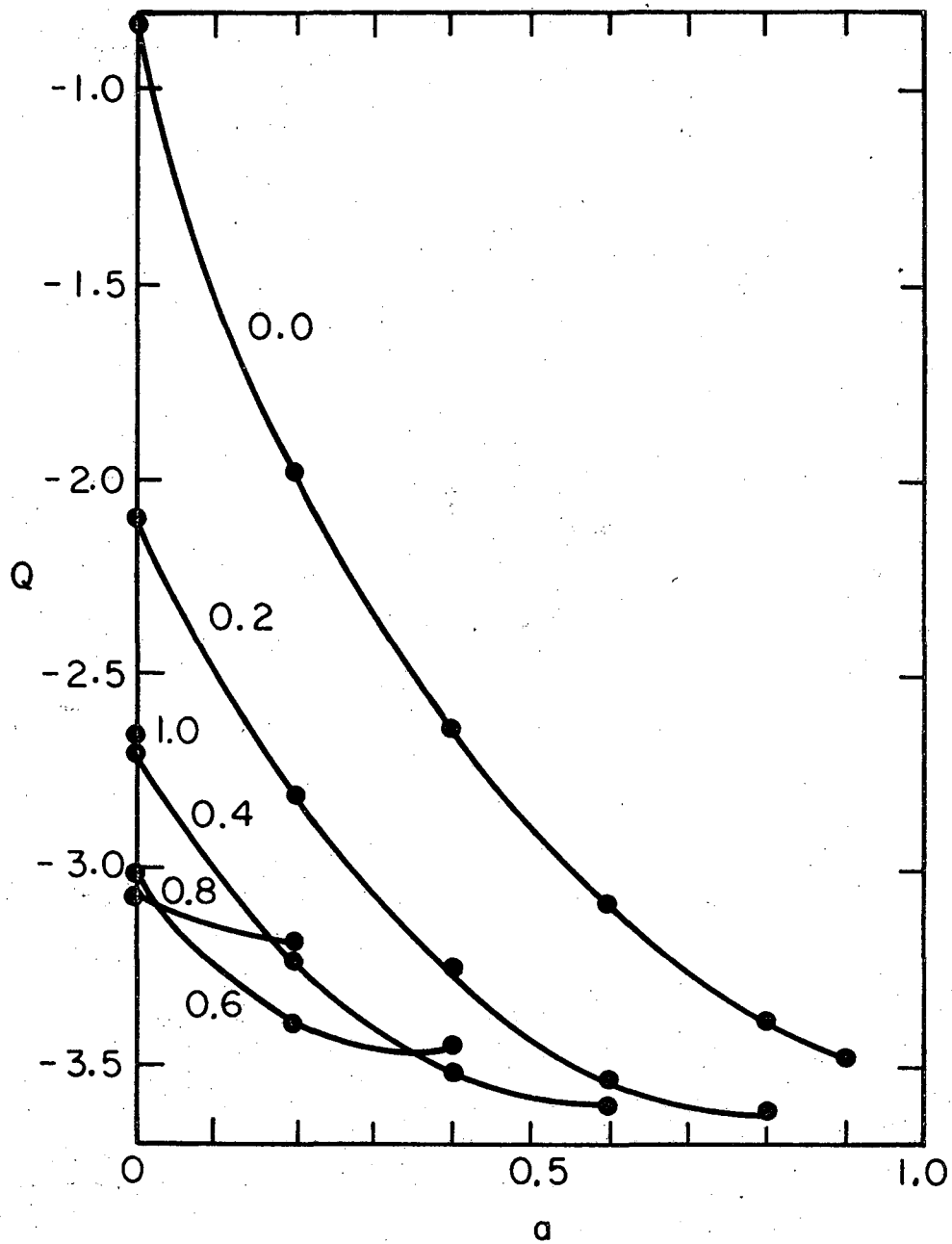
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Fig. 12



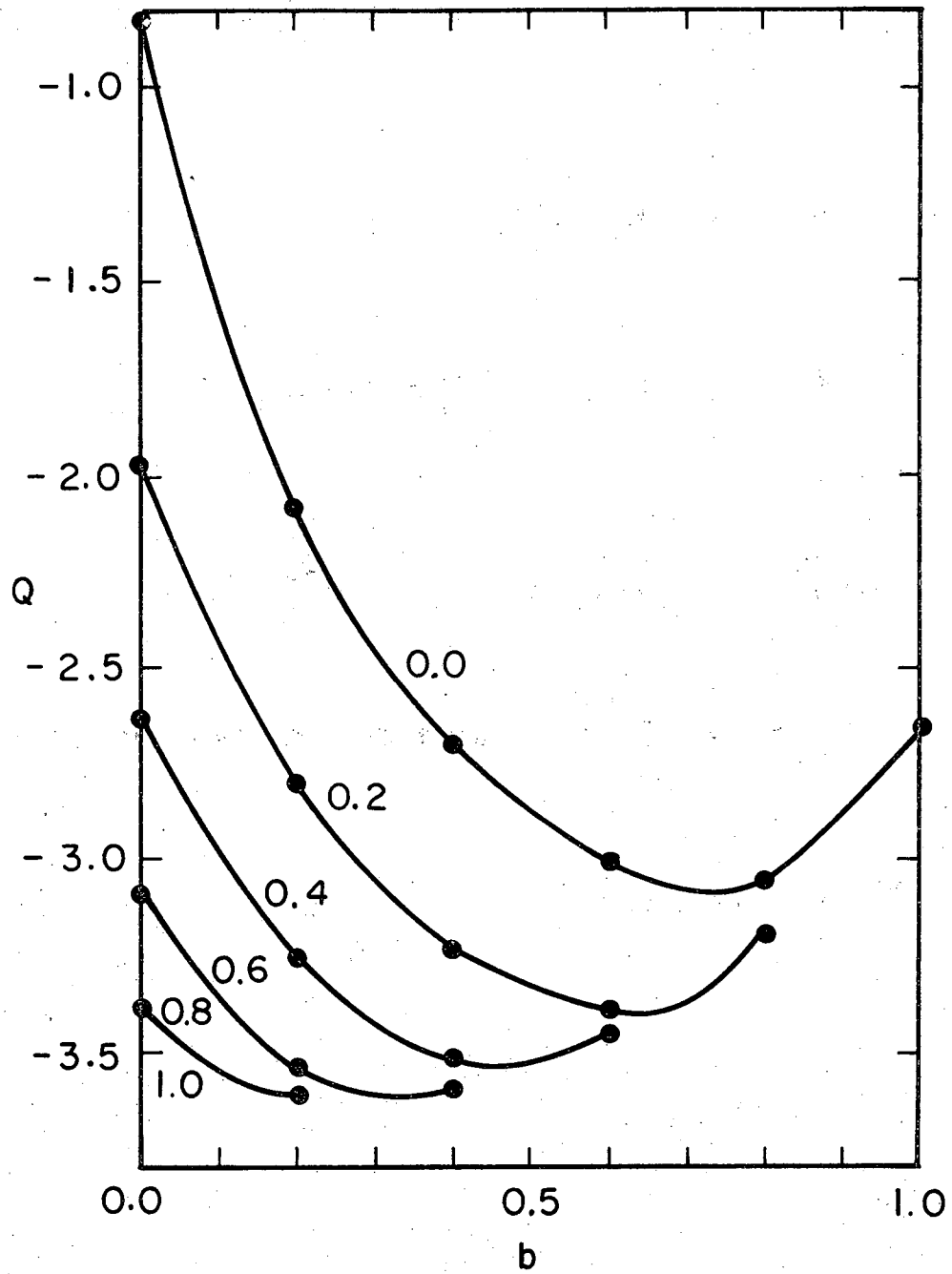
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Fig. 13



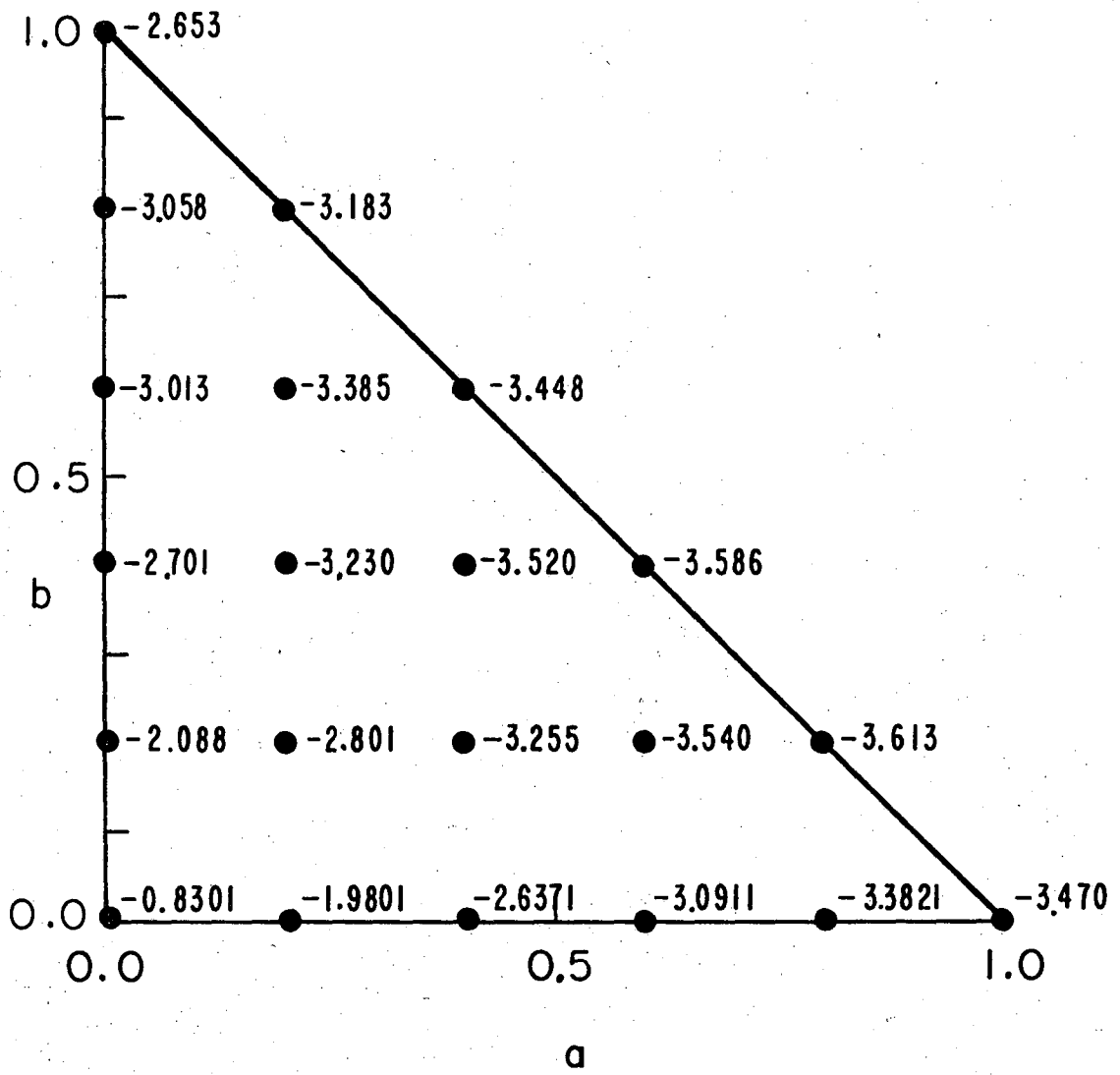
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Fig. 14



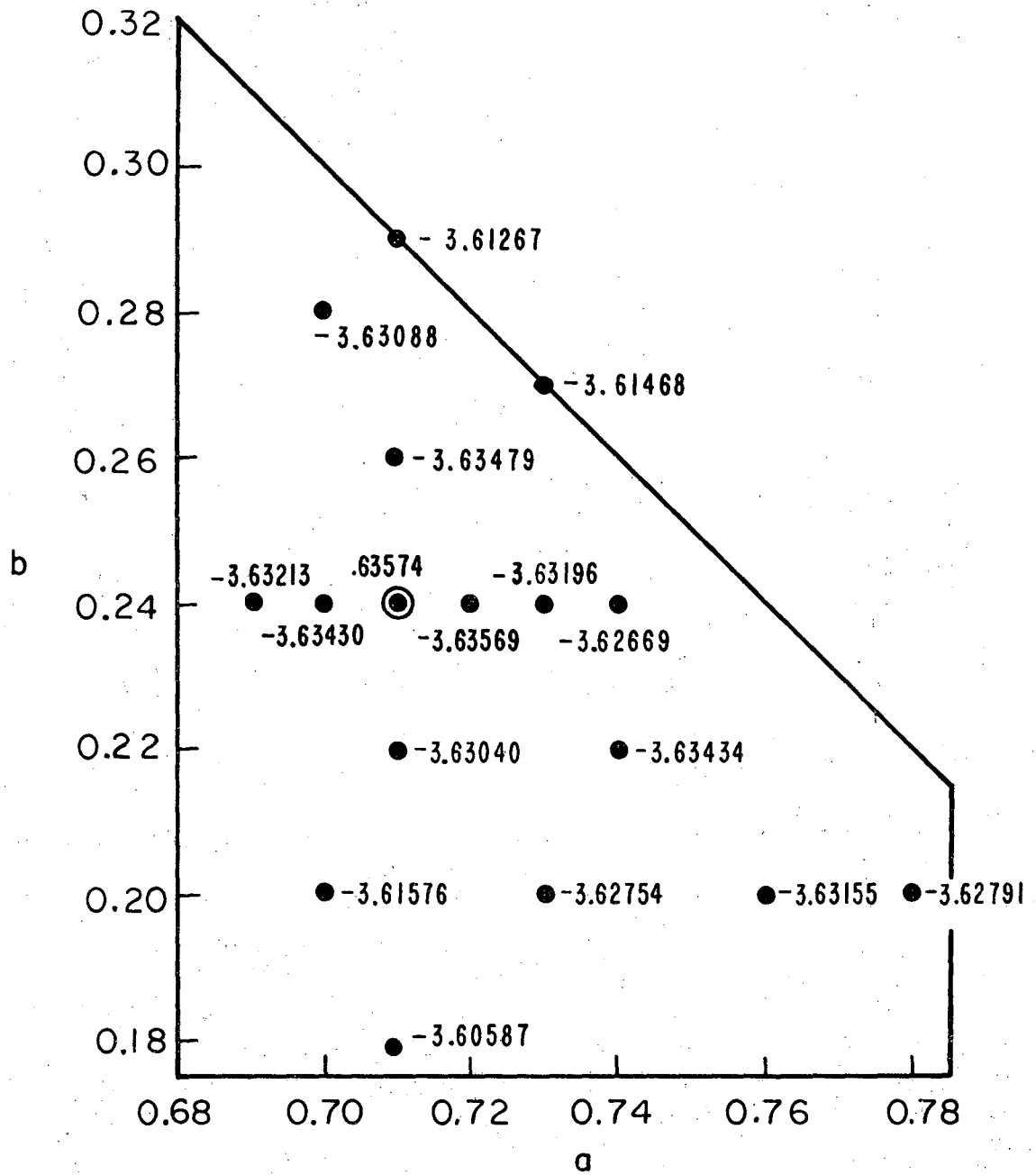
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Fig. 15



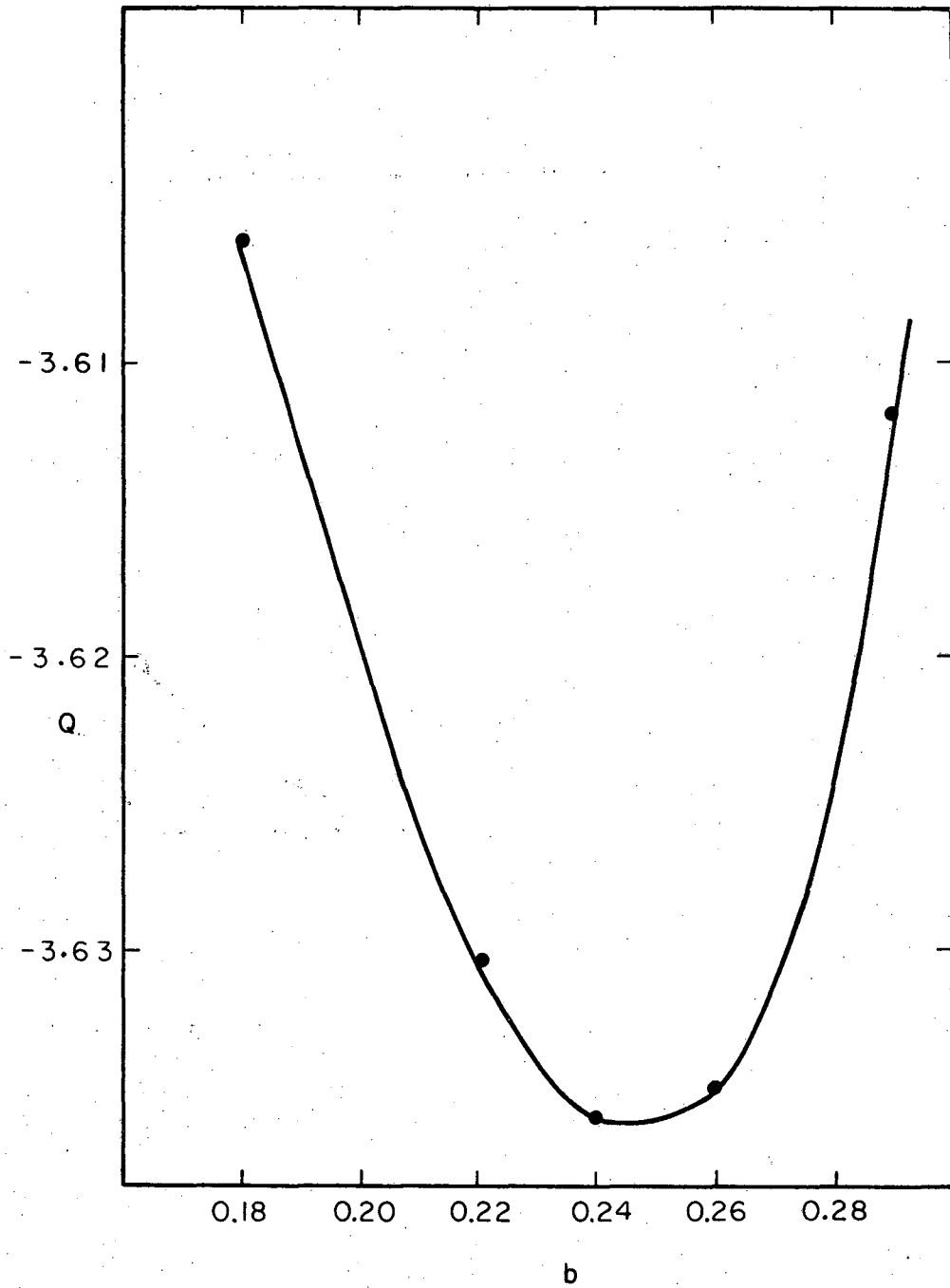
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Fig. 16



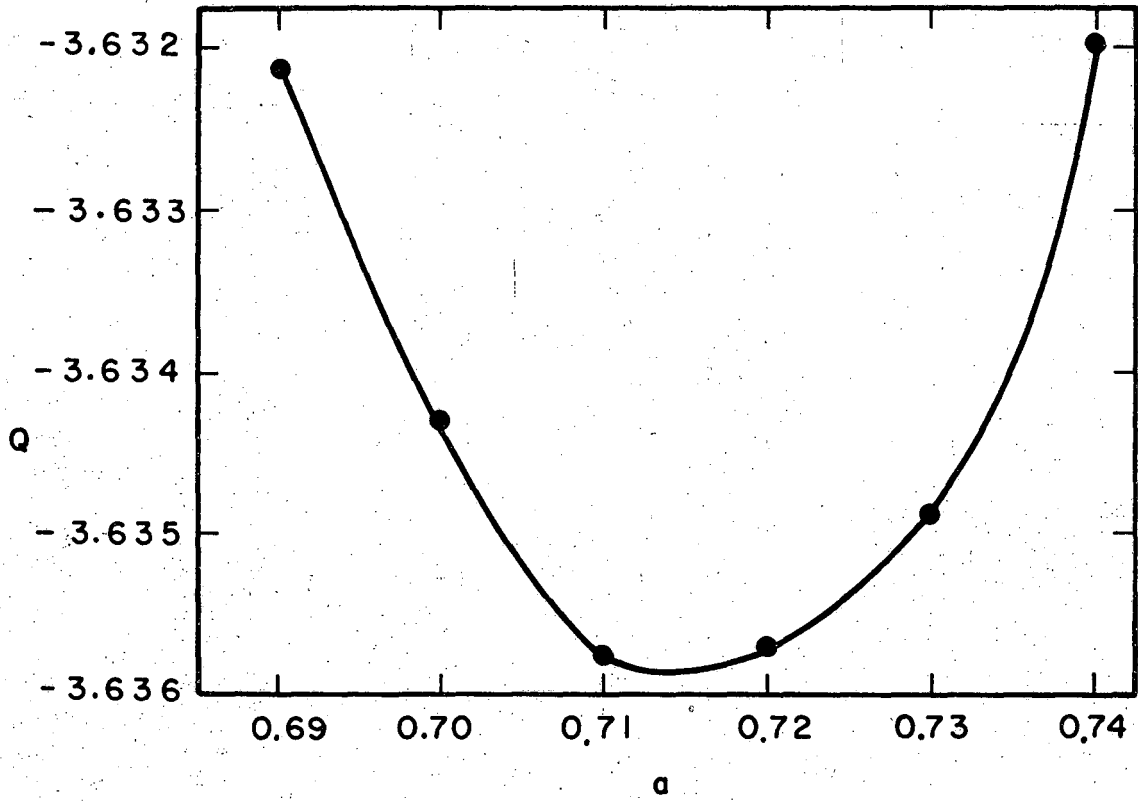
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Fig. 17



XBL6810-7011

Fig. 18



XBL6810-6996

Fig. 19

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