Prediction of the Thermodynamic Properties of Multicomponent Mixtures.

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ABSTRACT

The principle of corresponding states is developed for the prediction of the thermodynamic properties of both pure substances and mixtures. Three parameters are used in the defining equations - reduced temperature and volume (modified by shape factors) and an acentric factor. The thermodynamic consistency of the shape factor correlations was checked and found satisfactory. The acentric factor is constant for all conditions except for subcritical vapour-liquid equilibrium where it is varied with temperature or pressure.

A mixture is modelled either as a single hypothetical substance, or as an ideal mixture of hypothetical components. The former model is used throughout the work as tests showed that the latter had no great advantage over the former. Methane was used as the reference substance and the components of all mixtures were amongst light hydrocarbons to hexadecane, components of air, hydrogen sulphide and benzene.

Four computer programs have been written to predict the following properties.

1. Compressibility, internal energy and enthalpy at (120-623)K, (0-1000) atm. Agreement with experiment was good - 0.1% difference, with up to 5% maximum in the critical region.

2. Adiabatic and isothermal Joule-Thomson coefficients. These were 10% in disagreement with recent experimental work, and up to 25% with pre-1940 results.

3. Vapour-liquid equilibria. Nineteen binary systems were computed as either dew or bubble lines in the range (88-500)K, (0-200) atm. Bubble calculations were possible to within 5% of the critical point, and dew calculations up to the point of maximum concentration. For nine ternary mixtures, four 4- and 5-component mixtures and eight natural gases, point values on dew or bubble lines were computed in the range (90-370)K, (0-100)atm. Results agreed well with experimental work.

4. Isothermal flash separations. Computed phase compositions for twelve mixtures under various conditions agreed well with experimental work.

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Nomenclature.

$a_1 - a_5$	constants in Vennix's equation of state (2.7).
A	Helmholtz free energy.
$b_1 - b_5$	constants in Vennix's equation of state (2.8).
C	constant in Tait equation of state (2.26).
C_p	specific heat at constant pressure.
$C_A - C_F$	constants in Vennix's equation of state.
$d_1 - d_5$	constants in Vennix's equation of state (2.9).
e_1, e_2	constants in Vennix's equation of state (2.11).
f	corresponding states parameter.
f_1, f_2	constants in Vennix's equation of state (2.12).
F	a function.
$\mathfrak{F}$	fugacity.
G	1. a constant in Vennix equation (2.6). 2. Gibbs free energy.
h	corresponding states parameter.
$\bar{h}$	partial molal enthalpy.
H	1. a constant in Tait equation (2.26). 2. configurational enthalpy.
k	1. a constant in Vennix's equation (2.6). 2. Boltzmann constant (1.4). 3. $As(1-k_{12})$, Prausnitz's (12) unlike pair interaction constant.
K	ratio of vapour and liquid mole fractions.
n	number of moles.
N	1. number of molecules (Section 1, up to equation 1.4). 2. number of components in the mixture.
p	vapour pressure.
P	pressure.
q	mole fraction of a component in the feed to a flash.

Q	1. molar flow rate of feed to a flash (Section 2.5).
	2. configurational integral (Section 1).
r	1. intermolecular distance (Section 1).
	2. any molar property (Section 2.3).
R	gas constant.
$\bar{s}$	partial molal entropy.
S	entropy.
t_o	a constant in Vennix's equation of state (2.6).
T	temperature.
u	intermolecular potential.
U	configurational internal energy.
V	1. volume.
	2. ratio of vapour product to feed in a flash.
x	mole fraction of a component.
X	molar flow rate of liquid product in a flash.
y	mole fraction of a component.
Y	molar flow rate of vapour product in a flash.
Z	compressibility factor.
α	1. a constant in Vennix's equation of state (2.10)
	2. a general component
	3. relative volatility
β	1. a constant in Vennix's equation of state (2.10).
	2. a general component.
Δ	1. differential operator (Section 2.3).
	2. finite difference. (Section 2.6).
ϵ	characteristic energy.
μ	chemical potential.
η	adiabatic Joule-Thomson coefficient.

ρ density.

σ collision diameter.

φ isothermal Joule-Thomson coefficient.

ϕ shape factor for volume.

θ shape factor for temperature.

ω acentric factor.

ξ correction factor for interaction energy.

Subscripts

o reference compound.

s saturation state.

A actual state (given).

x pertaining to a hypothetical single substance.
replacing the mixture.

α pertaining to component α

Superscripts

C critical property.

E excess property.

R reduced state.

S saturation state.

t total property.

" second derivative.

' 1. variable in Gauss quadrature method of integration (2.59).
2. first derivative.

* ratio of critical properties only.

INTRODUCTION

Methods for the computation of multi-component vapour-liquid equilibrium and other thermodynamic properties have proliferated during the last two decades. Many factors have brought about this growth. The most dominant are the great increases in the production of oil, natural gas and petrochemicals, and the phenominally rapid development of electronic computers. Supply of technological know-how has been able to keep pace with demand, to bring about growth in the science of chemical engineering which once relied on the slide-rule and the engineer's experience. A further benefit from this expansion has been that theories and ideas in the past put aside as impractical - that is requiring what was thought near infinite computation times - can now be developed. Advances have been made too in the understanding of intermolecular forces and their relationship with thermodynamic properties.

The properties of real gases and liquids deviate from ideality. The knowledge of this deviation and how to calculate it, is thus of primary importance. The best methods are appropriate to both pure substances and mixtures. While calculations for pure substances usually present few computational difficulties, those for mixtures almost inevitably produce a mass of computations often beyond the limit of human endurance. This has brought about development of methods for calculation of thermodynamic properties by computer.

Basically there are two requirements - an equation of state and a method of computation. Equations of state have been developed since van der Waals first proposed his nearly a hundred years ago.

There are two types of thermodynamic data: one phase properties which need only an equation of state - such properties as compressibility, enthalpy; and multiphase properties which need additional computations to find equilibrium, properties such as fugacity and composition.

The first type - one phase properties - have been computed as long as the equations of state have been there to use.
The second type - which need so much more trial and error in order to find the equilibrium states - have been calculated with greater accuracy only since the advent of computers.

The first development of an equation of state specifically applicable to computer work was by Benedict Webb and Rubin in 1951 (111), and is usually known as the BWR equation of state.
It was developed for use with mixtures of light hydrocarbons. (C_1 - C_7) and various alkenes - in all twelve substances. Its range was (1-250)atm and (200-477)K. The thermodynamic equilibrium was achieved by balancing fugacities in each phase. Somewhat limited in application at first - it has been expanded and improved by its adherents, and, for many cases, still holds its own today.

In 1961, came the work of Chao and Seader (112), using the equation of state of Redlich and Kwong. Their method is also based on equating the fugacities in each phase to establish equilibrium. The method needs a large computer for solution of the equations involved, and has gained very widespread use.

Prausnitz and his colleagues (92) have done much work on this method, expanding and perfecting it. The Redlich-Kwong equation of state is an equation of state for the vapour phase which can be applied to a wide range of compounds, without the use of a reference substance, and provided suitable constants are available.

It has been claimed (123) that there are only two ways of predicting thermodynamic properties, either by the use of a completely empirical equation of state, or using an equation of state for the vapour phase and predicting the liquid phase deviations from ideality by empirical equations for the excess functions. There is another method however, developed first by Leland and his colleagues (6, 9, 11, 17, 121, 124), and later Rowlinson (1), and which uses an exact equation of state applicable to both vapour and liquid phases of a particular substance in conjunction with the principle of corresponding states. This method avoids the discontinuity between phases introduced by the other two methods just mentioned. This disadvantage of discontinuity between phases is acknowledged by Prausnitz (123). This third method of Leland's also has the advantage of being solidly based on theory.

The basic idea of the principle of corresponding states is that for very many substances, intermolecular forces can be defined by a relationship between intermolecular distance and energy only. The thermodynamic properties of a substance can be found from those of another whose properties are known simply by the appropriate adjustments to the parameters of this relationship.

Successful application of the principle of corresponding states needs a very exact equation of state for the reference substance. In recent years many such equations have been developed - especially for methane, as so much accurate P-V-T data are available for it. In this work, the equation of state developed by Vennix (16) is used. In addition the two parameter (critical temperature and volume) principle of corresponding states is enlarged to include a third parameter, the acentric factor. The acentric factor is included in such a way that parameters are modified by shape factors. These shape factors were proposed and developed by Leland and co-workers. Shape factors eliminate the slight lack of conformation of a P-V-T surface to make it a perfect match with that of the reference substance. Where there is conformality, the shape factors are all 1.0.

The application of the principle of corresponding states in this work is to hydrocarbons, rare and common gases, as both mixtures and pure substances. It is used to compute compressibility factors, enthalpies, Joule-Thomson coefficients, and vapour-liquid equilibria (both saturation and flash) in a wide range of temperature and pressure, (90-520)K and (0-1000)atm. Where possible, comparison is made both with properties experimentally determined and with properties computed by other methods, in order to evaluate this method of prediction.

The aim of this work has been to produce programs which are usable as chemical engineering tools. Wherever possible the procedures are general and no program contains any procedure specific to a system or compound. A copy of Leach's program PROPERTY (17) helped greatly in the development of the original program in this work - the one for computation of enthalpy and compressibility factors.

Original work has been done on the adjustment of acentric factors. In this work the acentric factor is allowed to vary with temperature and pressure to enable exact saturation data to be predicted for pure substances. The program to calculate flash separation uses a technique of matching chemical potential for equilibrium, which has not been used elsewhere, as far is known.

Section 1

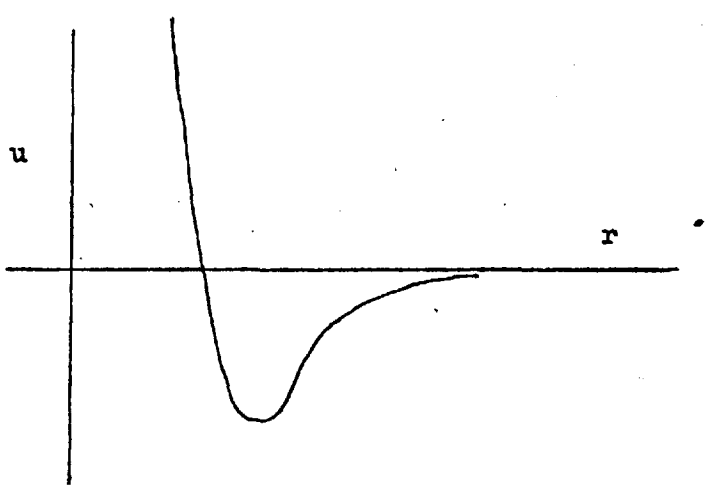
The Principle of Corresponding States.

Section 1

Configurational properties are the thermodynamic properties which define the equilibrium state of a system. This means that they arise from the forces of interaction between molecules - they depend on the configuration, and are independent of the internal properties of the molecules themselves. For a pair of simple molecules the energy of interaction between them is a function of their distance of separation, r, only (1).

Fig 1 shows a typical variation of intermolecular potential with separation.

Fig 1



Since for many substances, the variation of u with r is very similar, it should be possible to deduce one potential function from the knowledge of that for another species.

Suppose we have species 1 and 2, then we could write the intermolecular potentials u_{11}/ϵ_{11} and u_{22}/ϵ_{22} as functions of σ_{11}/r_1 and σ_{22}/r_2.

Now let species 1 be at conditions V and T, and species 2 be at a corresponding state such that the volume is $V(\sigma_{22}/\sigma_{11})^3$ and the temperature is T ($\epsilon_{22}/\epsilon_{11}$). In this way, there will be corresponding configurations in each systems. From this it follows that the configurational integral Q of species 1 is related to that of species 2 by the expression

$$Q_1[V,T] = (\sigma_{22}/\sigma_{11})^{-3N} \cdot Q_2[V(\sigma_{22}/\sigma_{11})^3, T(\epsilon_{22}/\epsilon_{11})] \qquad (1.1).$$

(The variables of thermodynamic functions are shown enclosed in square brackets.)

The ratio of the energies ϵ is abbreviated to f, and the ratio of the intermolecular distances is abbreviated to $h^{1/3}$. Equation (1.1) can be written in the form:

$$Q[V,T] = h_{11,o}^{N} \; Q_o [V/h_{11,o}, T/f_{11,o}] \qquad (1.2)$$

where $f_{11,o}$ means $\epsilon_{11}/\epsilon_{oo}$ and $h_{11,o}$ means $(\sigma_{11}/\sigma_{oo})^3$. In this way, the configuration integral of any substance 1,2,3 can be related to a reference compound O. From equation (1.2), we obtain for the configuration Helmholtz free energy,

$$A = -kT \ln Q \qquad (1.3)$$

and from (1.2) and (1.3)

$$A_1[V,T] = f_{11,o} A_o [V/h_{11,o}, T/f_{11,o}] - NkT \ln h_{11,o} \qquad (1.4)$$

Since $-(\partial A/\partial V)_T$ is equal to pressure P,

$$P_1\left[V,T\right] = f_{11,o}/h_{11,o}\, P_o\left[V/h_{11,o}, T/f_{11,o}\right] \qquad (1.5)$$

From the definitions of $f_{11,o}$ and $h_{11,o}$, it can be deduced that they can also be expressed

$$f_{11,o} = T_1/T_o \quad \text{and} \quad h_{11,o} = V_1/V_o \qquad (1.6)$$

where T_1, T_o and V_1, V_o are the temperatures and volumes at which substances 1 and 0 correspond.

Substituting (1.6) into (1.5) we have for the compressibility factor Z,

$$Z_1\left[V,T\right] = Z_o\left[V/h_{11,o},\ T/f_{11,o}\right] \qquad (1.7)\ .$$

Since the definitions of the parameters f and h above apply to any temperature or volume, they may also be written

$$f_{11,o} = T_1^c/T_o^c \quad \text{and} \quad h_{11,o} = V_1^c/V_o^c \qquad (1.8)$$

writing the reduced properties for species 1,

$$V_1^R = V/V_1^c\ ,\quad T_1^R = T/T_1^c$$

and substituting (1.8), we have for the reference substance,

$$V_o^R = V/V_o^c \cdot h_{11,o} = V_1^R$$

and

$$T_o^R = T/T_o^c. \quad f_{11,o} = T_1^R$$

Thus equation (1.7) can be written in the more familiar form of the Principle of Corresponding States

$$Z_1\left[V_1^R, \; T_1^R\right] = Z_o\left[V_o^R, \; T_o^R\right] \qquad (1.10)$$

The name "conformal" is applied to the members of a set of substances whose intermolecular potentials are of the form described above, and hence to which the principle of corresponding states applies, in the form defined in equation (1.10).

However, since in reality very few substances conform exactly, in order to apply the principle of corresponding states to a wider range of substances, a third parameter has been proposed, (3).

Treatment of the concept of corresponding states by dimensional analysis by Reid and Sherwood (4), Hakala (5) and others (6,7) shows that it depends on many more than the two parameters (V^c, T^c) assumed here. Hakala shows further that V^c and T^c are the fundamental critical constants in the law of corresponding states. The contribution of parameters such as polarizability, molecular mass, moment of inertia etc. to the accurate description of the P-V-T surface is generally negligible. They are all neglected in the work described here. The third parameter is sufficient to produce conformation.

Pitzer called this parameter the acentric factor, ω and defined it by the empirical equation

$$\omega = \log_{10} P^R - 1.000 \qquad (1.11)$$

P^R in equation (1.11) is the ratio of the vapour pressure (at $T^R = 0.7$) to the critical pressure.

It has also been proposed (6) that the critical compressibility Z^c could be used as the third parameter. This has the disadvantage that it makes an exact fit for corresponding states at the critical point, with increasing error at growing distance from the critical point. Furthermore Z^c can be determined only with the low accuracy of the critical volume, V^c which is rarely better than 2%. On the other hand, ω is defined at $T^R = 0.7$, which is a region of much greater practical interest. Any errors which will occur in the critical region are not of great importance.

This extension of the principle of corresponding states, to non-conformal substances may be effected by the introduction of shape factors (2). Since these are functions of ω (and Z^c) they describe how the third parameter is used in practice to fit the lack of conformation of different substances. When a pair of substances are not conformal, the parameters h and f are not constant but are slowly varying functions of V and T. The shape factors modify f and h in the following way.

$$f_{11,0}\,(V_1,T_1) = (T_1^c/T_o^c).\ \Theta_{11,0}\ (V_1^R,\ T_1^R) \qquad (1.12)$$

$$h_{11,)}\,(V_1,T_1) = (V_1^c/V_o^c).\ \Phi_{11,0}\ (V_1^R,\ T_1^R\ ) \qquad (1.13)$$

where

$$V_1^R = V_1/V_1^c \quad \text{and} \quad T_1^R = T_1/T_1^c \qquad (1.14)$$

(The variables of parameters are shown enclosed in parentheses).

So from (1.6), by substitution into (1.12) and (1.13)

$$\Theta_{11,0}\ (V_1^R, T_1^R) = T_1^R/T_o^R \qquad (1.15)$$

$$\Phi_{11,0}\ (V_1^R, T_1^R) = V_1^R/V_o^R \qquad (1.16)$$

If substance 1 is the reference compound instead of substance o, then the shape factors of substance o relative to 1, i.e. $\Theta_{oo,1}$, $\Phi_{oo,1}$, are directly connected with those defined above in (1.15) and (1.16).

$$\Theta_{oo,1}\ (V_o^R, T_o^R) = T_o^R/T_1^R$$

and so $\Theta_{oo,1} \cdot \Theta_{11,0} = 1$

and similarly for Φ. Although a seemingly simple method for transferring the values of shape factors for one reference substance to a system with another reference substance, it must not be forgotten that the arguments of $\Theta_{oo,1}$ and $\Theta_{11,0}$ are different, and so care must be taken in their evaluation.

Empirical formulae have been developed to express Θ and Φ as functions of T^R and V^R by Leach (8,9). The parameter ω has been incorporated in these formulae in the form $(\omega-\omega_o)$. This is consistent with the definition of the third parameter;

when a pair of substances are completely conformal, their ω and Z^c will be identical - and Θ and ϕ reduce to 1.0.

Leach's expressions for Θ and ϕ are for substance i relative to reference substance o.

$$\Theta_{ii,o} = 1 + (\omega_i - \omega_o).\left[0.0892 - 0.8493.\ \ln T_i^R + (0.3063 - 0.4506/T_i^R)\ (V_i^R - 0.5)\right] \quad (1.17)$$

$$\phi_{11,o} = \frac{Z_o^c}{Z_i^c}\left\{1 + (\omega_i - \omega_o).\left[0.3903\ (V_i^R - 1.0177) - 0.9462\ (V_i^R - 0.7663).\ \ln T_i^R\right]\right\} \quad (1.18)$$

The reference substance is methane, and the equations were developed for use with hydrocarbons. If V_i^R is outside the limits (0.5-2.0), then it should be set at 2.0, or 0.5 according to whether it is above or below the limit respectively. T_i^R, should lie between the limits 0.6 - 1.5.

Differentiation of equation (1.4) with respect to volume gives

$$Z_i\left[V,T\right] = Z_o\left[V/h_{11,o},\ T/f_{11,o}\right] +$$

terms in df/dV and dh/dV

If the principle of corresponding states is true for conformal substances, then these terms on the right hand side must sum to zero. The arguments below show how this is so.

Writing equation (1.4) in a slightly different form,

$$A_i\left[V,T\right] = f_{ii,o}A_o\left[V/h_{ii,o},\ T/f_{ii,o}\right] - RT\ln h_{ii,o}$$

$$\left(\frac{\partial A_i}{\partial V}\right)_T = f_{ii,o}\left(\frac{\partial A_o}{\partial V}\right)_T + A_o\left(\frac{\partial f_{ii,o}}{\partial V}\right)_T - RT\frac{\partial(\ln h_{ii,o})}{\partial V} \tag{1.19}$$

The parameters of A are omitted for clarity. A_o is a function of T_o and V_o, so that

$$\left(\frac{\partial A_o}{\partial V}\right)_T = \left(\frac{\partial A_o}{\partial T_o}\right)_{V_o}\cdot\left(\frac{\partial T_o}{\partial V}\right)_T + \left(\frac{\partial A_o}{\partial V_o}\right)_{T_o}\cdot\left(\frac{\partial V_o}{\partial V}\right)_{T_o} \tag{1.20}$$

and

$$\left(\frac{\partial T_o}{\partial V}\right)_T = -\frac{T}{f_{ii,o}^2}\cdot\left(\frac{\partial f_{ii,o}}{\partial V}\right)_T \tag{1.21}$$

$$\left(\frac{\partial V_o}{\partial V}\right)_T = \frac{1}{h_{ii,o}} - \frac{V}{h_{ii,o}^2}\cdot\left(\frac{\partial h_{ii,o}}{\partial V}\right)_T \tag{1.22}$$

Substituting (1.21) and (1.22) into (1.20), and then (1.20) into (1.19)

$$\left(\frac{\partial A_i}{\partial V}\right)_T = f_{ii,o}\cdot\left\{\left(\frac{\partial A_o}{\partial T_o}\right)_{V_o}\cdot\left(-\frac{T}{f_{ii,o}^2}\cdot\left(\frac{\partial f_{ii,o}}{\partial V}\right)_T\right) + \left(\frac{\partial A_o}{\partial V_o}\right)_{T_o}\cdot \left(\frac{1}{h_{ii,o}} - \frac{V}{h_{ii,o}^2}\cdot\left(\frac{\partial h_{ii,o}}{\partial V}\right)_T\right)\right\} + A_o\left(\frac{\partial f_{ii,o}}{\partial V}\right)_T - \frac{RT}{h_{ii,o}}\cdot\left(\frac{\partial h_{ii,o}}{\partial V}\right)_T \tag{1.23}$$

Simplification of (1.23) is possible :

$$\left(\frac{\partial A_o}{\partial T_o}\right)_{V_o} = -S_o \qquad \left(\frac{\partial A_o}{\partial V_o}\right)_{T_o} = -P_o$$

$$-\frac{P}{RT} = \frac{U_o}{RT}\cdot\left(\frac{\partial f_{ii,o}}{\partial V}\right)_T + \frac{1}{h_{ii,o}}\cdot\left(\frac{\partial f_{ii,o}}{\partial V}\right)_T\left(f_{ii,o}\cdot\frac{P_o V_o}{RT} - 1\right) -$$

$$P_o \frac{f_{ii,o}}{h_{ii,o}}\cdot\frac{1}{RT}$$

$$-Z = \frac{U_o}{RT_o}\cdot\frac{1}{f_{ii,o}}\left(\frac{\partial f_{ii,o}}{\partial V}\right)_T + \frac{1}{h_{ii,o}}\cdot\left(\frac{\partial h_{ii,o}}{\partial V}\right)_T\cdot(Z_o - 1) - Z_o$$

and so from equation (1.7)

$$\left\{\frac{U_o}{RT_o}\cdot\left(\frac{\partial f_{ii,o}}{\partial V}\right)_T\cdot\frac{1}{f_{ii,o}} + (Z_o-1)/h_{ii,o}\left(\frac{\partial h_{ii,o}}{\partial V}\right)_T\right\}$$

must be zero. This provides a useful method of testing the thermodynamic consistency of the expressions developed by Leach for Θ and Φ. Such a check is described in Section 4.

The defining equation for ω (1.11) does not exactly reproduce the vapour pressure curves for hydrocarbons, or other substances, at temperatures away from $T^R = 0.7$. Since accurate vapour pressure data are available for most substances, the idea is put forward that adjustment of ω using these data would make the prediction of properties by the principle of corresponding states more accurate. The ways in which this idea has been tried are discussed in Section 2.

Extension of the Principle of Corresponding States to Mixtures

In order to extend the principle of corresponding states to mixtures of different species, the intermolecular forces between unlike pairs of molecules must be defined. In a mixture of species 1 and 2, there will be interactions of the type 1-1, 2-2 and 1-2 (which is the same as 2-1).

Assuming that the mixture of different species is completely and randomly mixed, its configurational properties could be described as those of an equivalent hypothetical substance.

This postulate was proposed independently by several workers - Prigogine, Scott, Byers Brown (2), and is usually called the random mixture 1-fluid model . Another suggestion (2) is that the mixture could be considered an ideal mixture of hypothetical components, whose properties are functions of the real components. This is called the 2-fluid model, or nowadays is often called the average potential model.

Considering the 1-fluid model first: the free energy A, of the mixture is equal to that of the hypothetical substance plus the ideal entropy of mixing.

$$A_{mix}\left[V,T\right] = A_x\left[V,T\right] + RT.\sum\left(x \ln x\right) \tag{1.24}$$

where

$$A_x\left[V,T\right] = f_{x,o}.A_o\left[V/h_{x,o},\ T/f_{x,o}\right] - RT \ln h_{x,o} \tag{1.25}$$

Here $h_{x,o}$ and $f_{x,o}$ are parameters for the hypothetical substance. Many methods have been suggested for the calculation of $h_{x,o}$ and $f_{x,o}$ from $f_{ii,0}$ and $h_{ii,o}$. (From now on the subscript o on f and h will be omitted for simplicity). The method which gives the best results is that based on one originally developed by van der Waals; its advantage over other methods is that it deals well with combinations of molecules of very different sizes. For a mixture of N components.

$$h_x = \sum_{i=1}^{N} \sum_{j=1}^{N} \left(x_i x_j h_{ij} \right) \qquad (1.26)$$

and

$$f_x h_x = \sum_{i=1}^{N} \sum_{j=1}^{N} \left(x_i x_j f_{ij} h_{ij} \right) \qquad (1.27)$$

when i = j the pair interaction parameters f and h can be calculated from equations (1.12) and (1.13). T_i^c/T_o^c and V_i^c/V_o^c are referred to as f_{ii}^* and h_{ii}^* respectively in the following discussion. An iterative procedure is necessary to solve for Ω_{ii} and Φ_{ii} because they are functions of T_i^R and V_i^R which are themselves functions of Ω_{ii} and Φ_{ii} - equations (1.15) and (1.16).

Further assumptions are necessary to evaluate the terms in (1.29) and (1.30) where $i \neq j$. The Lorentz-Berthelot rules for combining like-pair interactions are used.

$$h_{ij} = \left(\frac{(h_{ii}^{1/3} + h_{jj}^{1/3})}{2} \right)^3 \qquad (1.28)$$

$$f_{ij} = \xi_{ij} \sqrt{f_{ii} \cdot f_{jj}} \qquad (1.29)$$

Where Berthelot's original proposal was that $\xi_{ij} = 1$.

The term ξ_{ij} is a factor by which agreement can be achieved between calculated configurational thermodynamic properties and experimental determinations of the same properties. Two studies on the determination of ξ , using similar methods, show how it is found either from the excess enthalpy H^E (11), or from the excess Gibbs free energy G^E (2). Using a guess for and calculating G^E or H^E, and adjusting this guess for in the light of the discrepancy between G^E (calc) and G^E (expt), values of ξ have been established. Although ξ is determined from one particular property, once it is established it can be used for all others, and extended to multicomponent mixtures as well.

Another method of finding ξ has been developed by Prausnitz (12). Several other workers have done similar work (13, 14). This approach used experimental virial coefficients, or experimental molar excess volume to calculate ξ . In Prausnitz's nomenclature ξ is $(1 - k_{12})$.

The alternative postulate for the application of the principle of corresponding states is the 2-fluid model. Since it is an ideal mixture, the free energy can be written.

$$A_{mix}[V,T] = \sum x_\alpha (A_\alpha [V,T] + RT \ln x) \qquad (1.30)$$

and from (1.4)

$$A_\alpha [V,T] = f_\alpha A_o [V/h_\alpha , T/f_\alpha] - RT \ln h_\alpha \qquad (1.31)$$

The parameters h_α and f_α now refer to the hypothetical component α . The van der Waals method for calculating the parameters h and f can be extended

$$h_\alpha = \sum_{\beta=1}^{N} x_\beta h_{\alpha\beta} \qquad (1.32)$$

$$f_\alpha h_\alpha = \sum_{\beta=1}^{N} x_\beta f_{\alpha\beta} h_{\alpha\beta} \qquad (1.33)$$

The unlike-pair interaction parameters, $f_{\alpha\beta}$, $h_{\alpha\beta}$ have definitions similar to those for f_{ii} and h_{ii} (cf equations (1.12), (1.13)).

For example

$$h_{\alpha\beta} = h^*_\alpha \Phi_{\alpha\beta} \left[\frac{T}{T^c_o} \cdot \frac{\Theta_{\alpha\beta}}{f_\alpha} , \frac{V}{V^c_o} \cdot \frac{\phi_{\alpha\beta}}{h_\alpha} \right] \qquad (1.34)$$

$$f_{\alpha\beta} = f^*_\alpha \Theta_{\alpha\beta} \left[\frac{T}{T^c_o} \cdot \frac{\Theta_{\alpha\beta}}{f_\alpha} , \frac{V}{V^c_o} \cdot \frac{\phi_{\alpha\beta}}{h_\alpha} \right] \qquad (1.35)$$

These parameters defined in (1.34) and (1.35) are only relevant in equation (1.32) and (1.33). For parameter h_β, $h_{\alpha\beta}$ would be a function of

$$\left[\frac{T}{T_o^c}\cdot\frac{\Theta_{\alpha\beta}}{f_\beta}\,,\ \frac{V}{V_o^c}\cdot\frac{\phi_{\alpha\beta}}{h_\beta}\right]$$

and similarly for f_β. Again, an iterative procedure is necessary to solve equations (1.34) and (1.35) for $h_{\alpha\beta}$ and $f_{\alpha\beta}$.

Section 2

Application of the Principle of Corresponding States to the Prediction of Thermodynamic properties.

SECTION 2

It has been shown in Section 1 how the thermodynamic properties of one substance, or of a mixture, are related to the corresponding properties of another - usually referred to as the reference compound. This section describes how these properties can be calculated, using an equation of state for the reference compound.

1. Compressibility factor

One of the pair of basic equations defining the principle of corresponding states is

$$Z_o \left[T_o^R, V_o^R \right] = Z_i \left[T_i^R, V_i^R \right] \qquad (2.1)$$

To determine the compressibility factor Z for substance i, the compressibility factor is determined for the reference compound i, at a temperature and volume which "correspond" to those of the compound i.

Thus $$T_o^R = T/T_o^c \cdot f_i \qquad (2.2)$$

$$V_o^R = V/V_o^c \cdot h_i \qquad (2.3)$$

or for a mixture, $$T_o^R = T/T_o^c \cdot f_x \qquad (2.4)$$

and $$V_o^R = V/V_o^c \cdot h_x \qquad (2.5)$$

However, h_x and f_x are functions of the shape factors Θ and ϕ. These in turn are both functions of $(T/T_o^c \cdot \Theta / f_x)$ and $(V/V_o^c \cdot \phi / h_x)$ as described in Section 1. This means that calculation of functions of V_o^R and T_o^R is rarely straightforward.

The reference substance used in this work is methane, and the equation of state is that developed by Vennix (15, 16). Another equation of state developed by Leach (8) was used initially to calculate compressibility factors, but that of Vennix is better, and subsequently all work has been based on the latter equation.

Vennix's equation of state for methane.

$$Z_o = 1 + C_B + \frac{C_A}{T_o^R} + \frac{C_C}{T_o^R} \cdot \exp(G - C_E(T_o^R - t_o)) + \frac{C_D}{T_o^R} \cdot \exp\left(k - \frac{C_E}{T_o^R}\right) \quad (2.6)$$

where

$$C_A = a_1\rho^R + a_2(\rho^R)^2 + a_3(\rho^R)^3 + a_4(\rho^R)^4 + a_5(\rho^R)^5 \quad (2.7)$$

$$C_B = b_1\rho^R + b_2(\rho^R)^2 + b_3(\rho^R)^3 + b_4(\rho^R)^4 + b_5(\rho^R)^5 \quad (2.8)$$

$$C_D = d_1\rho^R + d_2(\rho^R)^2 + d_3(\rho^R)^3 + d_4(\rho^R)^4 + d_5(\rho^R)^5 \quad (2.9)$$

$$C_C = \rho^R(\rho^R + \rho_o)^2[(\rho_o + \rho^R)^3 - (\alpha + \rho_o)^3][(\rho_o + \beta)^3 - (\rho_o + \rho^R)^3] \quad (2.10)$$

$$C_E = e_1 + e_2(\rho^R + \rho_o)^3 \quad (2.11)$$

$$C_F = f_1 + f_2 \cdot \rho^R \quad (2.12)$$

The constants (a_1, a_2 ..... f_2, G, t_o, k, α, β, ρ_o ,) are listed in Appendix (A). ^{R} is the reduced density.

$$\rho^R = 1/V^R$$

Although the variables of this equation (2.6) are T^R and ρ^R, it is almost universal to define process conditions in terms of temperature and pressure. Therefore solution of (2.6) for Z_o requires an iterative procedure. This means guessing a volume at the given temperature and pressure, using this to calculate shape factors and interaction parameters. From these Z_o can be calculated. By substituting into

$$\frac{Z_o \cdot T_o^R}{Z_o^c \cdot V_o^R} = P_o^R \qquad (2.13)$$

and comparing this P_o^R with the reduced pressure which defines the process, a measure of the error in the assumed volume (i.e. V_o^R) is known. By adjusting the volume, convergence of the pressure can eventually be achieved.

A method of convergence which works well for this particular case is the Newton-Raphson method. If V_i^R is the i-th estimate for the value of V^R which makes $F(V^R) = 0$, then an improved estimate V_{i+1}^R is found from

$$V_{i+1}^R = V^R - \frac{F(V^R)}{F'(V^R)} \qquad (2.14)$$

The function of reduced volume, $F(V^R)$, is $(P_A^R - P_o^R)$ - that is when the reduced volume is correct, the calculated pressure is identical to the specified pressure.

The first derivative $F'(V^R)$ in equation (2.15) is determined in the following manner

$$F(V^R) = P_A^R - P_o^R \tag{2.15}$$

$$\therefore \quad F'(V^R) = \left(\frac{\partial P_o^R}{\partial V_o^R}\right)_{T^R}$$

but from (2.13) $\quad P_o^R = \dfrac{Z_o \cdot T_o^R}{Z_o^c \cdot V_o^R}$

$$\therefore \left(\frac{\partial P_o^R}{\partial V^R}\right)_{T^R} = \frac{T_o^R}{Z_o^c}\left[V_o^R \cdot \left(\frac{\partial Z_o}{\partial V^R}\right)_{T^R} - Z_o\right] \cdot \frac{1}{(V^R)^2}$$

Since Z_o is a function of ρ^R, rather than V^R, $(\partial Z_o / \partial \rho^R)_{T^R}$ would be a more convenient differential to evaluate.

$$\left(\frac{\partial V^R}{\partial \rho^R}\right) = \frac{-1}{(\rho^R)^2}$$

$$\therefore \left(\frac{\partial P^R}{\partial \rho^R}\right) = \frac{T^R}{Z_o^C}\left[\rho^R \cdot \left(\frac{\partial Z}{\partial \rho^R}\right)_{T^R} + Z_o\right] \tag{2.16}$$

Differentiating equation (2.6) with respect to ρ^R

$$\left(\frac{\partial Z_o}{\partial \rho^R}\right)_{TR} = \left(\frac{\partial C_B}{\partial \rho^R}\right)_{TR} + \frac{1}{T_o^R}\left(\frac{\partial C_A}{\partial \rho^R}\right)_{TR} + \frac{1}{T_o^R}\left[C_c \frac{\partial}{\partial \rho^R}\left\{\exp(G - C_E(T_o^R - t_o))\right\}\right.$$

$$+ \left(\frac{\partial C_c}{\partial \rho^R}\right)_{TR} \cdot \exp(G - C_E(T_o^R - t_o)) + C_D \cdot \frac{\partial}{\partial \rho^R}\left\{\exp\left(k - \frac{C_F}{T_o^R}\right)\right\}$$

$$\left. + \exp\left(k - \frac{C_F}{T_o^R}\right) \cdot \left(\frac{\partial C_D}{\partial \rho^R}\right)_{TR}\right] \qquad (2.17)$$

where

$$\left(\frac{\partial C_A}{\partial \rho^R}\right)_{TR} = a_1 + 2a_2\rho^R + 3a_3(\rho^R)^2 + 4a_4(\rho^R)^3 + 5a_5(\rho^R)^4 \qquad (2.18)$$

$$\left(\frac{\partial C_B}{\partial \rho^R}\right)_{TR} = b_1 + 2b_2\rho^R + 3b_3(\rho^R)^2 + 4b_4(\rho^R)^3 + 5b_5(\rho^R)^4 \qquad (2.19)$$

$$\left(\frac{\partial C_D}{\partial \rho^R}\right)_{TR} = d_1 + 2d_2\rho^R + 3d_3(\rho^R)^2 + 4d_4(\rho^R)^3 + 5d_5(\rho^R)^4 \qquad (2.20)$$

$$\frac{\partial}{\partial \rho^R}\left\{\exp(G - C_E(T_o^R - t_o))\right\} = -\exp(G - C_E(T_o^R - t_o)) \cdot (T_o^R - t_o) \cdot \left(\frac{\partial C_E}{\partial \rho^R}\right)_{TR} \qquad (2.21)$$

$$\frac{\partial}{\partial \rho^R}\left\{\exp\left(k - \frac{C_F}{T_o^R}\right)\right\} = -\exp\left(k - \frac{C_F}{T_o^R}\right) \cdot \frac{1}{T_o^R} \cdot \left(\frac{\partial C_F}{\partial \rho^R}\right)_{TR} \qquad (2.22)$$

$$\left(\frac{\partial C_E}{\partial \rho^R}\right)_{TR} = e_2 \cdot 3(\rho^R + \rho_o)^2 \qquad (2.23)$$

$$\left(\frac{\partial C_F}{\partial \rho^R}\right)_{TR} = f_2 \qquad (2.24)$$

$$\left(\frac{\partial C_c}{\partial \rho^R}\right)_{TR} = C_c\left\{\frac{2\rho^R + (\rho^R + \rho_o)}{\rho_o(\rho_o + \rho^R)} + \left[\frac{1}{(\rho^R + \rho_o)^3 - (\rho_o + \alpha)^3} - \frac{1}{(\rho_o + \beta)^3 - (\rho^R + \rho_o)^3}\right] \cdot 3(\rho^R + \rho_o)^2\right\} \qquad (2.25)$$

A small approximation is introduced in the iterative cycle. The shape factors $\Theta_{i'o}$ and $\Phi_{i'o}$ are functions of V_i^R and T_i^R (equations (1.20) and (1.21), but the dependence on V_i^R is very weak - only a function of V^R at all between $V^R = 0.5$ and $V^R = 2.0$. So, shape factor dependence on V_i^R is left out of the convergence cycle while calculating the compressibility factor. When a constant value of V_i^R is obtained for a particular set of shape factors, these are recalculated using this V_i^R. The compressibility factor is calculated again from these. Three recalculations of shape factors has been found the maximum necessary for complete convergence on V_i^R.

For the liquid phase, the iterative procedure to find the compressibility factor can be avoided almost completely. The Tait equation of state gives V_o^R directly.

$$V_o^R = V_S^R - \ln \left\{ \frac{(P_A^R + H)}{(P_S^R + H)} \right\} \cdot \frac{1}{C} \qquad (2.26)$$

Empirical expressions for the saturation values of V^R and T^R were developed by Leach (8) from experimental data for methane.

$$V_S^R = 1/(1 + \exp(0.83531 + 0.4175105 \ln (1-T_o^R) + 0.214866.\exp (50.098 (T_o^R - 1)))) \qquad (2.27)$$

$$P_S^R = \exp (4.77726 - 4.72895/T_o^R + 0.73611 \ln T_o^R) \qquad (2.28)$$

$$H = - 17.4897 + 15.9008/T_o^R + \exp (10.5083 T_o^R - 11.0064) \qquad (2.29)$$

$$C = \frac{1.}{P_S^R} \exp\left(5.94009 - 2.105715/T_o^R - 0.986662/T_o^R\right)^2 \qquad (2.30)$$

From V^R, equation (2.26) the compressibility factor comes directly

$$Z_o = \frac{P_A^R \cdot V_o^R \cdot Z_o^C}{T^R} \qquad (2.31)$$

As for the vapour phase, three iterations are necessary to recalculate the shape factors, to include their dependence on V^R.

Since a second equation of state (Tait) has been introduced for the liquid phase, it becomes necessary to decide the phase of the mixture, before commencing any calculations.

An accurate expression for the vapour pressure of methane has been developed by Armstrong, Brickwedde and Scott (24), and slightly modified by Vennix (16) for use with his equation of state. By comparing the reduced vapour pressure of methane calculated from this expression at T_o ($= T/f_x$) with the reduced pressure of the system, the phase can be established. The reduced pressure is calculated

$$P_A^R = P/\left\{82.0567 \times \frac{Z_o^C \times T_o^C}{V_o^C} \cdot \frac{h_x}{f_x}\right\} \qquad (2.32)$$

If the reduced vapour pressure of the reference compound is less than P_A^R, then the mixture is in the liquid phase; if it is greater than P_A^R, the mixture is in the vapour phase.

In equation (2.26) the ratio $(P_A^R + H)$ can become negative or zero, and this will cause difficulty in calculating Z_o. This condition occurs when T_o^R is very close to 1.0, but not actually equal to 1.0. In his program PROPERTY, Leach (17), prepares for this condition by using the Tait equation only up to $T_o^R = 0.98$. In the program developed for this work, for any value of T_o^R which causes that ratio to be less than or equal to zero, control is transferred so that Z_o is calculated using Vennix's equation (2.6).

2. Internal Energy and Enthalpy

The Gibbs-Helmholtz relationship between A and U may be written.

$$U = A - \left\{\frac{\partial A}{\partial T}\right\}_V . T$$

For a mixture :

$$U_{mix} = A_{mix} - \left\{\frac{\partial A_{mix}}{\partial T}\right\}_V . T \qquad (2.33)$$

Using the 1-fluid model, from equations (1.27), and (1.28) we have

$$A_{mix}[V,T] = f_x A_o[V/h_x, T/f_x] - RT\ln h_x + RT\sum x\ln x$$

(2.34)

The parameters for A_{mix} and A_o will be omitted in the following derivation for simplicity. Differentiating equation (2.34) with respect to temperature :

$$\left(\frac{\partial A_{mix}}{\partial T}\right)_v = f_x \cdot \left(\frac{\partial A_o}{\partial T}\right)_v + A_o\left(\frac{\partial f_x}{\partial T}\right)_v - RT\left(\frac{\partial(\ln h_x)}{\partial T}\right)_v$$
$$-R\ln h_x + R\Sigma x \ln x \qquad (2.35)$$

Since A_o is a function of $(V/h_x, T/f_x)$ which is (V_o, T_o),

$$\left(\frac{\partial A_o}{\partial T}\right)_v = \left(\frac{\partial A_o}{\partial V_o}\right)_{T_o} \cdot \left(\frac{\partial(V/h_x)}{\partial T}\right)_v + \left(\frac{\partial A_o}{\partial T_o}\right)_{V_o} \cdot \left(\frac{\partial(T/f_x)}{\partial T}\right)_v \qquad (2.36)$$

Where

$$\left(\frac{\partial(V/h_x)}{\partial T}\right)_v = \frac{-V}{h_x^2} \cdot \left(\frac{\partial h_x}{\partial T}\right)_v$$

and

$$\left(\frac{\partial(T/f_x)}{\partial T}\right)_v = \frac{1}{f_x} - \frac{T}{f_x^2} \cdot \left(\frac{\partial f_x}{\partial T}\right)_v$$

Substituting these into (2.36), and then (2.36) into (2.35)

$$\left(\frac{\partial A_{mix}}{\partial T}\right)_v = f_x \cdot \left(\frac{\partial A_o}{\partial V_o}\right)_{T_o} \cdot \left(\frac{-V}{h_x^2}\left(\frac{\partial h_x}{\partial T}\right)_v\right) + A_o\left(\frac{\partial f_x}{\partial T}\right)_v$$

$$-R\ln h_x + f_x\left(\left(\frac{\partial A_o}{\partial T_o}\right)_{V_o} \cdot \left(\frac{1}{f_x} - \frac{T}{f_x^2}\left(\frac{\partial f_x}{\partial T}\right)_v\right)\right) - \frac{RT}{h_x}\left(\frac{\partial h_x}{\partial T}\right)_v$$

$$+ R\Sigma x \ln x$$

Using (2.33) and the basic relationships

$$\left(\frac{\partial A_o}{\partial T_o}\right)_{V_o} = -S_o \quad , \left(\frac{\partial A_o}{\partial V_o}\right)_{T_o} = -P_o \quad , U_o = A_o + T_o S_o$$

$$\frac{U}{RT}_{mix} = \frac{U_o}{RT_o} - \frac{U_o}{RT_o}\cdot\left[\frac{T}{f_x}\cdot\left(\frac{\partial f_x}{\partial T}\right)_V\right] - \frac{T}{h_x}\left(\frac{\partial h_x}{\partial T}\right)_V (Z_o - 1)$$

(2.37)

From this the enthalpy follows immediately since H = U + PV

$$\therefore \quad \frac{H}{RT} = \frac{U}{RT} + Z$$

so that

$$\frac{H_{mix}}{RT} = \frac{U_{mix}}{RT} + Z_{mix} \qquad (2.38)$$

The compressibility factor Z_o in equation (2.37) is evaluated at (V_o^R, T_o^R), and from equation (1.10) Z_o equals Z_{mix}.

A similar expression for the internal energy and enthalpy for a 2-fluid model of a mixture can be developed using the same arguments. The corresponding expressions are

$$\frac{U_{mix}}{RT_{mix}} = \Sigma x_\alpha \frac{U_o}{RT_o} - T\Sigma \frac{x_\alpha}{f_\alpha}\cdot\left(\frac{\partial f_\alpha}{\partial T}\right)_V \cdot \frac{U_o}{RT} \cdots$$

$$T\Sigma \frac{x_\alpha}{h_\alpha}\left(\frac{\partial h_\alpha}{\partial T}\right)_V \cdot (Z_o - 1)_\alpha \qquad (2.39)$$

Where Z_o and U_o are functions of V/h_α and T/f_α H_{mix} comes from (2.38) but

$$Z_{mix} = \Sigma x_\alpha Z_o \qquad (2.40)$$

Derivatives of f_x, h_x with respect to Temperature

The f and h parameters are defined, for the 1-fluid model:

$$f_x = \frac{\sum\sum x_i x_j f_{ij} h_{ij}}{\sum\sum x_i x_j h_{ij}} \tag{2.41}$$

and $$h_x = \sum\sum x_i x_j h_{ij}$$

$$\frac{df_x}{dT} = \left(h_x \cdot \frac{d(h_x f_x)}{dT} - h_x f_x \cdot \frac{dh_x}{dT} \right) / h_x^2 \tag{2.42}$$

where $$\frac{d(h_x f_x)}{dT} = \sum\sum x_i x_j \left(h_{ij} \frac{df_{ij}}{dT} + f_{ij} \frac{dh_{ij}}{dT} \right) \tag{2.43}$$

$$\frac{dh_x}{dT} = \sum\sum x_i x_j \frac{dh_{ij}}{dT} \tag{2.44}$$

To evaluate $\frac{df_{ij}}{dT}$ and $\frac{dh_{ij}}{dT}$, and iterative procedure is necessary.

Where i = j,

$$f_{ii} = f^*_{ii} \Theta_{ii}$$

so that $$\frac{\partial f_{ii}}{\partial T} = f^*_{ii} \cdot \frac{\partial \Theta_{ii}}{\partial T} \tag{2.45}$$

where $i \neq j$ $$f_{ij} = \xi_{ij} \sqrt{f_{ii} \cdot f_{jj}}$$

$$\frac{\partial f_{ij}}{\partial T} = \frac{1}{2 f_{ij}} \cdot \left(f_{ii} \cdot \frac{\partial f_{jj}}{\partial T} + f_{jj} \frac{\partial f_{ii}}{\partial T} \right) \tag{2.46}$$

It can be seen from (2.46) that differentials for $i \neq j$ can be determined from those for $i = j$. Similarly for the h parameter: where $i = j$,

$$h_{ii} = h^*_{ii}\,\Phi_{ii}$$

$$\therefore \quad \frac{\partial h_{ii}}{\partial T} = h^*_{ii} \cdot \frac{\partial \Phi_{ii}}{\partial T} \tag{2.47}$$

f^*_{ii} and h^*_{ii} are defined by equation (1.8)

Where $i \neq j$, the correct expression for h_{ij} is

$$h_{ij} = \left(\frac{1}{2}\left(h_{ii}^{1/3} + h_{jj}^{1/3}\right)\right)^3$$

The differential of this is complicated, so a small approximation is introduced. For the purposes of producing a differential,

$$h_{ij} = 1/2\ (h_{ii} + h_{jj})$$

so that

$$\frac{\partial h_{ij}}{\partial T} = \frac{1}{2}\left(\frac{\partial h_{ii}}{\partial T} + \frac{\partial h_{jj}}{\partial T}\right) \tag{2.48}$$

Next arises the problem of how to evaluate $\partial \Theta / \partial T$ and $\partial \Phi / \partial T$. The shape factors Θ_{ii} and Φ_{ii} are functions of T_i^R and V_i^R, thus

$$\left(\frac{\partial \Theta_{ii}}{\partial T}\right)_V = \left(\frac{\partial \Theta_{ii}}{\partial T_i^R}\right)_{V_i^R} \cdot \left(\frac{\partial T_i^R}{\partial T}\right)_V + \left(\frac{\partial \Theta_{ii}}{\partial V_i^R}\right)_{T_i^R} \cdot \left(\frac{\partial V_i^R}{\partial T}\right)_V \tag{2.49}$$

$$\left(\frac{\partial \Phi_{ii}}{\partial T}\right)_V = \left(\frac{\partial \Phi_{ii}}{\partial T_i^R}\right)_{V_i^R} \cdot \left(\frac{\partial T_i^R}{\partial T}\right)_V + \left(\frac{\partial \Phi_{ii}}{\partial V_i^R}\right)_{T_i^R} \cdot \left(\frac{\partial V_i^R}{\partial T}\right)_V \tag{2.50}$$

From equations (1.17) and (1.18) for Θ and Φ we have :

$$\left(\frac{\partial \Theta_{ii}}{\partial T_i^R}\right)_{V_i^R} = (\omega_i - \omega_o).(-0.8493/T_i^R + (0.4506/T_i^R)(V_i^R - 0.5)) \tag{2.51}$$

$$\left(\frac{\partial \Theta_{ii}}{\partial V_i^R}\right)_{T_i^R} = 0.3063 - 0.4506/T_i^R \tag{2.52}$$

$$\left(\frac{\partial \Phi_{ii}}{\partial T_i^R}\right)_{V_i^R} = \frac{Z_o^c}{Z_i^c}\left\{(\omega_i - \omega_o)(0.3903(V_i^R - 1.0177) - 0.9462/T_i^R (V_i^R - 0.7663))\right\} \tag{2.53}$$

$$\left(\frac{\partial \Phi_{ii}}{\partial V_i^R}\right)_{T_i^R} = \frac{Z_o^c}{Z_i^c}.(\omega_i - \omega_o)(0.3903 - 0.9462 \ln T_i^R) \tag{2.54}$$

From equations (1.15) and (1.16)

$$\left(\frac{\partial T_i^R}{\partial T}\right)_V = T_i^R\left[\frac{1}{\Theta_{ii}} \cdot \left(\frac{\partial \Theta_{ii}}{\partial T}\right)_V + \frac{1}{T} - \frac{1}{f_x}\left(\frac{\partial f_x}{\partial T}\right)_V\right] \tag{2.55}$$

$$\left(\frac{\partial V_i^R}{\partial T}\right)_V = V_i^R\left[\frac{1}{\Phi_{ii}} \cdot \left(\frac{\partial \Phi_{ii}}{\partial T}\right)_V - \frac{1}{h_x} \cdot \left(\frac{\partial h_x}{\partial T}\right)_V\right] \tag{2.56}$$

The iterative procedure arises out of the fact that in equations (2.43) and (3.44), $(\partial h_{ij}/\partial T)_v$ and $(\partial f_{ij}/\partial T)_v$ are functions of $(\partial h_x/\partial T)_v$ and $(\partial f_x/\partial T)_v$. So, in order to solve for $(\partial h_x/\partial T)_v$ and $(\partial f_x/\partial T)_v$ a small initial value is given to $(\partial T_i^R/\partial T)_v$ and $(\partial V_i^R/\partial T)_v$, and equations (2.49) and (2.50), followed by (2.45, 2.46, 2.47, 2.48), leading to(2.42) and (2.44) are solved. Then beginning again with (2.55) and (2.56) convergence on $(\partial h_x/\partial T)_v$ and $(\partial f_x/\partial T)_v$ can eventually be reached.

Evaluation of Uo

A basic thermodynamic relationship between U and pressure, volume and temperature is

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \qquad (2.57)$$

The residual internal energy U* is defined

$$U^* = \int_\infty^V \left\{\left(\frac{\partial U}{\partial V}\right)_T - \left(\frac{\partial U^{p.g.}}{\partial V}\right)_T\right\} dV$$

But the internal energy of a perfect gas is zero, so

$$U^* = \int_\infty^V \left(\frac{\partial U}{\partial V}\right)_T dV = U$$

Where U is the configurational part of the internal energy.

From (2.57)

$$U = \int_\infty^V \left\{T\left(\frac{\partial P}{\partial T}\right)_V - P\right\} dV$$

For the reference compound we write $U = U_o$. Using reduced variables and changing the variable of integration from volume to density.

$$\frac{U_o}{RT_o} = -\int_0^{\rho_R} \left\{ \frac{T_o^R}{\rho_o^R} \cdot \left(\frac{\partial Z_o}{\partial T_o^R} \right)_{\rho^R} \right\} d\rho^R \qquad (2.58)$$

When Zo is calculated from the Vennix equation of state, the integral in (2.58) is evaluated by the Gaussian quadrature method.

$$\text{Integral} = \frac{b - a}{2} \sum_{m=1}^{m=8} T_m g(W_m)$$

Where a and b are the former limits of integration, T_m and W_m are tabulated constants (18), and g is a function of W_m.

Equation (2.58) becomes

$$\frac{U_o}{RT_o} = -T_o^R \rho^R \sum_{m=1}^{m=8} \left[\frac{1}{\rho'^R_m} \left(\frac{\partial Z'}{\partial T^R} \right) \right] \frac{T_m}{2} \qquad (2.59)$$

$$\rho'^R_m = 1/2 (\rho^R + \rho^R . W_m)$$

Z' is the compressibility factor calculated from equation (2.6) as a function of ρ'^R

$$\left(\frac{\partial Z'}{\partial T^R} \right)_{\rho^R} = \frac{1}{T_o^R} \left(\frac{-C_A}{T_o^R} - C_c \left(C_E + \frac{1}{T_o^R} \right) \exp\left(G - C_E \left(T_o^R - t_o \right) \right) \right)$$

$$+ \frac{1}{T_o^R} C_D \left(\frac{C_F}{T_o^R} - 1 \right) \exp\left(k - \frac{C_F}{T_o^R} \right) \qquad (2.60)$$

In the liquid phase, or where the Tait equation of state is used to calculate Z_o, equation (2.58) may be calculated analytically.

$$Z_o = \frac{Z_o^c . P_A^R}{\rho_o^R . T_o^R}$$

$$\therefore \left(\frac{\partial Z_o}{\partial T_o^R} \right)_{\rho_o^R} = \frac{Z_o^c}{\rho_o^R} \cdot \left(T_o^R \left(\frac{\partial P_A^R}{\partial T^R} \right)_{\rho^R} - P_A^R \right) \cdot \frac{1}{(T_o^R)^2} \qquad (2.61)$$

Substituting equation (2.61) into (2.58)

$$\frac{U_o}{RT_o} = \int_0^{\rho^R} \frac{Z^c}{(\rho^R)^2} \cdot \left(\frac{\partial P_A^R}{\partial T_o^R}\right)_{\rho^R} \cdot d\rho^R + \int_0^{\rho^R} \frac{Z^c P_A^R}{(\rho^R)^2 \cdot T_o^R} \cdot d\rho^R \tag{2.62}$$

From the Tait equation

$$P_A^R = \exp\left(C(V_S^R - V_o^R)\right).(P_S^R + H) - H$$

$$\therefore \left(\frac{\partial P_A^R}{\partial T_o^R}\right)_{\rho^R} = \exp\left\{C(V_s^R - V_o^R)\right\}.\left\{\frac{dP_s^R}{dT_o^R} + \frac{dH}{dT_o^R}\right.$$

$$\left. + (P_s^R + H).\left[\frac{dC}{dT_o^R}\left(V_s^R - V_o^R\right) + C\,\frac{dV_s^R}{dT_o^R}\right]\right\} - \frac{dH}{dT_o^R} \tag{2.63}$$

In the liquid phase, the integral in (2.58) can be divided into the integral from infinite volume to the volume of saturated vapour, and the integral from saturation to the volume of the liquid. The former integral we write as U_o^S, and this can be determined from the empirical expression found by Leach (8).

$$\left(\frac{U_o^S}{RT_o}\right)_{V_S^R} = \frac{1}{V_S^R} \cdot \left(-0.29152279 + 1.934121/T_o^R - (0.251244 + 0.3800509/T_o^R)\exp\left(15.0\,(T_o^R - 1)\right)\right) \tag{2.64}$$

Since the Tait equation is in terms of V^R (instead of ρ^R)

$$\frac{U_o}{RT_o} = \frac{U_o^s}{RT_o} + \int_{V_s^R}^{V^R} \frac{T_o^R}{V_o^R}\left(\frac{\partial Z_o}{\partial T_o^R}\right)_{V^R} \cdot dV^R$$

Rewriting (2.61)

$$\left(\frac{U_o}{RT_o}\right) = \left(\frac{U_o^s}{RT_o}\right) + Z_o^c\left[\frac{dP_s^R}{dT_o^R} + \frac{dH}{dT_o^R} + (P_s^R+H).C.\frac{dV_s^R}{dT_o^R}\right].$$

$$\int_{V_s^R}^{V^R} \exp(C(V_s^R - V_o^R))\,dV^R - Z_o^c\int_{V_s^R}^{V^R}\frac{dH}{dT_o^R}.dV^R$$

$$+\frac{Z_o^c}{T_o^R}\int_{V_s^R}^{V^R} H.dV^R - Z_o^c(P_s^R+H)\int_{V_s^R}^{V^R}\exp(C(V_s^R-V_o^R))\,dV^R$$

$$+ Z_o^c(P_s^R+H)\frac{dC}{dT_o^R}\int_{V_s^R}^{V^R}(V_s^R - V_o^R)\exp(C(V_s^R-V_o^R))\,dV^R$$

This reduces to :

$$\frac{U_o}{RT_o} = \frac{U_o^s}{RT_o} + \frac{Z_o^c}{C}.(P_A^R - P_s^R)\left[\left(\frac{dP_s^R}{dT_o^R} + \frac{dH}{dT_o^R}\right)\Big/(P_s^R+H) + \frac{1}{T_o^R}\right.$$

$$\left. + \frac{1}{C}.\frac{dC}{dT_o^R} - C.\frac{dV_s^R}{dT_o^R}\right] + Z_o^c(V_o^R - V_s^R)\left(\frac{H}{T_o^R} + \frac{dC}{dT_o^R}.\frac{1}{C}.(P_A^R+H) - \frac{dH}{dT_o^R}\right)$$

(2.65)

Where

$$\frac{dV_s^R}{dT_o^R} = -(V_S^R)^2\exp(0.83531 + 0.4175105\ln(1-T_o^R)$$
$$+ (0.214866\exp(50.908(T_o^R - 1))).(0.4175105/(T_o^R - 1)$$
$$+ 10.938398\exp(50.908(T_o^R - 1))) \qquad (2.66)$$

$$\frac{dH}{dT_o^R} = -15.9008/(T_o^R)^2 + 10.5083\exp(10.5083.T_o^R - 11.0064) \qquad (2.67)$$

$$\frac{dP_s^R}{dT_o^R} = P_S^R(4.72895/T_o^R + 0.73611)/T_o^R \qquad (2.68)$$

$$\frac{dC}{dT_o^R} = \exp(5.94009 - 2.105715/T_o^R - 0.986772/(T_o^R)^2)/P_S^R \cdot \left[(2.105715 + 1.973533/T_o^R)/(T_o^R)^2 - \frac{dP_s^R}{dT_o^R} \cdot \frac{1}{P_o^R}\right] \qquad (2.69)$$

3. Chemical Potential and Fugacity

A multiphase system of one component or more is in equilibrium when all phases are at the same temperature and pressure and the chemical potential, μ of each component is the same in each phase. The chemical potential of the i-th component is related to the configurational Gibbs free energy of the phase by the definition

$$\mu_i(P,T,x) = \left(\frac{\partial G(P,T,x)}{\partial n_i}\right)_{T,P,n_j(j\neq i)}$$

In order to determine the right hand term, G(P,T,x) must be defined. As for the Helmholtz free energy, (1.27) and (1.28), we can write the Gibbs free energy of a mixture as the sun of G_x (for the hypothetical substance replacing the mixture) and the ideal mixing term.

$$G_{mix}(P,T,x) = G_x(P,T) + \Sigma x RT \ln x \qquad (2.70)$$

And as for A_x (equation (1.24)

$$G_x(P,T) = f_x \cdot G_o(P_o,T_o) - RT \ln h_x \qquad (2.71)$$

The term $(\partial G_{mix}/\partial n_i)$, where n_i is the number of moles of component i, and G_{mix} is a function of mole fractions, presents a difficulty. Mole fractions of the components of a mixture are not independent variables. However, we can treat them as independent variables by the following manipulation. Brown (1) and Rowlinson and Watson (1, 10) introduce a differential operator :

$$\Delta_1 = \left[\frac{D}{Dx_1} - \sum x_\alpha \frac{D}{Dx_\alpha} \right]_{P,T} \qquad (2.72)$$

Where (D/Dx_1) is a differentiation treating x as an independent variable. It can be shown (1) that for the molar property r_α of a component in a mixture - e.g. component α, that

$$r_\alpha = r + \Delta_\alpha r$$

Where r without a subscript is the same property for the whole mixture. So, for component i,

$$\mu_i = G_{mix} + \Delta_i G_{mix}$$

$$\Delta_i G_{mix} = \frac{dG_{mix}}{dx_i} - \sum_{\beta=1}^{\beta=N} x_\beta \frac{dG_{mix}}{dx_\beta} \qquad (2.73)$$

Using equations (2.73) and (2.70) the operator Δ can be transferred to G_x

$$\mu_i = (1 + \Delta_i)G_x + RT \ln x_i \qquad (2.74)$$

From equation (2.71) and omitting the parameters for simplicity,

$$\Delta G_x = \Delta f_x \cdot G_o + f_x \cdot \Delta G_o - \frac{RT}{h_x} \cdot \Delta h_x \qquad (2.75)$$

Substituting (2.75) back into (2.74)

$$\mu_i = RT \ln x_i + G_x + \Delta_i f_x \cdot G_o + f_x \cdot \Delta_i G_o - \frac{RT}{h_x} \cdot \Delta h_x \qquad (2.76)$$

But G_o is a function of T_o, P_o (ie T/f_x, Ph_x/f_x)

$$\therefore \Delta G_o = \left(\frac{\partial G_o}{\partial f_x}\right)_{h_x} \cdot \Delta f_x + \left(\frac{\partial G_o}{\partial h_x}\right)_{f_x} \cdot \Delta h_x \qquad (2.77)$$

Differentiating (2.71) with respect to f_x and h_x

$$\left(\frac{\partial G_x}{\partial f_x}\right)_{h_x} = \left(\frac{\partial G_o}{\partial f_x}\right)_{h_x} \cdot f_x + G_o \qquad (2.78)$$

$$\left(\frac{\partial G_x}{\partial h_x}\right)_{f_x} = f_x \left(\frac{\partial G_o}{\partial h_x}\right)_{f_x} - \frac{RT}{h_x} \qquad (2.79)$$

Substituting (2.77, 2.78, 2.79) into (2.76)

$$\mu_i = RT \ln x_i + G_x + \Delta f_x \frac{\partial G_x}{\partial f_x} + \Delta h_x \cdot \frac{\partial G_x}{\partial h_x} \qquad (2.80)$$

From (2.78) and (2.79)

$$\left(\frac{\partial G_x}{\partial f_x}\right)_{h_x} = U_o \quad \text{and} \quad \left(\frac{\partial G_x}{\partial h_x}\right)_{f_x} = \frac{1}{h_x}(VP - RT)$$

Substituting these into (2.80) and dividing by RT (or $RT_o f_x$)

$$\frac{\mu_i}{RT} = \ln x_i + \frac{G_x}{RT} + \frac{\Delta f_x}{f_x} \frac{U_o}{RT_o} + \frac{\Delta h_x}{h_x}(Z_o - 1) \qquad (2.81)$$

U_o and Z_o can be evaluated at T_o and V_o (P_o), but the problem remains how to find G_x. Since $T_o = T/f_x$ and $V_o = V/h_x$ we can rewrite equation (1.28) as

$$A_1[V,T]/RT + \ln V_1 = A_o[V_o,T_o]/RT_o + \ln V_o$$

Using (1.7) we have

$$G_o[P_o,T_o]/RT_o - \ln(P_o/T_o) = G_1[P,T]/RT - \ln(P/T)$$

From the definition of chemical potential,

$$\mu_o^{resid}[P_o,T_o]/RT_o = \mu_i^{resid}[P,T]/RT \qquad (2.82)$$

A residual property is defined as the difference between the configurational property of the real substance and the same property of the equivalent ideal substance.

This (2.82) is one of the basic equations defining the principle of corresponding states; another is (2.1).
The definition of fugacity in terms of μ was first proposed by G.N. Lewis (20).

$$\mu_i = RT \ln \mathfrak{f}_i + \Theta$$

For the chemical potential of a component i in a mixture, and where Θ is some function of temperature.

For a perfect gas $\mathfrak{f} = Px_i$.

i.e. $$\mu_i^{p.g.} = RT \ln P x_i + \Theta$$

Combining these definitions of μ we have

$$\frac{\mu_i^{resid}}{RT} = \frac{(\mu_i - \mu_i^{p.g.})}{RT} = \frac{\ln \mathfrak{f}_i}{Px_i} \qquad (2.83)$$

Combining equations (2.83) and (2.81)

$$\frac{\mu_i^{resid}}{RT} = \frac{G_x}{RT} + \frac{\Delta f_x}{f_x}\left(\frac{U_o}{RT_o}\right) + \frac{(Z_o - 1)}{h_x}\Delta h_x - \ln P \qquad (2.84)$$

For a single component - a pure substance such as the hypothetical one denoted by subscript x

$$\lim_{x_\alpha \to 1} \Delta_\alpha = 0$$

$\therefore$ in (2.84)

$$\frac{\mu_x^{resid}}{RT} = \frac{G_x}{RT} - \ln P \qquad (2.85)$$

Combining (2.84) and (2.85)

$$\frac{\mu_i^{resid} - \mu_x^{resid}}{RT} = \frac{\Delta f_x}{f_x} \cdot \frac{U_o}{RT_o} + \frac{\Delta h_x}{h_x} \cdot (Z_o - 1) \qquad (2.86)$$

But from (2.83)

$$\frac{\mu_i^{resid} - \mu_x^{resid}}{RT} = \ln \frac{\mathcal{F}_i}{Px_i} - \ln \frac{\mathcal{F}_x}{P}$$

Since for equilibrium the chemical potential of each component must be the same in all phases, and since fugacities can be calculated directly from P-V-T data, it is convenient to write (2.86)

$$\ln\left(\frac{\mathcal{F}_i}{P}\right) = \ln x_i + \ln\left(\frac{\mathcal{F}_x}{P}\right) + \frac{\Delta f_x}{f_x} \cdot \frac{U_o}{RT_o} + \frac{\Delta h_x}{h_x}(Z_o - 1)$$

Joffe (22) derived a similar relationship for fugacity coefficients using the principle of corresponding states. However since

$$\frac{\mu_x^{resid}}{RT} = \ln \frac{\mathcal{F}_x}{P}$$

and from (2.82)

$$\frac{\mu_x^{resid}}{RT}[P,T] = \frac{\mu_o^{resid}}{RT_o}[P_o,T_o]$$

$$\frac{\mu_o^{resid}}{RT_o} = \ln\left(\frac{\mathcal{F}_o}{P}\right)$$

$$\ln\left(\frac{\mathcal{F}_i}{P}\right) = \ln x_i + \ln\left(\frac{\mathcal{F}_o}{P}\right) + \frac{\Delta f_x}{f_x} \cdot \frac{U_o}{RT_o} + \frac{\Delta h_x}{h_x}(Z_o - 1) \qquad (2.87)$$

Equation (2.87) is used for the calculation of phase equilibria.

Calculation of ln ($\mathcal{F}_o/P$)

The fugacity coefficient $\mathcal{F}/P$ is defined in terms of pressure, volume and temperature by

$$\ln\left(\frac{\mathcal{F}}{P}\right) = \int_0^P \left(V - \frac{RT}{P}\right) dP \qquad (2.88)$$

Since $Z = PV/RT$

$$\frac{dP}{dZ} = \frac{RT}{V} + ZRT\,\frac{d\rho}{dZ} \tag{2.89}$$

$\frac{1}{V}$ has been replaced by ρ, so that the final expression of (2.88) is compatible with the integration for U_o (2.59).

Thus, (2.88) becomes

$$\ln(\mathfrak{F}/P) = \int_1^Z \frac{(Z-1)}{Z}\,Z + \int_0^\rho \frac{Z-1}{\rho}\,d\rho$$

$$\therefore \quad \ln(\mathfrak{F}/P)_o = Z_o - 1 - \ln Z_o + \int_0^\rho \frac{Z-1}{\rho}\,d\rho \tag{2.90}$$

The integral in (2.90) is evaluated by an 8-point Gauss quadrature method, and which has been described previously in the section 2.2 for U_o.

For a liquid phase, the integration in (2.90) can be divided, to account for the change of phase; equation (2.88) becomes, with subscript S for saturation

$$\ln(\mathfrak{F}/P) - \ln(\mathfrak{F}/P)_s = \int_{\rho_s}^{\rho} \frac{(V-RT)}{P}\,dP$$

$$\therefore \quad \ln\left(\frac{\mathfrak{F}}{P}\right)_o = \ln\left(\frac{\mathfrak{F}}{P}\right)_s + Z_o - Z_s - \ln\left(\frac{Z_o}{Z_s}\right) + \int_{\rho_s}^{\rho} \frac{Z-1}{\rho}\,d\rho \tag{2.91}$$

Splitting the integral in (2.91) still further

$$\int_{\rho_s}^{\rho} \frac{Z-1}{\rho}\,d\rho = \int_{\rho_s}^{\rho} \frac{Z}{\rho}\,d\rho - \int_{\rho_s}^{\rho} \frac{1}{\rho}\,d\rho$$

in which

$$-\int_{\rho_s}^{\rho} \frac{1}{\rho}\,d\rho = -\ln\left(\frac{\rho}{\rho_s}\right) \tag{2.92}$$

Finally, substituting $Z = Z_o^C \cdot P_A^R V_o^R / T_o^R$ and $dV_R = -1/(\rho^R)^2 . d\rho^R$ into the remaining integral, we have

$$-\frac{Z_c}{T^R}\int_{\rho_s^R}^{\rho^R} (P^R)\, dV^R \qquad (2.93)$$

From the Tait equation,

$$P_A^R = (P_S^R + H)\ \exp\left[C(V_S^R - V_o^R)\right] - H$$

and changing the limits of integration to P_S^R and P^R equation (2.93) becomes

$$\frac{-Z_o^C}{T_o^R}\left[-(P_S^R + H).\ \frac{(P^R - P_S^R)}{(P_S^R + H)}.\ \frac{1}{C} - C\ (V_S^R - V_o^R)\right] \qquad (2.94)$$

Substituting (2.94) and (2.92) into (2.81)

$$\ln\ (\mathfrak{F}/P)_o = \ln\ (\mathfrak{F}/P)_S - (Z_o - Z_s) - \ln\left(\frac{P^R}{P_S^R}\right)$$

$$+ \frac{Z_o^C}{T_o^R}\left[\frac{(P^R - P_S^R)}{C} + C\ (V_S^R - V_o^R)\right] \qquad (2.95)$$

Leach (8) has developed an empirical equation for methane for the calculation of $\ln\ (\mathfrak{F}/P)_s$

$$\ln(\mathfrak{F}/P)_s = -\exp\ (3.5197242 - 4.4195532/T_o^R - 1.2808837.\ln T_o^R) \qquad (2.96)$$

Calculation of $\Delta_\alpha h_x$ and $\Delta_\alpha f_x$

Equation (2.72) gives the definition of the Δ function. For the parameters f and h,

$$\Delta_\alpha h_x = \frac{\partial h_x}{\partial x_\alpha} - \sum_{\beta=1}^{\beta=N} x_\beta \cdot \frac{\partial h_x}{\partial x_\beta} \qquad (2.97)$$

$$\Delta_\alpha f_x = \frac{\partial f_x}{\partial x_\alpha} - \sum_{\beta=1}^{\beta=N} x_\beta \frac{\partial f_x}{\partial x_\beta} \qquad (2.98)$$

Taking (2.97) we can transfer the operator Δ to the shape factor ϕ:

$$\Delta_\alpha h_x = 2h_\alpha - 2h_x + \Sigma\Sigma x_\alpha x_\beta h^*_{\alpha\beta} \Delta_\alpha \phi_{\alpha\beta} \tag{2.99}$$

where

$$h_\alpha = \Sigma x_\beta h_{\alpha\beta} \tag{2.100}$$

and $(2h_\alpha - 2h_x)$ is what would be $\Delta_\alpha h_x$ if x_α could be considered constant.

Since $\phi_{\alpha\beta}$ is a function of T^R_α and V^R_α

$$\Delta_\alpha \phi_{\alpha\beta} = \left(\frac{\partial \phi}{\partial T^R}^{\alpha\beta}\right)_{V^R} \cdot \Delta_\alpha T^R + \left(\frac{\partial \phi_{\alpha\beta}}{\partial V^R}\right)_{T^R} \cdot \Delta_\alpha V^R \tag{2.101}$$

and since

$$T^R_\alpha = \frac{T}{T^c_o} \cdot \frac{\Theta_{\alpha\beta}}{f_x} \quad , \quad V^R_\alpha = \frac{V}{V^c_o} \cdot \frac{\phi_{\alpha\beta}}{h_x} \tag{2.102}$$

$$\Delta_\alpha T^R = T^R_\alpha \left[\frac{1}{\Theta_{\alpha\beta}} \cdot \Delta_\alpha \Theta_{\alpha\beta} - \frac{1}{f_x} \cdot \Delta_\alpha f_x\right]$$

and

$$\Delta_\alpha V^R = V^R_\alpha \left[\frac{1}{\phi_{\alpha\beta}} \Delta_\alpha \phi_{\alpha\beta} - \frac{1}{h_x} \cdot \Delta_\alpha h_x\right] \tag{2.103}$$

Expanding (2.88) for $\Delta_\alpha f_x$,

$$\Delta_\alpha f_x = \frac{2h_x f_x}{h_x}\left[\frac{f_\alpha h_\alpha}{f_x h_x} - \frac{h_\alpha}{h_x}\right] +$$

$$\frac{1}{h_x} \Sigma\Sigma x_\alpha x_\beta h_{\alpha\beta} f^*_{\alpha\beta} \Delta_\alpha \Theta_{\alpha\beta} +$$

$$\frac{1}{h_x} \Sigma\Sigma x_\alpha x_\beta h^*_{\alpha\beta} \Delta_\alpha \phi_{\alpha\beta} \left(f_{\alpha\beta} - \frac{h_x f_x}{h_x}\right) \tag{2.104}$$

Where the first term is what would be $\Delta_\alpha f_x$ if x_α were a constant, and

$$f_\alpha h_\alpha = \Sigma x_\beta h_{\alpha\beta} f_{\alpha\beta} \qquad (2.105)$$

and since $\Theta_{\alpha\beta}$ is a function of V_α^R and T_α^R

$$\Delta_\alpha \Theta_{\alpha\beta} = \left(\frac{\partial \Theta_{\alpha\beta}}{\partial T^R}\right)_{V^R} \cdot \Delta_\alpha T^R + \left(\frac{\partial \Theta_{\alpha\beta}}{\partial V^R}\right)_{T^R} \cdot \Delta_\alpha V^R \qquad (2.106)$$

The partial derivatives in (2.106) are given in equations (2.51) - (2.54).

An iterative procedure must be followed to evaluate $\Delta_\alpha h_x$ and $\Delta_\alpha f_x$. First h_α and $h_\alpha f_\alpha$ - (2.100) and (2.105) respectively and $\partial\Theta_{\alpha\beta}/\partial T^R$ etc (2.51 - 2.54) are calculated. Then $\Delta_\alpha h_x$ and $\Delta_\alpha f_x$ are assumed equal to 2 ($h_\alpha - h_x$) and $2f_x$ $(f_\alpha h_\alpha / h_x f_x - h_\alpha / h_x)$ respectively, $\Delta_\alpha \Theta_{\alpha\beta}$ and $\Delta_\alpha \phi_{\alpha\beta}$ both equal to 0., and all these are substituted into (2.102) and (2.103). Next equations (2.101) and (2.106) are solved, followed by (2.99) and (2.104) for $\Delta_\alpha h_x$ and $\Delta_\alpha f_x$. These are compared with the values assumed in equation (2.102) and (2.103), and whether or not they are satisfactorily close, so the iterations continue.

4. Calculation of Vapour-Liquid Equilibria

In a multicomponent system of N components, and two phases, there will be 2N variables, made up of (2N-1) mole fractions, temperature and pressure. The phase rule states :

F	+	P	=	C	+	2
Degrees of freedom		no. of phases		no. of compts.		

Substituting C = N and P = 2, we have F = N. Thus by fixing, say pressure and the composition of one phase, the composition of the other and the temperature may be calculated. Other combinations of the variables are possible :

Fixed (deg. of freedom)	Calculated
$P, y_1, y_2, \ldots\ldots y_{N-1}$	$T, x_1, x_2 \ldots\ldots x_{N-1}$
$P, x_1, x_2, \ldots\ldots x_{N-1}$	$T, y_1, y_2 \ldots\ldots y_{N-1}$
$T, y_1, y_2, \ldots\ldots y_{N-1}$	$P, x_1, x_2 \ldots\ldots x_{N-1}$
$T, x_1, x_2, \ldots\ldots x_{N-1}$	$P, y_1, y_2 \ldots\ldots y_{N-1}$

In the case of a flash, there is one independent phase : thus there will be (N+1) degrees of freedom - i.e. temperature, pressure and the composition of that phase. The composition of the phases that result from the flash can be calculated from those data.

A flash is the separation of a single phase into two phases by a sudden change in temperature or pressure. For a 2 component system, shown in Fig 2, at a flash pressure P_F, and a fixed temperature, the mixture containing mole fraction q_A of component A will "flash" into two phases containing x_A in the liquid phase and y_A in the vapour phase. Point F cannot be outside the region bounded by the dew and bubble point lines, if a flash is to occur - as study of equation (2.109) in Section 2.5 will show.

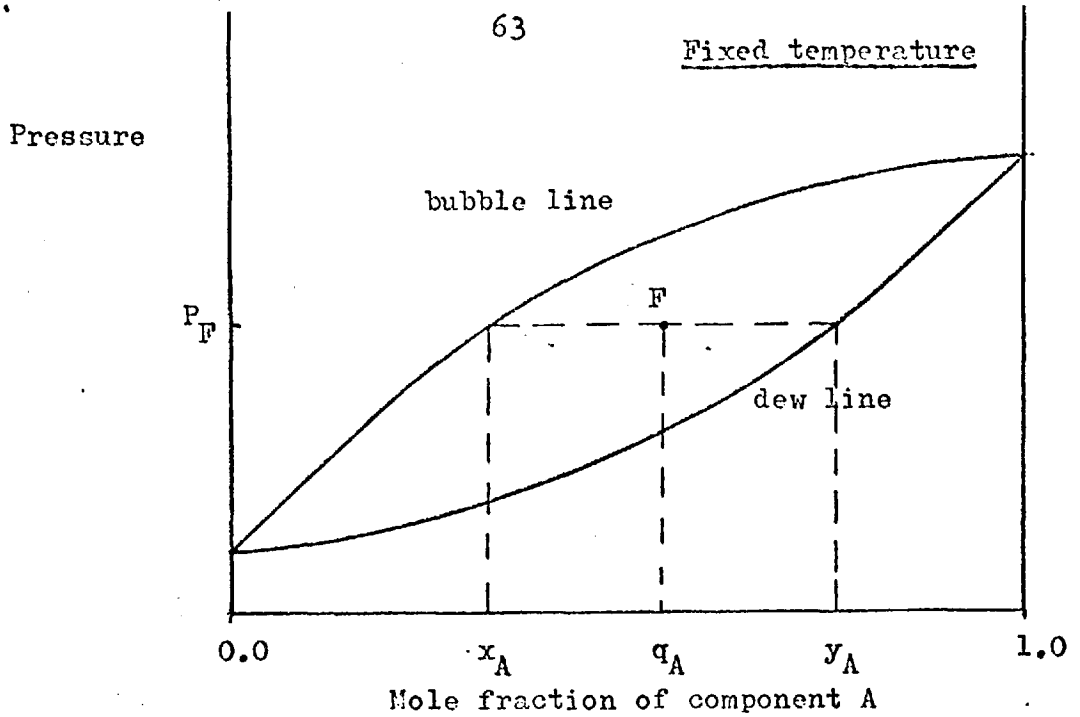


Fig 2. Flash seperation of a two component system.

Calculation of Saturation Equilibrium

The chemical potential is calculated, at the fixed temperature (or pressure) and composition y say, using a guess for the pressure (or temperature) respectively. Using a set of guessed mole fractions for the other phase x say, one can calculate for each component :

$$\left\{ \ln\left(\frac{f_i}{P}\right) - \ln\left(\frac{f_o}{P}\right) - \frac{U_o}{RT_o}\cdot\frac{\Delta f_x}{f_x} - \frac{(Z_o-1)}{h_x}\cdot\Delta h_x \right\} \quad (2.107)$$

and this should equal ln x_i (2187). By comparing these x_i with the set of x_i assumed to calculate (2.107) above, an iterative procedure can be used to converge on a set of x. The additional requirement for equilibrium is that Σx must equal 1.0.
If Σx is not 1.0, then the assumed temperature (or pressure) is not correct, and a further iterative loop of calculations is necessary.

By adjusting temperature or pressure until Σx is both constant on successive iterations and equal to 1.0, the saturation points in the phase diagram can be determined. The secant method has been found to be a satisfactory method to adjust temperature or pressure.

The Secant Method

Fig. 3 shows an arbitrary function, F(T) plotted against temperature T. Two points, 1 and 2, are determined by calculation and the line joining them is extrapolated to point 3 where it cuts the abscissa.

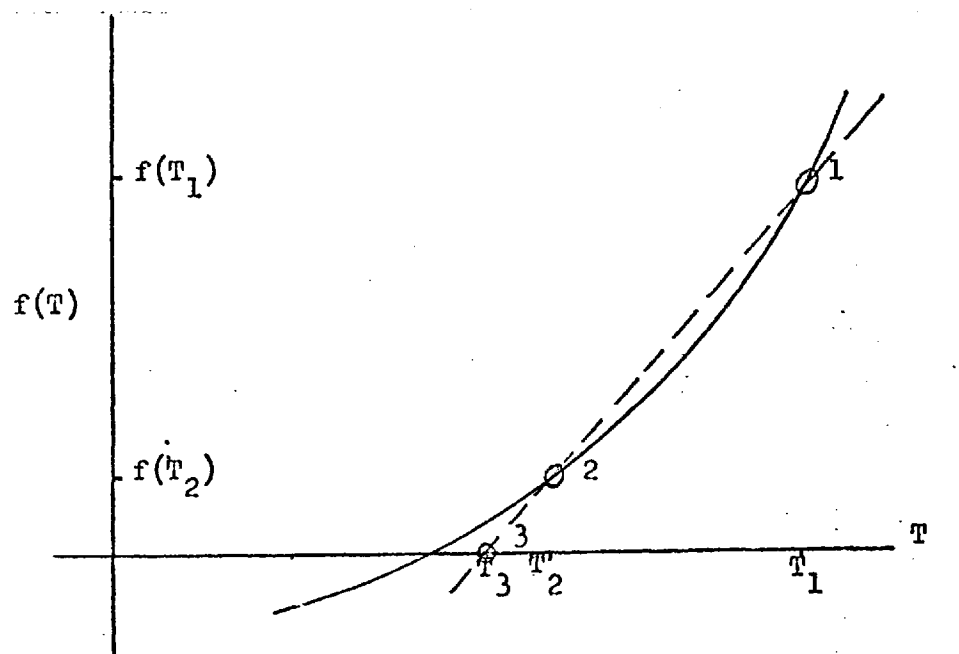


Fig 3. The secant method of convergence.

The temperature at 3, T_3, can be calculated from :

Slope of line 1 - 2 = slope of line 2 - 3

which is

$$\frac{F(T_1) - F(T_2)}{T_1 - T_2} = \frac{F(T_2) - 0}{T_2 - T_3}$$

Rearranging

$$T_3 = T_2 - \frac{F(T_2)(T_1 - T_2)}{F(T_1) - F(T_2)}$$

or in more general terms

$$T_n = T_{n-1} - \frac{F(T_{n-1})(T_{n-2} - T_{n-1})}{F(T_{n-2}) - F(T_{n-1})}$$

Hence $F(T_3)$, $F(T_4)$ ..... can be calculated successively until $F(T_n)$ is close enough to zero. In this case F(T) could be $(\Sigma x - 1)$ or $(\Sigma y - 1)$.

Adjustment of the Acentric Factor

Although the vapour pressure curves of hydrocarbon and various other compounds are very similar, the expression (1.11) for ω is only exactly true at a reduced temperature of 0.7. The use of ω as defined by Pitzer therefore introduces slight inconsistencies into the calculation of vapour-liquid equilibrium. So, adjustment of ω using accurate vapour pressure data has been tried.

(a) Using Pitzer's own Method

In their paper Pitzer and Curl (3) give tabulated values of $\log P_o^R$ and $(d \log P_o^R/d\omega)$ in the expression

$$\omega = \frac{\log P_R - \log P_o^R}{\left(\frac{\partial \log P_o^R}{\partial \omega}\right)} \qquad (2.126)$$

Vapour pressure data is used to calculate P_o^R. This method gives better results for vapour liquid equilibrium calculations than those using ω defined at 0.7, but since it is based on generalised vapour pressure curves, it does not exactly reproduce the real vapour pressures.

(b) Extrapolation method

The bubble point or bubble pressure is calculated twice for a set of mixtures which each contain, in turn 95% and then 97.5% of a particular component. The first time ω is the value given by Pitzer, and then for the second time, ω is increased by 10%.

It is assumed that mole fractions vary linearly with temperature or pressure at concentrations close to unity. So, by extrapolation, pressure or temperature at a mole fraction of 1.0 can be found. Fig. 4 shows how ω varies with pressure or temperature. This too, is assumed to be a straight line relationship. By extrapolation to the vapour pressure or temperature, an acentric factor which will exactly reproduce this saturation data can be determined.

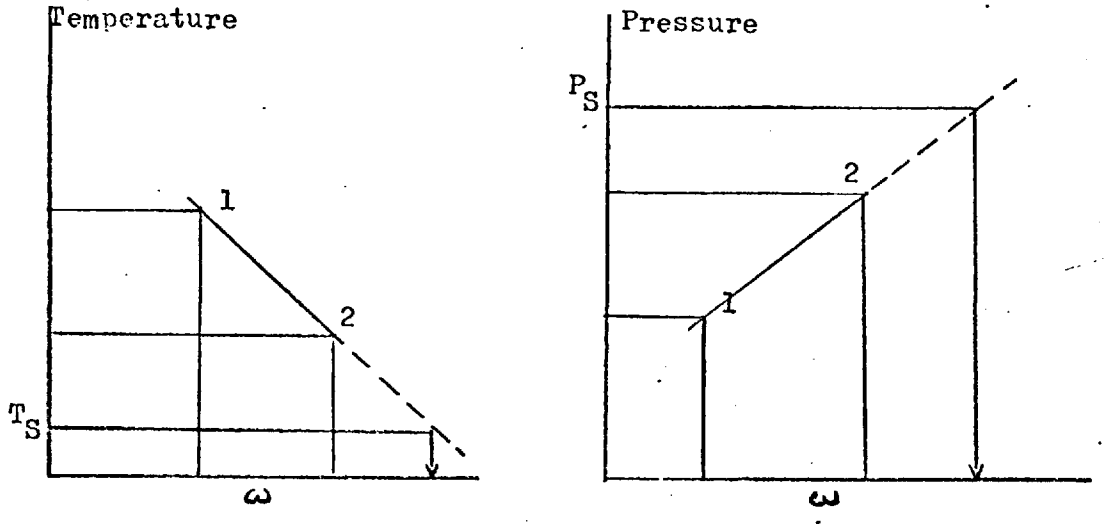


Fig 4. Variation of ω with temperature or pressure.

(1) calculations using Pitzer's ω

(2) calculations using Pitzer's ω increased by 10%.

5. Flash separation

For a flash separation, the calculation of equilibrium follows a similar procedure to that for the saturation points.

Consider the mass balance over the flash system shown in Fig. 5 below.

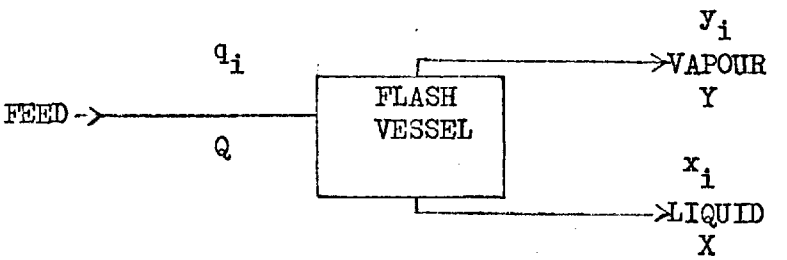


Fig 5.

Q, X, Y are total molar flows; q, x, y are mole fractions.

Writing the mass balances:

for component i $\quad q_i Q = y_i Y + x_i X$

for total flows $\quad Q + Y + X$

Let $y_i/x_i = K_i$ and $Y/Q = V$

then
$$x_i = \frac{q_i}{K_i V + (1 - V)} \qquad (2.108)$$

or
$$V = \frac{q_i - x_i}{y_i - x_i} \qquad (2.109)$$

This last equation (2.109) is a useful test for the consistency of flash results, since it must apply equally to all components.

By guessing the composition of one phase and calculating the composition of the other, at a particular vapour fraction V, constant K-values can be found. However the sum of the calculated mole fractions must equal 1.0, and this will only be true when V is correct - i.e.

$$\Sigma y = 1 = \Sigma x \qquad \text{or} \quad \Sigma x - \Sigma y = 0 \qquad (2.110)$$

An iterative procedure enveloping the one to determine the K values is necessary to converge on a solution for V satisfying (2.110). In this work the convergence procedure described by Rohl and Sudall (19) is used, known as the Richmond method.

The Richmond method

Searching for the value of V which makes F(V)=0, at the (n + 1)th iteration,

$$V_{n+1} = V_n - \frac{2F(V_n).\ F'(V_n)}{2(F'(V_n))^2 - F(V_n).F''(V_n)} \qquad (2.111)$$

If the ratio V is correct, equation (2.110) will be true. The Richmond method of convergence has been shown to be faster than the Newton-Raphson method, despite the extra computation involved (19). Taking equation (2.110) and substituting (2.108) into it,

$$\Sigma\left\{\frac{K_i q_i}{K_i V + (1-V)}\right\} - \Sigma\left\{\frac{q_i}{K_i V + (1-V)}\right\} = 0$$

Combining these,

$$\Sigma\left(\frac{(K_i - 1)q_i}{K_i V + (1-V)}\right) = 0 \qquad (2.112)$$

Equation (2.112) is now the function of V_n ($F(V_n)$) in (2.111) and

$$F'(V_n) = -\sum\left(\frac{(K_i - 1)^2 q_i}{((K_i - 1)V + 1)^2}\right) \qquad (2.113)$$

and

$$F''(V_n) = 2 \cdot \sum\left(\frac{(K_i - 1)^3 q_i}{((K_i - 1)V + 1)^3}\right) \qquad (2.114)$$

Estimation of Initial Values for K and V

Many workers (21, 23, 29) developing computed programs for flash separations use an initial value of 1.0 for all K_i and 0.5 for V. This procedure was followed at first in this work, but subsequently refinements were introduced.

Raoult's law can be written.

$$P = p_1x_1 + p_2x_2 + \ldots\ldots$$

where p_1, p_2 ..... are vapour pressures of components 1, 2 .....
Dalton's law states : $y_1P = P_1$, $y_2P = P_2$ etc.

where P_1, P_2 .... are partial pressures. Combining these two laws we have

$$y_1 = \frac{P_1x_1}{P}, \quad y_2 = \frac{P_2x_2}{P} \quad \text{etc.}$$

Since $K_1 = y_1/x_1$, an initial set of K can be based on the ratio of the vapour pressure, at the fixed flash temperature, and the fixed total pressure.

When the flash conditions are supercritical for any particular component a further expedient is necessary. The vapour pressure curve is extrapolated and a pseudo-vapour pressure is used.

An initial value for V is based on the fact that a plot of V vs temperature for any mixture has approximately the shape shown in Fig 6. This can be expressed as

$$V \quad \left(\frac{T - T_{Dew}}{T_{Bubble} - T_{Dew}} \right)^{0.25}$$

In some cases this method is not so useful and V = 0.5 is used instead.

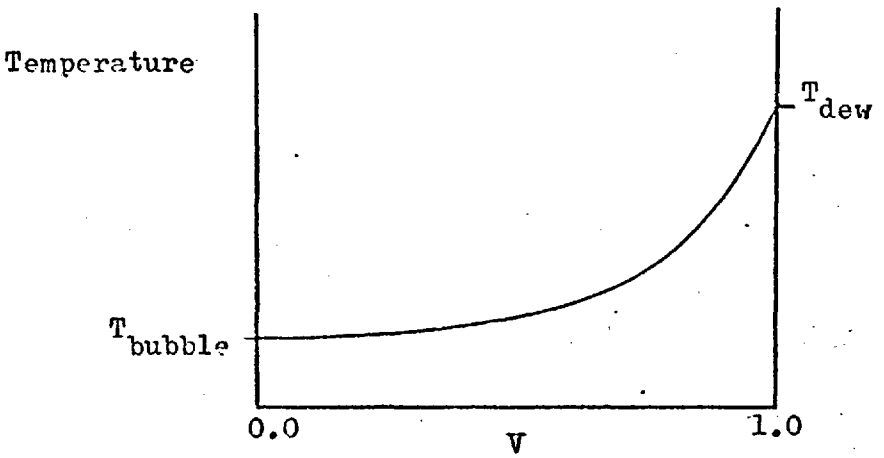


Fig 6. Approximate shape of a flash curve from dew to bubble point.

6. Partial Molal Enthalpies

The partial molal enthalpy of a component i in a mixture is defined by

$$\left\{ \frac{\partial H}{\partial n_i} (P,T,x) \right\}_{T,P,n_j (j \neq i)} = \bar{h}_i (P,T,x) \qquad (2.115)$$

The relationships between partial properties are the same as those between total properties, so that where,

$$G = H - TS \qquad (2.116)$$

for component i

$$\mu_i = \bar{h}_i - T\bar{s}_i$$

Also $$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,x} = -\bar{s}_i \qquad (2.117)$$

so that substituting (2.117) into (2.116) we have

$$\mu_i = \bar{h}_i + T\left(\frac{\partial \mu_i}{\partial T}\right)_{P,x} \qquad (2.118)$$

For a perfect gas,

$$\mu_i^{p.g.} = \bar{h}_i^{pg} + T\left(\frac{\partial \mu_i^{p.g.}}{\partial T}\right)_{P,x}$$

and from the definition of chemical potential, for a perfect gas

$$\mu_i^{p.g.} = RT\ln(Px) + \theta$$

θ here is a function of temperature.

$$\therefore \left(\frac{\partial \mu^{pg}}{\partial T}\right) = R\ln(Px) + \frac{d\theta}{dT}$$

and hence $$\bar{h}_i^{pg} = \theta - \frac{d\theta}{dT}$$

For a real gas $$\mu_i = RT\ln \mathfrak{F}_i + \theta$$

and $$\left(\frac{\partial \mu_i}{\partial T}\right) = RT\frac{\partial \ln \mathfrak{F}_i}{\partial T} + R\ln \mathfrak{F}_i + \frac{d\theta}{dT}$$

so that by substituting into (2.118)

$$\bar{h}_i = \bar{h}_i^{pg} - RT^2\left(\frac{\partial \ln \mathfrak{F}_i}{\partial T}\right) \qquad (2.119)$$

Residual partial molal enthalpies can be computed from (2.119). Analytical differentiation of (2.87) for $(\partial \ln \mathfrak{F}/\partial T)$ involves very complicated terms for the operator Δ, and so differentiation by finite differences was used instead. The interval was 1.0 K.

It is only possible to calculate residual partial molal enthalpies because h_i^{pg} is unknown; although $\Sigma x h^{pg} = RT$. Consistency of the computation of enthalpy can be tested by comparing the residual configurational enthalpy, $(H_{mix} - 1)RT$ from equation (2.38) and $\Sigma x(-RT^2 \partial \ln \mathfrak{F}/\partial T)$ from equation (2.119). They should be the same for each phase of the flash separation. Results are shown in Section 4.

Retrograde behaviour of Multicomponent mixtures

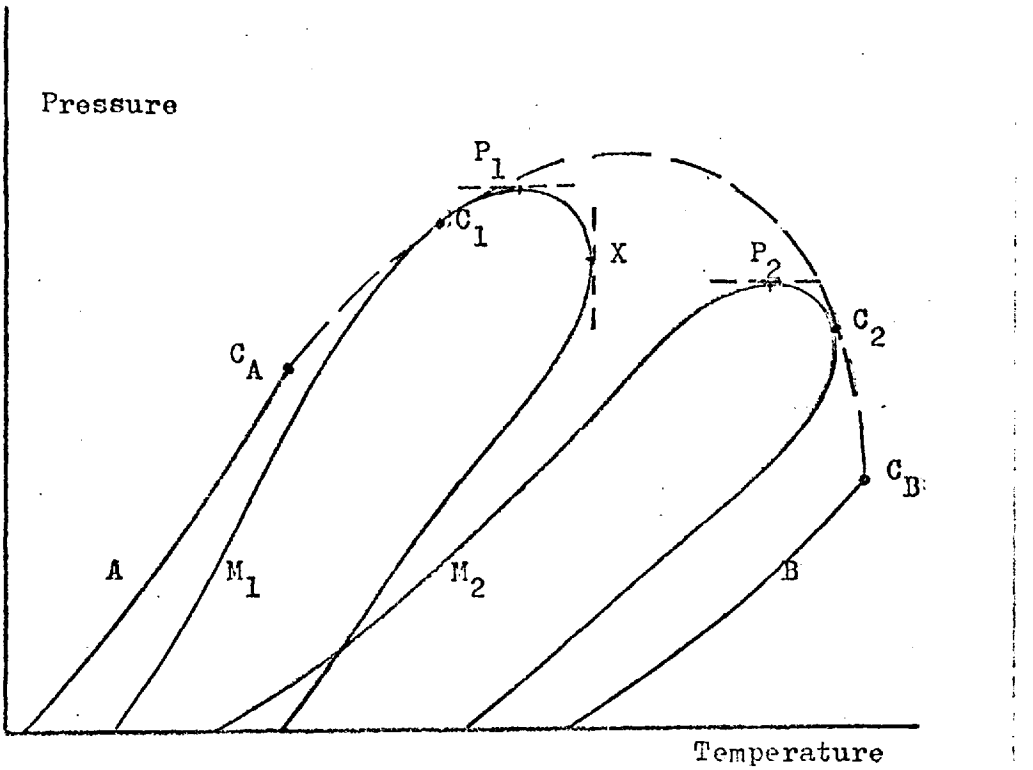


Fig 7. Retrograde behaviour of a multicomponent system.

The phenomenon of retrograde behaviour imposes limits on the extent of the calculations. Fig 7 shows the phase diagram for a two-component mixture. In the figure the vapour pressure curves of A and B are shown, ending at their critical points C_A, C_B respectively, and the line joining these points, through C_1 and C_2 is the critical locus. C_1 is the critical point for mixture 1 and C_2 is the critical point of mixture 2. P_1 and P_2 are the points of maximum pressure for H_1 and H_2. The right hand side of each loop, up to the critical point is the bubble point curve and the left hand side is the dew point curve. On line M_1, the part P_1X shows the phenomenon of retrograde condensation - increasing temperature with decreasing pressure.

Similarly on line M_2, the part P_2C_2 shows retrograde behaviour on the bubble point line. Apart from the disadvantages this phenomenon brings to industrial processes, it means the reduced temperatures (or pressures) are greater than 1.0. This imposes difficulties on the liquid phase integrations due to the nature of equation (2.64). Apart from this, if the initial guesses for composition are sufficiently good, and the reduced temperature or pressure are not too close to 1.0, the calculations will proceed.

7. Joule-Thomson coefficients

Suppose a gas at a temperature and pressure P_1, T_1 is allowed to move through a porous plug to a region of lower pressure P_2; this region will have a temperature of T_2. The temperature T_2 might be greater or less than T_1. This change of state is called the Joule-Thomson effect. In an industrial context, this is known as throttling, and the porous plug is actually a valve or pressure reducer. The conditions of throttling are such that pressure and volume changes are small and the whole process is kept at adiabatic conditions.

Thus we can say that the Joule-Thomson process occurs at constant enthalpy.

Since H^t is a function of temperature and pressure,

$$dH^t = \left\{\frac{\partial H^t}{\partial T}\right\}_P . dT + \left\{\frac{\partial H^t}{\partial P}\right\}_T . dP$$

and since the enthalpy is constant, i.e. $\Delta H = 0$

$$\left\{\frac{\partial H^t}{\partial T}\right\}_P .dT = \left\{\frac{\partial H^t}{\partial P}\right\}_T .dP$$

Using the Maxwell relationship

$$-\left(\frac{\partial H^t}{\partial P}\right)_T \cdot \left(\frac{\partial H^t}{\partial T}\right)_P = \left(\frac{\partial T}{\partial P}\right)_H$$

we have

$$\frac{dT}{dP} = \left(\frac{\partial T}{\partial P}\right)_H = -\frac{\left(\partial H^t/\partial P\right)_T}{\left(\partial H^t/\partial T\right)_P} = \eta \qquad (2.120$$

which is the definition of the adiabatic Joule-Thomson coefficient.

Computation of η

In equation (2.120), H^t is the total enthalpy. This may be separated into two parts; the configurational enthalpy and the molecular enthalpy.

$$H^t = H + H^{mol} \qquad (2.121)$$

Taking reasonably small increments for temperature and pressure we may write (2.120)as

$$\eta = -\frac{(H^t[P_2,T_1] - H^t[P_1,T_1])/\Delta P}{(H^t[P_1,T_2] - H^t[P_1,T_1])/\Delta T} \qquad (2.121)$$

and the partial differentials in (2.120) can be evaluated directly. Taking the numerator of (2.122), at temperature T_1

$$\frac{(H[P_2] - H[P_1] + H^{mol}[P_2] - H^{mol}[P_1])}{\Delta P} \qquad (2.123)$$

where $\Delta P = P_2 - P_1$

Molecular properties are a function of temperature only, so that $H^{mol}[P_2] = H^{mol}[P_1]$. Therefore equation (2.123) reduces to

$$(H[P_2] - H[P_1])/\Delta P \qquad (2.124)$$

The denominator of (2.122) at pressure P_1 can be written

$$(H\ T_2 - H\ T_1 + H^{mol}\ T_2 - H^{mol}\ T_1)/\Delta T \qquad (2.125)$$

where $$\Delta T = T_2 - T_1$$

Now $$\Delta H^{mol} = \left(\frac{\partial H^{mol}}{\partial T}\right)_p \cdot \Delta T$$

and $$\left(\frac{\partial H^{mol}}{\partial T}\right)_p = C_p^{mol}$$

From the division of total free energy into configurational and molecular parts, we have

$$C_p^t = C_p + C_p^{mol}$$

For a perfect gas $H = RT$ and therefore $C_p = R$ and $C_p^{mol} = C_p - R$ (2.126)

Substituting (2.126) into (2.125) we now have

$$((H[T_2] - H[T_1]) + (C_p^{mol} - R).\Delta T)/\Delta T \qquad (2.127)$$

η can now be calculated from equations (2.123) and (2.127).

Isothermal Joule-Thomson coefficient φ

The term $(\partial H/\partial P)_T$ is the definition of the isothermal Joule-Thomson coefficient φ. From (2.120)

$$\varphi = -\eta\left(\frac{\partial H^t}{\partial T}\right)_p \qquad (2.128)$$

or $$\varphi = \eta . C_p^t$$

Equation (2.128) can be transformed, using the basic relationship

$$dH^t = TdS^t + Vdp$$

into $$\varphi = -\frac{RT^2}{P}.\frac{(\partial Z)}{(\partial T)_p} \qquad (2.129)$$

Equation (2.129) could be used as a measure of the deviation of a gas from the ideal gas behaviour.

Computation of φ

To evaluate φ, the same approach as for η is used.

$$\left(\frac{\partial H}{\partial P}\right)_T = \frac{\Delta H}{\Delta P}$$

$$\therefore \quad \varphi = \frac{(H[P_1,T_1] - H[P_2,T_1])}{\Delta P} \qquad (2.130)$$

H^{mol} has been eliminated because this is a constant temperature process.

Section 3

Description of Programs developed in this work.

Section 3

Program Descriptions

Four main programs have been developed.

1. Calculation of compressibility factors and enthalpies.
2. Calculation of vapour-liquid equilibria.
3. Calculation of isothermal flash separation.
4. Calculation of adiabatic and isothermal Joule-Thomson coefficients.

It will be seen from the description of the theory in Section 2 that these programs will have much in common. All four programs calculate Z_o and U_o in the same way, and the following subroutines are common to all.

1. Subroutine THEPHI to calculate $\Theta, \phi, h_x, h_x f_x$.
2. Subroutine DIFFER to calculate the differentials of fx and hx with respect to temperature.
3. Subroutine LIQ to calculate Z_o and U_o for the liquid phase.
4. Subroutine ZEDU to calculate Z_o and U_o for the vapour phase.

and in common for programs 3 and 4 above, subroutine DELTA, to calculate Δf_x and Δh_x.

The original program to calculate Z_o and U_o and enthalpy was one based on the program PROPERTY written by Leach (8), and which was modified to use the f and h convention for the corresponding states parameters by Watson (10).

1. Program to calculate compressibility factors, internal energies and enthalpies.

This program will calculate these properties either for a mixture or for a pure substance, using either the 1-fluid or a 2-fluid model to describe the mixture. However, the 2-fluid model cannot be used for a pure substance - for obvious reasons.

The data which must be supplied for the calculation of Z, U and H are :

1. The pressure and temperature, and the volume if known. The units of pressure and volume are identified by using the following code.

	Volume		Pressure
1	g/cm^3	1	psia
2	mol/l	2	atm
3	amagat density	3	bars
4	cm^3/g	4	Kg/cm^2
5	V amagat	5	P amagat
6	mol/cm^3		
7	cu ft/lb		
0	volume not in the data		

2. Critical constants for each component:

critical volume in cc/mol

critical temperature K

acentric factor

critical compressibility

3. A set of ξ for unlike pair interactions.
   The factors are listed in various sources (2, 11, 12), or obtained in the course of this work.

4. A set of mole fractions for the composition of the mixture.

All volume and pressure data are converted to atmospheres and cm^3/mol and the set of ξ are rearranged to an array containing 1.0 for all ξ_{ii} . f^*_{ii} and h^*_{ii} (1.8) are calculated using the critical constants, and h_x, $h_x f_x$ are determined from these. The titles are printed out and calculation for Z begins. An initial value for the reduced volume is calculated from

$$V_o^R = \frac{RT}{PV}c \qquad (3.1)$$

and arrays of T_i^R and V_i^R are set up for the calculation of shape factors (1.17) and (1.18). The logical variable DONE remains FALSE until the three outer iterations on reduced volume are complete, and then it is changed to TRUE. The shape factors and h_x and $h_x f_x$ are calculated in subroutine THEPHI. The counter NUMBER counts the outer iterations on reduced volume and the counter NCONV counts the iterations on V_o^R using the Newton-Raphson technique (which ignores shape factor dependence on reduced volume).

In the first iteration, if the reduced temperature is less than 1.0 the phase is established by calculation of the vapour pressure at T_o and comparing it (as P_o^R) with the actual reduced pressure P_A^R.

This decides whether the compressibility factor shall be calculated using subroutine LIQ (Tait equation of state) or with subroutine ZEDU (Vennix equation of state). In the case of the 2-fluid model it is also necessary to check that all components are in the same phase. In the first iteration, the variable PHASE is set .FALSE. for vapour and .TRUE. for a liquid, and another variable REGION is set 2 or 1 respectively. Then the vapour pressure of methane is calculated at T/f_{α} for each component and compared with P_A^R. Variable PHASE is not altered after the first iteration, but REGION is, showing which phase has been detected. At the first iteration the combinations are :

vapour: PHASE = .FALSE. and REGION = 2

liquid: PHASE = .TRUE. and REGION = 1

In following iterations any change in these combinations is detected and the run is abandoned.

When Z_o is calculated with the Vennix equation of state, the Newton-Raphson convergance procedure follows to improve the estimate of V^R. Not more than 5000 (NCONV) iterations are allowed, and the error between assumed V_o^R and calculated V_o^R is :

$$\text{ERROR} = \left\{ \frac{P_{calc}^R}{P_A^R} - 1 \right\} \times 100 \qquad (3.2)$$

For the calculation of internal energies and enthalpies to proceed this error must not be greater than 0.001.

Where Z_o is calculated using the Tait equation of state, the arguments T^R and V_o^R transferred from the main program to subroutine LIQ have to be adjusted slightly because the critical constants for methane used in the main program are different to those used in the development of the Tait equation. The factors are :

$$P^R_{Tait} = P^R_A \times 0.99848$$

$$T^R_{Tait} = T^R_o \times 0.99691$$

When Z_o has been calculated, the volume follows :

$$Vol = \sum_{n=1}^{n=N} \left(\frac{Z_n . R . T}{P} \right) X_n \qquad (3.3)$$

Where N is 1 for a 1-fluid model and is equal to the number of components for 2-fluid model, X_n is 1.0 for a 1-fluid model and equal to the mole fractions of the components for a 2-fluid model. T_i^R and V_i^R are recalculated with the best values of θ and ϕ (from the final iteration on V_o^R) and these are used to calculate the derivations of f_x and h_x with respect to temperature. The internal energy and enthalpy follow, (2.37) and (2.38) respectively. The results can now be printed and the program is ready for the next set of P-V-T data.

2. Program to calculate Joule-Thomson coefficients

To calculate the adiabatic coefficient η (2.123, 2.127) or the isothermal coefficient φ (2.130) the configurational enthalpy H is calculated at three (or two) sets of conditions. These are (T, P), (T + ΔT, P), (T, P + ΔP) for η and (T, P) and (T, P + ΔP) for φ . The enthalpies are calculated in the manner described in the preceding program.

The data required are as follows.

1. A list of the component identification numbers (see Appendix B) and the mole fraction of each.

2. The temperature and pressure and molar specific heat (for η) of the mixture. The molecular specific heat is calculated from

$$(C_P^{mol})^{mixture} = \sum x_i C_{P_i}^{mol}$$

3. A set of the unlike pair interaction parameters ξ .

4. The logical variable ADIAB set to .TRUE. for η and .FALSE. for φ .

The adiabatic coefficients are calculated and printed in the units K/atm. The results are converted to an alternative set of units, F/psia and are printed alongside those in K/atm.

Similarly for φ ; calculated in Cal/mol, they are converted to J/mol as well, and both are printed.

3. Program to calculate two-phase vapour-liquid equilibrium with adjustment to the acentric factor.

This program calculates the phase composition and temperature (or pressure) of either the liquid or the gas phase, given the composition of the other phase and pressure or temperature respectively. To distinguish within the program between the different types of calculation, an identifying number is assigned; this number is the logical variable WHICH.

WHICH	Calculation type
1	T, y from P, x
2	P, y from T, x
3	T, x from P, y
4	P, x from T, y

Vapour pressure data is required, so that the acentric factor ω can be adjusted. If WHICH is 1 or 3, the vapour temperature TEM (I) at fixed pressure must be given, or if WHICH is 2 or 4, the vapour pressure VP(I) at fixed temperature must be given. If the fixed temperature or pressure is super-critical, no saturation data can be supplied and the acentric factor will be unchanged throughout the calculation. This means it has the value calculated by Pitzer (3).

The counter NCONV is set to zero at the beginning of the calculation. NCONV counts the number of iterations on temperature or pressure. If it goes above fifty, the results computed so far are printed including a warning that this is not a complete calculation, and after that the program proceeds to the next set of data.

The pressure data are corrected to atms, according to the unit identifier PDIM.

PDIM =	1 means pressure data is	psia
	2	atm
	3	bars
	4	Kg/cm^2
	5	mm Hg

The first part of the equilibrium calculation is to reset the acentric factor. The fixed parameter (i.e. pressure or temperature) is checked for supercriticality against the critical data at the beginning of the program for each component. If it is supercritical, the logical variable SUPER (I) is set .TRUE., otherwise it stays .FALSE. Also, if ω is zero (Pitzer value) for any component, then SUPER (I) also becomes .TRUE.

At the beginning of the ω adjustment calculation, the logical variable SETW is set .FALSE. This means ω is not set completely yet, and so there is no adjustment made to temperature or pressure in the program.

Equilibrium calculations are done at two concentrations, for two values of ω for each component. The results are extrapolated back to a mole fraction of 1.0 for each ω to obtain a temperature (or pressure) in each case. A further extrapolation of ω against temperature or pressure gives an acentric factor at the fixed vapour temperature (TEM (I)) or pressure (VP (I)). The concentrations are $x_i = 0.975$, where $x_{j \neq i} = (1-x_i)/N$, and the first value of ω is that in DATAW (3), and the second value is (ω_{first} x 1.1).

After the acentric factor has been calculated - now called WNEW - the parameters in the program for calculation of vapour-liquid are set up. SETW becomes .TRUE., and GUESS and WHICH are reset to the values given in the input data.

The internal energy UMIX and enthalpy HMIX are calculated for the fixed phase at fixed temperature (or pressure) and the guess for pressure (or temperature). Note that if WHICH is 1 or 2 the fixed phase is liquid and Z_o and U_o are calculated using subroutine LIQ (Tait equation of state); if WHICH is 3 or 4 the fixed phase is vapour and the Z_o and U_o are calculated in subroutine ZEDU (Vennix equation of state). The terms Δh_x and Δf_x are calculated in subroutine DELTA, and thus μ/RT is calculated - equation (2.87). This establishes the fixed phase completely. Now using a guess for the composition of the other phase, and using equation (2.107), an improved estimate for the composition of this phase is obtained.

This set of compositions is used in a fresh calculation of equation (2.107), until the sum of the mole fractions is constant. When this is so, it is compared with 1.0 and if not within 0.0001, this means the temperature (or pressure) is not correct. It is adjusted by the secant method described in Section 2. The procedure now restarts and recalculates the fixed phase chemical potential at the new temperature (or pressure). This is continued until the sum of the mole fractions in the guessed phase is 1.0, and then results are printed.

Another program has been written which calculates vapour-liquid equilibrium, but without adjustment to the acentric factor. It is similar to the program described above, but for the calculations for ω adjustment.

4. Program to calculate a flash separation

This program is very similar to the foregoing program above for vapour-liquid equilibria.

The dewpoint and bubble point of the feed is calculated and a check is made that the feed temperature is within the range of the dew and bubble points. An initial value for the K ratio is computed using vapour pressures and the vapour-liquid ratio V is given an initial value.

Now using (2.87) for the liquid phase composition, the chemical potential for the liquid phase is calculated.

From this, the vapour phase composition is calculated (2.107) and this is compared with the K-value assumed - in the following way.

$$\left(\frac{y}{x_{ass}}\right) \quad : \quad \left(\frac{y\ calc}{x\ ass}\right) \qquad (3.4)$$

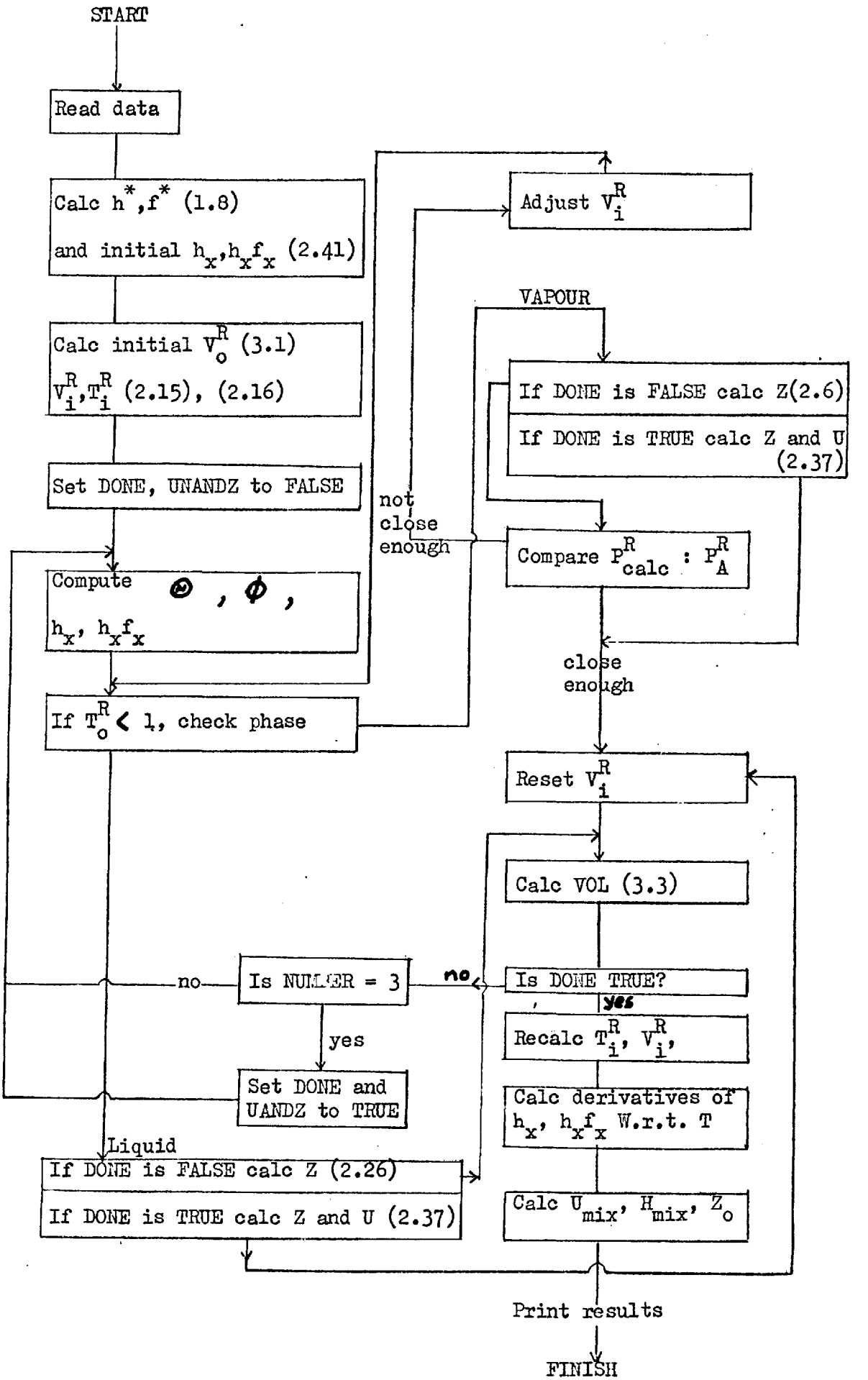
or $\quad K_{ass} \quad : \quad K\ calc$

$$\text{ERROR} = \sqrt{\frac{\Sigma (\Delta K)^2}{N}} \qquad (3.5)$$

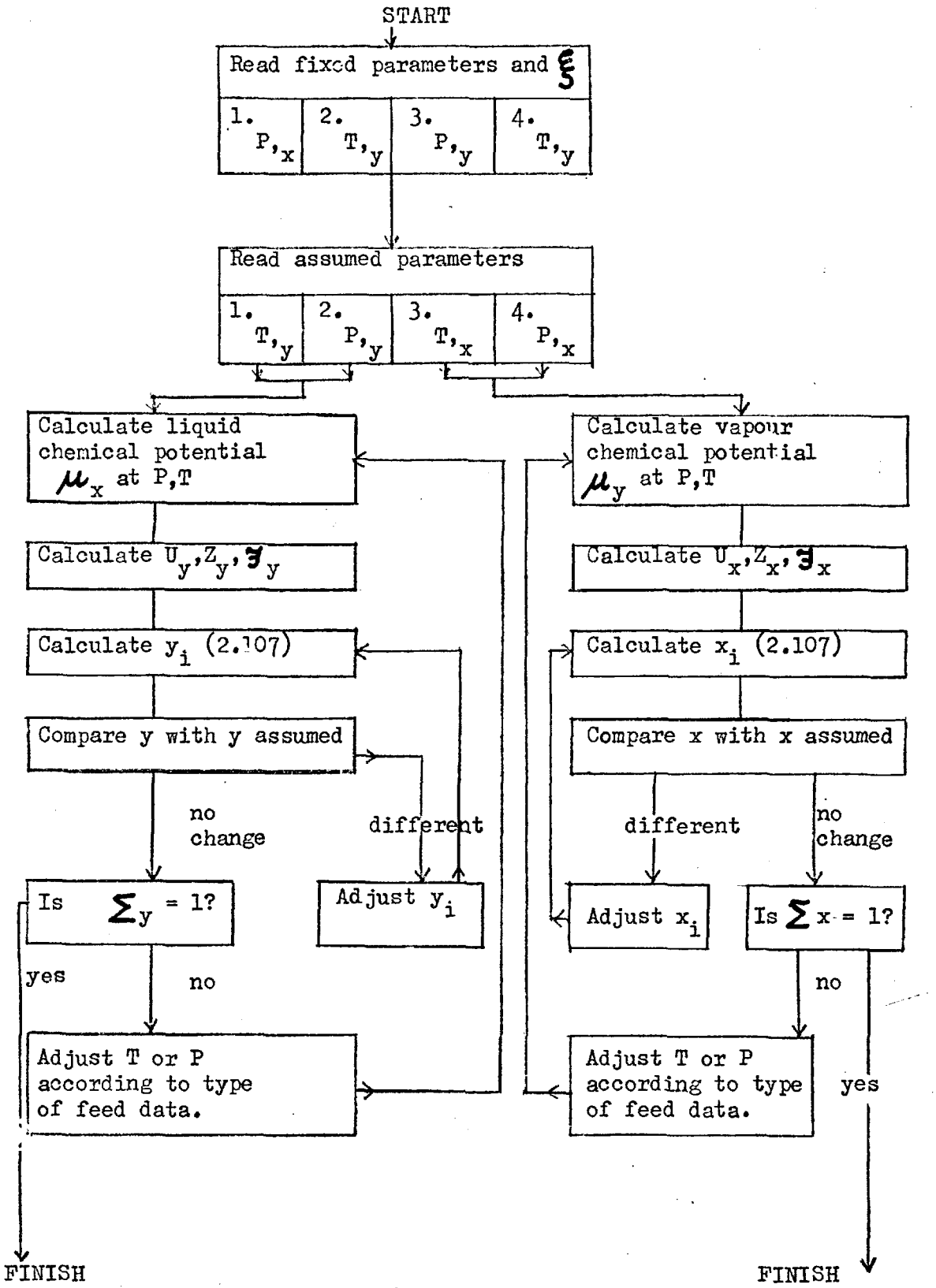
If this ERROR is greater than 0.001, the K ratio's are reset, and the chemical potentials are recalculated. If the error is less than 0.001, the vapour ratio V is adjusted by the Richmond method (2.111). When V is constant, the molar flow rates and enthalpies are calculated, and the results of the flash are printed.

The FORTRAN statements for these programs are to be found at the back of this thesis.

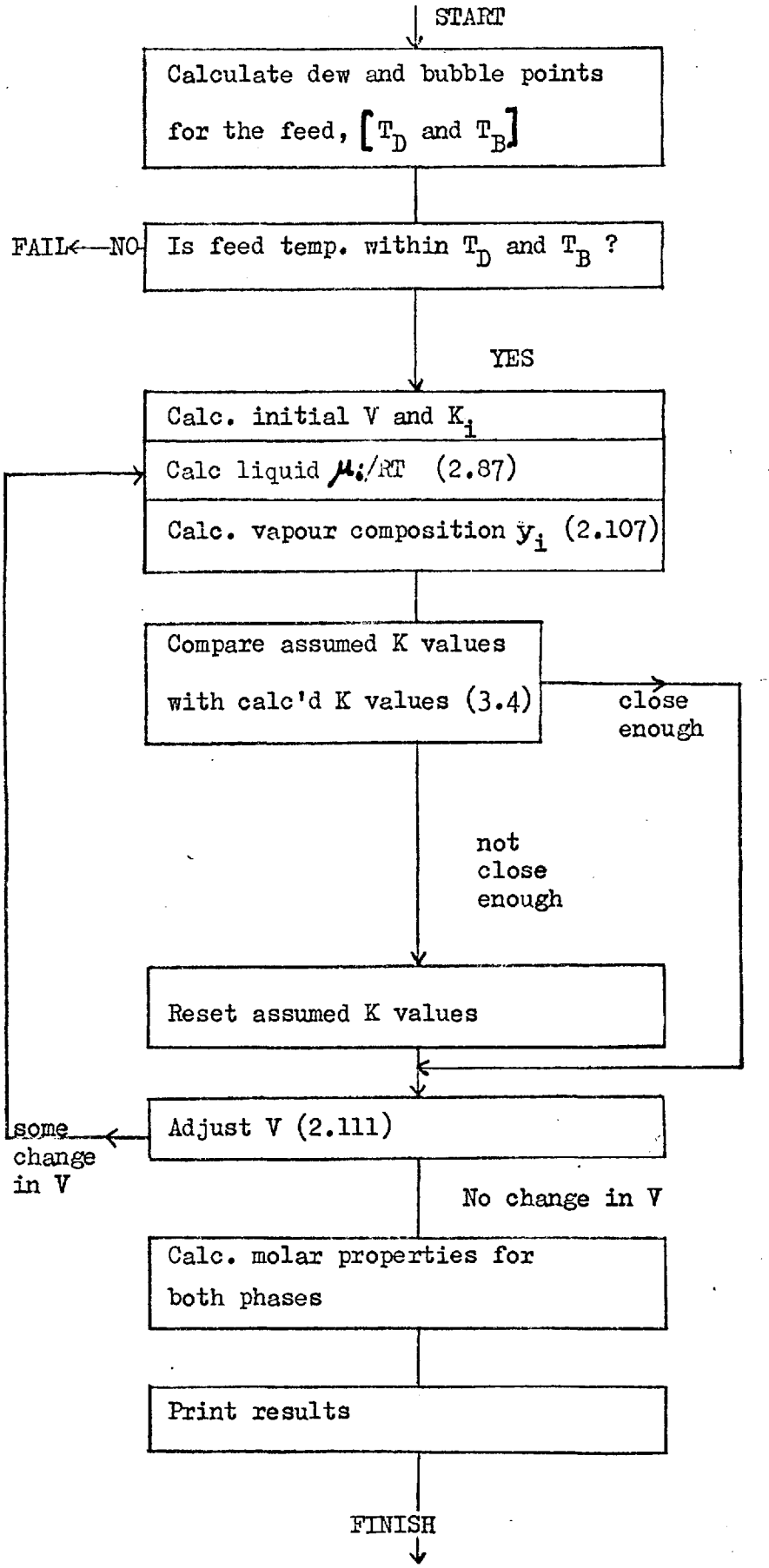
Flow diagram for the Computation of Z_o, U_{mix}, H_{mix}.



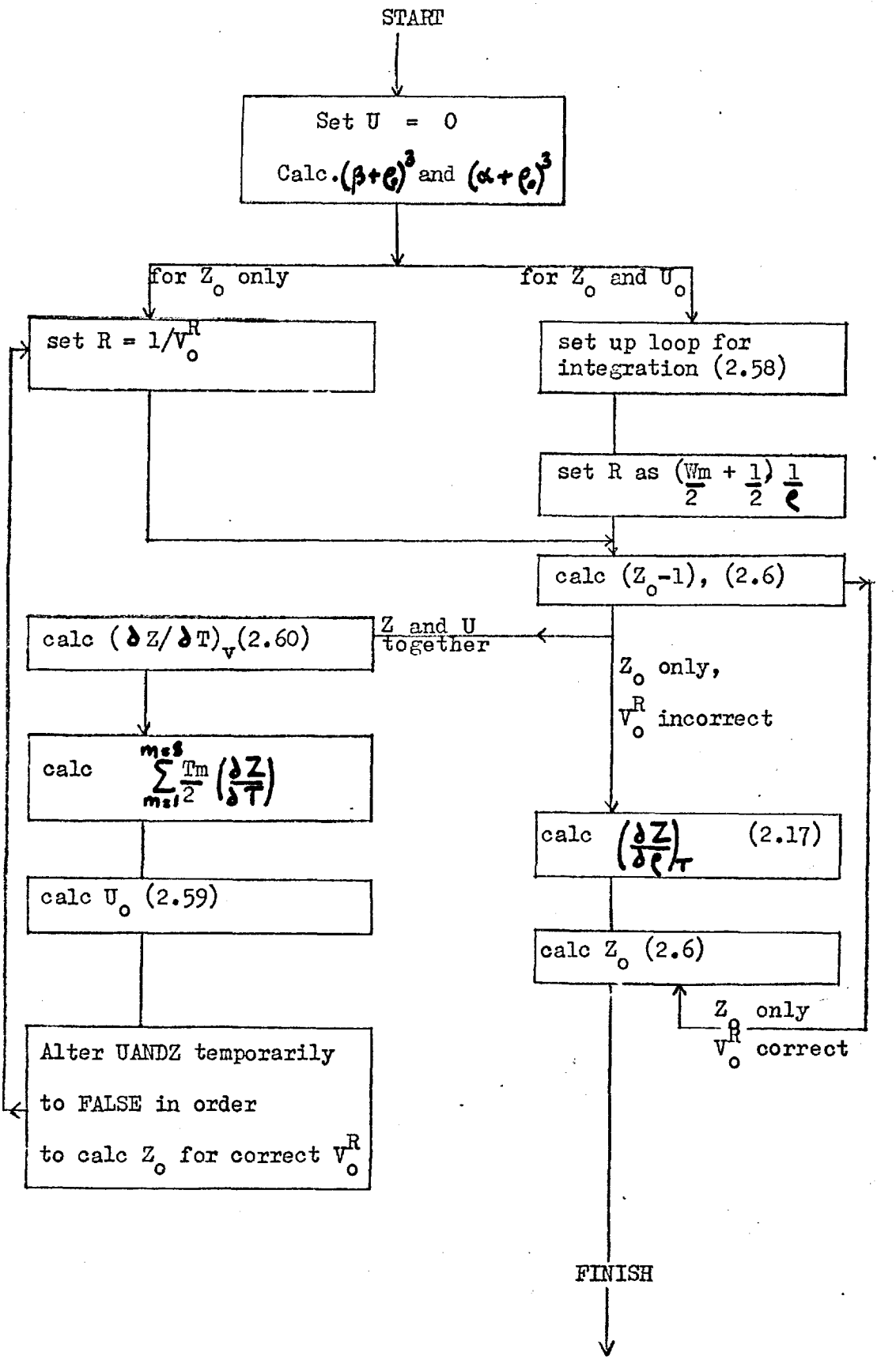
Flow diagram for dew and bubble calculations



Flow diagram for the Flash Program

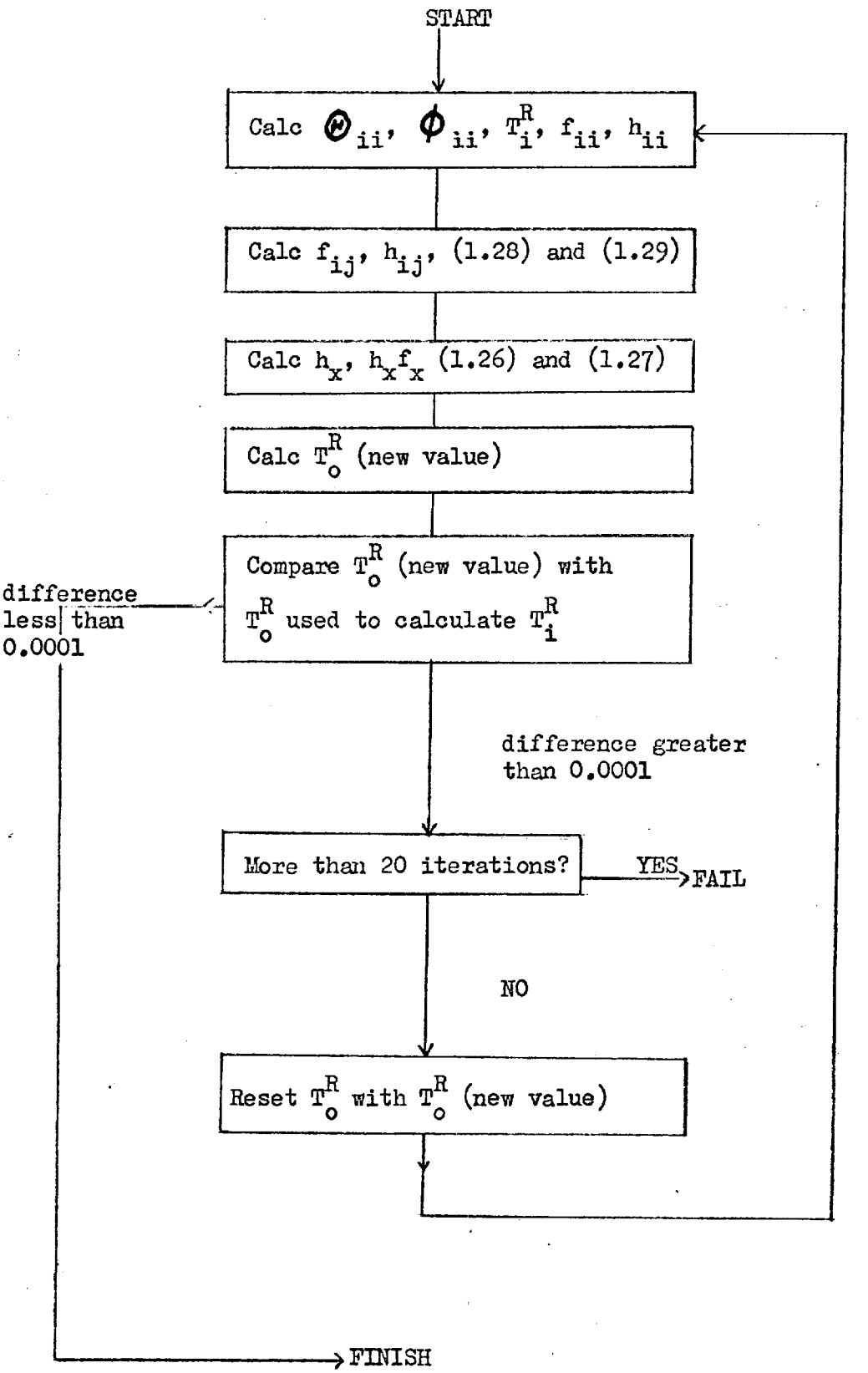


Flow diagram for subroutine ZEDU



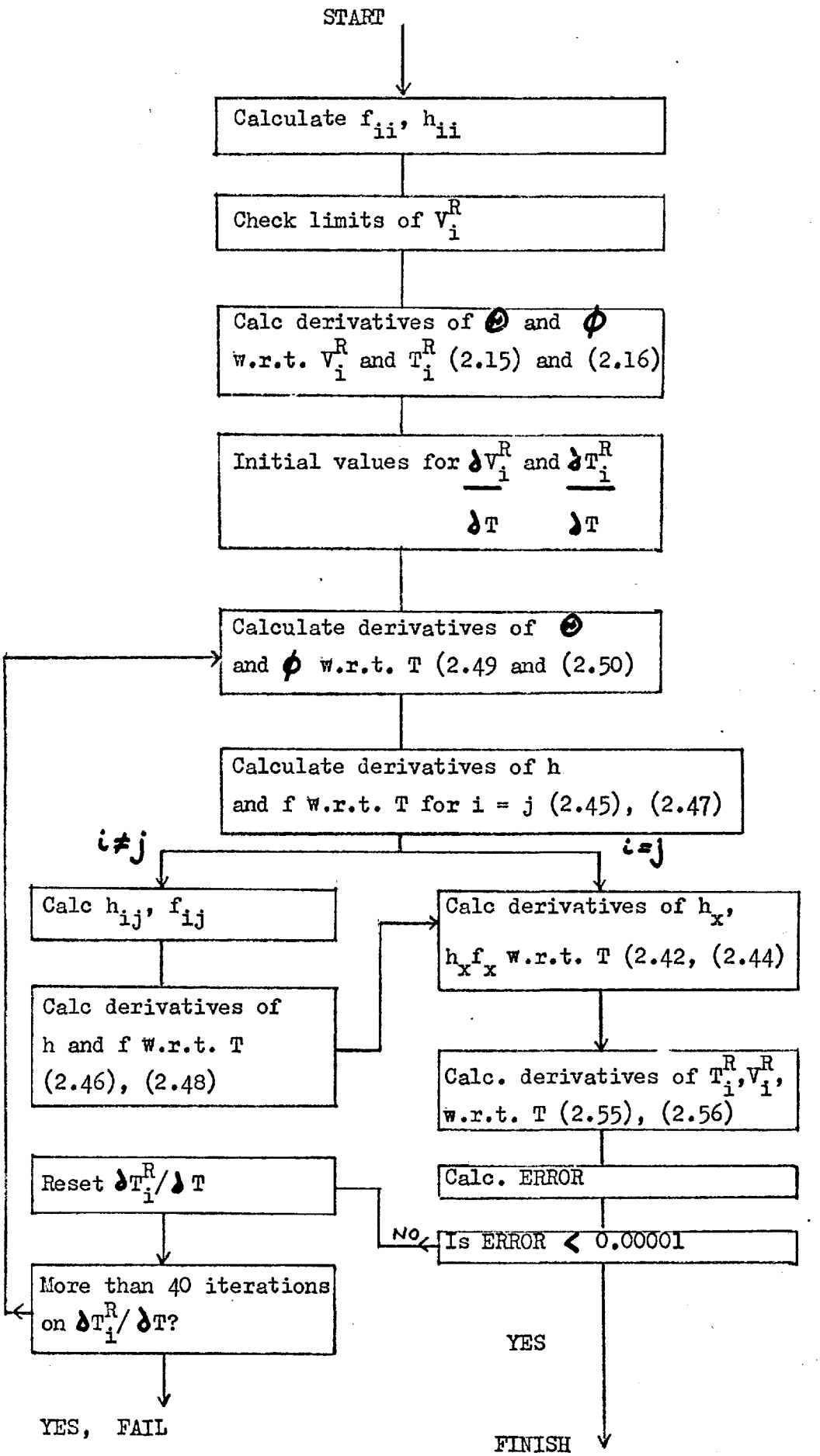
Flow diagram for subroutine THEPHI

1-fluid model



Flow diagram for subroutine DIFFER

1-fluid model



Section 4

Results

Section 4

Results

1. Compressibility factors

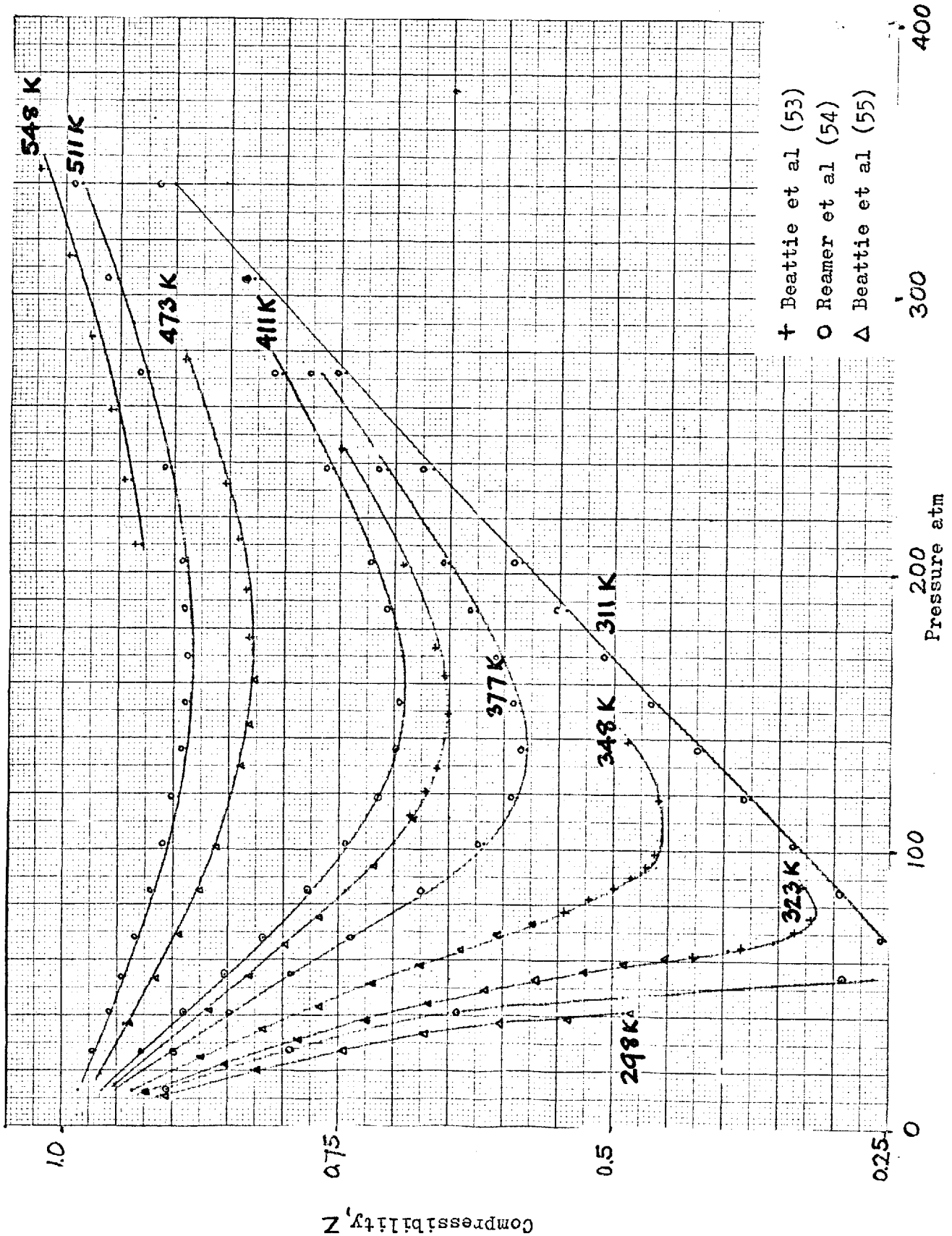
The compressibility factors for both gas and liquid phases were computed for eleven pure substances and four mixtures. It is hoped that these substances cover the range of applicability of the principle of corresponding states using the Vennix equation of state for methane as a reference substance.

1. Ethane

The compressibility factor Z was computed for ten isotherms from (298-548)K for a pressure range of (0-350)atm. This range of pressure and temperature is covered by the experimental work of Beattie et al (55, 53) and Reamer, Olds, Sage and Lacey (54). Together they give results at 18 temperatures. The first (55) covers (298-523)K and (11-192)atm, the next (53) covers (323-548) and (60-350)atm and the last (54) covers (310-511) and (13-408)atm. Fig 17 shows a plot of Z against pressure, with selected experimental results. The results of Beattie (53) and Reamer are consistently above computed results and those of Beattie et al (55) are consistently below.

Beattie and co-workers (53) state that this work is more reliable than their earlier work (55), especially where the isotherms meet - i.e. at a density of 5 moles/litre. Reamer et al, also claim their work to be an improvement on the early work of Beattie et al (55) and also on previous work by Sage, Webster and Lacey (114). This latter work disagreed with both Beattie's results by as much as 2%.

Fig 17. Ethane, compressibility factor.

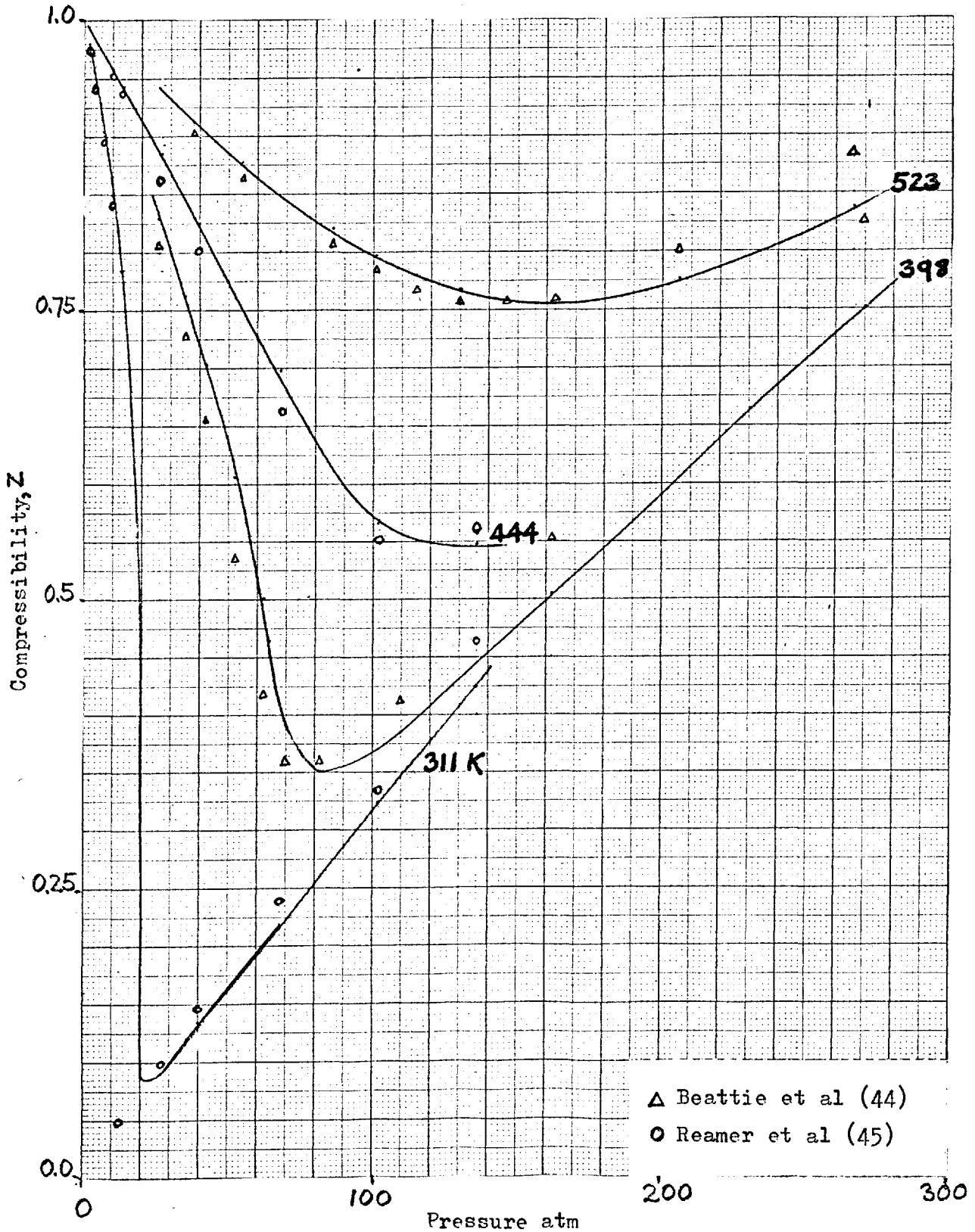


Computed results agreed well with the experimental work except at very low Z. The maximum error is about 0.7% at high temperatures. At lower temperatures the error is 0.4 - 0.5%. The critical constants for ethane used in these computations are listed in Appendix C.

2. Propane

The compressibility factor of propane has been measured by two groups of co-workers - Beattie, Kay and Kaminsky (44) and Reamer, Sage and Lacey (45). The former covered the range (23-305)atm and (370-548)K and the latter (2-136)atm and (311-344)K. Beattie et al claim that their experimental work is more accurate than that of Reamer et al - whose propane was none too pure. Compressibility factors for propane were computed in this work at twelve different temperatures, four of which are plotted in Fig 18. Experimental results are shown and there is considerable divergence at high pressures. The sets of experimental work are fairly consistent amongst themselves. This divergence is rather an unexpected result, unless the experimental work is not accurate. Beattie et al (44) also give computed compressibility factors which they obtain from the Beattie-Bridgeman equation of state. There is increasing deviation between calculated and experimental values of Z, with increasing pressure. They do not give computed values of Z past the point at which experiment begins to deviate considerably from the computed values of Z in this work - approximately 120 atm. Maybe Beattie et al found this increasing divergence too.

Fig 18. Propane, compressibility factor.



3. Propylene

Marchman, Prengle and Motard (52) give experimental results for the compressibility factor of propylene in the range (0-215)atm and (348-523)K. Compressibility factors were calculated at six of the temperatures used by Marchman et al and computed and experimental results are plotted in Fig 19. There is very close agreement between the two; the greatest deviation is at low Z at 398 and 373K - about 1%. Elsewhere in the range studied it is less than 0.5%.

4. Butane

The compressibility factor of butane has been experimentally determined by Beattie et al (50), and by Sage et al (51). Beattie et al worked in the range (423-573)K and covered a pressure range of (14.7 - 117)atm, and (37-357)atm. Sage et al worked at (311-393)K. The compressibility factor was computed at six temperatures, four of which are shown in Fig 20 with the corresponding experimental work of Beattie et al. There is extremely close agreement with experiment over a wide range of temperature and pressure. Maximum error - about 5% - occurred at low Z near the critical point, but elsewhere the error was about 0.3%.

Liquid phase was detected by the program at 423K and the compressibilities were calculated with the Tait equation of state.

Fig 19. Propylene, compressibility factor.

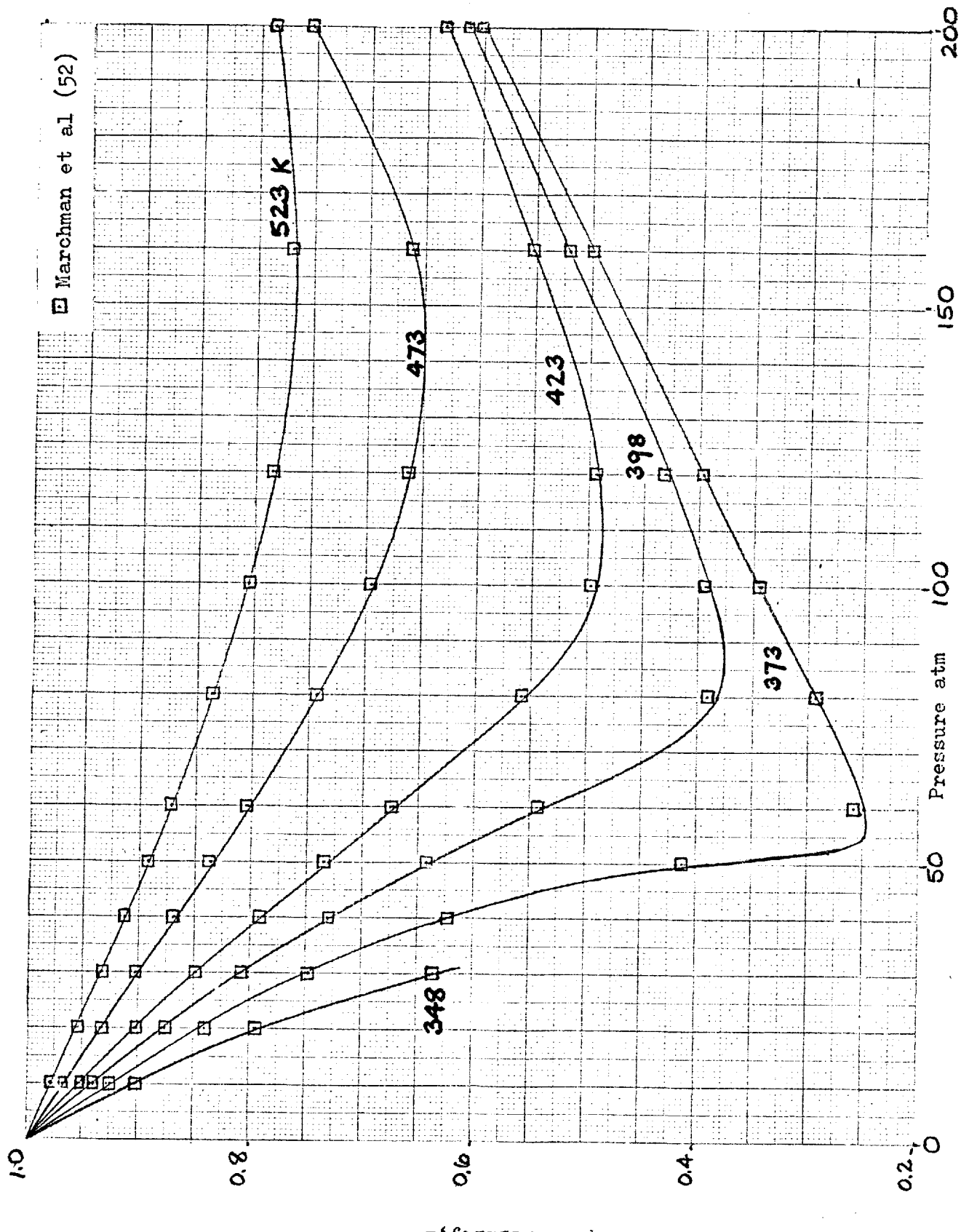
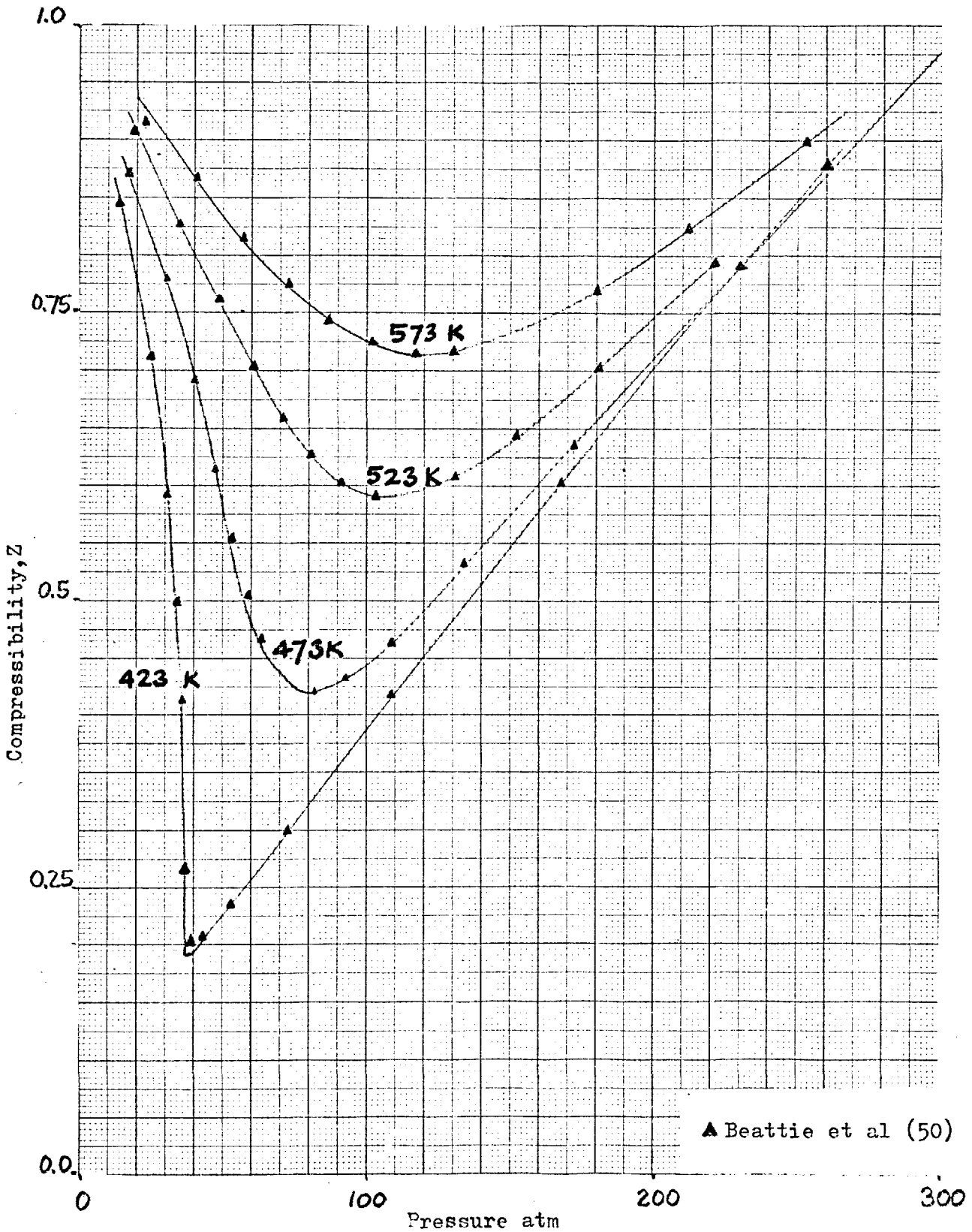


Fig 20. Butane, compressibility factor.



5. Pentane

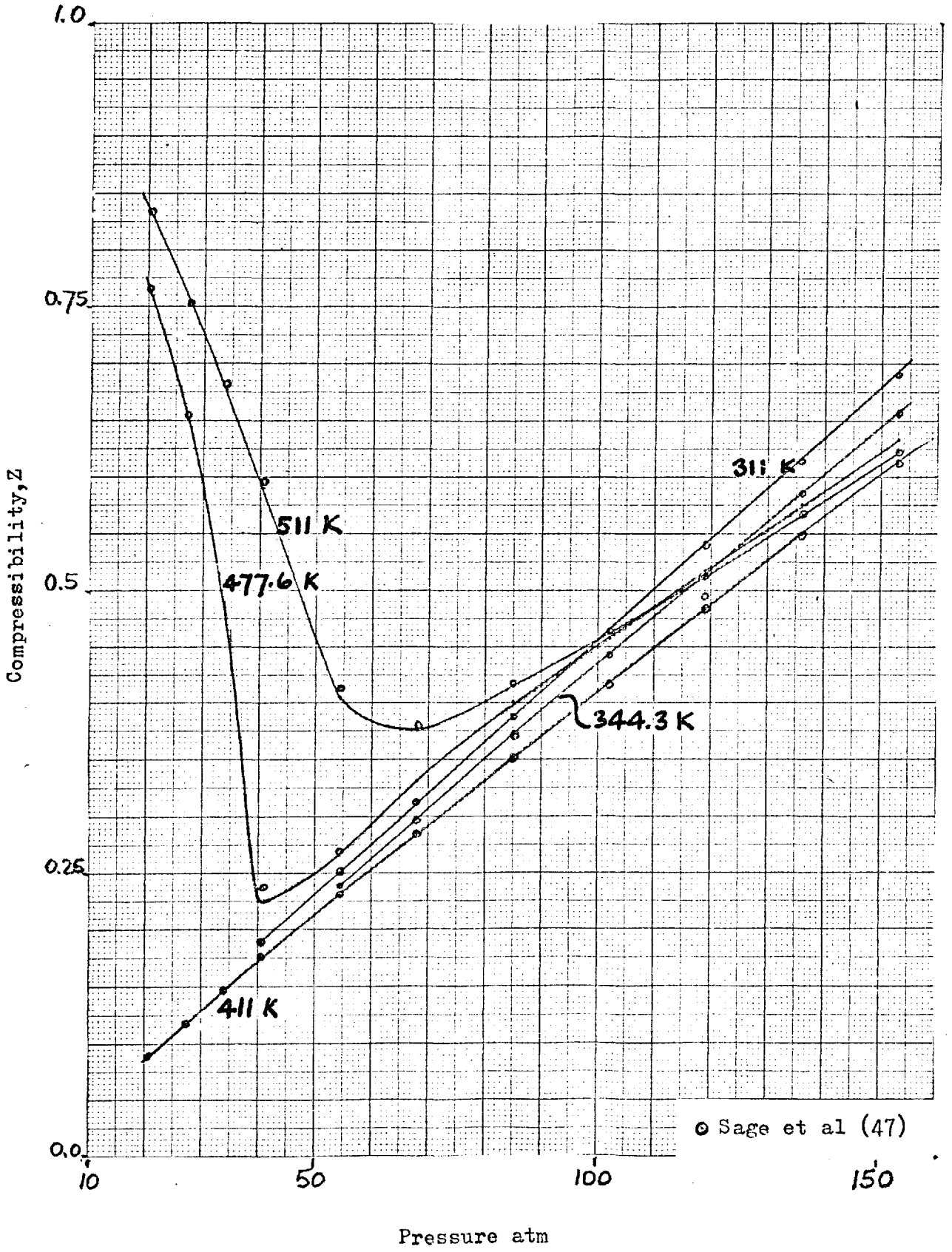
The experimental work of Sage and Lacey (47), covers a very wide range of temperature and pressure - (311-511)K and (20-340)atm. This range is mostly liquid phase, and this is correctly established by the program. Compressibility factors were calculated at seven temperatures for the pressure range used by Sage and Lacey. Five of the isotherms are shown in Fig 21, with experimental results of Sage and Lacey. There is close agreement throughout - about 0.2% error, except at low Z and 477.6K where it is 5.0%. However 477.6K is very close to the critical point of pentane (469K), and, as in the case of butane, results cannot be expected to be as good as at conditions not close to the critical point.

Sage and Lacey also give tabulated enthalpies - calculated from their experimental P-V-T data. Their results were converted to dimensionless configurational enthalpies for direct comparison with computed results in this work.

Some examples :

T K	P atm	H/RT(47)	H/RT(this work)
311.0	119.0	- 8.80	- 8.72
344.3	54.4	- 7.45	- 7.42
444.3	20.4	- 0.23	- 0.17
	34.0	- 4.06	- 4.08
511.0	20.4	+ 0.25	+ 0.403
	27.0	+ 0.05	+ 0.148

Fig 21. Pentane, compressibility factor.



These results agree fairly well, there being least agreement near the critical region. This is not unexpected as calculation of enthalpy involves partial differentials of (equation 2.58)) and this always magnifies small discrepancies. The critical region is where there is greatest slope in the isotherm, and this will mean greater errors in any properties dependent on derivatives.

6. Hexane

Kelso and Felsing (48) and Watson and Dodge (46) have both determined experimental compressibility factors for hexane. These two sets of experimental work are in good agreement. Watson and Dodge report three isotherms in the range (523-573)K for pressures (15-100)atm, and Kelso and Felsing give Z for (373-573)K for a pressure range (2.5 - 300)atm. In this range of pressure, compressibility factors were computed at nine different temperatures. Four of these isotherms are shown in Fig 22 with experimental results of Kelso and Felsing, and Watson and Dodge.

Stewart, Sage and Lacey (49) have experimentally determined the compressibility factors for liquid hexane for temperatures (311-511)K and pressures (6.8 - 680)atm. The temperatures at which they worked do not coincide with those of the other experimental results (48, 46), but in Fig 22, Z at 377.6K from (49) is shown on the isotherm at 373K. This is only a 1% error in temperature, and,in view of the closeness of the isotherms,is a negligible error in these circumstances. As with previous hydrocarbons discussed the greatest error in computed Z for hexane is where Z is very low and where the isotherms have greatest slope. Fig 23 shows a single isotherm computed at 448K including the experimental results at 444K (49).

Fig 22. Hexane, compressibility factor.

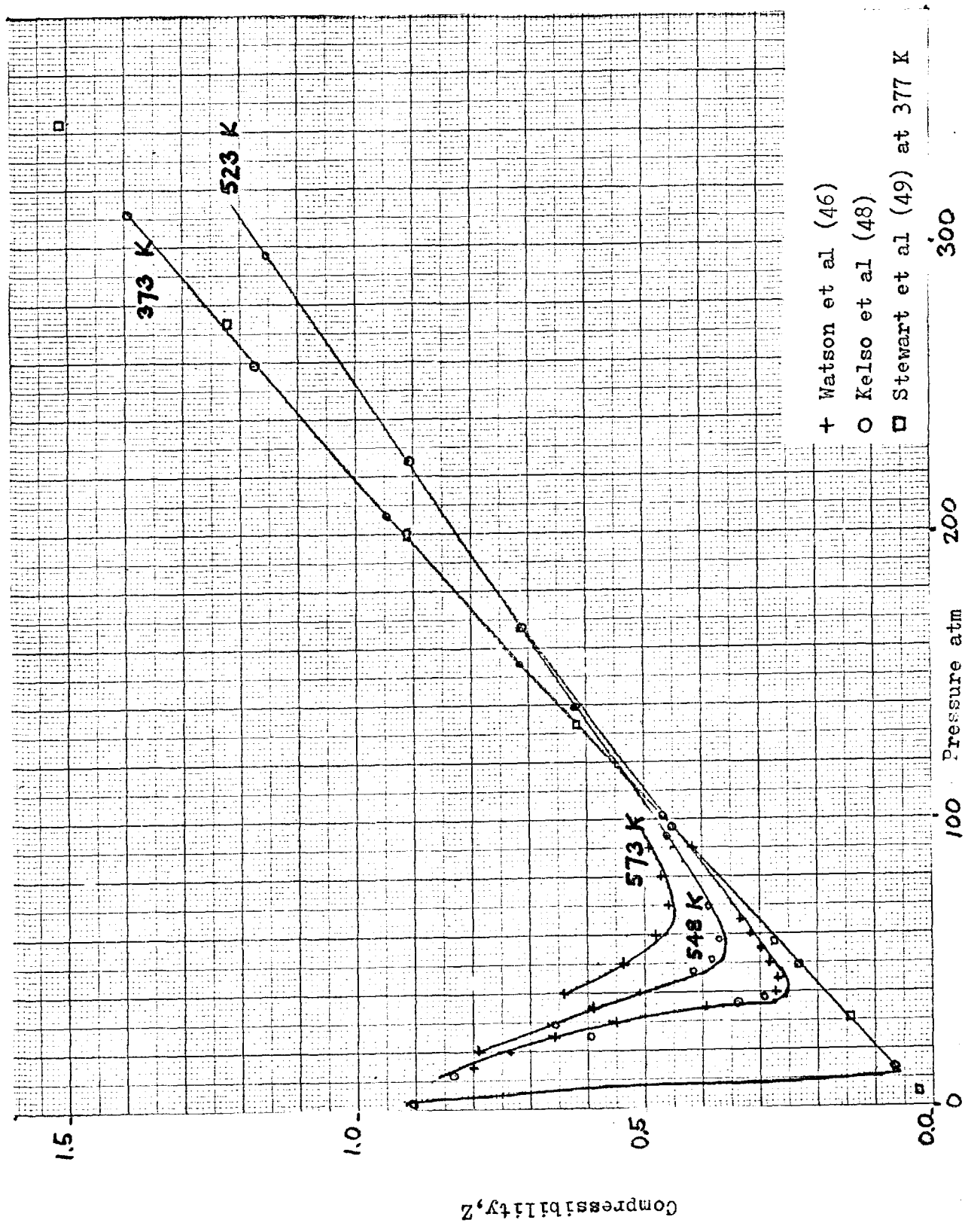
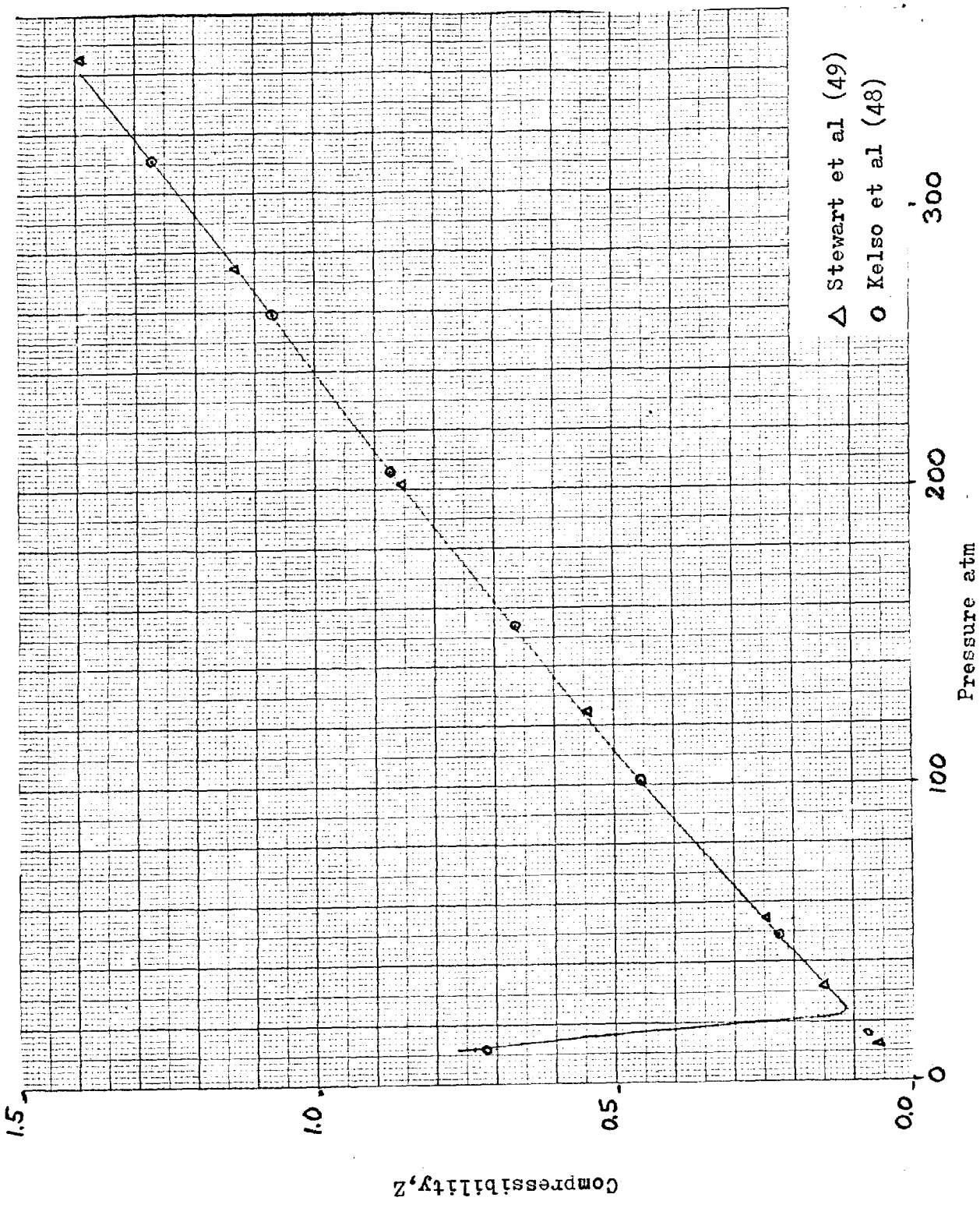


Fig 23. Hexane, compressibility factor at 444 K and 448 K.



This shows more clearly the accuracy of prediction away from the region of minimum Z, and the consistency between different experimental work.

7. Heptane

Smith, Beattie and Kay (56) determined experimental compressibility factor for heptane at (303-623)K and (0-350)atm. Computed compressibility factors at four of the same temperatures as those used by Smith et al, are shown in Fig 24. In all, Z was computed at nine temperatures in the range (303-623)K. Agreement between computation and experiment is very close - at low temperatures about 0.1 - 1.0% error, with increasing pressure, and at high temperature 0.1 - 0.4% error with increasing pressure. Smith et al state that the estimated experimental error in density, in the liquid phase is less than 0.3% for densities up to 2.5 moles/litre and 0.6% for higher densities. In the gas phase, the error in temperature is (0.01-0.02)degrees, in pressure less than 0.03% and in volume 0.1%. Thus the deviation of computed results from experimental work is within experimental error. An additional calculation using the Vennix equation was done for the liquid phase compressibility factors - and this gave results as satisfactory as those the Tait equation gave.

8. Toluene

Experimental compressibility factors for toluene were determined by Watson and Dodge (46), at three temperatures (523, 548, 573)K for (10-32)atm. The compressibility factor was computed at these same three temperatures and the results are shown in Fig 25. Agreement is poor, but not unexpected, and no reflection on the validity of the experimental work.

Fig 24. Heptane, compressibility factor.

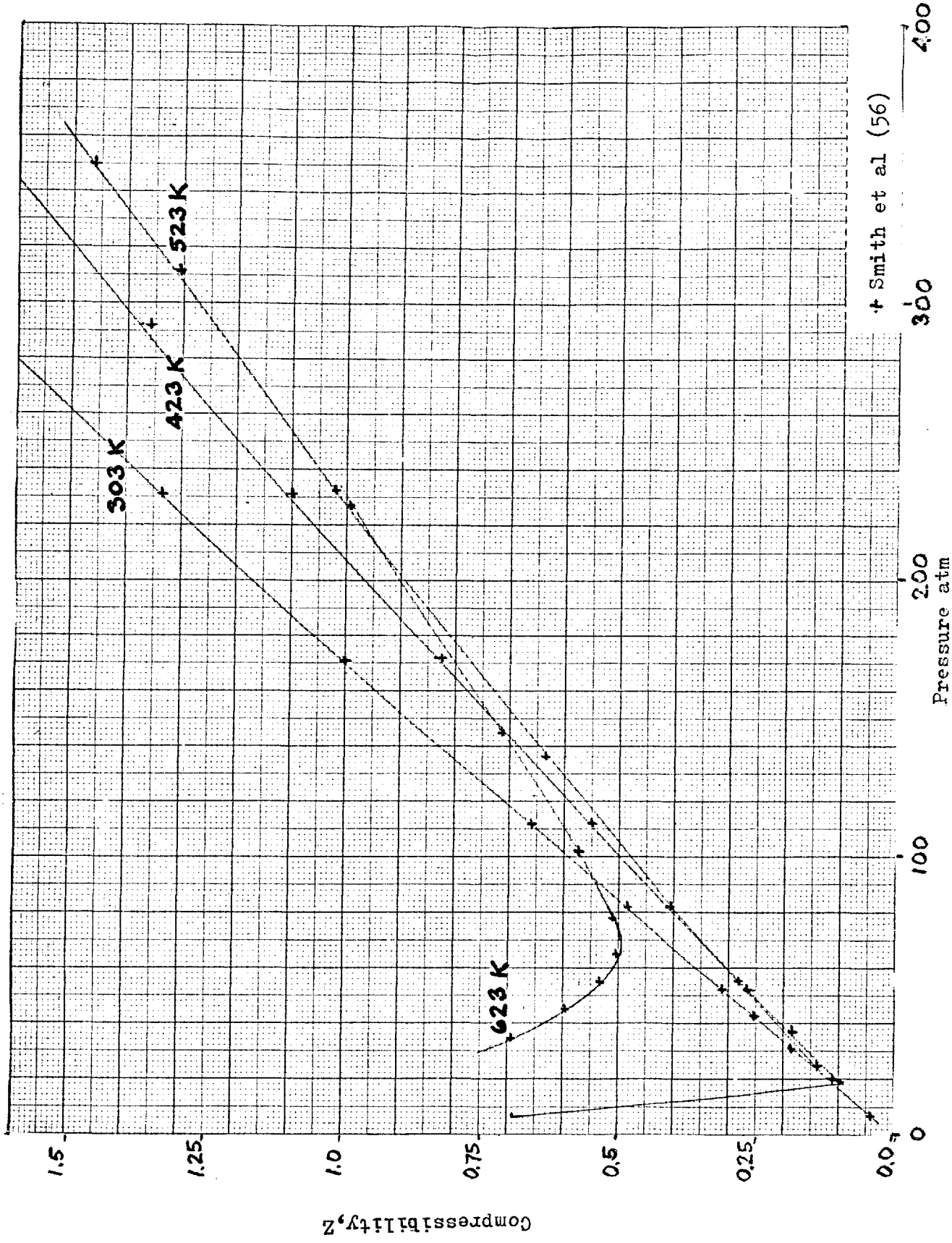
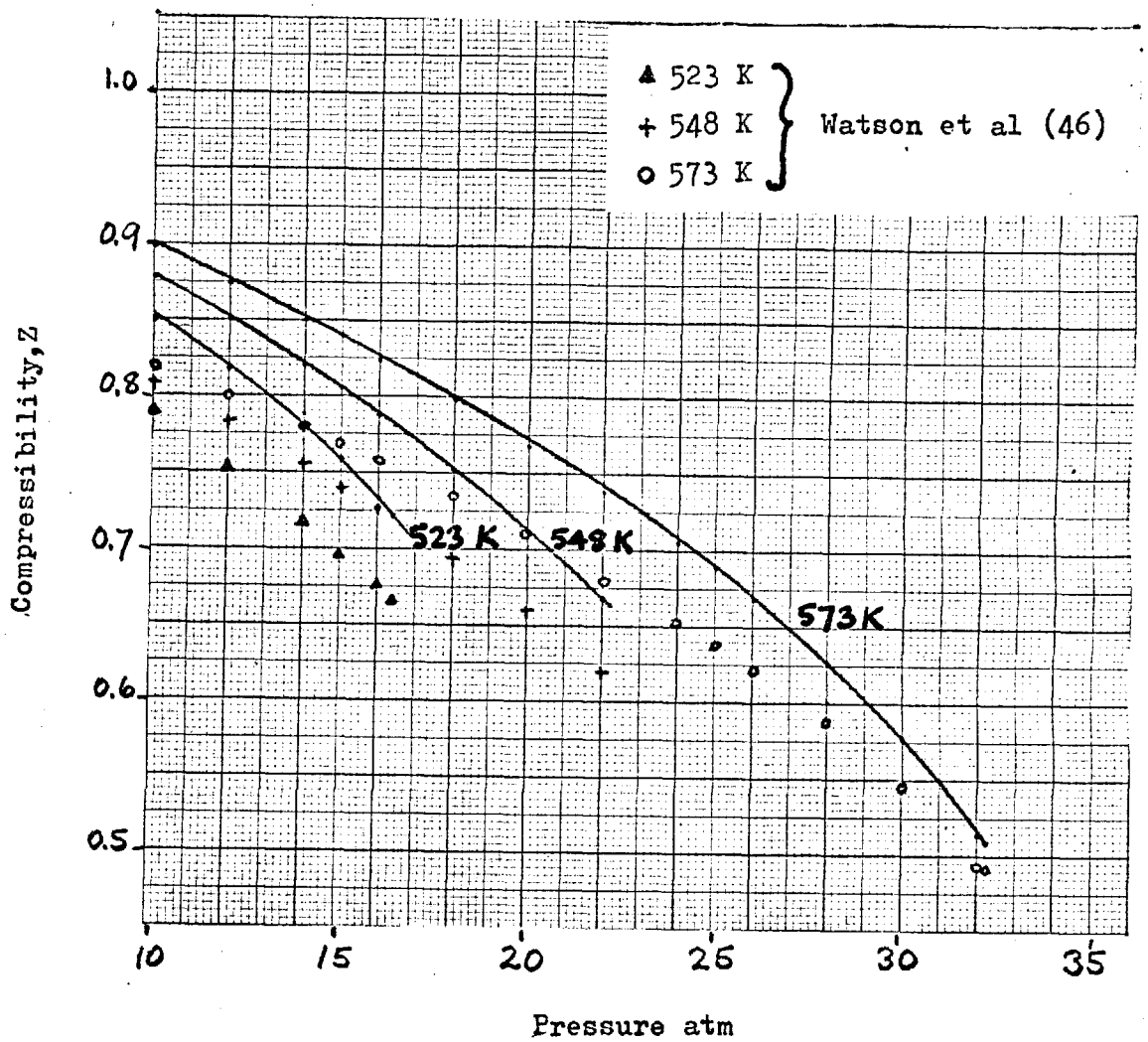


Fig 25. Toluene, compressibility factor.



It is straining the principle of corresponding states somewhat to use an equation of state for methane to predict the properties of such a substance as toluene.

9. Oxygen

Extensive experimental P-V-T data for oxygen is available throughout the published literature. Two sources used in this work for comparison with computed compressibility factors are Wasserman et al (37), and Michels et al (57). The former covers the range (0.25 - 1000)bar and (80 - 1300)K, and the latter (22 - 130)atm and (273 - 323)K. Computed results are shown in Fig 26 with the experimental work of Wasserman et al. Also in Fig 26 are the experimental results of Michels et al at 298K, shown on the isotherm at 300K. At this temperature (about 300K), there appears to be less error between computed Z and Michels' experimental work than between computed Z and Wasserman's work - respectively 0.25% and 0.31%. However, comparing computed Z with Wasserman's work only, there is greater deviation at lower temperatures and high pressures than elsewhere. The deviation rises to as much as 2.2%. At low pressures, the deviation drops to 0.05%.

An earlier program was developed using an equation of state for methane given by Leach (8). The same isotherms as in Fig 26 were also computed using this earlier program, but results showed insignificant differences from those computed with the Vennix equation of state. The compressibility factors were consistently better at low pressures using the Leach equation, but at 200 bars and above, the Vennix equation gave better results - in both cases by only a very small percentage.

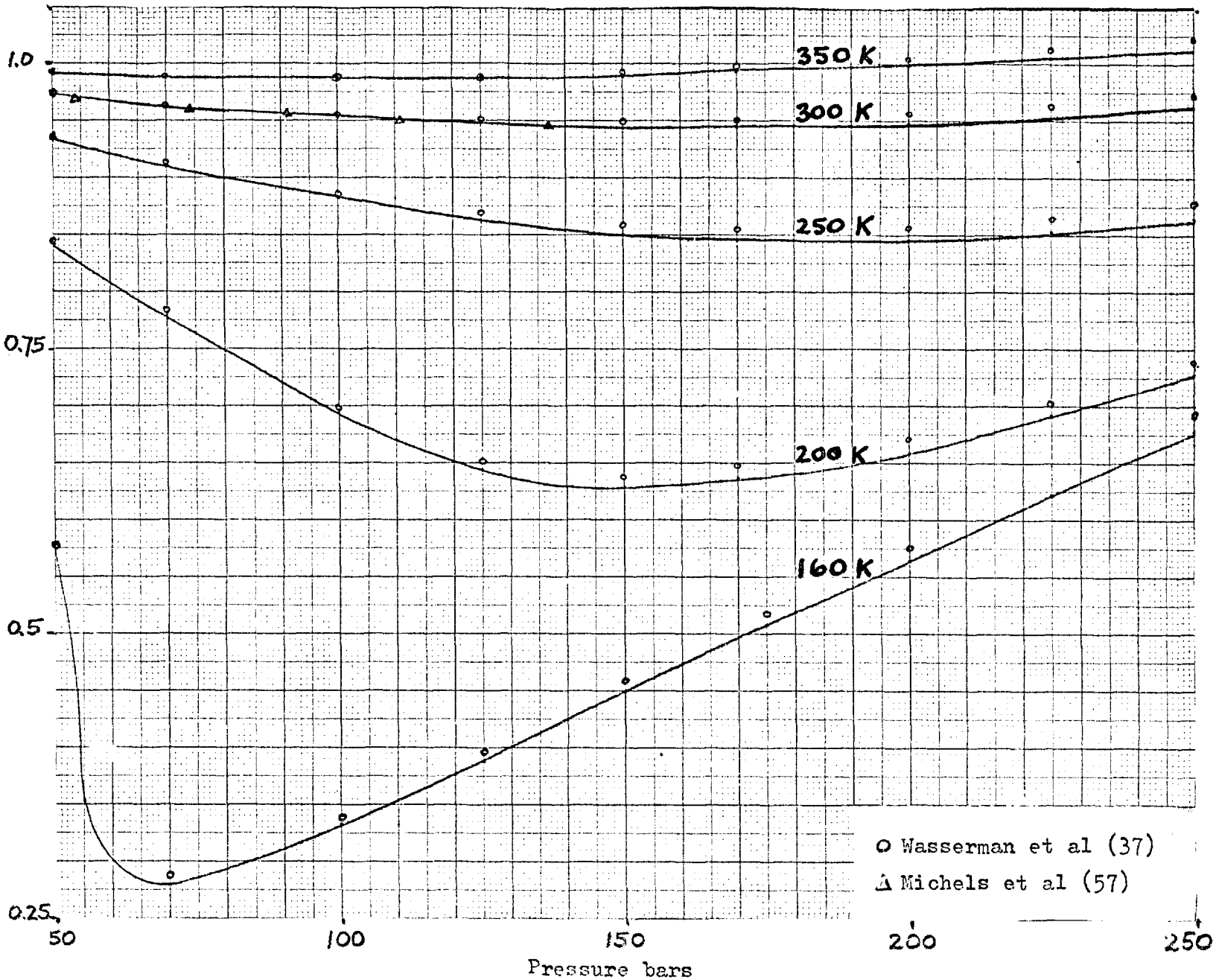


Fig 26. Oxygen, compressibility factor.

However, the Vennix equation is easier to handle and so that was the equation of state finally selected for computation work.

10. Argon

Michels and co-workers have worked extensively on the determination of experimental P-V-T data (34, 35, 36) for argon. Wasserman et al (37) have published tables of smoothed experimental data in the range (0.25 - 1.000 bars) and (85-1300)K. Michels work covers (118-423)K and (0-1050)atm. Fig 27 shows a few selected isotherms of computed compressibility factors and corresponding experimental values of Z. Agreement between computations and experiment is good for 153K to 423K and all experimental work appears extremely consistent. Although not shown in Fig 27, some compressibility factors were computed at pressures up to 1000 atm. Such a pressure is far beyond the stated limit of application of the Vennix equation of state (15,16), but even so, calculated Z was only 0.5 - 1% in disagreement with experimental work (37).

Crain and Sonntag (33) report P-V-T data on argon and nitrogen and mixtures of the two. They also compare many published values of compressibility factor for pure argon and nitrogen with their own experimental values, at temperatures used in these computations. Computed Z agrees with these values extremely well - 0.02 - 0.5% error.

Fig 28 shows H/RT plotted against temperature for various isobars. At 50 and 200 atm, some of Michels' data have been converted to H/RT, where H is configurational enthalpy, and are also shown in Fig 28.

Fig 27. Argon, compressibility factor.

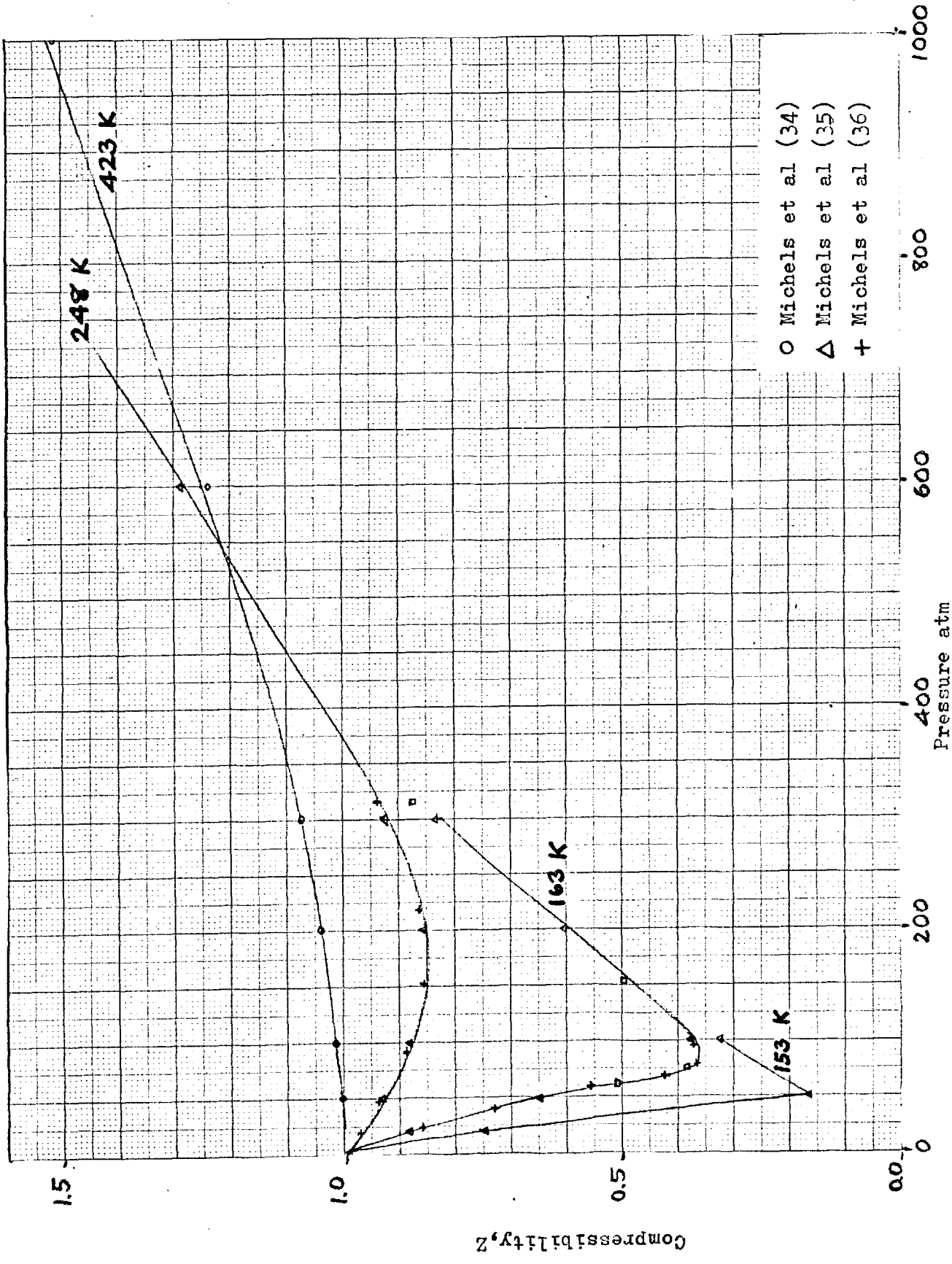
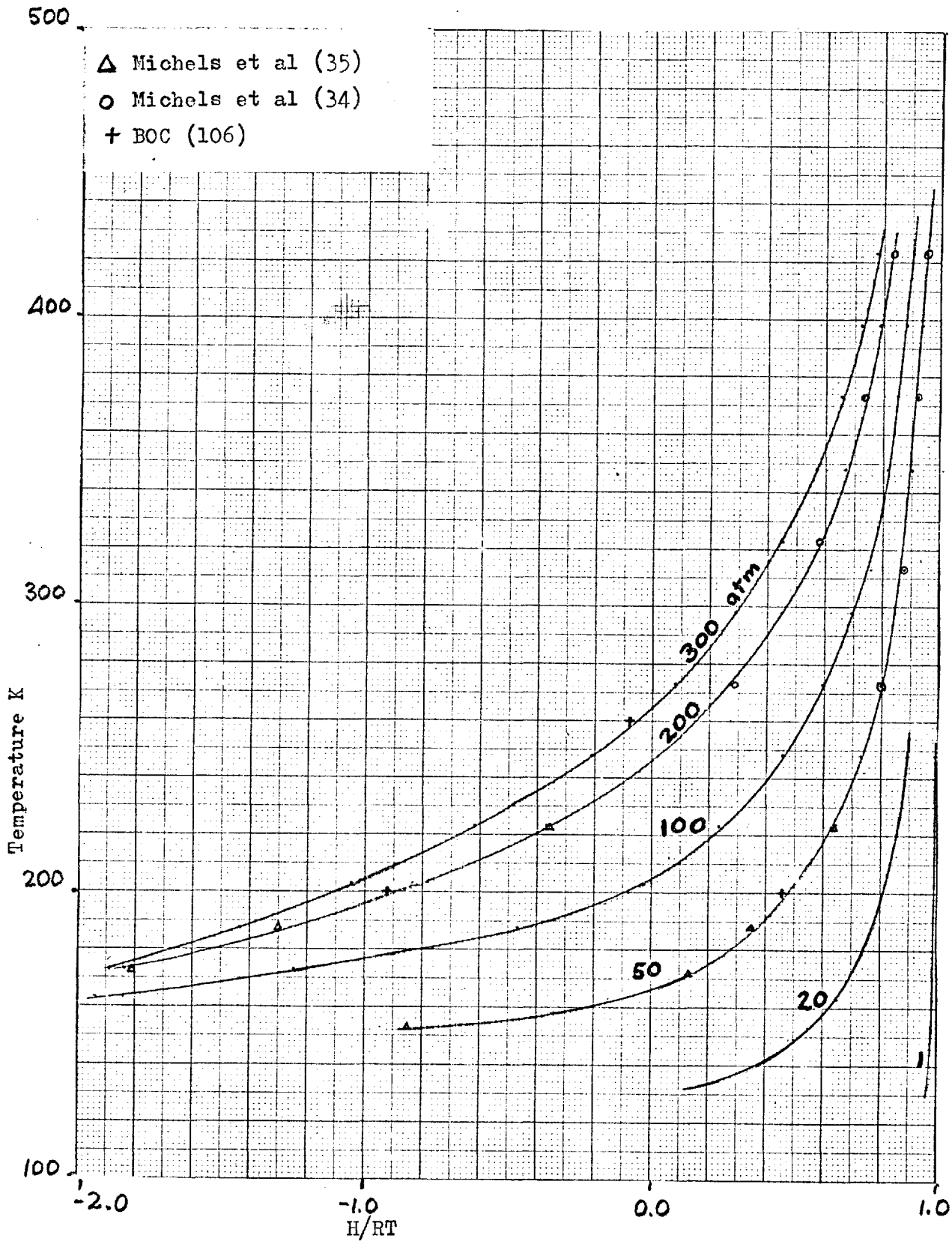


Fig 28. Argon, dimensionless configurational enthalpy, H/RT.



Michels' enthalpies (34, 35) are calculated from his own P-V-T data. Agreement with computed H/RT is good, but could be expected from the excellent agreement between his compressibility factors and those computed here. The British Oxygen Company (115) have published tables of P-V-T data for oxygen, nitrogen, argon and air. Their data also agree well with these computations. For example :

P atm	T K	H/RT(115)	H/RT*(this work)
50	200	+ .46	+ 0.48
200	200	- .92	- 0.90
300	260	- .082	- 0.055

* by interpolation on Fig 28.

11. Nitrogen

Wasserman et al (37) have published a table of smoothed P-V-T data for nitrogen (0.25 - .000 bar) and (70 - 1300)K, and Lunbeck et al (43) have determined experimental P-V-T data for the range (148 - 423)K and (0 - 6000)atm. The compressibility factor was computed at nine temperatures and these are shown in Fig 29. The temperatures used correspond to those in the experimental work (37, 43). In Fig 29 results from both sources have been included - the slight variation in temperature ($\gtrsim$ 1. %) is not considered significant.

	Ref (43)	Ref (37)
Temperatures for which experimental points are shown in Fig 27.	-	120 K
	148	150
	198	200
	248	250
	323	320

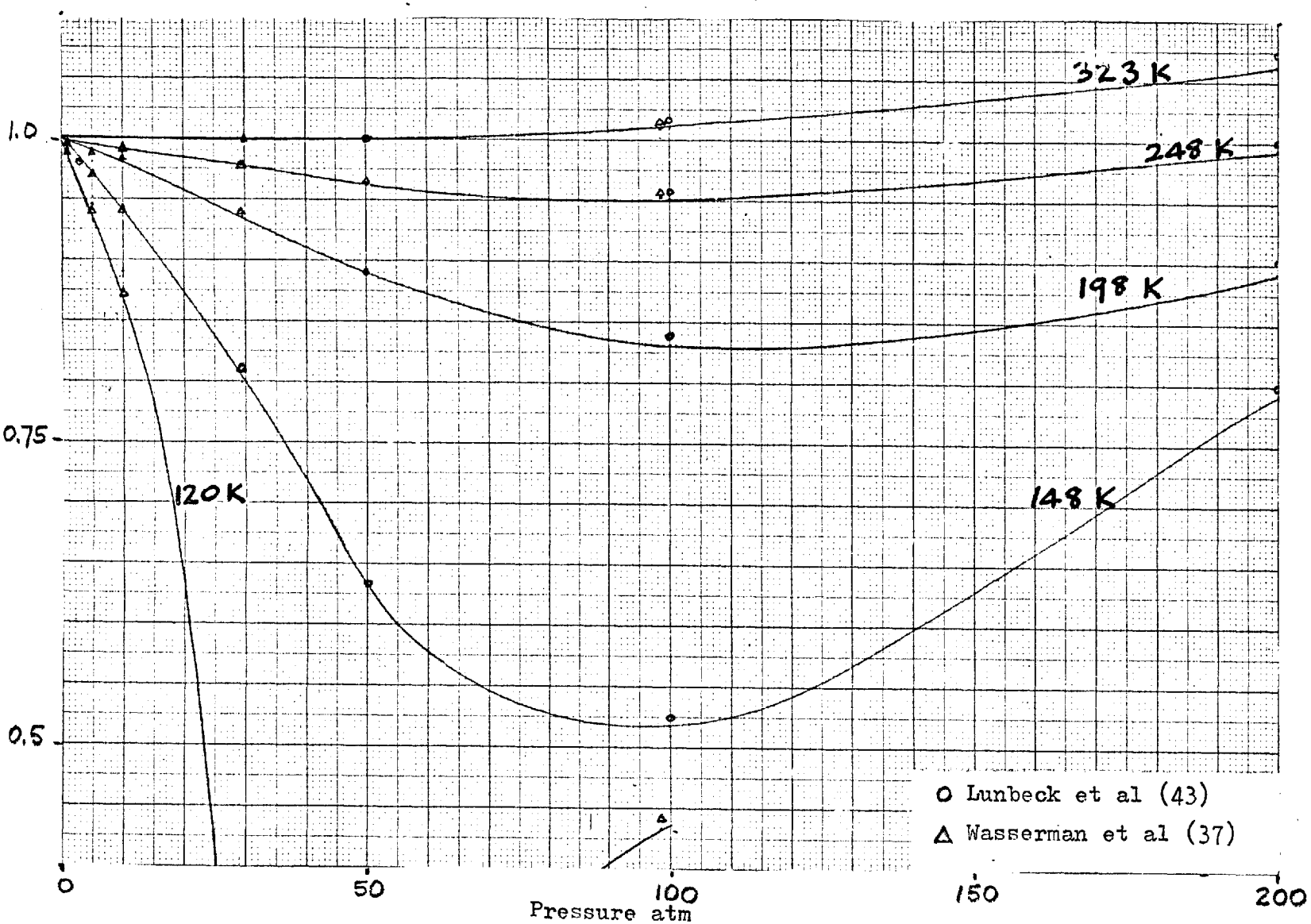


Fig 29. Nitrogen, compressibility factor.

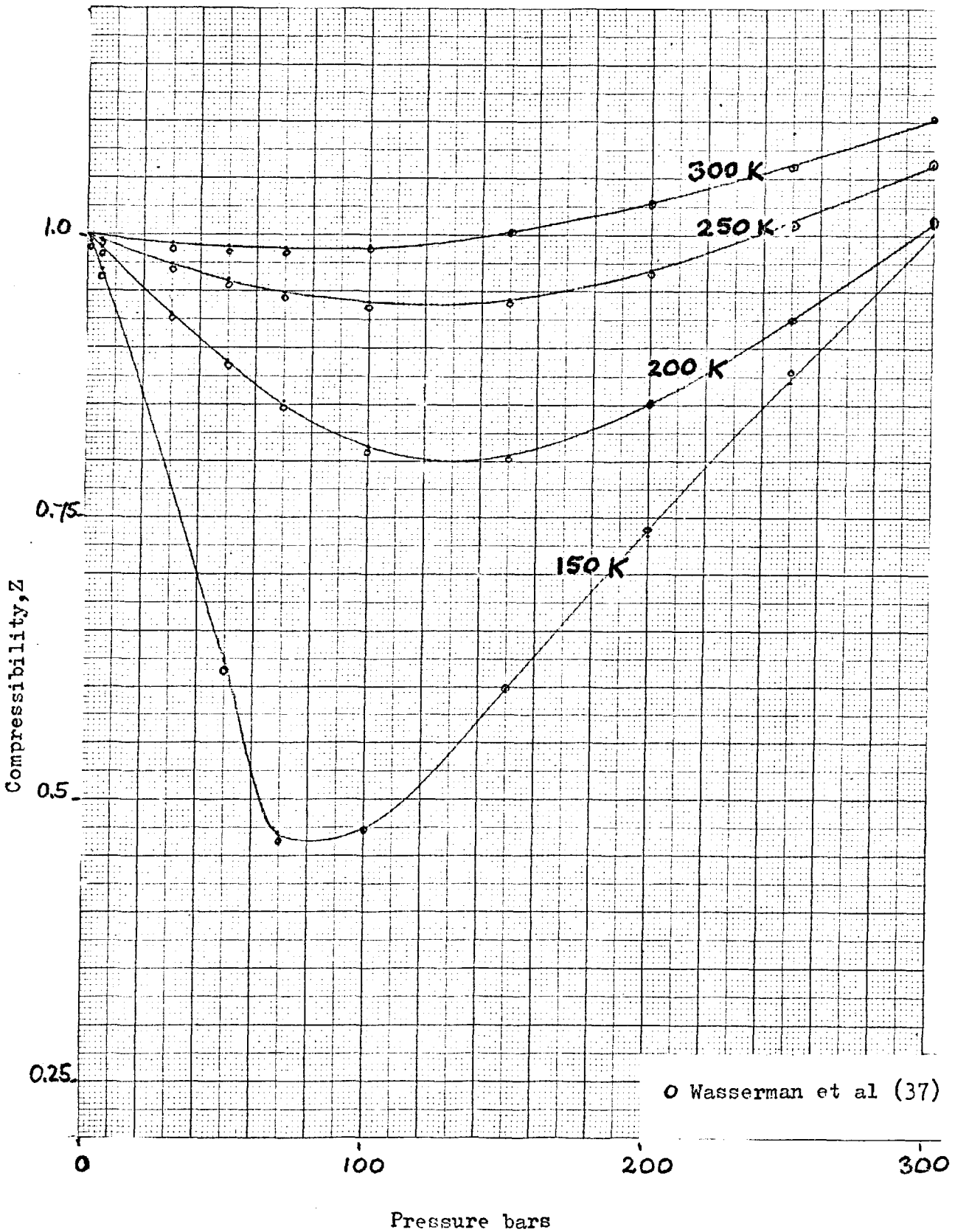
The computed results are those corresponding to the temperatures for (43). At 1 bar, the experimental values are all less than the computed Z, but above 1 bar, they are greater than computed Z. All Lunbeck's experimental Z are greater than computed Z.

These same data were used in the program mentioned in the section for oxygen which uses Leach's equation of state. The differences in computed Z were minimal - sometimes a fraction of a percent higher, sometimes lower. Perhaps this was due to rounding error in the data (both (43) and (37) are smoothed data) and in the program. Lunbeck et al also endorse the validity of their experimental work by comparing their own work with that of Keesom (116). Crain and Sonntag (33) list many experimentally determined compressibility factors and compare these with their own experimentally determined Z. Computed Z in this work compares well - to within 0.2%, but up to 1% error at high pressures.

12. Air

Smoothed P-V-T data for air, are given by Wasserman et al (37) for the range (0.25 - 7000) bars and (75 - 1300)K. Michels et al (58) give smoothed P-V-T data, and calculated thermodynamic properties for the range (203 - 348)K and up to 1200 atm. The data published by B.O.C. (115) is that of Wasserman et al. In Fig 30 a few of the computed isotherms are shown with experimental results of Wasserman et al. In all Z was computed at seventeen temperatures in the range (160 - 320)K.

Fig 30. Air, compressibility factor (1-fluid model).



There is less error in computed results at higher temperatures and pressures - most error is at low temperature and pressure, being about 0.5%. It is interesting to note that all computed values of Z lie below experimental Z (37) whereas for oxygen all computed Z lie above experimental Z (37).

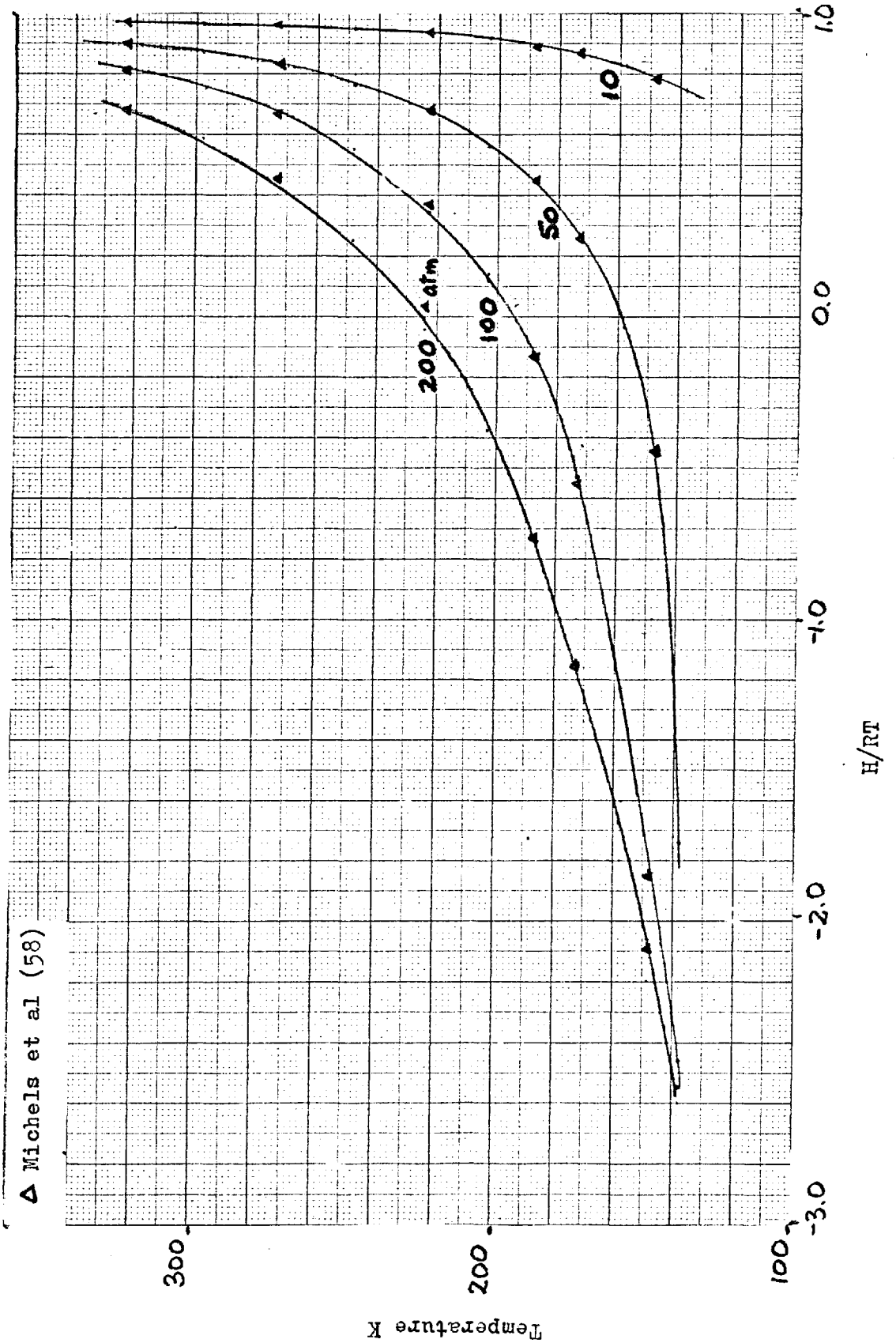
The pair interaction parameters were taken from the work by Leland et al (11) and the composition of air was taken as :

Component	Mole fraction
N_2	0.78
O_2	0.21
Ar	0.01

Species pair	ξ_{12}
N_2 - O_2	0.995
N_2 - Ar	0.995
O_2 - Ar	0.988

These data (Fig 30) were also used in computations for Z using a two-fluid model, and in the program which uses Leach's equation of state, again using both 1- and 2-fluid models. The 2-fluid model using Leach's equation of state is marginally the best at low pressure and temperature, with nothing to choose between the other three. At high pressures, the 1-fluid model with the Vennix equation of state gives rather poor results. The disadvantages of the 2-fluid model are that only fractionally better results are achieved by considerably more complicated programming, and at low temperatures near the phase boundary, a mixture can appear to be in two phases - as explained in Section (3.1).

Fig 31. Air, dimensionless configurational enthalpy, H/RT.



In Fig 31 a plot of H/RT against temperature shows computed results and some enthalpies from Michels work (58). The experimental work was converted here to configurational properties. Below are tabulated some of the points shown in Fig 31.

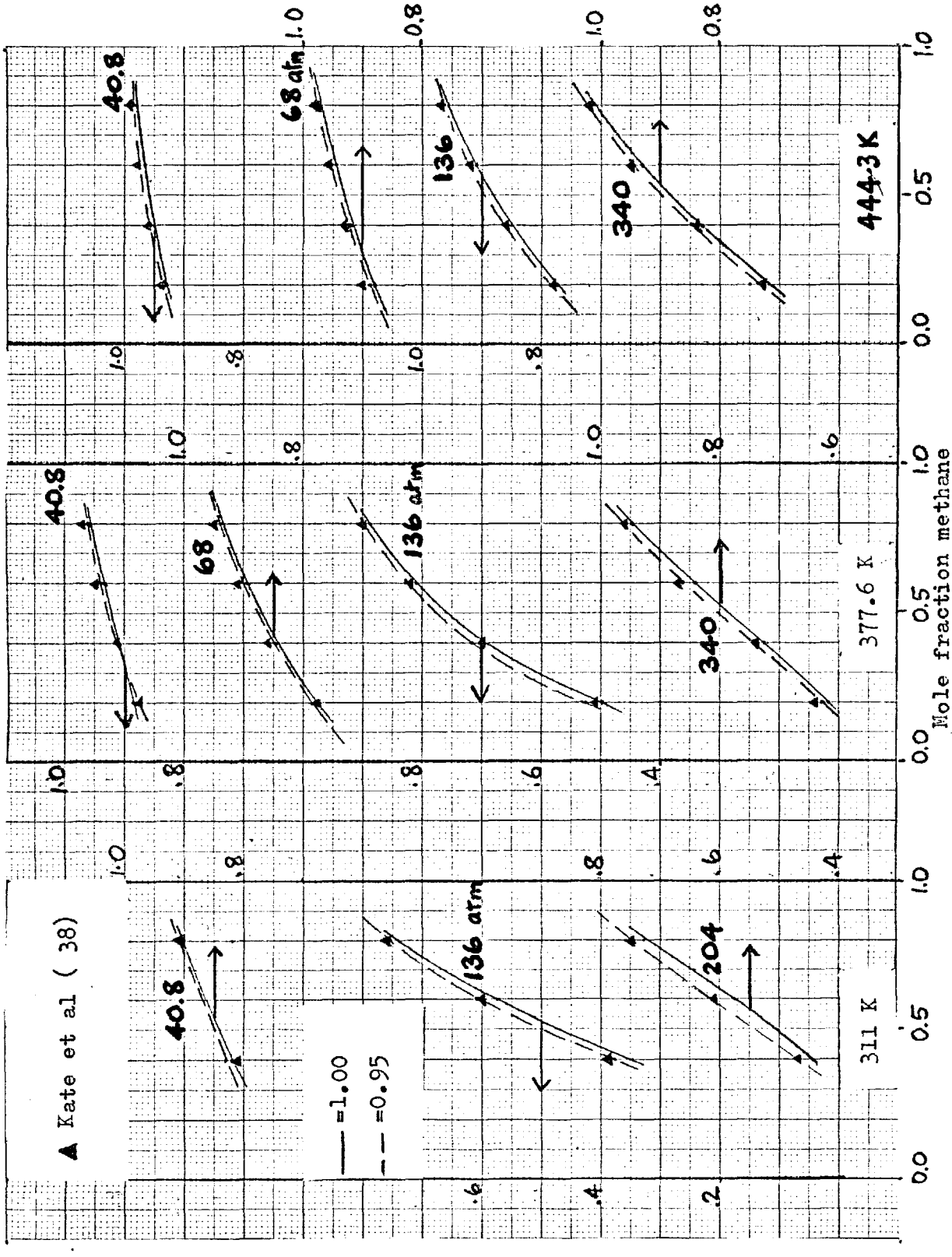
T K	P atm	H/RT(58)	H/RT(this work)
148	10	+ 0.790	+ 0.798
	50	- 0.445	- 0.443
	100	- 1.853	- 1.829
	200	- 2.093	- 2.085
188	10	+ 0.896	+ 0.896
	50	+ 0.446	+ 0.449
	100	- 0.131	- 0.121
	200	- 0.743	- 0.718
273	10	+ 0.965	+ 0.964
	50	+ 0.829	+ 0.827
	100	+ 0.675	+ 0.674
	200	+ 0.447	+ 0.448

Agreement with Michels' work is close.

13. Hydrogen Sulphide-Methane

Kate, Robinson and Chao (38) investigated partial volume at infinite dilution in order to find an interaction constant for the B-W-R equation of state, for mixtures of hydrogen sulphide and methane. To test the constant they found, they used the experimental results of Reamer, Sage and Lacey (39) and plotted compressibility factor against mole fractions of methane.

Fig 32. Methane-hydrogen sulphide system, compressibility factor.



The work of Reamer et al agrees very well with the experimental work of Kohn and Kurata (40). Agreement of predicted Z (38) from BWR equation with the results of Reamer et al was quite good, best at low concentrations of either component and worst at equimolar concentrations. Fig 32 shows computed Z in this work plotted in the same way as in the paper of Kate et al, to make comparison easy. Calculations were made using $\xi_{12} = 1$ and $\xi_{12} = 0.95$ (12).

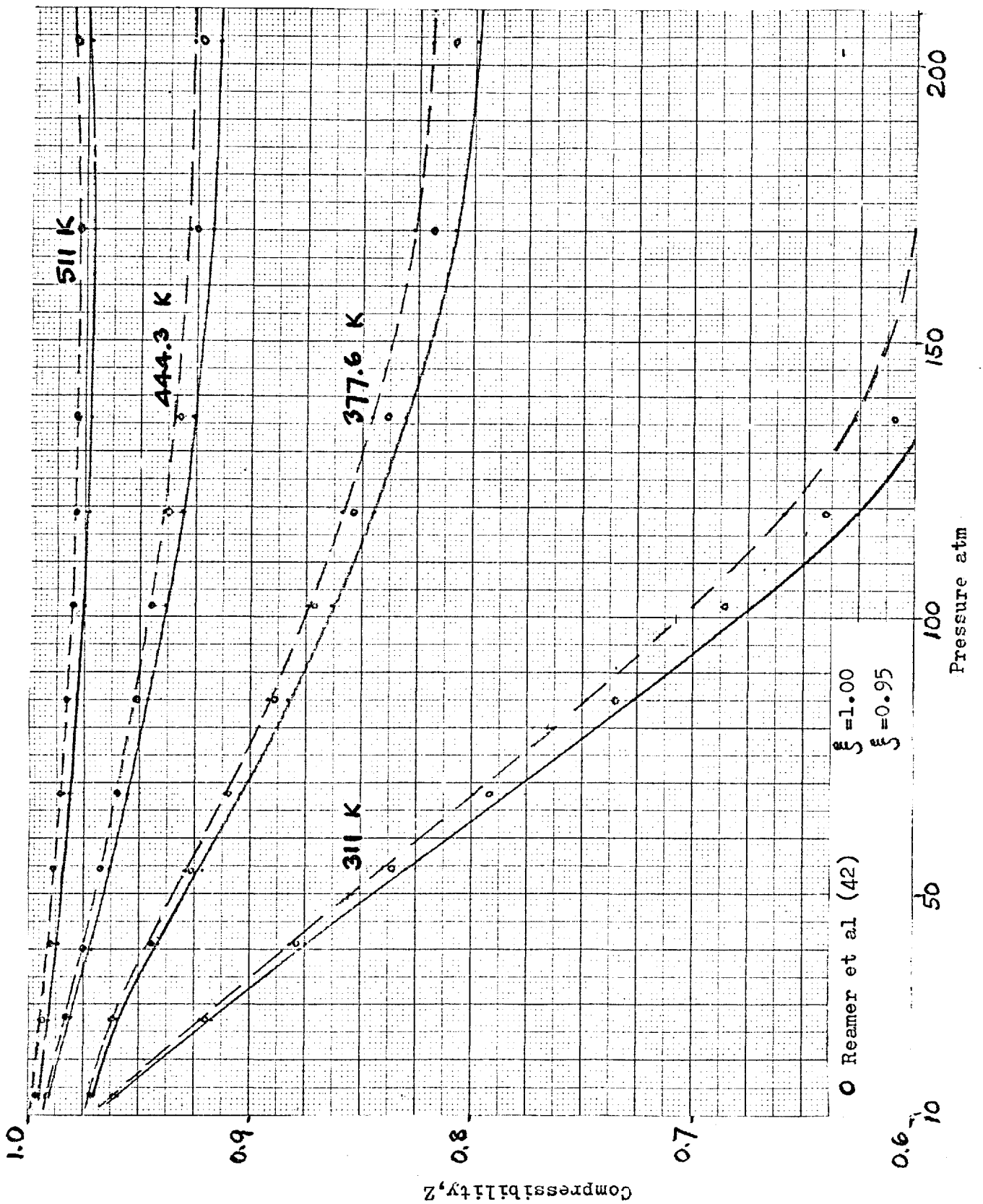
For $\xi_{12} = 1$, at low temperature and low pressure, agreement with experiment is good with very slight increase in error as pressure and temperature increase. These computed Z are closer to the experimental results than the predictions using BWR equation are, except at very low concentrations of either component.

For $\xi_{12} = 0.95$, the computed values of Z agree extremely well with the experimental work for almost all temperatures and pressures, but it is least good at low hydrogen sulphide concentrations at low pressures.

14. Carbon dioxide-Methane

Compressibility factors of mixtures of carbon dioxide and methane at seven temperatures (311 - 511)K for a pressure range up to 680 atm have been experimentally determined by Reamer et al (42). They used four concentrations of methane in carbon dioxide. Compressibility factors were calculated over the entire range in given in (42) for all concentrations. In Fig 33, four isotherms, using $\xi_{12} = 1$, for the mixture 0.4055 methane, are shown. Also shown are the computed results using $\xi_{12} = 0.95$ (12).

Fig 33. Methane-carbon dioxide system, compressibility factor. Mole fraction of methane, 0.4055.



Using $\xi_{12} = 0.95$ gives excellent results at high temperatures, but at lower temperatures (e.g. 311 K) $\xi_{12} = .96$ might be a better value.

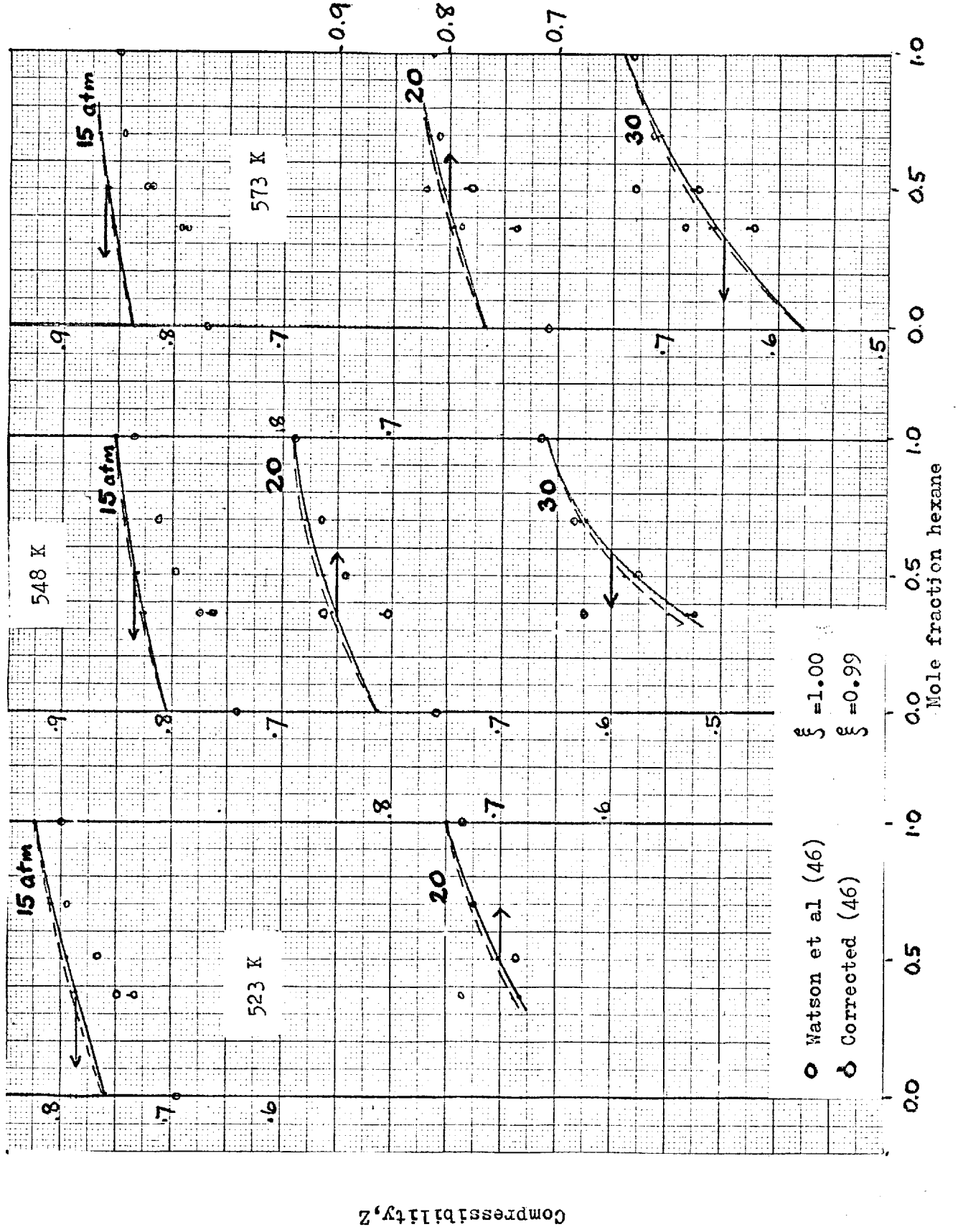
Work on excess enthalpies - described further on in this Section for carbon dioxide-methane mixtures shows that $\xi_{12} = .96$ is probably a better value for ξ_{12} than 0.95, and from Fig 33 this would seem to be borne out - especially at low temperatures.

For the other compositions - i.e. 0.2035, 0.6050, 0.8469 methane, only $\xi_{12} = 1.0$ was used in computing Z. As might be expected, results were better at lower concentrations of carbon dioxide, about 0.1% error, and up to 0.16% at high carbon dioxide concentrations for low temperature and pressure. The same error occurs at high temperature and pressure. At low temperature and high pressure, the error was 0.8% for low carbon dioxide concentration up to 1.1% for high concentrations; and at high temperature and low pressure the error was 0.08% to 0.16% for increasing carbon dioxide concentration.

15. Toluene-Hexane

Watson and Dodge (46) give Z for three concentrations of hexane in toluene (0.7, 0.505, 0.336), for temperatures (498 - 573)K and pressures (13 - 95)atm. There appears to be a misprint in their tables of results and in Fig 34, corrected experimental values are shown as well as the literal values from (46).

Fig 34. Toluene-hexane system, compressibility factor.



Agreement between computed results at these temperatures and pressures with experiment is not too good, worse at high toluene concentrations. The data were rerun with $\xi_{12} = 0.99$ (12), and had the effect of increasing Z throughout, but with least effect at low pressure and high temperature and with most effect at high temperature and low pressure. A similar phenomenon occurred in the prediction of Z for carbon dioxide-methane mixtures. Agreement for pure hexane does not at first appear good, but referring to Fig 22, these pressures are where the isotherms for hexane have greatest slope, and where the least accuracy can be expected in predicted compressibility factors.

Enthalpy

Enthalpies for an equimolar mixture of methane and propane were computed at a selection of temperatures and pressures, in order to compare with experimentally determined enthalpies - and to assess the accuracy of the predicted enthalpies. Five temperatures (144-394)K and pressures (136-34)atm were used. The experimental work was that of Yesavage (Ph.D thesis, Rice Univ., 1966) and was taken here as quoted in a paper by Fisher and Leland (125). They compare their own computed enthalpies with those of Yesavage.

In the computations in this work an unlike pair interaction parameter of 0.98 was used initially, and predicted enthalpies were extremely close to experimental results. The enthalpies quoted by Fisher and Leland are residual enthalpies, so in order to compare with these computations they were converted to H/RT. The table below shows all three results expressed as H/RT.

Equimolar concentration is the best test for the accuracy of prediction since errors due to the mixing rules are greatest at this concentration.

Another set of computed enthalpies were made with $\xi = 0.99$. This value of ξ was found by Teja (109) to be the best value for the prediction of the critical locus of methane-propane mixtures.

However, the enthalpies were not nearly so close to the experimental values as those computed as $\xi = 0.98$. Sole exceptions were at high temperature and pressure (394K, 136 and 103 atm), where there was a slight improvement.

T K	P atm	H/RT (This work)	(Expt, Yesavage)	Fisher (125)
144.0	136.1	- 10.72	- 10.79	- 10.85
	102.0	- 10.82	- 10.89	- 10.95
	34.0	- 11.04	- 11.09	- 11.12
	17.0	- 11.09	- 11.12	- 11.21
200.0	136.1	- 6.48	- 6.55	- 6.37
	102.0	- 6.55	- 6.58	- 6.44
	68.0	- 6.61	- 6.63	- 6.55
	34.0	- 6.67	- 6.69	- 6.57
311.0	136.1	- 2.34	- 2.34	- 2.35
	102.0	- 2.16	- 2.15	- 2.17
	27.2	0.42	0.33	0.41
338.0	136.1	- 1.56	- 1.58	- 1.56
	102.0	- 1.17	- 1.22	- 1.19
	68.0	- 0.34	- 0.44	- 0.36
	51.0	0.095	0.0	0.07
	34.0	0.45	0.38	0.43
	17.0	0.74	0.71	0.74
394.0	136.1	- 0.41	- 0.47	- 0.43
	102.0	- 0.08	- 1.41	- 0.10
	68.0	0.29	0.24	0.28
	51.0	0.48	0.38	0.37
	34.0	0.56	0.64	0.66
	17.0	0.84	0.82	0.83

Dimensionless configurational enthalpies for an equimolar mixture of methane and propane.

Excess Enthalpies

A reliable method of computing accurate enthalpies can be used further to find excess enthalpies (or heats of mixing) for mixtures. An excess enthalpiy is the difference between the total enthalpy of the real mixture and that of the ideal mixture. The magnitude of excess enthalpies increase and therefore become more significant near the critical region and especially in the dense fluid region.

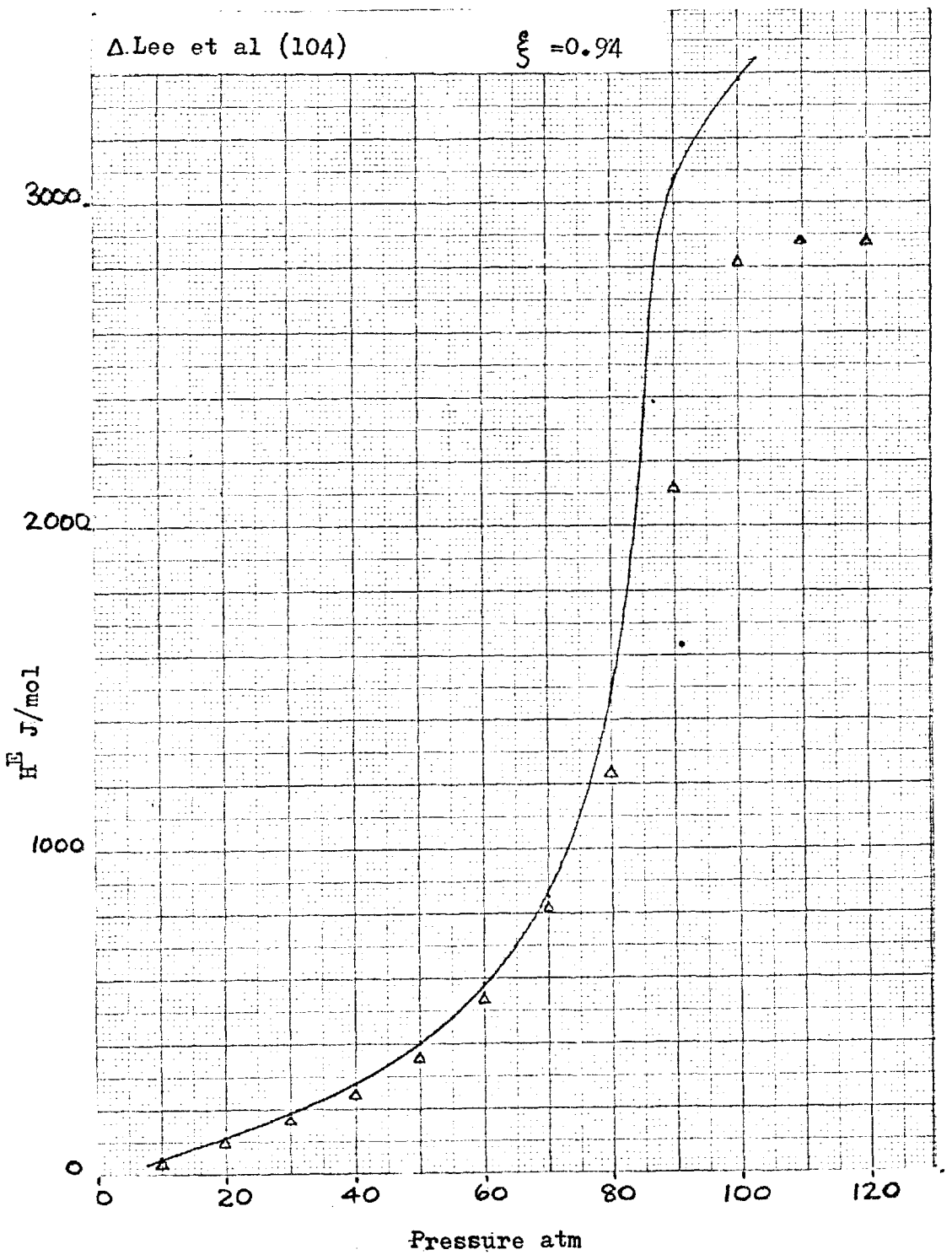
The excess enthalpies are defined :

$$H^E = H^t_{mix} - \sum_{i=1}^{i=N} x_i H^t_i \qquad (4.5)$$

where H^t_{mix} in these calculations is H configurational.

The configurational enthalpies H_{mix} and H_i are computed by the programs developed in this work, and then processed further in equation (4.5). Lee and Mather (104) have measured excess enthalpies for mixtures of nitrogen and carbon dioxide in a flow calorimeter at 313.2K for the range (4-131)atm. They compare their experimental results with those of others, and there is good agreement. They have also calculated H^E at equimolar concentration using several different theories. Agreement between their computations and their own experiments is good at low pressures but divergence occurs with the rapid increase of H^E with pressure at 60 atm. Above 120 atm there is approximately 100% difference. between the highest and lowest predicted H^E (1600 and 3300 J/mol respectively).

Fig 67 Carbon dioxide-nitrogen system, excess enthalpy at equimolar composition at 313.2 K.



On Fig 67, H^E is plotted against pressure showing computed values for this work and smoothed experimental points of Lee and Mather. Agreement between the two is good. Several values of ξ were tried to obtain a good match of computation and experiment; 0.94 was the best value obtained here.

To make comparisons with experiment, the published enthalpies had to be converted from residual or total enthalpies to dimensionless configurational enthalpies (i.e. H/RT).
The computations on the carbon dioxide - nitrogen system have shown that the values of H/RT for components and the mixture are good enough to obtain agreement of computed H^E with experimental H_E. Excess enthalpies are a stiff test of enthalpy predictions as their (H^E) calculation involves many rounding errors.

3. Joule-Thomson Coefficients

Experimental measurements of adiabatic and isothermal Joule-Thomson coefficients are not as plentiful as other types of thermodynamic data - such as compressibility factors and two-phase equilibrium data. In recent years it has been shown that some Joule-Thomson measurements are quite inaccurate and inconsistent. It is interesting to note that in the past, when P-V-T data at low pressures and temperatures (below 373K and 10 atm) were difficult to determine experimentally Joule-Thomson coefficients were considered a good source of information to fill these gaps. Now that the P-V-T data is more easily available it can be used to calculate Joule-Thomson coefficients. It is in this way that the inconsistencies in older published experimental work have been shown up.

1. Carbon Dioxide

Both adiabatic and isotherm coefficients were computed in this work. The adiabatic coefficients of carbon dioxide have been determined by many workers, and those determined by Roebuck (23) are taken to be the best available. Johnson and White (36) reviewed Joule-Thomson data available at the time (1948), and they came to the conclusion that the work of Roebuck and co-workers was the most accurate and reliable. The adiabatic coefficients published by Roebuck are calculated from very careful measurements of pressure and temperature changes and constant enthalpy.

Fig 16. Carbon dioxide, adiabatic Joule-Thomson coefficients.

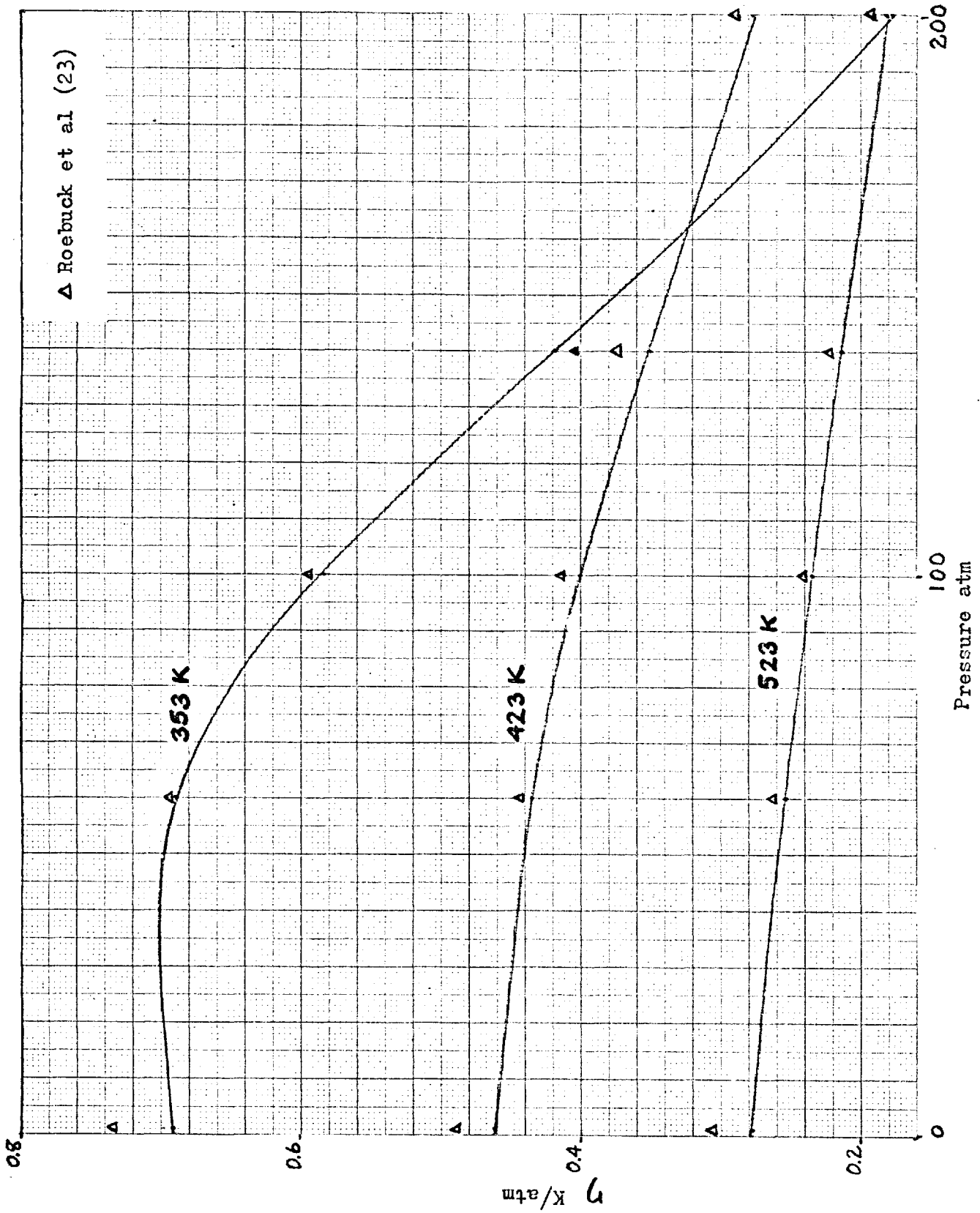
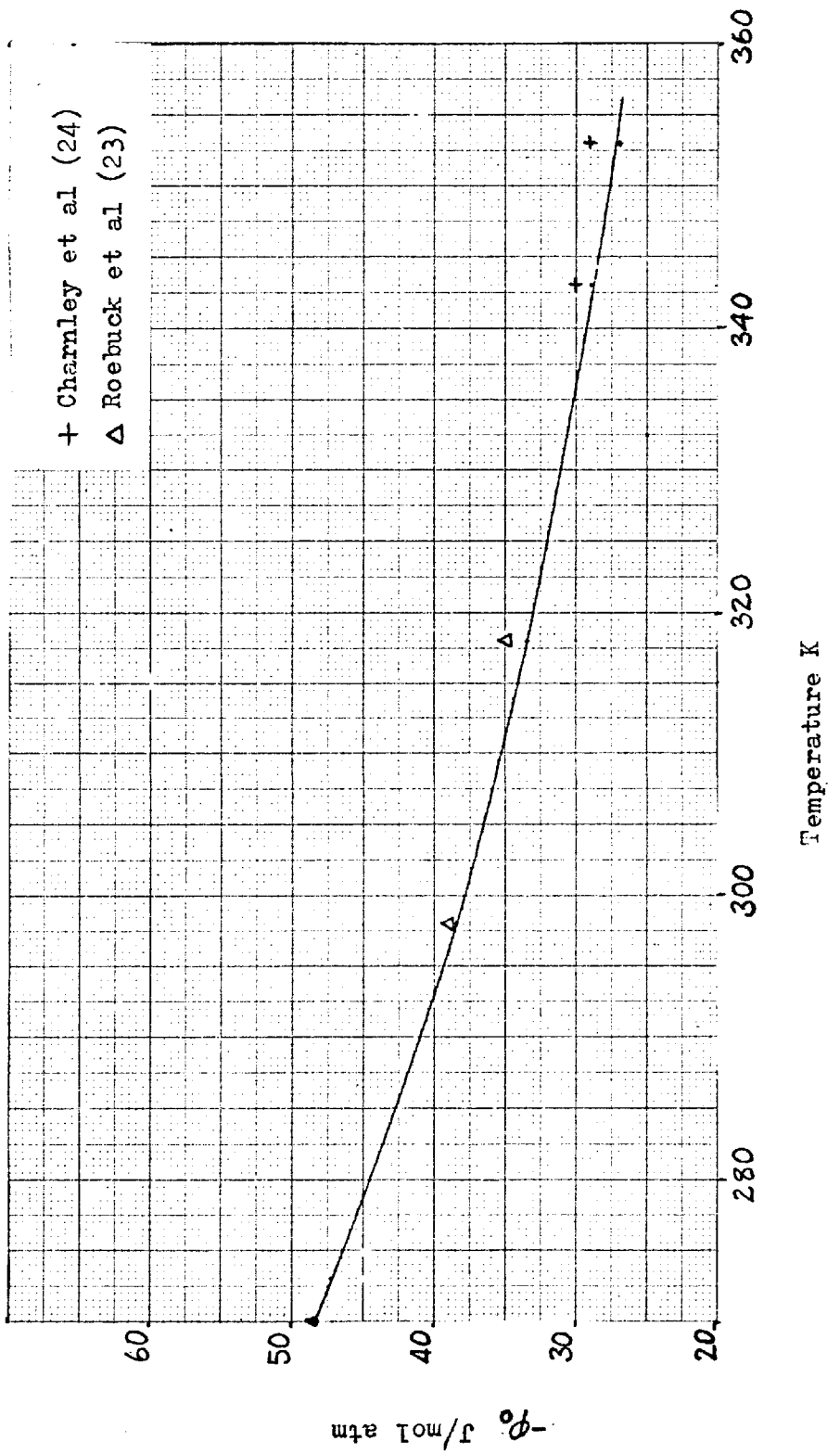


Fig 10. Carbon dioxide, variation of computed isothermal Joule-Thomson coefficient at zero pressure with temperature.



Charnley and co-workers (24) measured experimental isothermal Joule-Thomson coefficients of carbon dioxide in a study of the coefficients of mixtures of carbon dioxide and ethylene. They give their results expressed as the coefficients at zero pressure φ_o. φ_o is obtained by extrapolation to P = 0 for measurements of φ at pressures in the range (4-10)atm.

Adiabatic coefficients were computed in the pressure range (1-200)atm, on nine isotherms. The temperatures were the same as those used by Roebuck. Fig 16 shows three of the isotherms for η and some of Roebuck's experimental measurements. Agreement with experiment is to within 5% except at low pressure. Different values of Δ P and ΔT (equations (2.123) and (2.127)) were tried in the computations, but the difference in computed results for η were negligible.

Computed isothermal coefficients at 1, 5, 10 atm are shown in Fig 9, extrapolated to zero pressure. In Fig 10, $-\varphi_o$ is plotted against temperature for computed φ_o and the experimental results of Roebuck and Charnley. The adiabatic coefficients of Roebuck have been extrapolated to zero pressure and multiplied by the appropriate value of the ideal specific heat - to give isothermal coefficients at zero pressure. ($-\varphi_o = \eta . C_{p_o}$). This plot shows the consistency of the two sets of experimental data - despite the scatter in the measurements of Charnley et al (see Fig 8). The ideal specific heats were taken from the National Bureau of Standards Hand Book (25).

Fig 8. Carbon dioxide-ethylene system, isothermal Joule-Thomson coefficient at zero pressure.

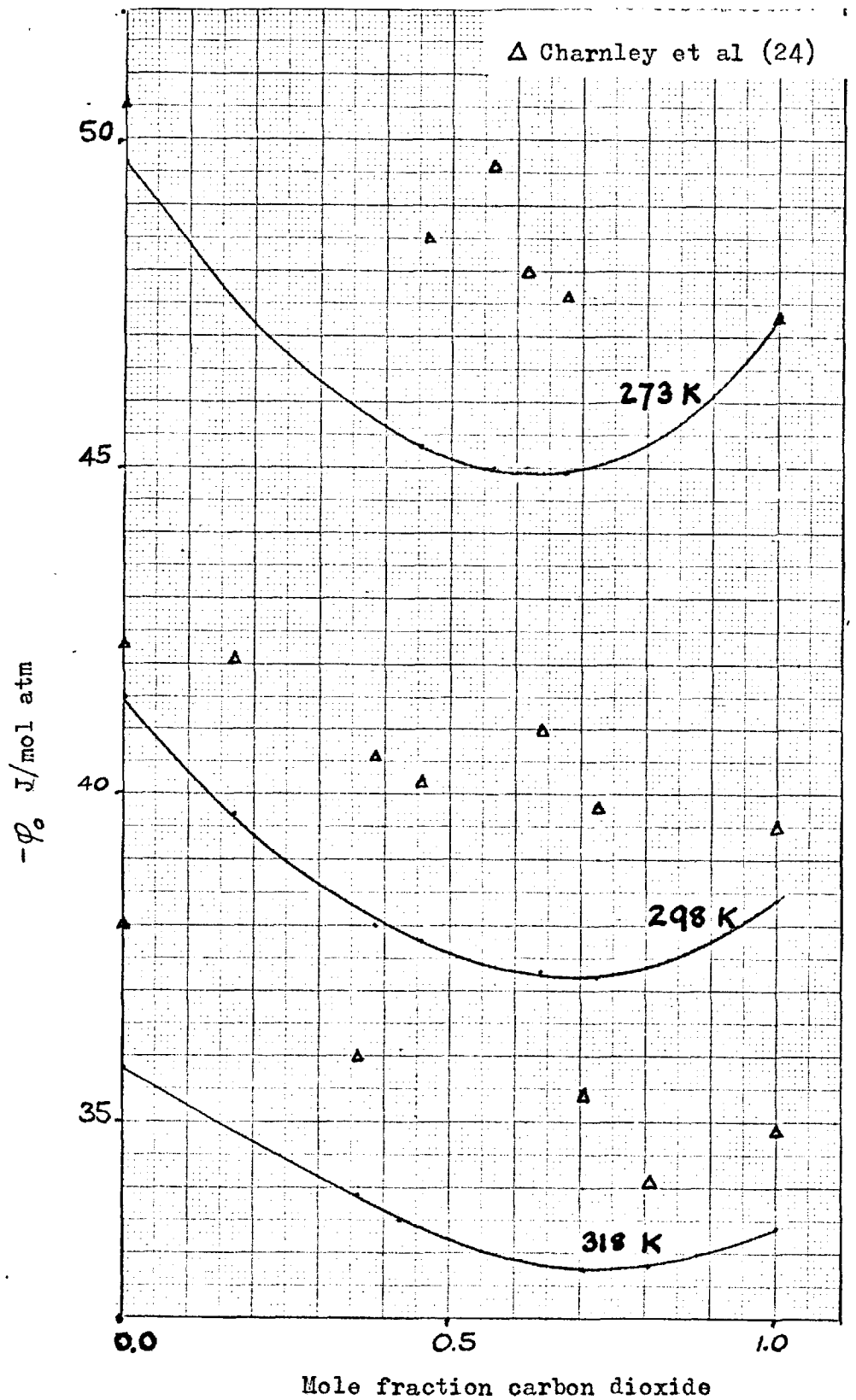
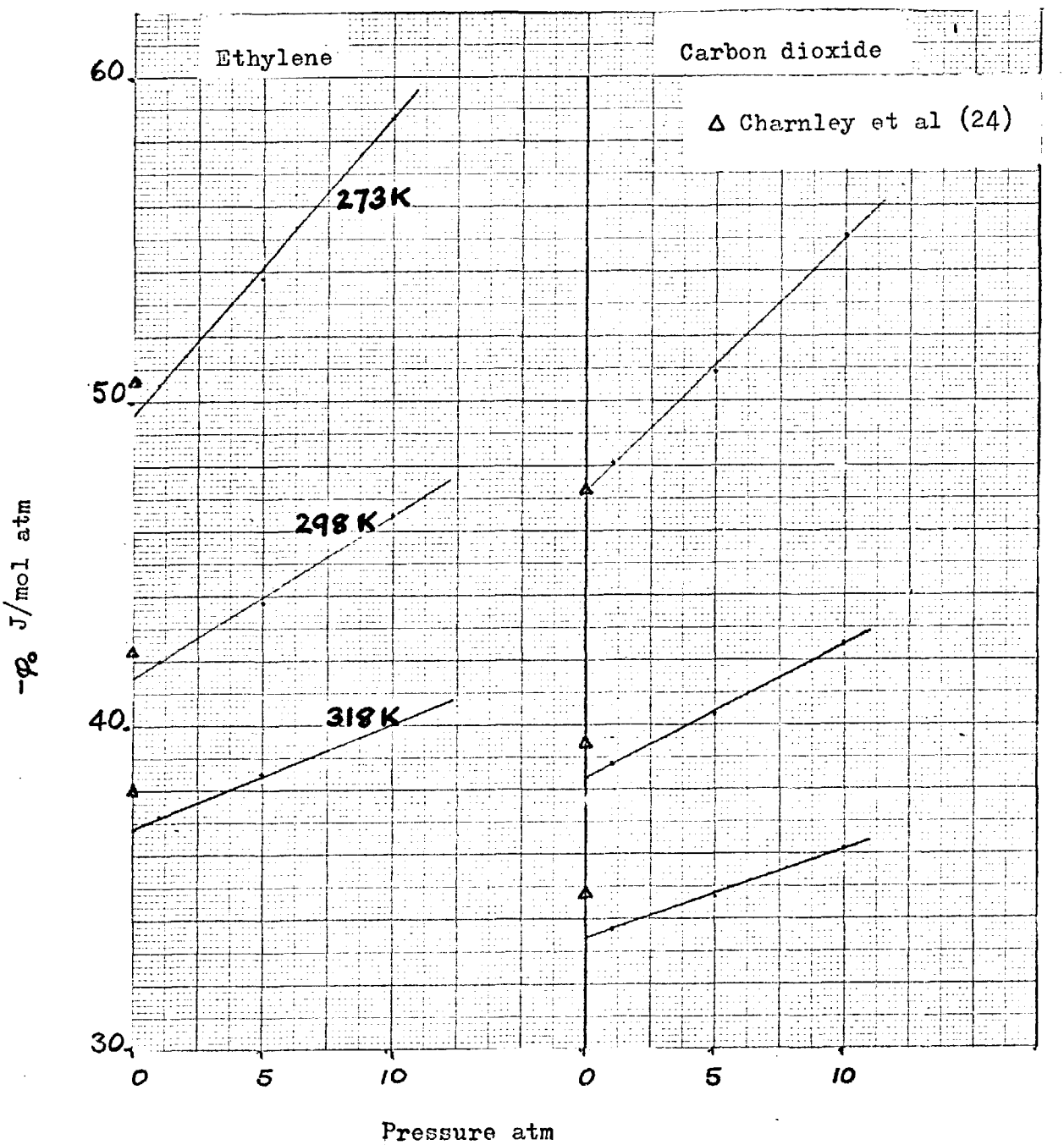


Fig 9. Carbon dioxide-ethylene system, extrapolations of computed isothermal Joule-Thomson coefficients to zero pressure.



2. Carbon dioxide - Ethylene

Charnley et al (24) give isotherms for φ_o at 273, 298, 318K for four or five different compositions of carbon dioxide and ethylene, for isothermal Joule-Thomson coefficients. φ was computed at these temperatures for 1,5,10 atm, and φ_o found by extrapolation to zero pressure. The results are shown in Fig 8. Agreement is not too good, even considering the scatter of the experimental work. The unlike pair interaction parameter was 0.94 (12).

3. Propane

Adiabatic Joule-Thomson coefficients were determined experimentally by Sage et al (28) for a wide range of temperatures - up to 377K and pressures - up to 38 atm. Both adiabatic and isothermal coefficients for propane were measured by Yesavage et al (29). They give φ for the range (266-393)K and (0-136)atm, and the adiabatic coefficients for the same pressure range at approximately 268K.

Computed adiabatic coefficients are shown in Fig 11 with some of the experimental results of Sage (28). Agreement between computation and experiment is only good at 377.4K. This result is borne out by a study made by Manning and Canjar (26). In this study, they compare experimental adiabatic coefficients at zero pressure, - i.e. η_o, with their own computed values of η_o. They compute η_o from the relation

$$(C_{Po} \cdot \eta) = T^2 \frac{d(B/T)}{dT} \qquad (4.2)$$

Where B is the second virial coefficient.

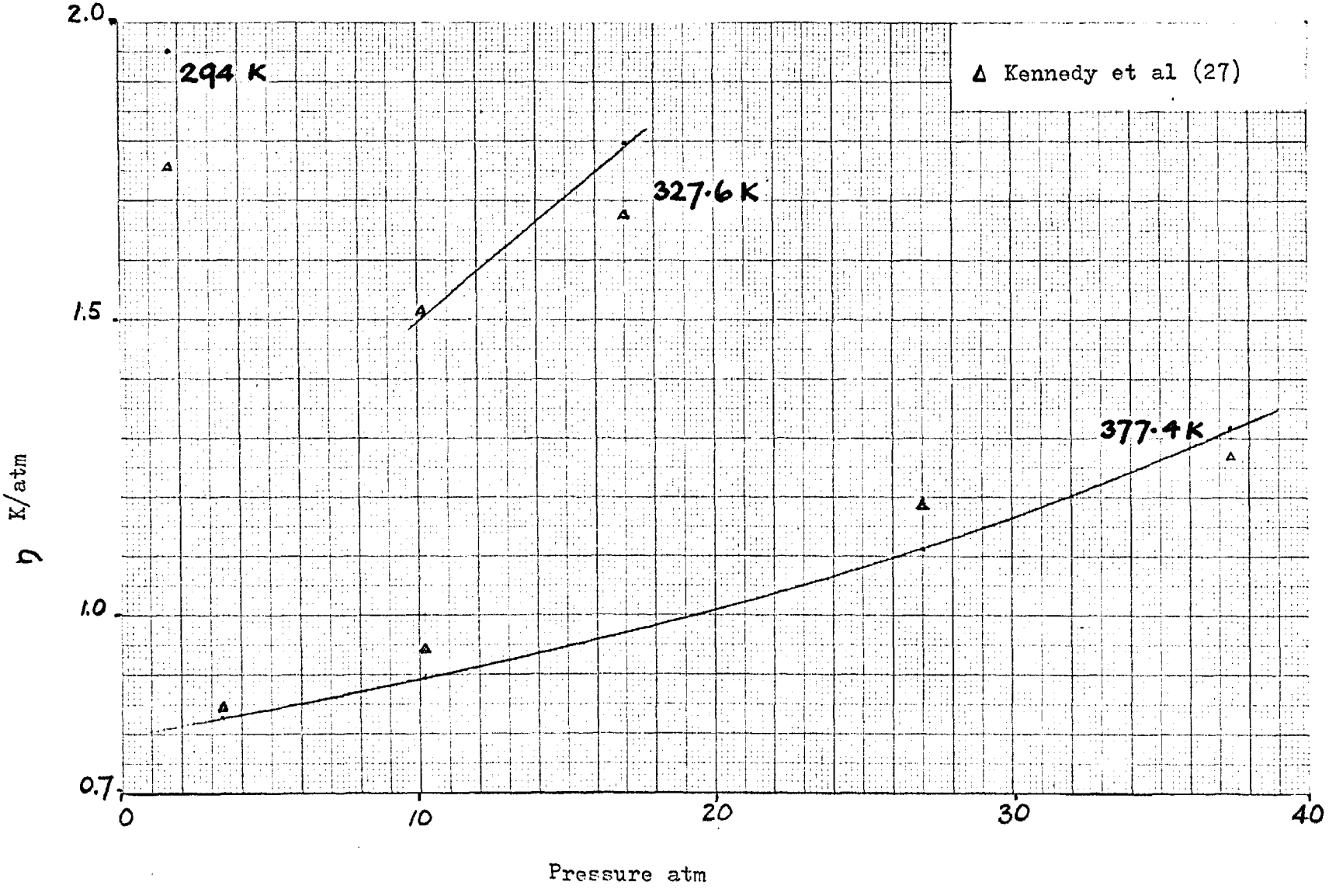


Fig 11. Propane, adiabatic Joule-Thomson coefficient.

Equation (4.2) is only exact at zero pressure, and Manning and Canjar used the virial coefficients accurately determined by McGlashan and Potter (30). They plot η_o against temperature and their computed η_o only agrees with experimental η_o (28), at a temperature approximately equal to 377K.

4. Butane

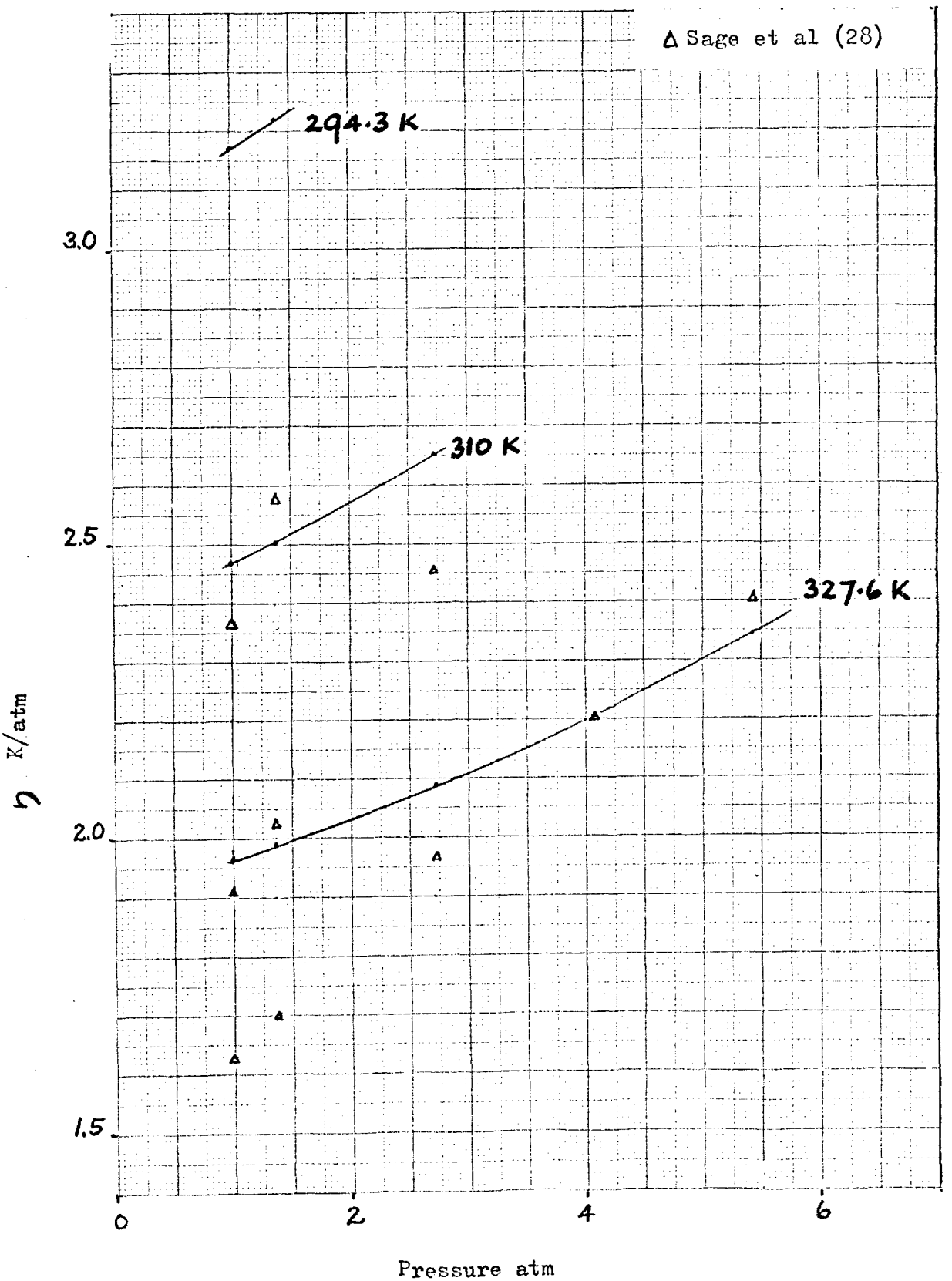
Kennedy et al (27) determined adiabatic coefficients calorimetrially for temperatures (284-377)K and pressures (1-15) atm. Computations of η were made at some of the temperatures used by Kennedy et al. Fig 12 shows three isotherms at 294.3, 310.0, 327.6K. Agreement with experiment is poor; but the computed η_o of Manning and Canjar (26) for butane agrees well with η_o in this work. η_o here is obtained by extrapolation in Fig 12.

Examples of η_o at two temperatures:

T K	Expt'l η_o (28)	Calc'd η_o (26)	η_o (this work)
327.6	1.4	1.88	1.90
294.3	1.8	2.53	3.05

η_o in K/atm.

Fig 12. Butane, adiabatic Joule-Thomson coefficients.



5. Pentane

Brown and Pattee (31) measured the adiabatic Joule-Thomson coefficient at 1 atm using a throttling calorimeter. Their temperature range was (390-730)K. Kennedy et al (27) also did experimental work on η for pentane. They covered the range (327-377) and (1-6)atm. In this work, η was computed at 327.6, 344.3 and 361K. Fig 13 shows these isotherms with some experimental work from Brown (31) and Kennedy (27).
The experimental work shows great disparity at 361 K, and neither agree with computed η . Manning and Canjar also note this divergence at zero pressure for η . Their computed η_o agrees with a value of η_o obtained from computed η in this work. For example:

T K	Computed coefficients		Expt'l coefficients	
	η_o(this work)	η_o(26)	η_o(31)	η_o(27)
361.0	1.8	1.71	2.44	1.3
344.3	2.18	2.28	3.43	1.47

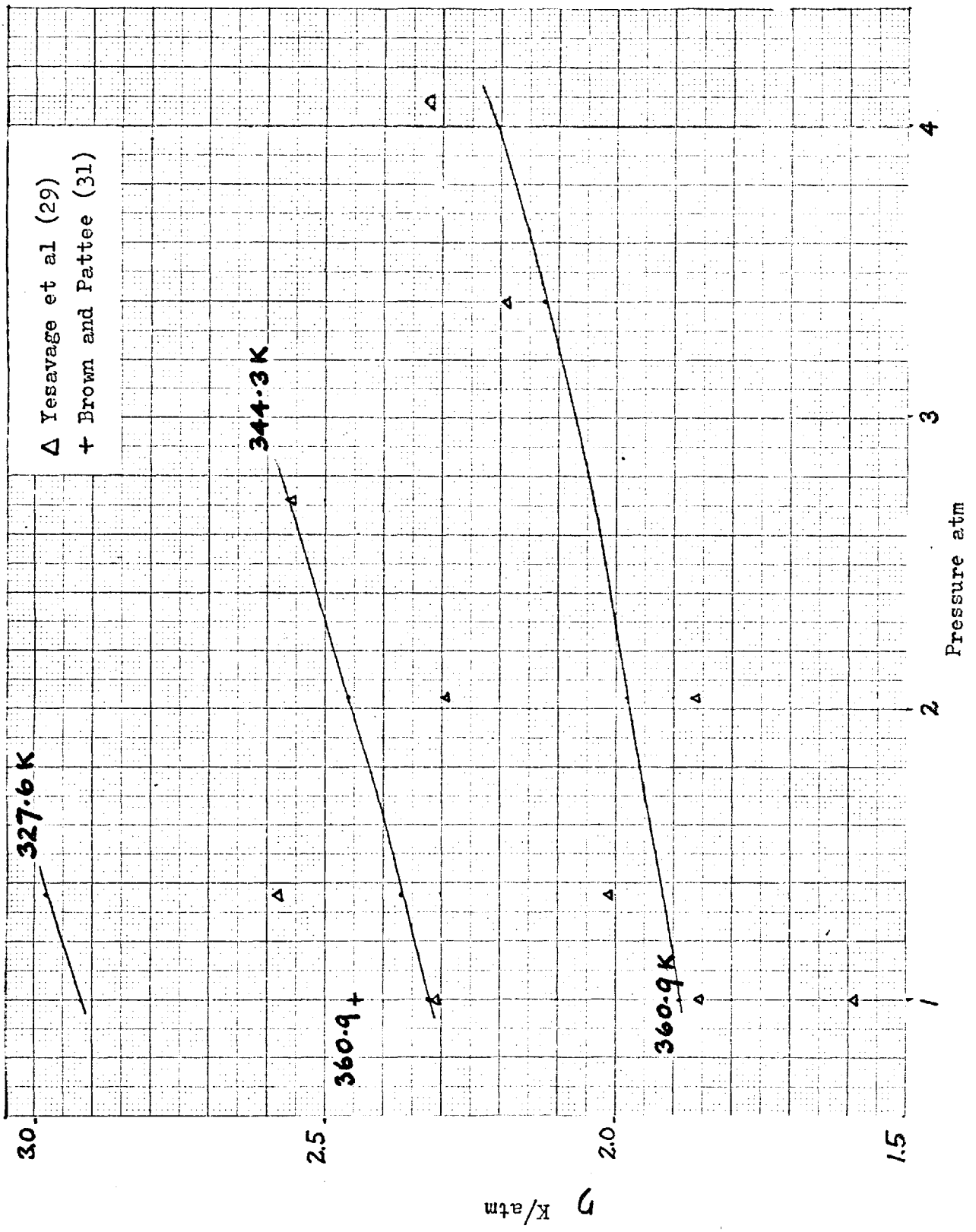
η_o in K/atm.

Sage and Lacey (47) have calculated isothermal coefficients for pentane from P-V-T measurements for a wide range of temperature and pressure - (311-509)K and up to 680 atm. Taking a few of their values at 344.3K, and comparing with computed values of η multiplied by the specific heat, we have

P atm	Computed $\varphi[\eta.C_p]$ this work	Expt'l φ (47)
2.6	352.0	342.0
1.3	324.0	259.0*
0.0	311.0	182.0*

φ in J/mol atm.

Fig 13. Pentane, adiabatic Joule-Thomson coefficients.



* These values are reasonably consistent with values of φ (actually $\eta \times C_p$) measured by Kennedy et al (27) - 276, 192 J/mol, atm respectively. However this does not mean that the computed results are wrong, as it has already been shown that experimental work for both φ and η shows great scatter.

6. Air

Michels et al (32) calculated adiabatic Joule-Thomson coefficients for air from their own experimental PVT data. It is believed that they calculated η from

$$\eta = \frac{RT^2}{P} \cdot \left(\frac{\partial Z}{\partial T}\right)_p \cdot \frac{1}{C_p} \qquad (4.3)$$

Six of the isotherms computed in this work are shown in Fig 14. The temperatures range from 138K to 323K. Agreement with Michels' work is very close. Where there is disagreement, the differences are consistent with those between computed compressibility factors for air and Michels' experimental Z for air. A plot of Z against temperature should show similar trends for divergence as those in Fig 14 since from equation (4.3) at constant T,

$$\eta = \text{a constant} \times \left(\frac{\partial Z}{\partial T}\right)_p$$

Fig 14. Air, adiabatic Joule-Thomson coefficients.

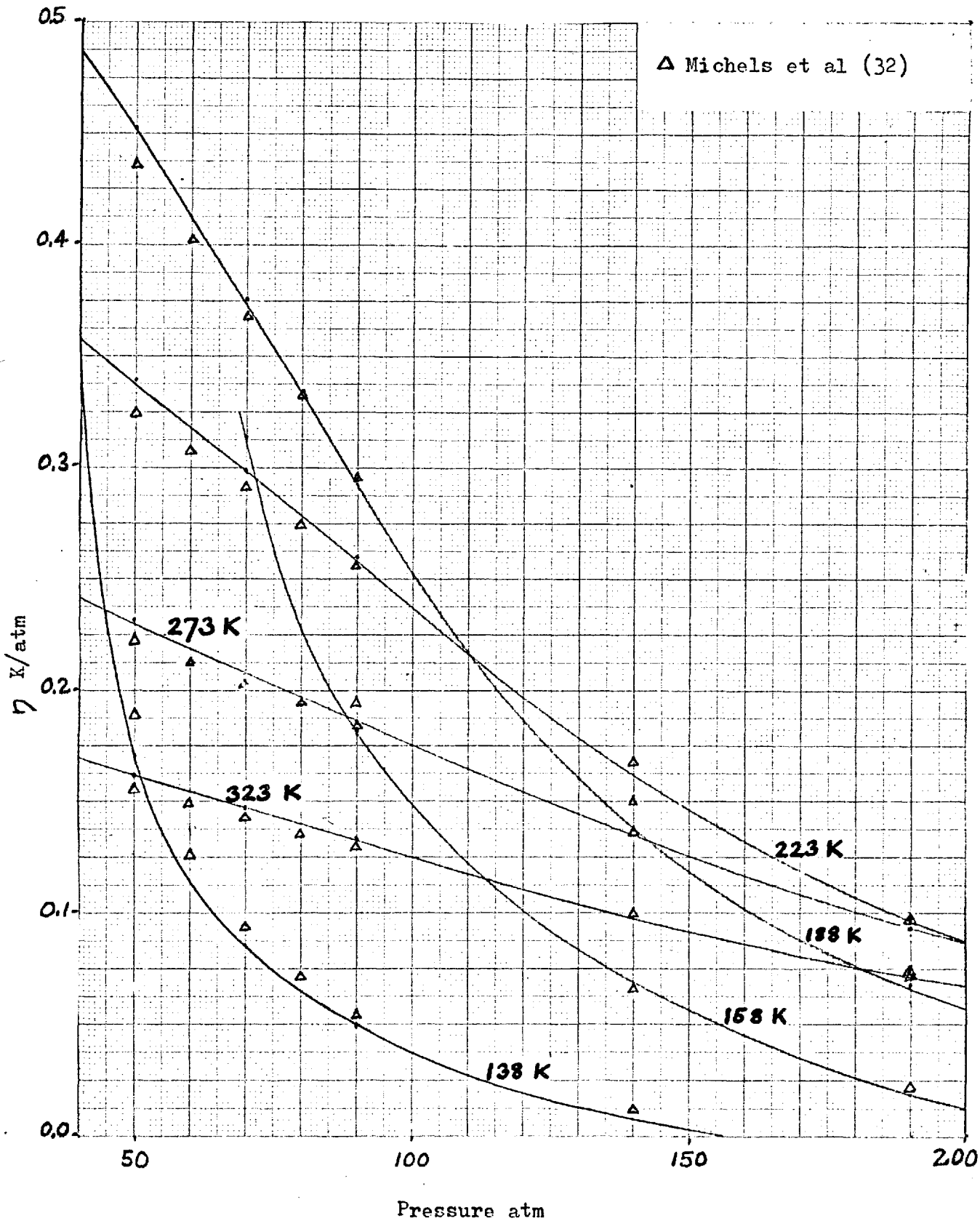


Fig 15. Air, compressibility factor against temperature.

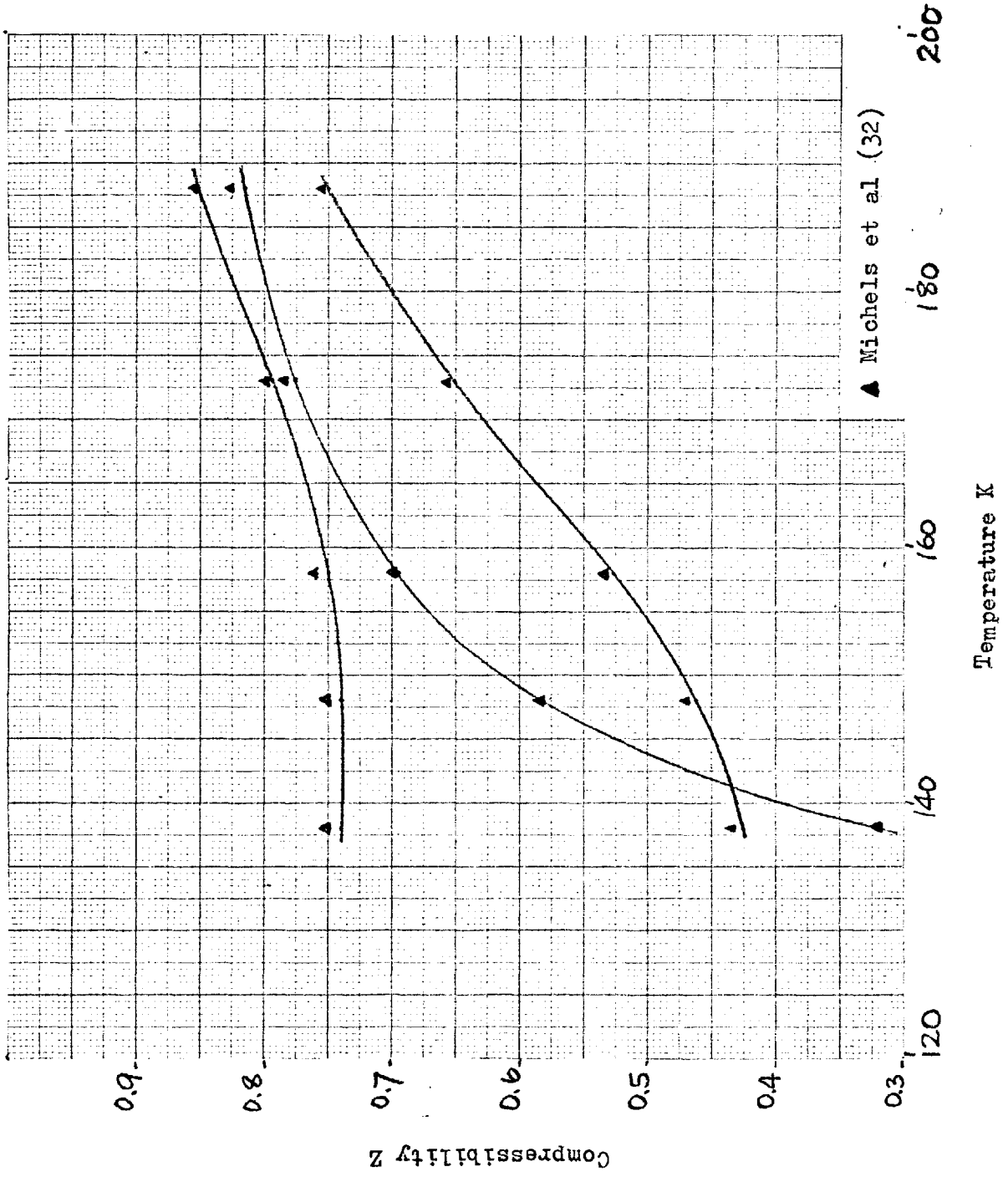


Fig 15 shows Z plotted against temperature - and error trends are consistent.

7. Methane-Ethane-Nitrogen

Alkasab et al (117) compare their experimental work on isothermal Joule-Thomson coefficients with computed φ using the BWR equation of state. There is quite good agreement between experiment and computation. Alkasab et al have used analytical differentials of the equation of state (BWR) for equation

$$\varphi = V + T\left[\left(\frac{\partial P}{\partial T}\right)_V \Big/ \left(\frac{\partial P}{\partial V}\right)_T\right] \qquad (4.4)$$

In this work, finite differences were considered satisfactory for equation (2.130). Isothermal coefficients were computed at two temperatures - 255.5K and 274.7K, using two of the mixtures which Alkasab et al investigated. The compositions were :

	Mixture 1	Mixture 3*
C_1	0.7373	0.2286
C_2	0.2624	0.7675
C_4	-	0.0006
N_2	0.0003	0.0033

* The numbers correspond to those in Alkasab's paper.

The table below shows a comparison between computations in this work and the work of Alkasab.

Mixture 1	T = 255.5 K	φ in J/mol atm	
P atm	φ expt (117)	φ computed (117)	φ (this work)
24.16	- 9.76	- 9.31	- 8.73
34.70	- 10.22	- 10.37	- 9.79
44.23	- 11.14	- 11.44	- 11.02
54.78	- 13.43	- 13.12	- 12.75
Mixture 3	T = 274.7 K		
5.44	- 15.24	- 15.23	- 13.02
12.25	- 16.98	- 16.79	- 14.68
20.41	- 19.49	- 19.61	- 17.62
31.30	- 27.37	- 28.03	- 25.67

There appears to be a misprint in the text of Alkasab's paper - the units given for φ are BTU/mol psi. Checking their results against φ for a similar mixture investigated by Budenholtzer et al, (118), and assuming consistency between the two sets of experimental results, the units must almost certainly be BTU/lb psi. The results of Budenholtzer and Alkasab are in quite good agreement although the concentrations in the former's work is 0.25 ethane and 0.75 methane.

Agreement between φ computed in this work and φ experimentally determined by Alkasab is good, but not as close as the predictions using the BWR equation of state. Wenzel (119) also compared computed and experimental Joule-Thomson coefficients for mixtures of methane, ethane and nitrogen. He found that predictions using the BWR equation of state for an equation such as (4.4) were within 1.7% of experiment, and were closer than other methods he tried.

Several combinations of ξ_{12} were used in an attempt to get better agreement, but they made negligible difference to the computed φ. Results given here are those calculated with ξ_{12} from Prausnitz's table of values (12).

4. Vapour Liquid Equilibrium

Binary Systems

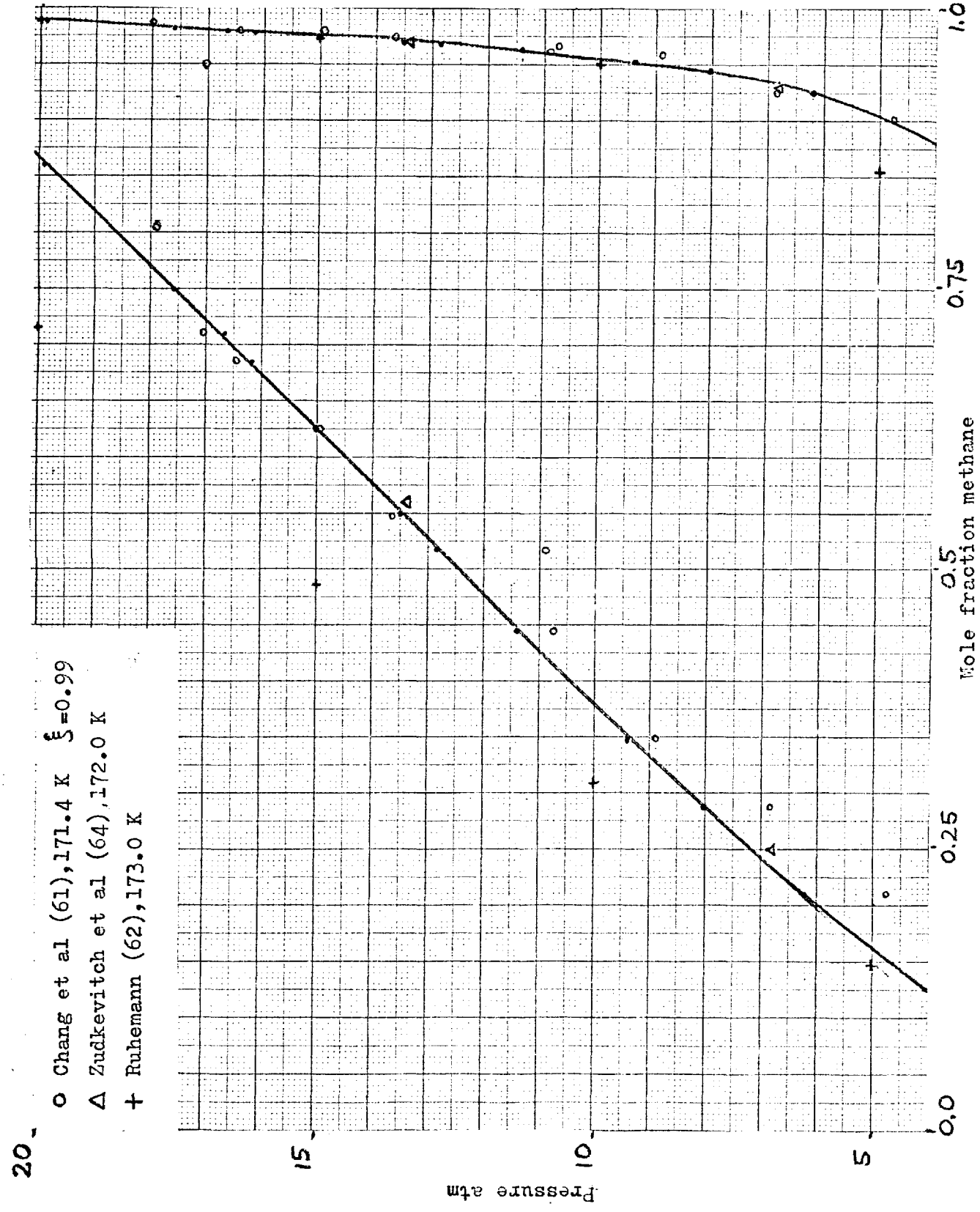
Nineteen binary systems were studied, They were chosen partly because they showed typical vapour liquid phase equilibrium phenomena and partly because experimental data was available in the published literature. The phase conditions studied include those where both components are subcritical, where only one is super-critical and where both are super-critical.
Calculations have been done with and without adjustment to the acentric factor, and using ξ_{12} equal to one, and otherwise.

1. Methane-Ethane

A bubble pressure line at 171.4K was computed for a range of compositions of methane-ethane. Experimental work at this temperature on vapour liquid equilibrium has been done by Chang and Lu (61), at 171.4K, Price and Kobayashi (63) at 172K and Ruhemann (62) at 173K. Experimental and computed results are shown in Fig 35. The experimental work is in good agreement, except Ruhemann's results in the liquid phase. However these points are smoothed interpolations of experimental results at other temperatures, and referring to Ruhemann's P-x diagrams of his original results, their scatter makes debatable the best position for the isotherm.

The computed results used adjusted acentric factors, for which the vapour pressures were taken from(82) and (80).
The unlike pair interaction parameter was 0.99.

Fig 35. Methane-ethane system, bubble pressure calculation at approximately 172 K.



Zudkevitch and Joffe (64) have developed a method of predicting vapour liquid equilibrium using the Redlich-Kwong equation of state. They compare some of their computed equilibria with experiment - for example this system, methane-ethane. The experimental results they quote are those of Price and Kobayashi, and they use K values (K = y/x) for comparisons of computation and experiment. For example :

at 171 K

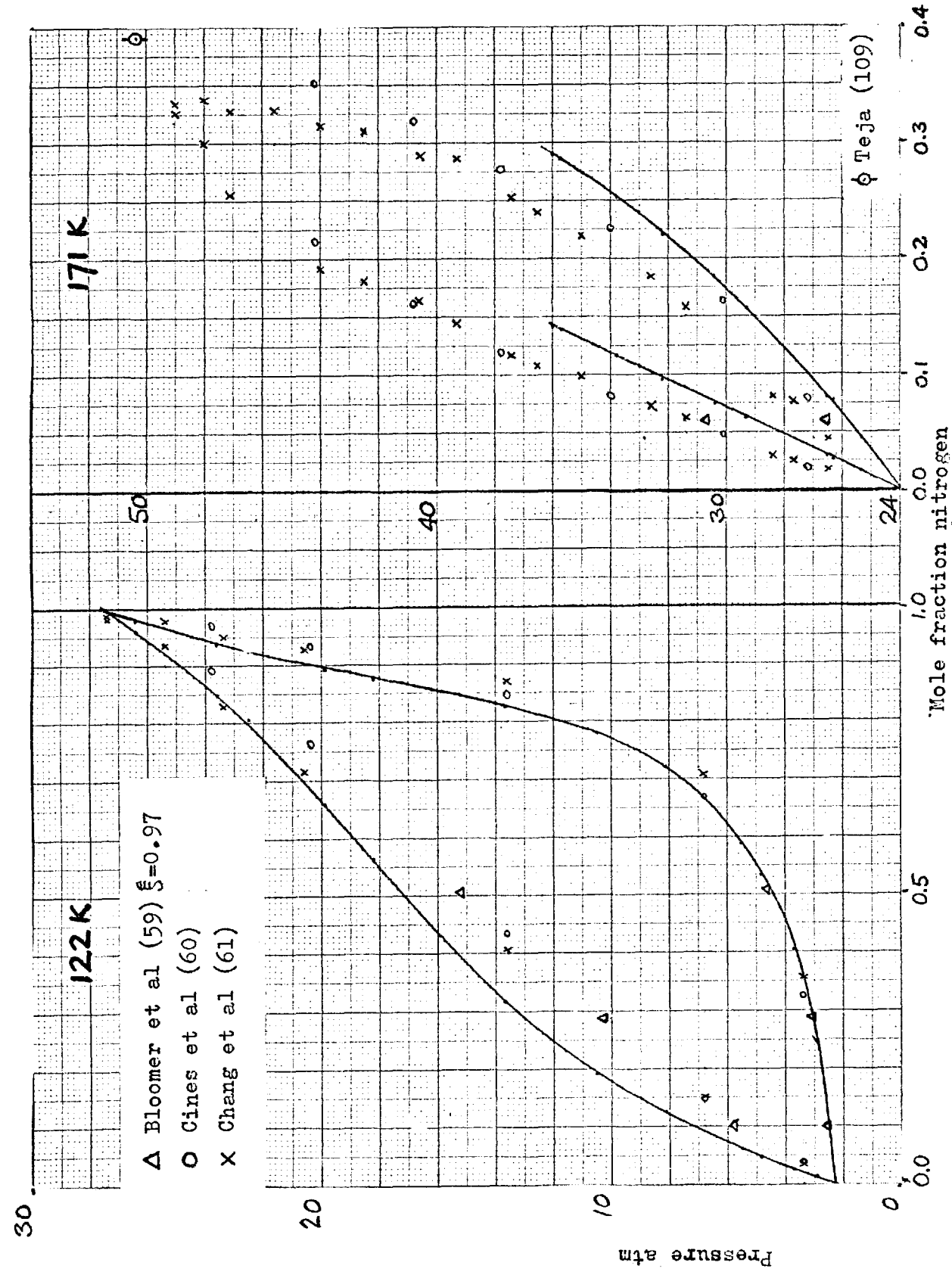
P atm	Component	x given	y calc'd	K(this work)	K(64) predict'd	K(63) expt.
6.8	C_1	0.235	0.935	3.900	3.820	3.710
	C_2	0.765	0.065	0.085	0.087	0.088
13.4	C_1	0.555	0.9725	1.750	1.760	1.780
	C_2	0.445	0.0275	0.062	0.062	0.068

Slight differences in compositions - and hence K - are inevitable because Zudkevitch and Joffe's method uses a flash procedure. This way both pressure and temperature are held constant and the vapour fraction is converged to 1.0 or 0.0 for a bubble or dew calculation respectively.

2. Methane-Nitrogen

Two isotherms were calculated for methane nitrogen mixtures. At 122K both components are subcritical and at 171K only methane is subcritical. Three sets of experimental work are available at these temperatures; Bloomer and Parent (59) investigated dew and bubble pressures at a wide range of temperatures for many compositions.

Fig 36. Nitrogen-methane system, dew pressure calculation at 122 K and 171 K.



Cines et al (60) also worked at a wide range of temperatures - 100K to 171K and they give eight smoothed isotherms in this range. Chang and Lu (61) studied the mixture at 120K and 171K only.

Isotherms at these two temperatures were computed by dew pressure calculation and are shown in Fig 36 along with experimental results. The unlike pair interaction parameter was taken as 0.97 and the vapour pressures for acentric factor adjustment were taken from (25) for nitrogen and (16) for methane.

At 122K, the predicted vapour phase is closer to experiment than the predicted liquid phase, and at 171K agreement for both phases is not so good. The three sets of experimental work agree well at this temperature except for the vapour phase at high pressures. However the critical point for this mixture at 171K calculated by Teja (109) is shown in Fig 36 and the apparently diverging vapour line of Cines et al seems consistent with this critical point. The computations of dew pressure at 171K broke down at a nitrogen mole fraction of 0.31 in the vapour. This is the point of maximum concentration and is the pressure at which 171K is a maximum temperature. Further discussion on the breakdown of dew calculations is in Section 5.

Where a component is supercritical, no adjustment to the acentric factor ω is possible, and it is kept at the accepted value given by Pitzer et al (3). Some results below are for methane-nitrogen equilibrium, computed with no ω adjustment (regardless of whether the temperature is supercritical or not).

Dew Pressure at 152.8K

	y (given)	x(calc'd) $\xi = 1$	x(calc'd) $\xi = 0.97$	x*(expt)	P(calc)atm $\xi = 1$	P(calc)atm $\xi = 0.97$	P*(expt)
CH_4	0.4912	0.7798	0.7997	0.8	24.3	25.4	25.5
N_2	0.5088	0.2202	0.2003	0.2			

Bubble point at 15.48 atm

	x (given)	y(calc'd) $\xi = 1$	y(calc'd) $\xi = 0.97$	y*(expt)	T K $\xi = 1$	T K $\xi = 0.97$	T*(expt)
CH_4	0.9705	0.89	0.87	0.86	156.4	155.7	156.0
N_2	0.0295	0.11	0.13	0.14			

* These results were obtained by interpolation from P-T-x curves from (59).

A value of 0.97 for ξ_{12} seems satisfactory at 122K and for the two points above but at 171K maybe a lower value would be better.

3. Methane-Carbon Dioxide

Donnelly and Katz (65) have done experimental work on the phase equilibria of methane carbon dioxide mixtures at seven temperatures between 271K and 200K. Dew and bubble pressures were computed at five of these temperatures and are shown in Figs 37,38. The dew calculations broke down at the maximum concentration (about 0.8 methane at 223K and 0.5 methane at 259.7K) and the bubble calculations broke down at a pressure a small percentage from the critical point. The liquid and vapour lines were successfully extended at 223K by bubble calculation to within a fraction of the critical point. This result is shown in Fig 37 as a dotted line.

Fig 37. Methane-carbon dioxide system, dew pressure calculation at 223 K and bubble pressure calculations at 219 K and 241 K.

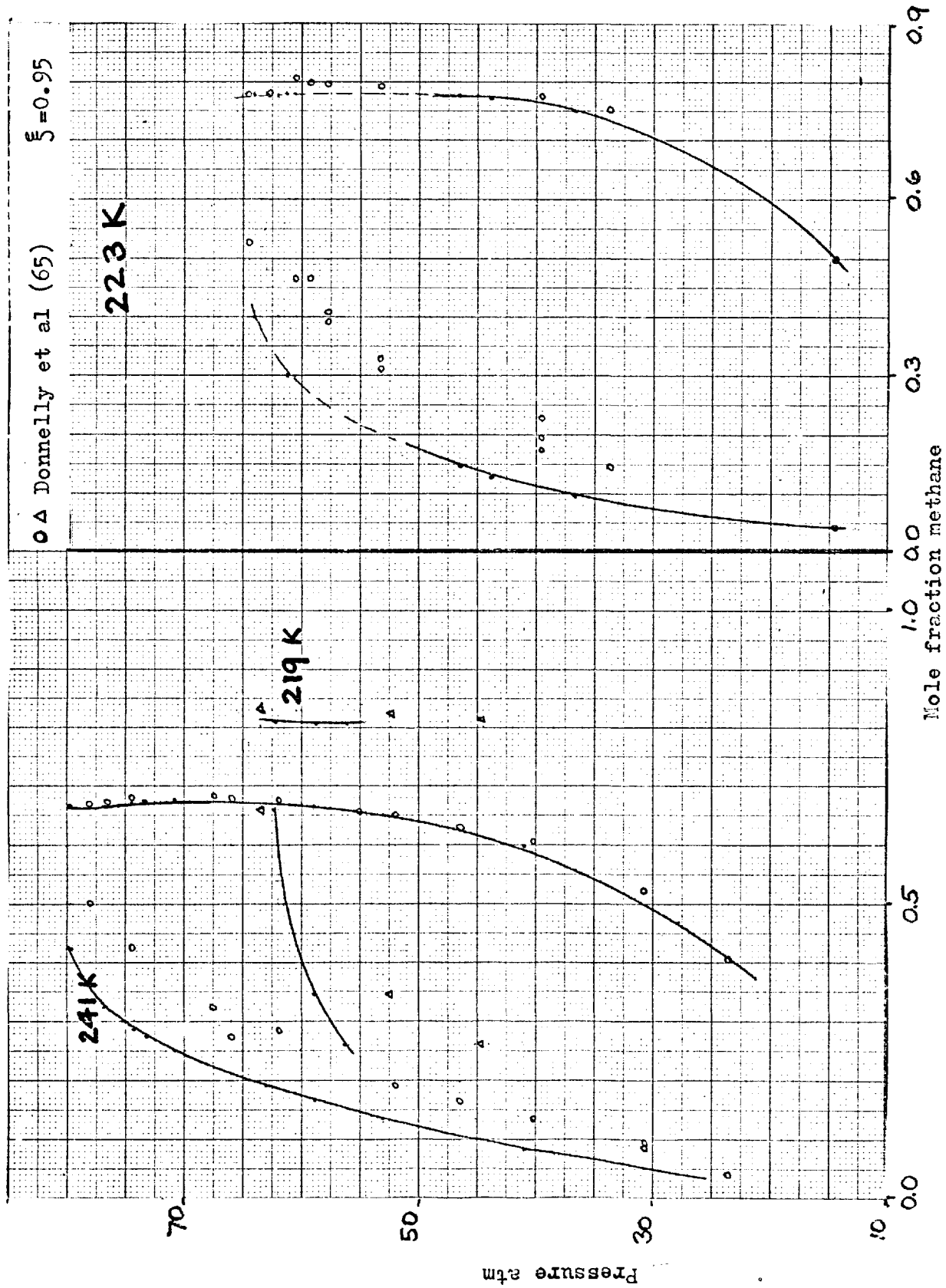
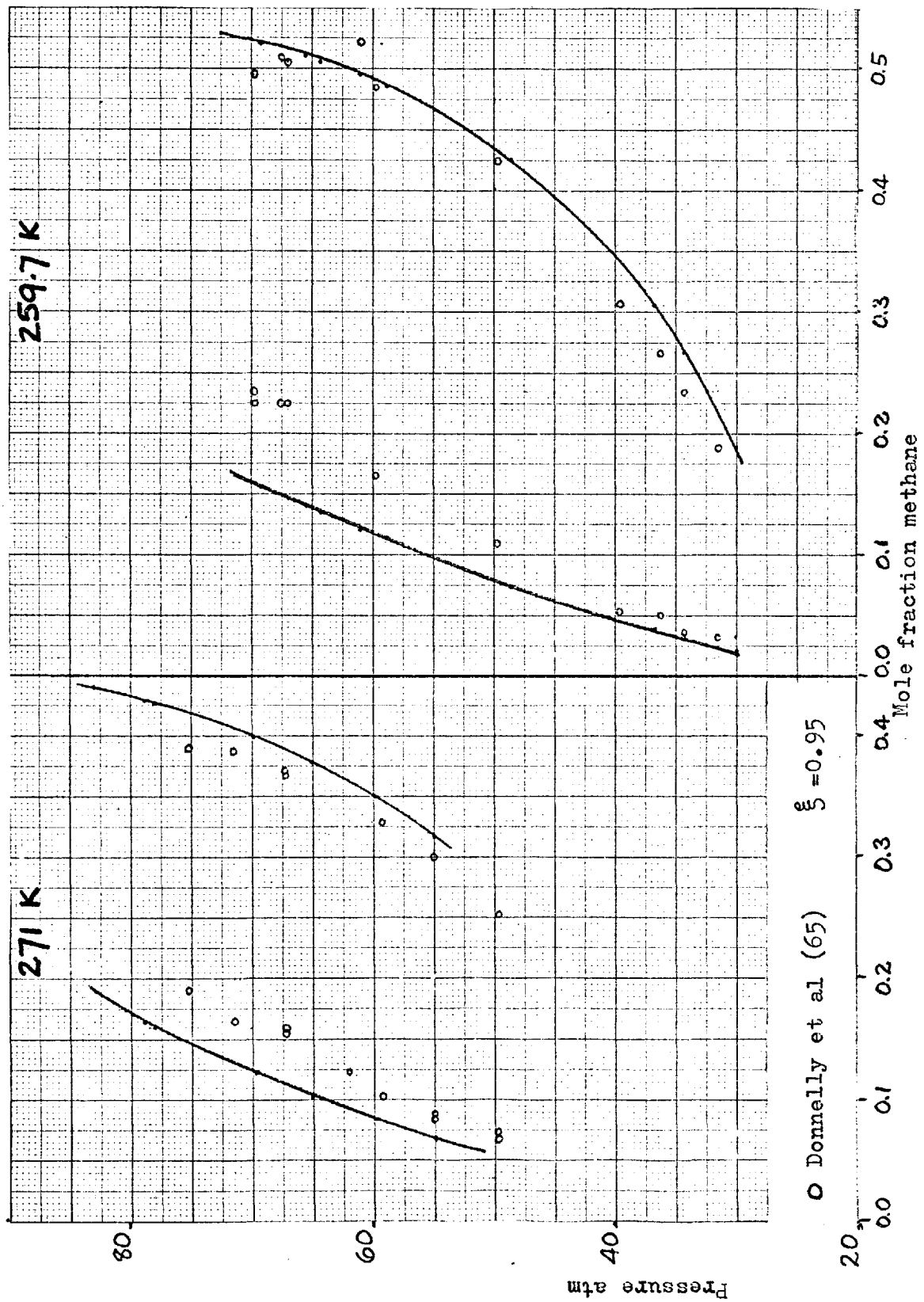


Fig 38. Methane-carbon dioxide system, bubble pressure calculation at 271 K and dew pressure calculation at 259.7 K.



For all temperatures, the liquid lines are in poor agreement with experiment. It is difficult to predict accurately phase equilibria for mixtures containing carbon dioxide, especially for the liquid phase, because its behaviour is so dissimilar to methane (the reference substance) in the liquid phase. The lower the temperature the greater the inaccuracy - a similar observation was made for the prediction of single phase compressibility factors for this mixture.

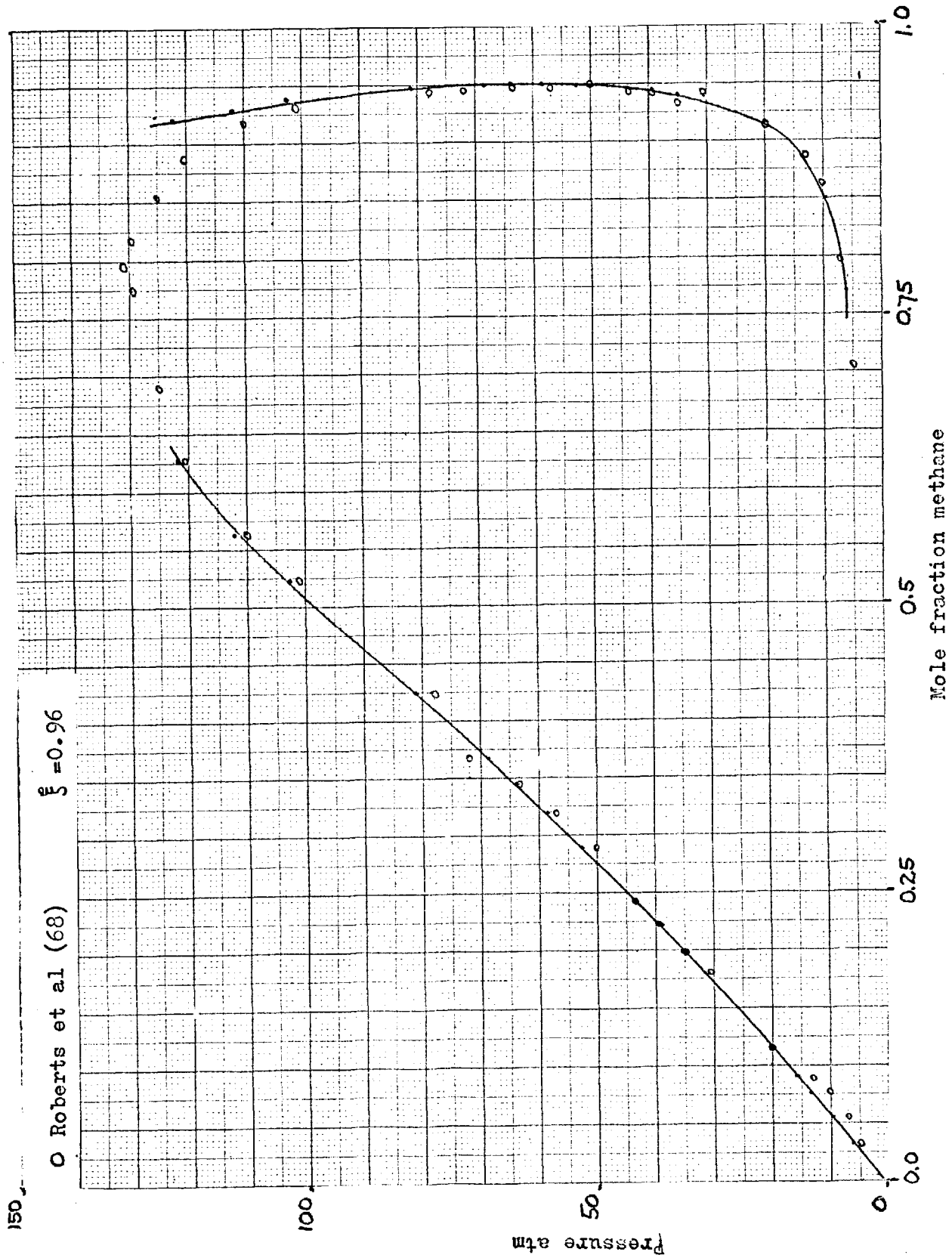
ξ_{12} was taken as 0.95.

4. Methane-Butane

Vapour liquid equilibrium for methane-butane mixtures has been measured experimentally by Roberts et al (68) at five temperatures in the range (411-210)K and by Sage et al (67) in the range (311-359)K. The latter also give the critical locus and the maximum temperature and pressure lines for various concentrations of methane. Hsi and Lu (69) calculated vapour liquid equilibria of methane with various hydrocarbons, including butane, using the Redlich-Kwong equation of state. They particularly chose conditions where one component was supercritical. They give an isotherm for the mixture at 294K and compare with the experimental results of Sage et al (67). There is good agreement between the two and their calculation breaks down at about 95% of the critical pressure of the mixture.

In this work, a bubble pressure line was computed at 277.6K using $\xi_{12} = 0.96$. Hsi and Lu also use a parameter to correct the interaction term in the mixture critical temperature calculated by the mixing rule (equation 1.29), and their value is 0.9602.

Fig 39. Methane-butane system, bubble pressure calculation at 277.6 K.



However their value found by fitting computed vapour-liquid equilibrium to experimental work (67). Agreement between the isotherm computed here at 277.6K and the experimental work of Roberts et al was extremely good and is shown in Fig 39. The calculation broke down at 125 atm which is about 5% less than the critical point.

Attempts to calculate isotherms at 411, 244 and 211K (all experimentally determined by Roberts et al) were not so successful. These failures can be explained in several ways. At 211K, the reduced temperature is less than 0.5, and this is below the lower limit of the Vennix equation of state. At 411K, the experimental work (67, 68) do not agree so well. From Sage's maximum temperature and pressure curves, the critical pressure is at a mole fraction of methane of 0.1 and from Robert's work it is 0.2 methane. In addition, 411K is within 3% of the critical point of pure butane, and possibly too close for the computation to proceed normally. The experimental bubble pressure lines are almost vertical, so that if an initial guess were slightly unsuitable, then intermediate calculations searching for a solution could easily become super-critical, and the computations cease. This is probably the case at 244K, as well as the fact that the reduced temperature might well be under 0.5 in some iterations, causing further inaccuracies to build up.

5. Methane-Isobutane

The mixture methane-isobutane was studied because the data given by Olds et al (70) were given in weight fractions, and data were required to test a program written to process data given as weight fractions. Olds et al give three experimental isotherms of smoothed vapour-liquid equilibria, at 311.0, 344.3, 377.6K.

Fig 40. Methane-isobutane system, bubble pressure calculation at 311 K.

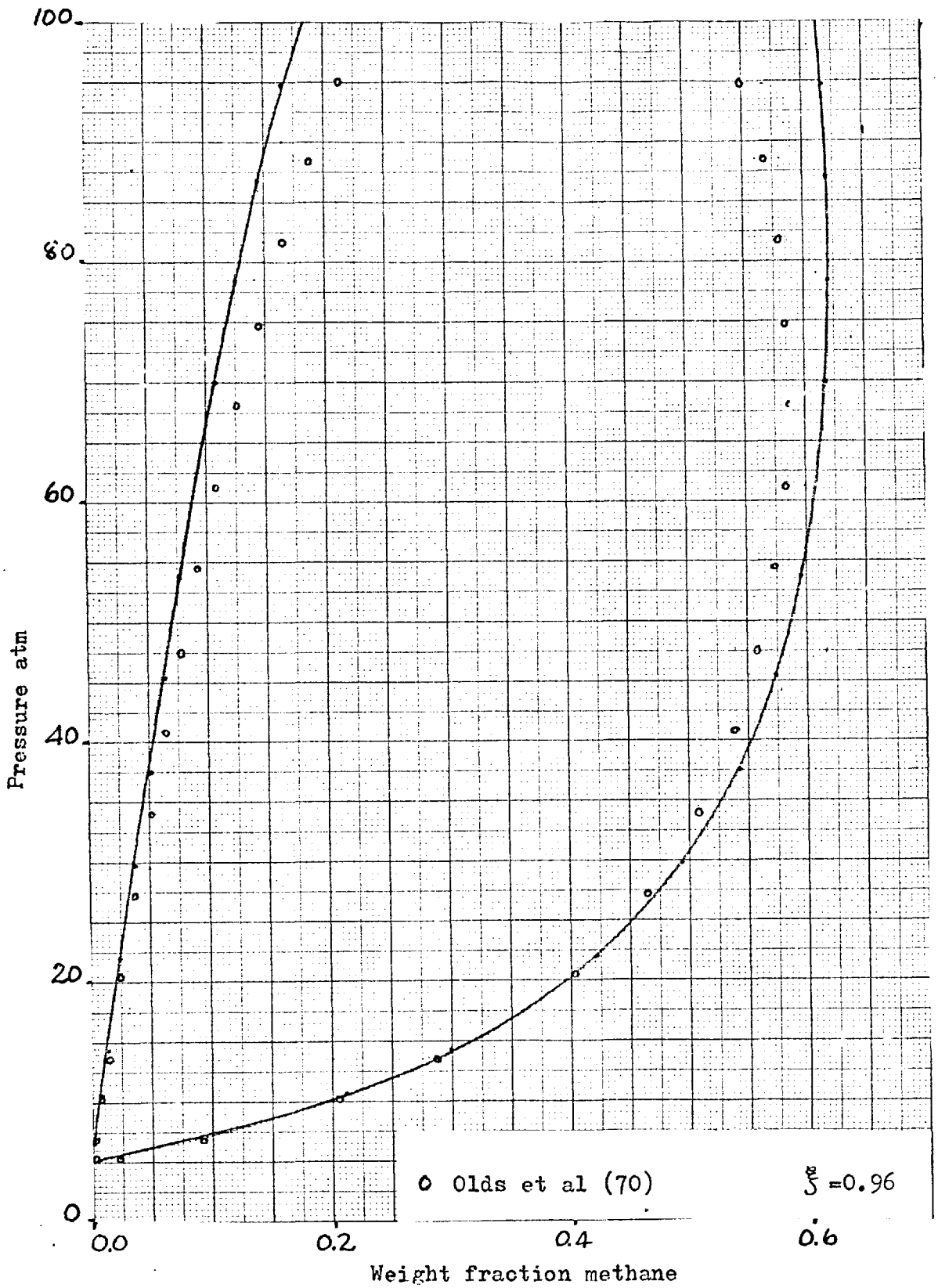
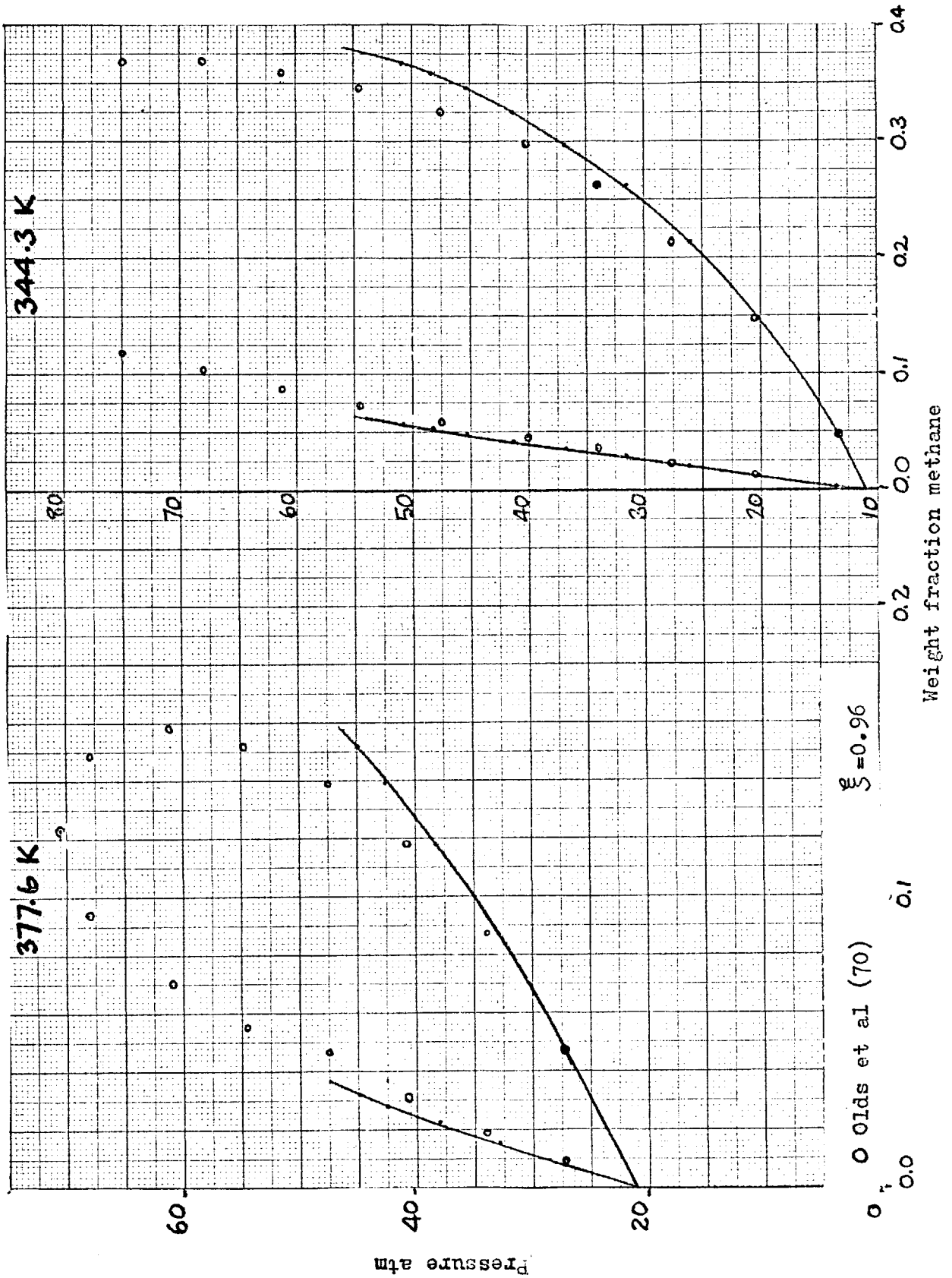


Fig 41. Methane-isobutane system, dew pressure calculations at 377.6 K and 344.3 K.



One bubble pressure line and two dew pressure lines were computed at these temperatures respectively. Figs 40,41 show these computed isotherms and the experimental points. The bubble pressure calculation breaks down near the critical point - not actually shown in Fig 40, and the dew calculations broke down at the points of maximum concentration. Vapour pressure data was taken from (120) and ξ_{12} was 0.96.

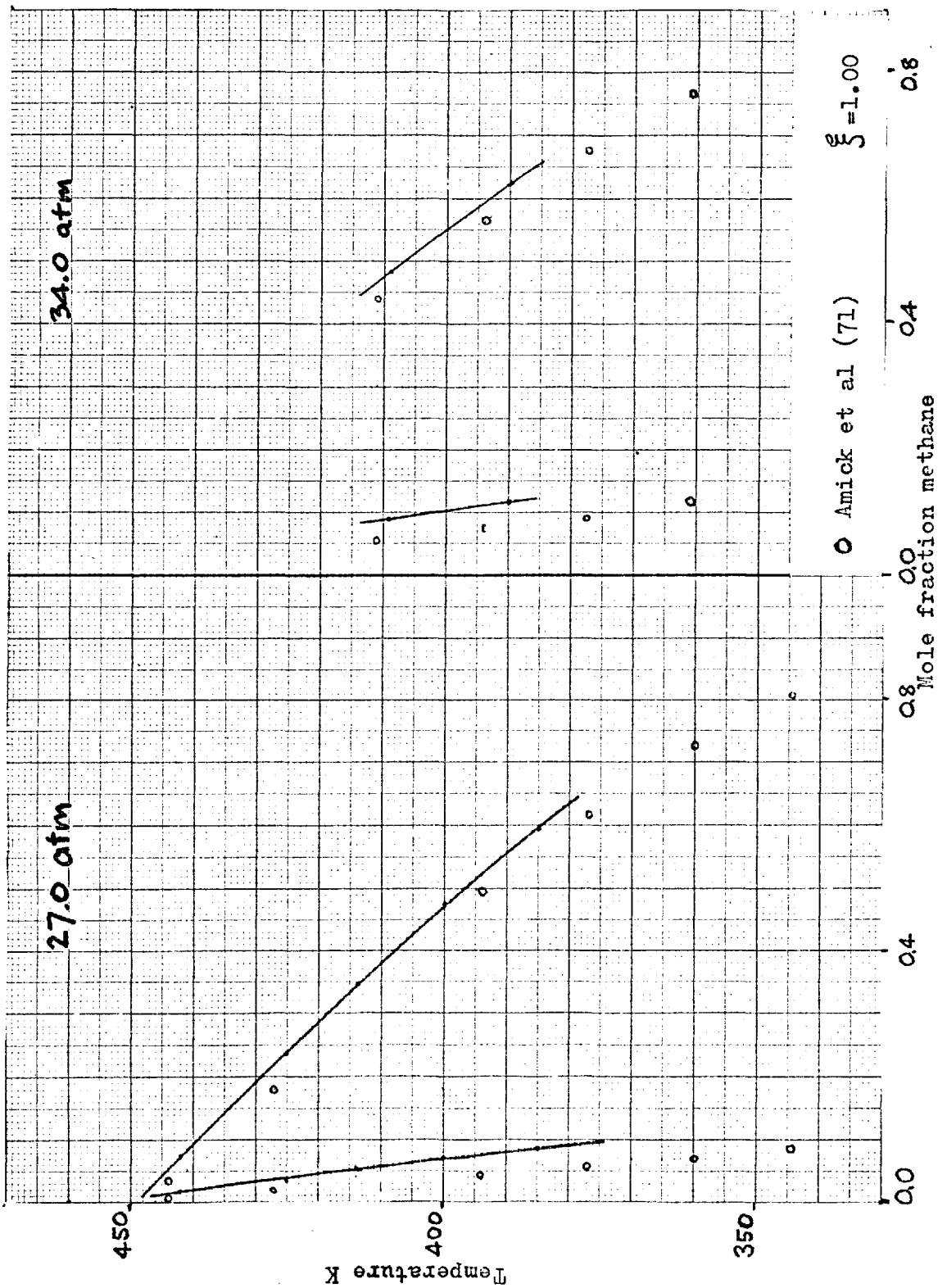
Agreement of computed equilibria and experiment is good, with slightly greater divergence on the vapour lines at higher pressures.

6. Methane-Isopentane

The phase equilibria of methane-isopentane was studied in detail by Amick et al (71). They measured compressibility factors in the superheated region of several different mixtures of the two components, and in the two-phase region, they measured phase composition for temperatures (344-450)K at pressures between 27 and 68 atm. They compare K values for their experimental compositions with those predicted from generalised correlations. However the correlations they use do not take into consideration the effect of composition. They do acknowledge that this assumption of an ideal solution is not really valid for such a mixture as methane and isopentane.

Attempts to compute coexisting vapour and liquid compositions as bubble point lines met with difficulties. At 27 and 37 atm a measure of success was had but only for $\xi_{12} = 1.0$ and no adjustment to the acentric factor.

Fig 42. Methane-isopentane system, bubble point calculations at 27.0 atm and 34.0 atm.



Modification to either of these caused failure. The reason possibly is that these conditions are too close to the critical point of isopentane - 32.9 atm, 461K. Modification of the acentric factor at a temperature within about 2% of the critical temperature has been found to fail for various systems on several occasions.

In spite of this, the agreement between experiment and computation is quite good - they are shown in Fig 42.

7. Methane-Decane

Vapour-liquid equilibrium of methane-decane mixtures has been measured by Reamer et al (72). They give tables of smoothed data for seven isotherms (311-511)K, expressed in weight fractions. Although the tables extend to the critical point of each composition, actual experimental work was not done near the critical region. Computations of the phase equilibria were produced in weight fractions to enable easy comparison between computation and experiment. The data are converted into mole fractions within the program and back again to weight fractions in the printed results. Weight fractions make the vapour-liquid equilibria of such mixtures as methane-decane (molecules of widely differing size and properties) easier to plot in a graph since weight fractions are numerically less than mole fractions. For example 0.7 weight fraction of methane is 0.95 mole fraction, 0.8 is 0.97, 0.9 is 0.987 and so on.

Fig 43. Methane-decane system, dew point calculation at 477.6 K and bubble point calculation at 411 K.

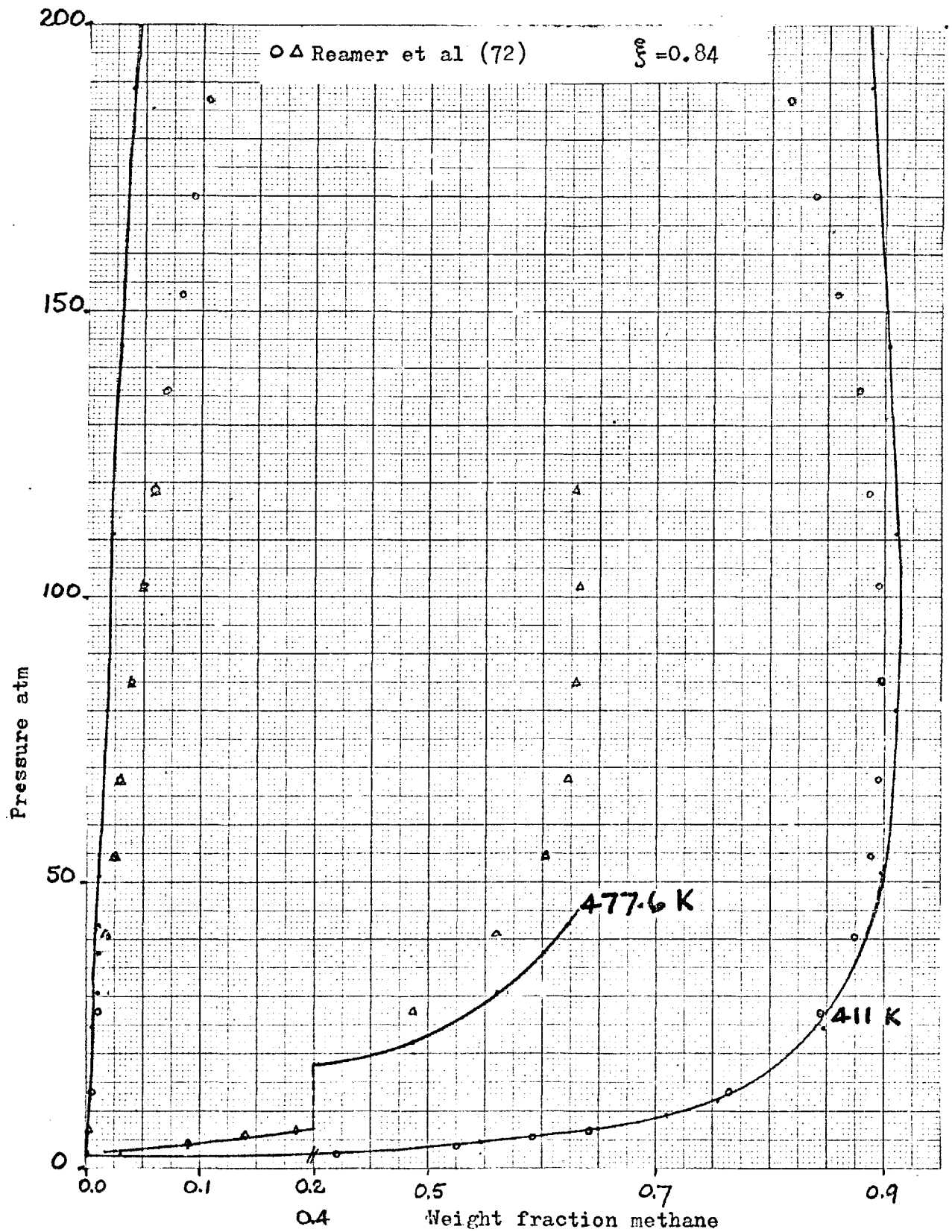


Fig 43 shows two isotherms at 477.6K and 411.0K, dew and bubble pressures respectively. The dew pressure computations broke down at the point of maximum concentration - 0.625 weight fraction of methane, and the bubble pressures continue up towards the critical point. In fact the program continued to calculate bubble pressures which were greater than the experimental critical point, and broke down at 580 atm. In this work, ξ_{12} was 0.84, and except for very high pressures, results were in good agreement with experiment. Teja (109) found that for mixtures of very different sized molecules, a volume correction factor (similar to ξ) was necessary. The factor η is defined by Teja as

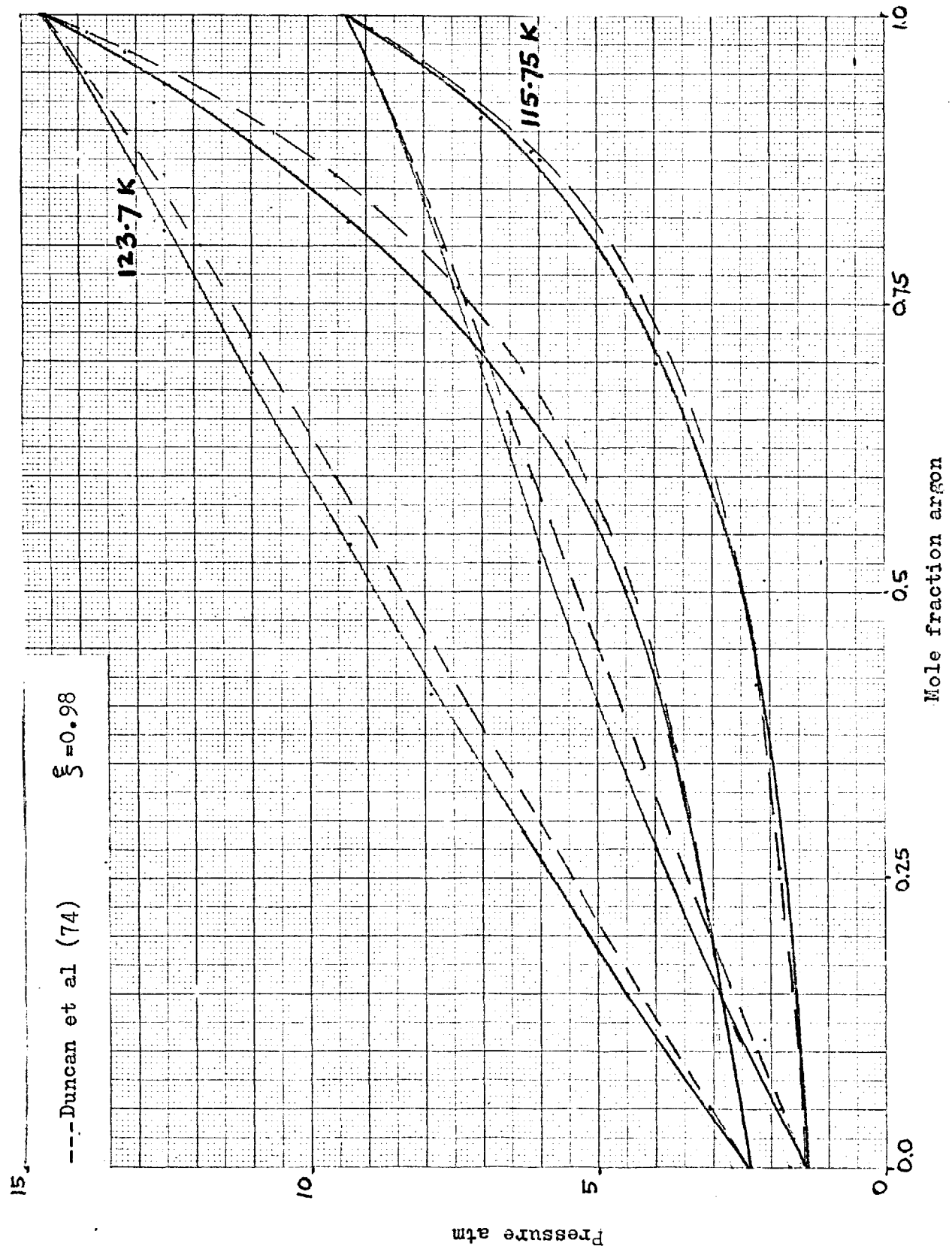
$$h_{ij} = \eta_{ij} \left[\frac{(h_{ii}^{1/3} + h_{jj}^{1/3})}{2} \right]^3$$

This factor has been assumed 1.0 in all the computations in this thesis, but Teja found that a value of 0.94 gave a locus closer to the experimental one. Even so the predictions for vapour-liquid equilibrium were not as close to experiment as for other binary mixtures.

8. Methane-Argon

Three isotherms for vapour-liquid equilibrium of methane-argon were measured experimentally by Duncan and Hiza (74). Work at very similar temperatures was done by Gravelle and Lu (73), 115.2, 123.4 and 137.1K, and they also predict vapour-liquid equilibria at these temperatures using the Redlich-Kwong equation of state. They use an interaction parameter ξ_{12}, which they determine by fitting their computations to their experimental results, and minimising deviations from vapour composition. They found that this parameter varies with temperature although it is generally assumed independent of volume and temperature (10,12).

Fig 44. Methane-argon system, bubble pressure calculations at 123.7 K and 115.75 K.



Leland et al (121) have calculated ξ_{12} for methane-argon and found it to be 0.979 using excess Gibbs free energy, and 0.989 using virial coefficients.

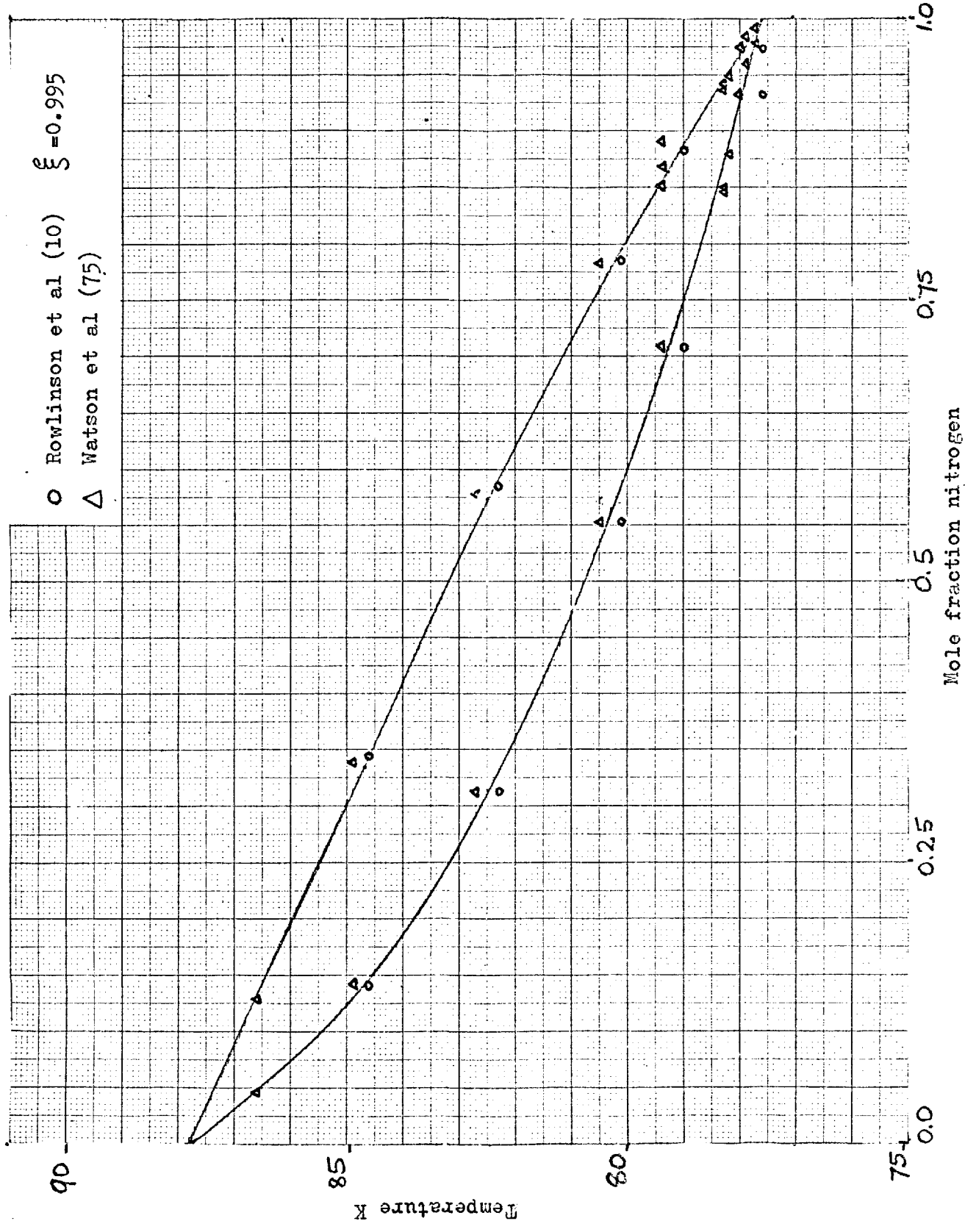
The interaction parameter for the computations was taken first as 0.98, and then as 0.979. The results at 0.979 showed very slight differences from those at 0.98, but it is impossible to show them in Fig 44 as significantly different. Gravelle and Lu found the following values of ξ .

T K	ξ_{12}
1152.	0.979
123.4	0.977
137.1	0.974

Computations were made in this work of bubble pressure lines at 123.7, 119.73 and 115.75K. The first and last are shown in Fig 44. The solid line is a copy (as close as possible) of the coexistence curves given by (74) on a small plot of pressure against composition. The broken lines are the computed results. There is good agreement with experiment, greatest deviation being at equimolar concentrations.

Argon vapour pressures were taken from an Antoine formula given by National Bureau of Standards (25), and for methane from Vennix (16).

Fig 45. Nitrogen-argon system, bubble point calculation at 1 atm.



9. Nitrogen-Argon

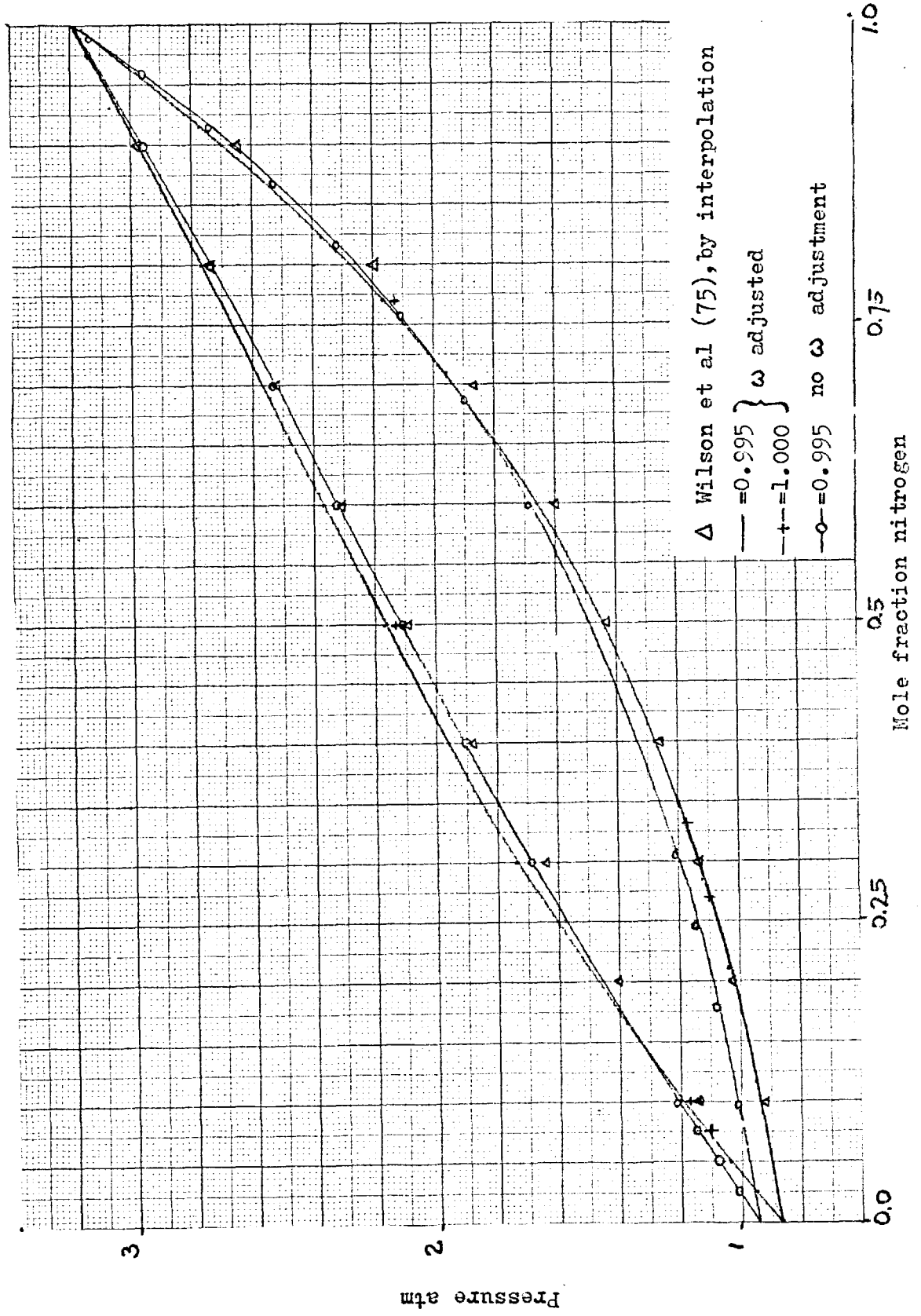
Watson and Rowlinson (10) have published a comprehensive set of figures comparing computed vapour liquid equilibria with experimental work. They worked on binary systems in the N_2 - Ar - O_2 mixture, as well as the ternary system. The program they used was similar to that developed here, but as well as minor differences, they did not adjust the acentric factor.

In this work, a calculation of bubble temperatures at 1 atm (using 1-fluid model) was made to compare with the work of Watson and Rowlinson. The experimental work used was that of Wilson, Silverberg and Zellner (75). In Fig 45 are shown the two sets of computed equilibria and the experimental points. The adjustment to the acentric factor obviously improves the prediction of the bubble point line, and agreement of computations in this work and experiment is very good. The acentric factor of argon is 0. and this was unchanged even though the pressure was subcritical ξ_{12} was 0.995 (10).

10. Nitrogen Oxygen

A bubble pressure line at 88.88K was computed for a nitrogen oxygen mixture. Experimental results to compare with this line were taken from the work of Wilson et al (75). Their work is given as compositions at constant pressures, so compositions and pressures at 88.88K (exactly 160 R) were obtained by interpolation. Fig 46 shows several sets of computed results with these interpolated experimental results. The bubble pressures were computed with and without acentric factor adjustment, both with ξ_{12} equal to 0.995 (10); then with ξ = 1 and adjustment to the acentric factor.

Fig 46. Nitrogen-oxygen system, bubble pressure calculation at 88.88 K.



It can be seen what a difference adjustment to ω makes - for oxygen the correct vapour pressure is predicted. For nitrogen, 88.88K is 0.7 of the critical temperature, and so adjustment of the acentric factor is really unnecessary - which is why both lines coincide at 100% nitrogen. Using $\xi = 1$ shows a slight lowering of bubble pressures, especially on the liquid line.

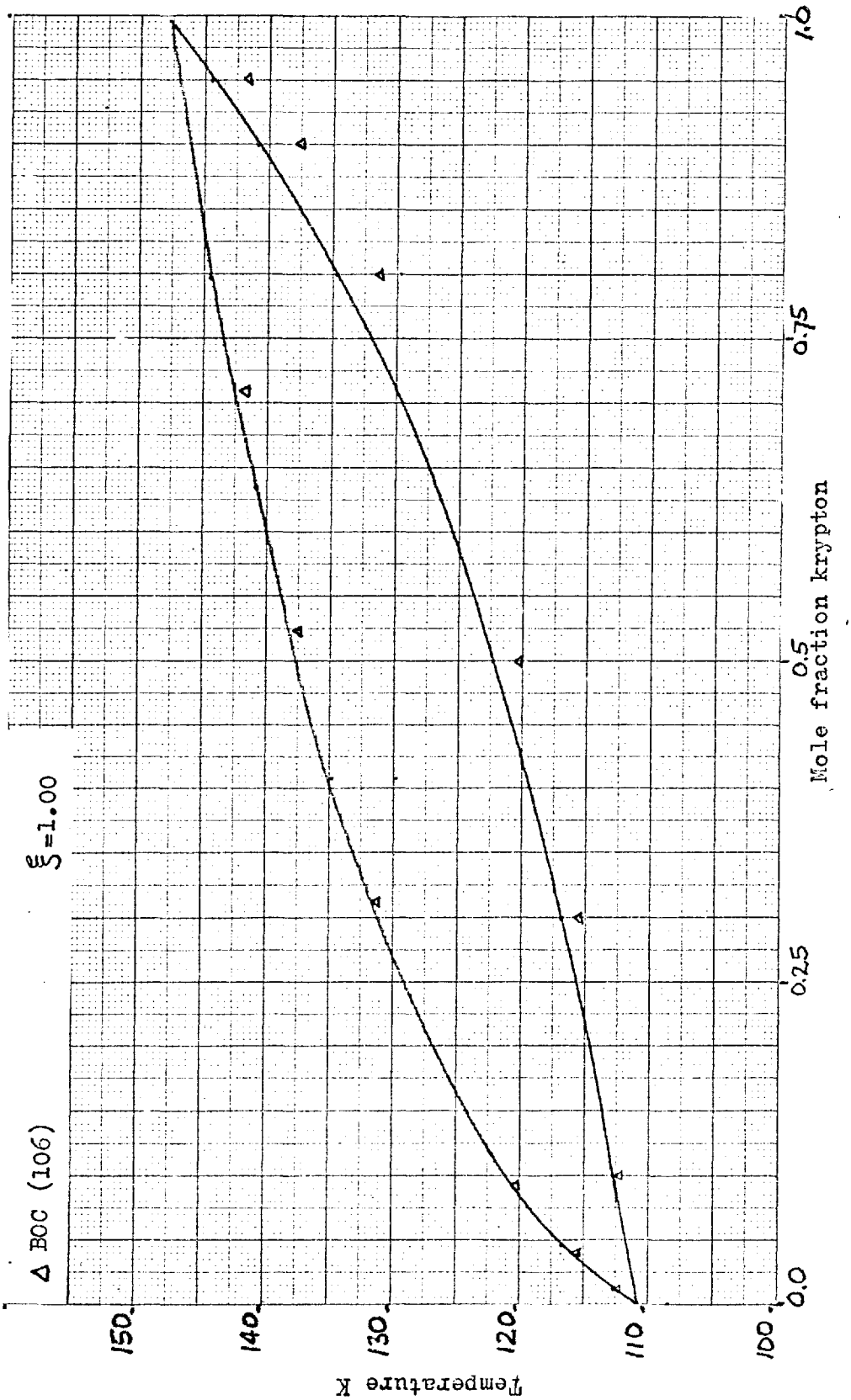
11. Krypton-Oxygen

A bubble point line at 6 atm was computed for krypton-oxygen mixture. The interaction parameter ξ_{12} was 1.0 and no adjustment was made to the acentric factor because, at the time, the vapour pressure data for krypton was not available. Fig 47 shows the computed bubble point line and some other computed points using the BWR equation of state (106). The bubble points agree well, but the liquid compositions are lower than those computed by the BWR equation. The vapour temperature of pure oxygen is predicted fairly accurately by both methods (this work and by BWR) - it should be 111.64 K. This is probably due to the fact that this temperature is approximately 0.7 of the critical temperature.

Some other computations of bubble pressures were made for various temperatures and compositions in the range (114-145)K and a mole fraction of krypton (0.001-0.95) respectively.

The bubble pressures were in the range (7.28-6.6)atm and the vapour mole fraction of krypton was (0.0001-0.798) respectively. It has not been possible to compare these figures with computations using other methods, or with experimental work.

Fig 47. Krypton–oxygen system, bubble point calculation at 6.0 atm; no ω adjustment.



12. Propane-Carbon dioxide

Vapour-liquid equilibrium of propane carbon dioxide mixtures has been measured by Poettmann and Katz (76), and by Reamer et al (78). Poettmann and Katz measured the bubble and dew points of six different mixtures for a range of temperatures. They smoothed their results, giving four isotherms (355-233)K on a pressure against composition plot, and four pressures (34-54.5)atm on a temperature against composition plot. These ranges cover those investigated by Reamer et al. They give tables of compositions for smoothed temperatures and pressures in the range (277-344)K and (5-65)atm. Agreement between these two experimental measurements, away from the critical region is not too good, and Reamer et al state that they think there is a systematic error in the compositions of Poettmann and Katz.

Computations at three temperatures (277.6, 311.0 and 344.3K) were made in this work. The first and last temperatures were bubble pressure lines and the other was a dew pressure line.

At 277.6K, both components were subcritical and the vapour pressures were taken from the extrapolations to the pure components in Reamer's tables of vapour-liquid equilibrium (78). Fig 48 shows the computations at this temperature and experimental points from both Reamer and Poettmann. The computed results follow, but do not coincide with the work of Reamer et al, although agreement is best at high concentration of propane. ξ_{12} was taken as 0.89 (12).

Fig 48. Carbon dioxide-propane system, dew pressure calculation at 311 K.

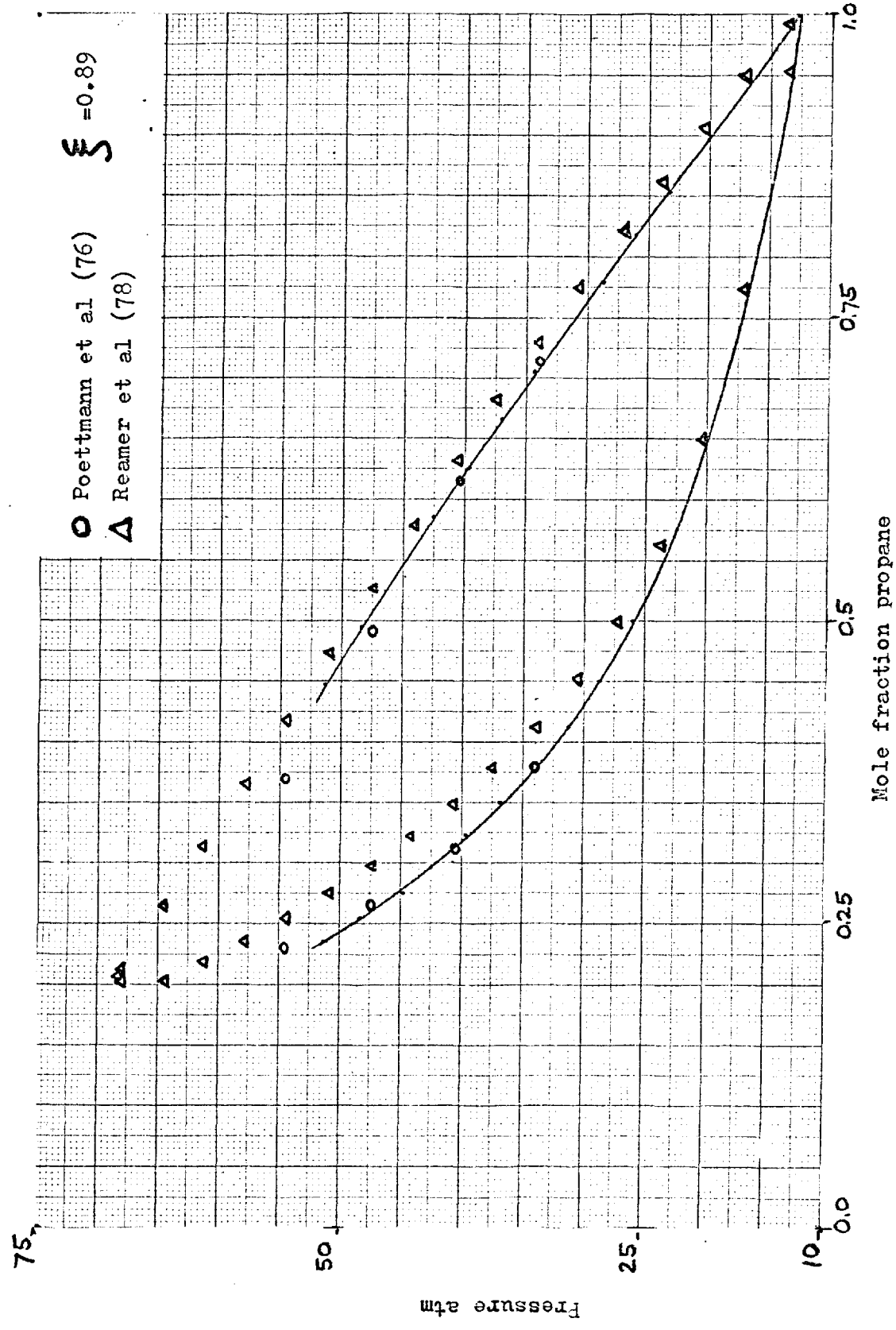
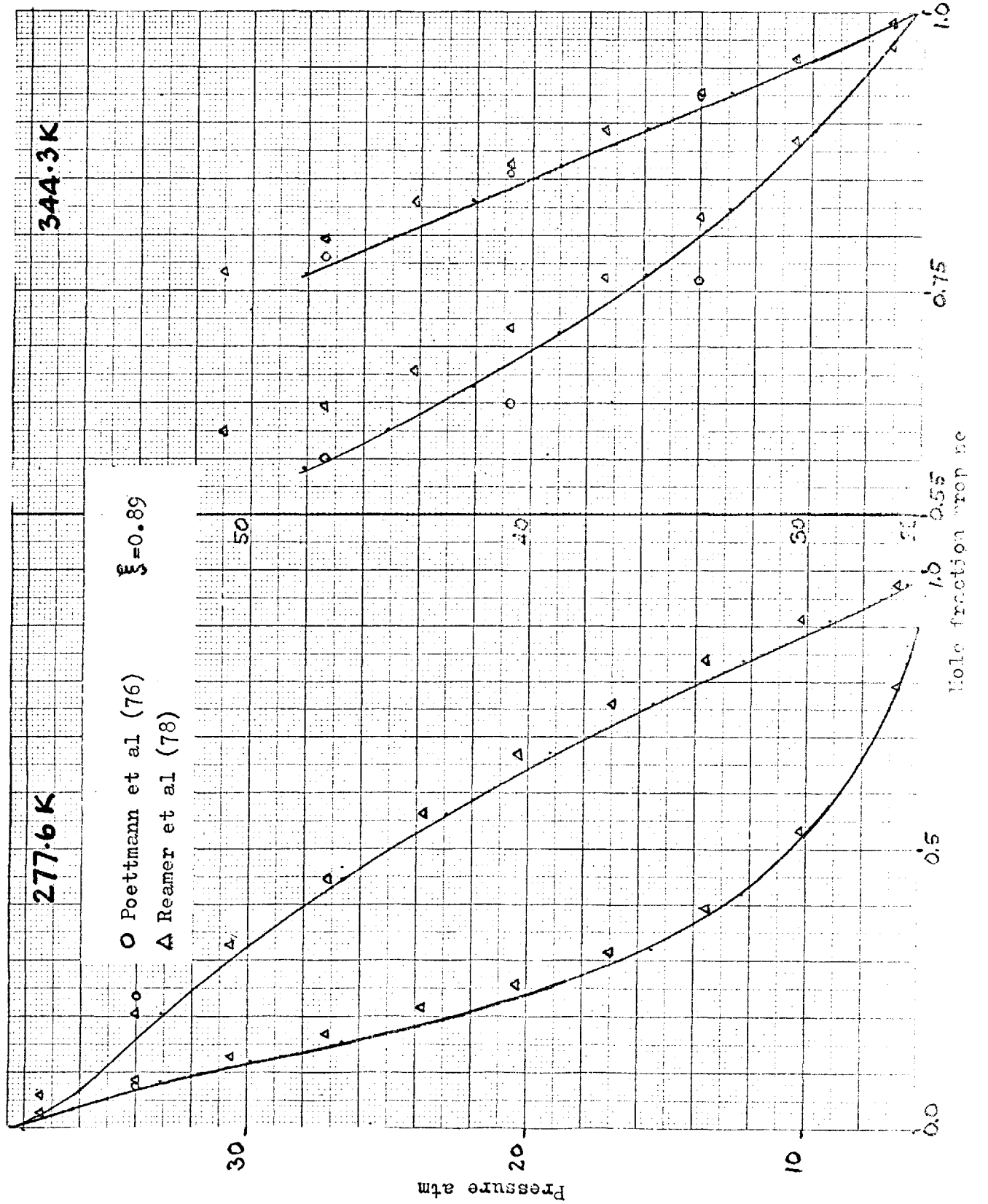


Fig 49. Carbon dioxide-propane system, bubble pressure calculations at 277.6 K and 344.3 K.



At 311K, the dew pressure line computation break down at the point of maximum temperature given by Poettmann, a mole fraction of propane 0.215. Reamer et al gives 0.2 at the same temperature as the maximum concentration. The computations agree better with the experimental work of Poettmann in both phases.

At 344.3K, the computations broke down at about 50 atm. Although unusual for bubble pressure computations to break down at the point of maximum concentration (i.e. maximum temperature), this temperature (344.3K) is only 6% from the critical point of propane, and in addition the change of critical pressure with critical temperature is almost vertical. Closeness to the pure component critical temperature is often the cause of breakdown in the computation of vapour liquid equilibrium. The reduced temperature of the liquid phase at the point of breakdown in this case was greater than 1.0 - the initial guess of liquid composition being based on the experiment values of Reamer et al (78).

Zudkevitch and Joffe (64) have developed prediction methods for vapour-liquid equilibrium using the Redlich-Kwong equation of state and they use the experimental work of Reamer et al as a comparison with their computations. They give their results expressed as K values. A few examples below compare their work with this work.

T K	P atm	K expt(78)	K calc(64)	K(this work)
277.6	13.6	0.472	0.464	0.500
	30.6	0.399*	0.395	0.365
311.0	20.4	0.715	0.710	0.722
	47.6	0.567	0.557	0.510
344.3	34.0	0.881	0.858	0.887
	54.4	0.828	0.821	-

* rather uncertain (78).

Although the figures above are not in complete agreement, K values do mask considerable deviations in bubble calculations - being relatively insensitive to variation in pressure.
In addition, Zudkevitch and Joffe calculate their vapour liquid equilibria by flash procedure, which will make both their phase compositions different to experiment. The K values given for this work in the table above were taken from the computations shown in Figs 48, 49.

13. Butane-Carbon Dioxide

The phase equilibria of butane and carbon dioxide mixtures has been experimentally measured by Olds et al (79), and the results were smoothed and presented at four temperatures (311-411)K for a range of pressures. At all these pressures, carbon dioxide is supercritical. Poettmann and Katz (76) also studied this mixture, and they give dew and bubble points at six temperatures. In this work, bubble pressures were computed at 311.0 and 377.6K, and dew pressures at 344.3K. The bubble pressures are shown on Fig 50, with experimental results from both Olds et al and Poettman and Katz. At 311.0K, agreement is good, but computations break down at a pressure close to the critical point.

At 377.6K, agreement is not so good, particularly in the vapour phase. Computations break down at the pressure corresponding to a maximum temperature - 64 atm. This breakdown for a bubble calculation might be due to an unfortunate choice of concentration - corresponding exactly to the maximum temperature which caused iterations to produce reduced temperatures well over 1.0.

Fig 50. Carbon dioxide- butane system, bubble pressure calculations at 311 K and 377.6 K.

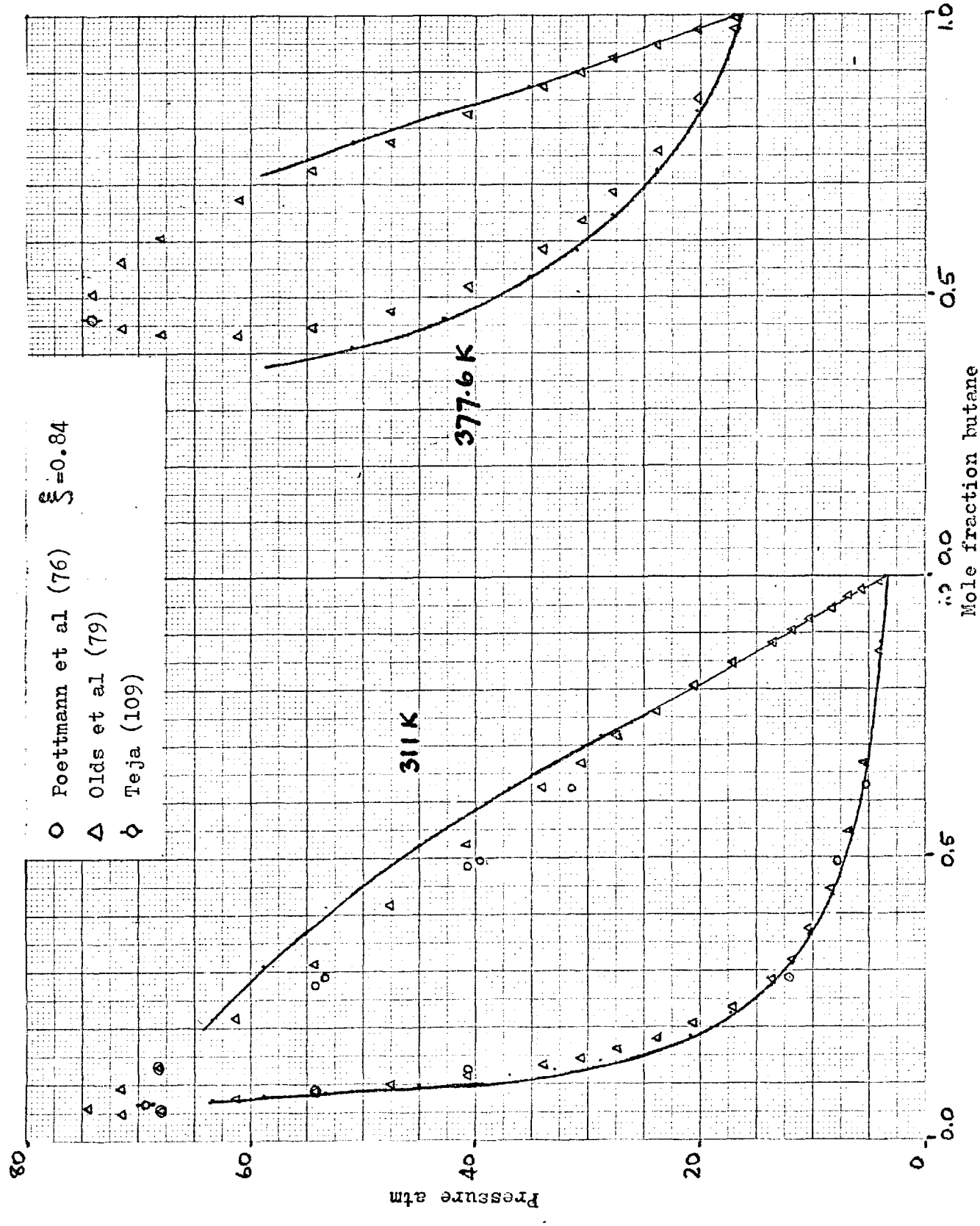
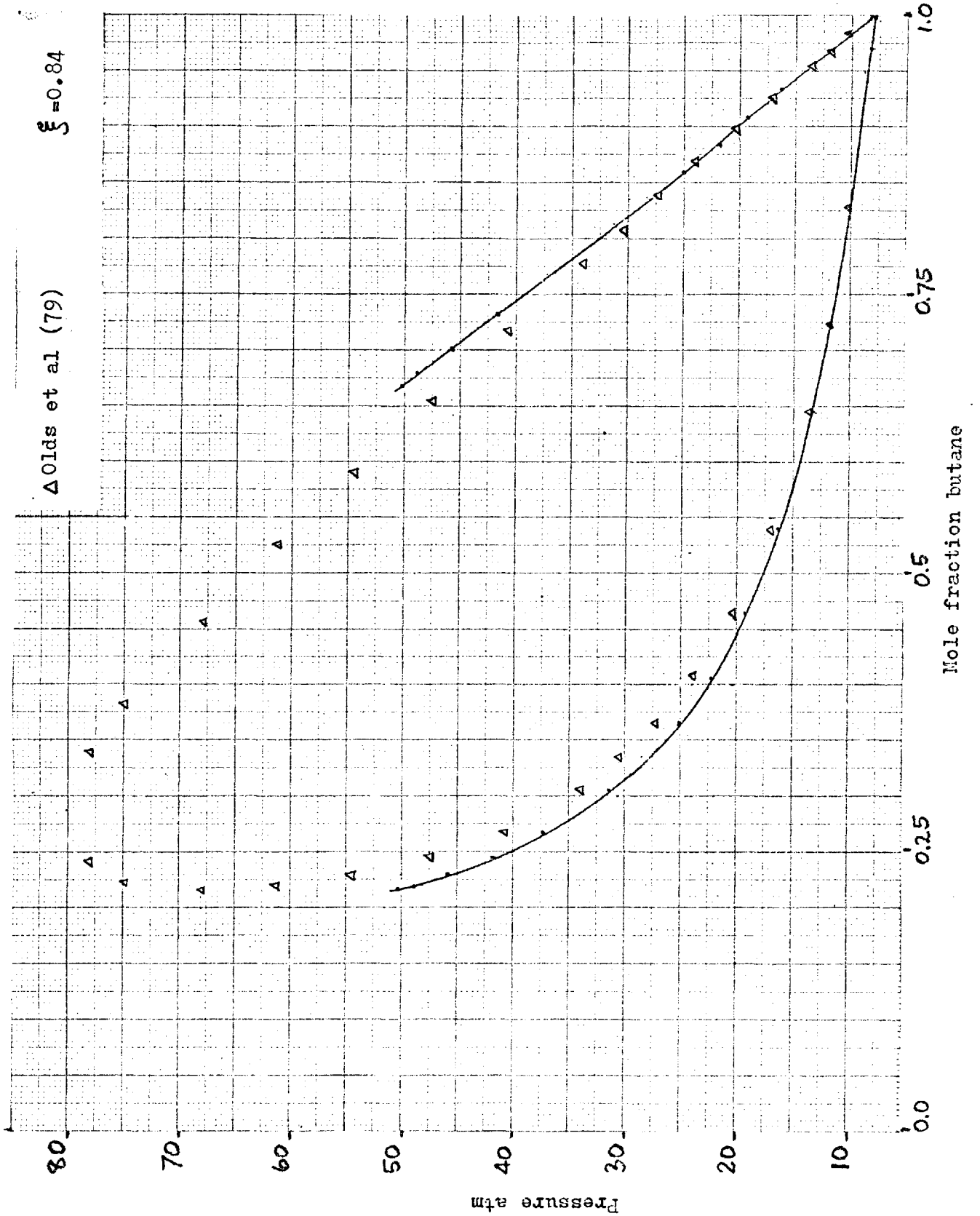


Fig 51. Carbon dioxide-butane system, dew pressure calculation at 344.3 K.



The dew pressure computations at 344.3K are shown in Fig 51, with experimental results of Olds et al. The computations broke down at the maximum concentration of 0.21 carbon dioxide, where the pressure is 50 atm.

14. Ethane-Propylene

McKay et al (80) made experimental measurements of the volumetric and phase behaviour of ethane-propylene mixtures. They measured the properties of the co-existing phases at three compositions and present their results as interpolations for regular pressure intervals for four temperatures (261-344)K.

Computations were made at these four temperatures - two dew pressure lines at 277.6 and 344.3K and two bubble pressure lines at 261.0 and 311.0K.

At 261.0K, two values of ξ were used, 1.0 and 0.99. The latter gave a far better agreement with experiment, as shown in Fig 52. Similarly, there was good agreement using ξ = 0.99 for the dew pressure computation at 277.6K - also shown in Fig 52. At 344.3 and 311.0K the ethane is supercritical. The bubble pressure computations using ξ = 1 at 311.0K broke down at 45 atm - which is approximately 5% from the critical point which would have been predicted had the program been able to continue. The reduced temperature also became greater than 1.0 for the liquid phase - not surprising since 311.0K is so close to the critical point of ethane. The computations are shown in Fig 53.

Fig 52. Ethane-propylene system, bubble pressure calculation at 261.0 K and dew pressure calculation at 277.6 K.

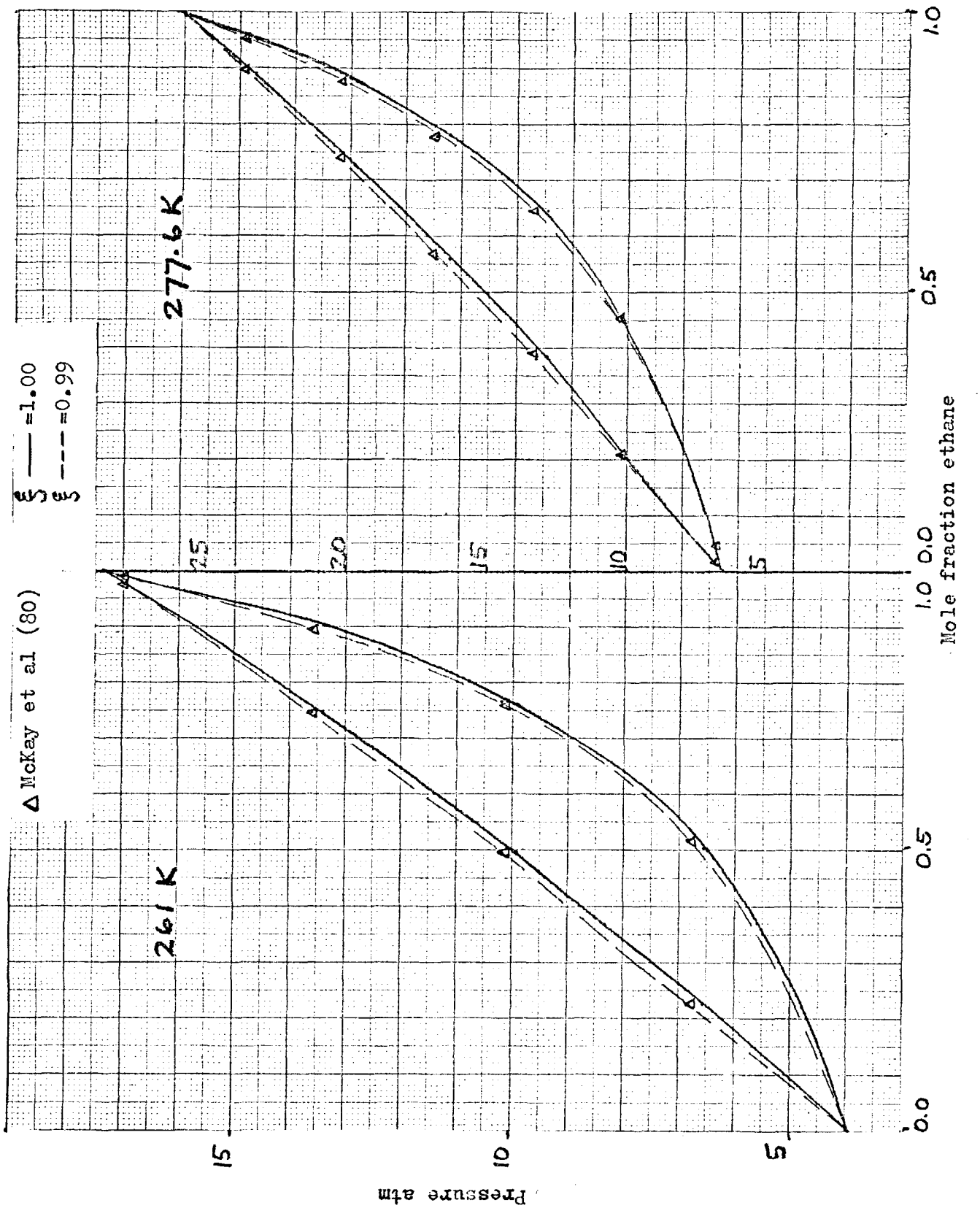
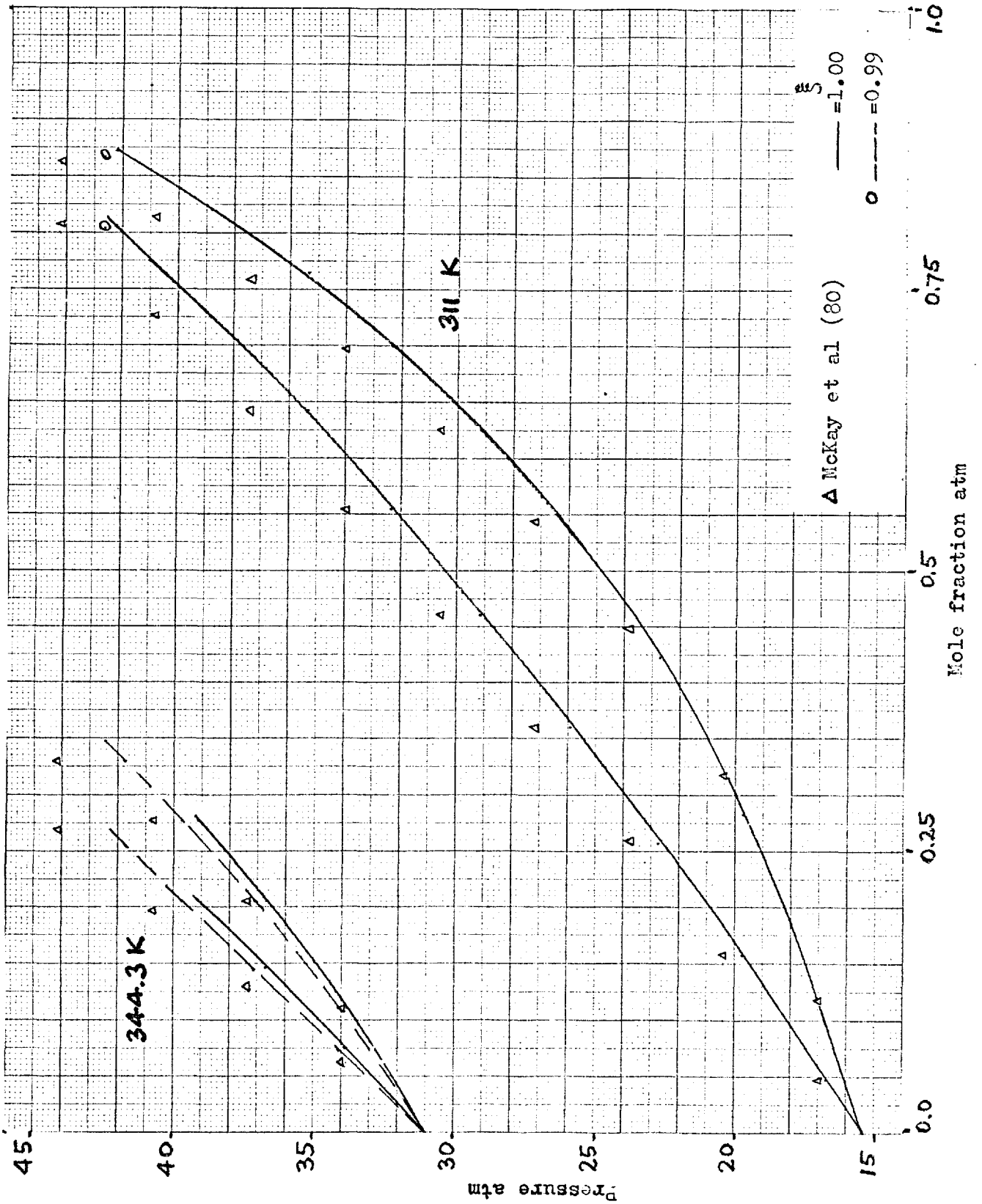


Fig 53. Ethane-propylene system, dew pressure calculation at 344.3 K and bubble pressure calculation at 311 K.



The dew pressure computations at 344.3K (also shown in Fig 53) break down near point of maximum concentration, 0.35 mole fraction of ethane. Agreement with experiment is not so good as for the lower temperatures, and this suggests that lower value of ξ would improve agreement. Decrease of ξ with increasing temperature is consistent with the findings of Gravelle and Lu (73).

It is interesting to note that computations were able to proceed further using $\xi = 0.99$ than $\xi = 1.0$. However, the actual experimental measurements of McKay et al ceased at 40.7 atm at 344.3K and 44 atm at 311.0K. Their tabulated results are extrapolations. If these extrapolations are in error, then use of these as a basis for guesses in the data for the computation of vapour-liquid equilibrium could lead to failures. This might be the case in dew pressure computations at 344.3K in this work.

McKay et al compare their experimental results with the much earlier work of Lu, Newitt & Ruhemann (81), using K values. Two examples below compare these two experimental determinations with the computations in this work. The computed K values are not so close to the earlier work nor is the work of McKay. Although use of K values can be a misleading basis for comparison of co-existing phase compositions, the results below suggest that Lu's work might be incorrect.

T K	P atm	K expt(81)	K expt(80)	K(this work)
311.0	40.8	0.8	1.60	1.10($\xi = 1.0$)
344.3	40.8	1.375	1.54	1.31($\xi = 0.99$)

15. Ethane-Benzene

The system ethane-benzene was considered an interesting mixture for the prediction of vapour liquid equilibrium because benzene is an aromatic compound, and somewhat dissimilar to methane, and because experimental data were available for conditions where both components were supercritical. Kay and Nevens (82) worked on this system and they give their temperature measurements at regular pressure intervals for six different compositions. They also give tables of temperatures at various pressures for smoothed compositions at regular intervals, and they give the loci of the maximum temperature and pressure lines.

Bubble point lines were computed at 20.4, 34.02 and 68.04 atm. At the first two, both components are subcritical and at the last, both are supercritical. In Fig 54, the subcritical computations are shown with the experimental points. Three different values of ξ were tried at 20.4 atm - 0.95, 0.97, 0.98. The best agreement at 20.4 atm is with 0.95 for the liquid line - results for all three values of ξ were indistinguishable in the vapour phase. At 34.02 atm ξ = 0.97 gives agreement with experiment which could hardly be bettered.

At 68.04 atm, there are interesting results shown in Fig 55. Two values of ξ (0.95, 0.97) were tried. They give very different values for the liquid line, but the vapour lines are indistinguishable. 0.97 gives the better agreement with experiment. Near the upper critical point, 530K, computations began at a mole fraction of ethane 0.25.

Fig 54. Ethane-benzene system, bubble point calculations at 20.4 atm and 34.02 atm.

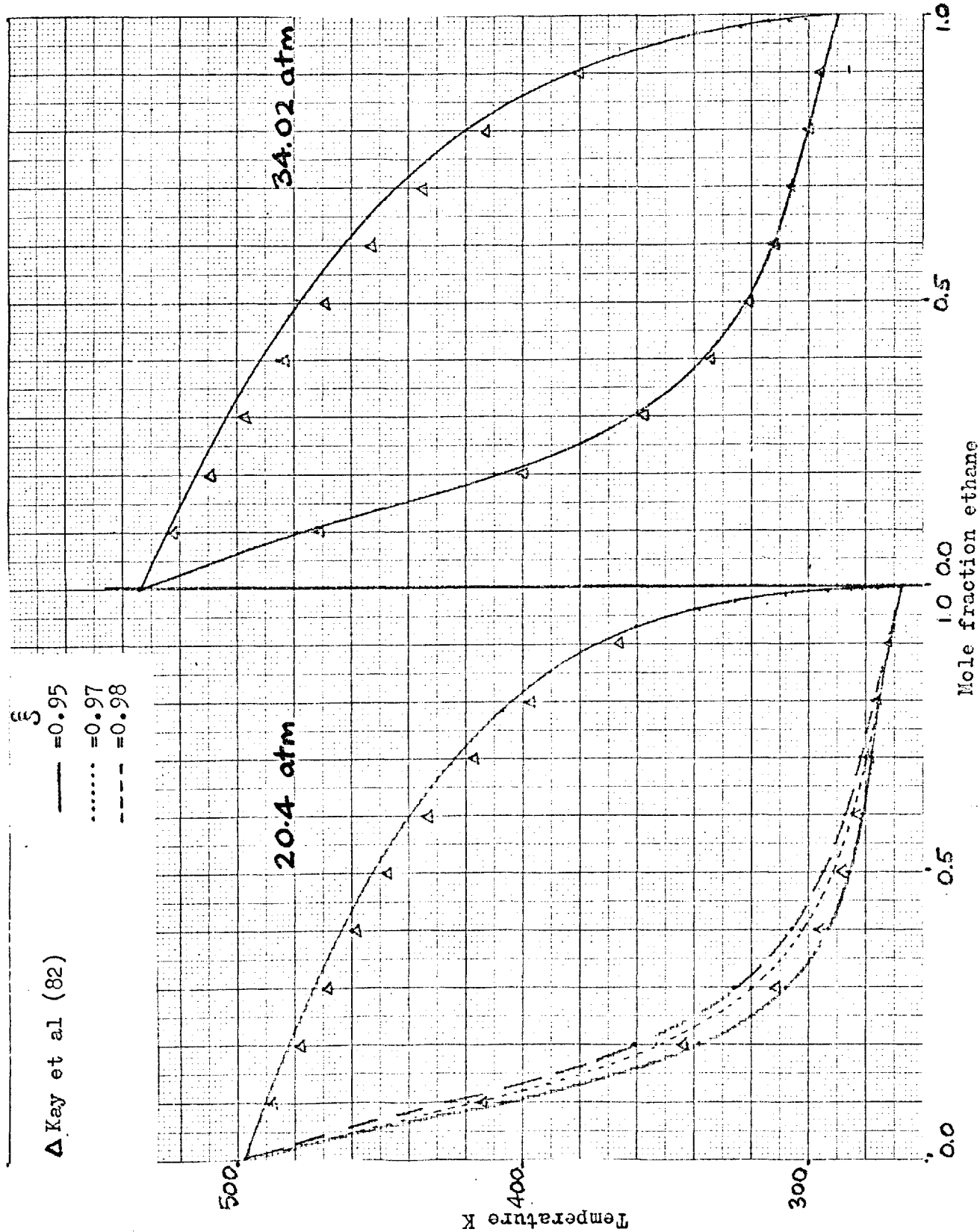
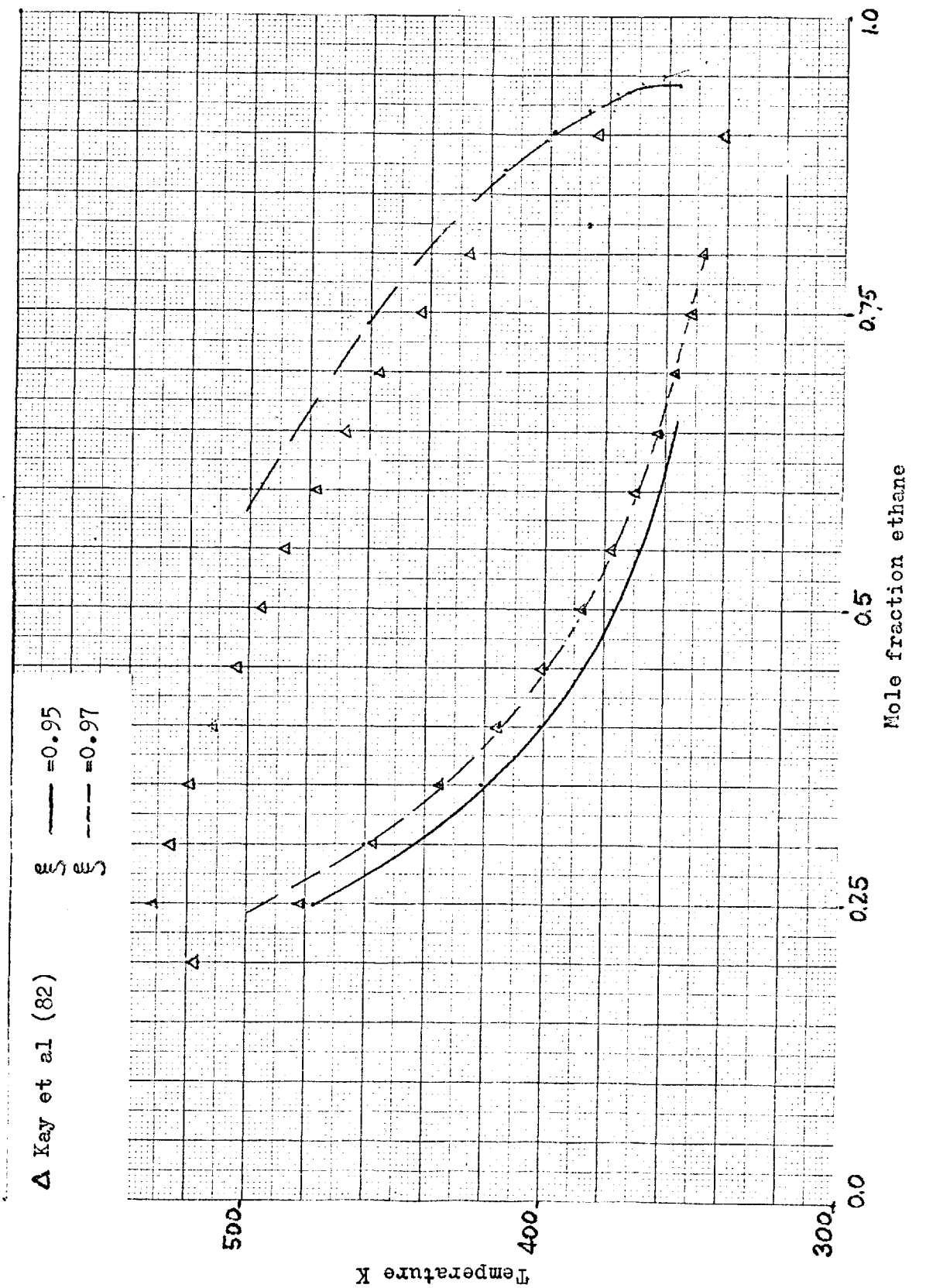


Fig 55. Ethane-benzene system, bubble point calculation at 68.04 atm.



This is fortuitously just below the point of maximum concentration; even so, the reduced temperature did go above 1.0 during intermediate calculations. At the lower end of the phase diagram, computations continued right up to the point of maximum concentration - 0.94 mole fraction of ethane, at 350K. At this point reduced temperatures went above 1.0 and computations broke down.

16. Propane-Pentane

Of the pressures chosen for computation of bubble temperatures of propane-pentane mixtures, only that one where both components are subcritical was successful. This was 27.23 atm. The results are shown in Fig 56, with the experimental points of Kay (83). In this paper, Kay gives a wide range of two-phase equilibria at regular composition intervals for pressures (20.4 - 44)atm.

At 27-23 atm agreement of computed bubble temperatures with experiment is good - ξ_{12} was 0.99. However isobars at 40 and 44 atm were impossible to calculate. Studying the temperature composition plot given by Kay, the maximum pressure locus is very nearly coincident with the dewpoint lines at both 40 and 44 atm. This means that anywhere along the dewpoint line would almost be a "maximum pressure" point. Thus computations are almost bound to fail due to iterations wandering into the one phase regions.

17. Propane-Propylene

The vapour-liquid phase equilibria of the system propane-propylene has been investigated in detail by several workers - Reamer and Sage (84), Hanson et al (86), Hirata et al (85), Hirata and co-workers worked in the range (228-233)K.

Fig 56. Propane-pentane system, bubble point calculation at 27.23 atm.

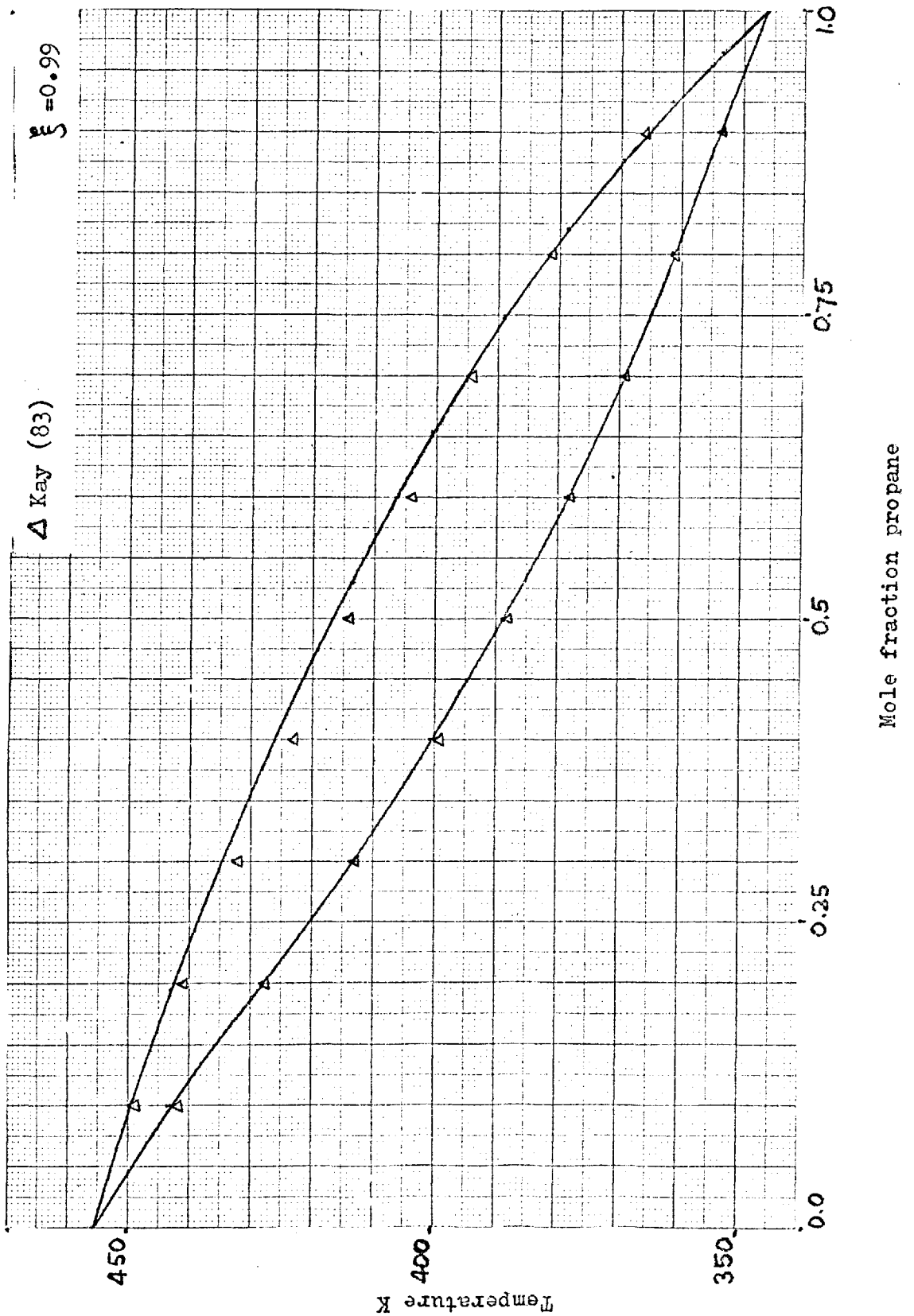
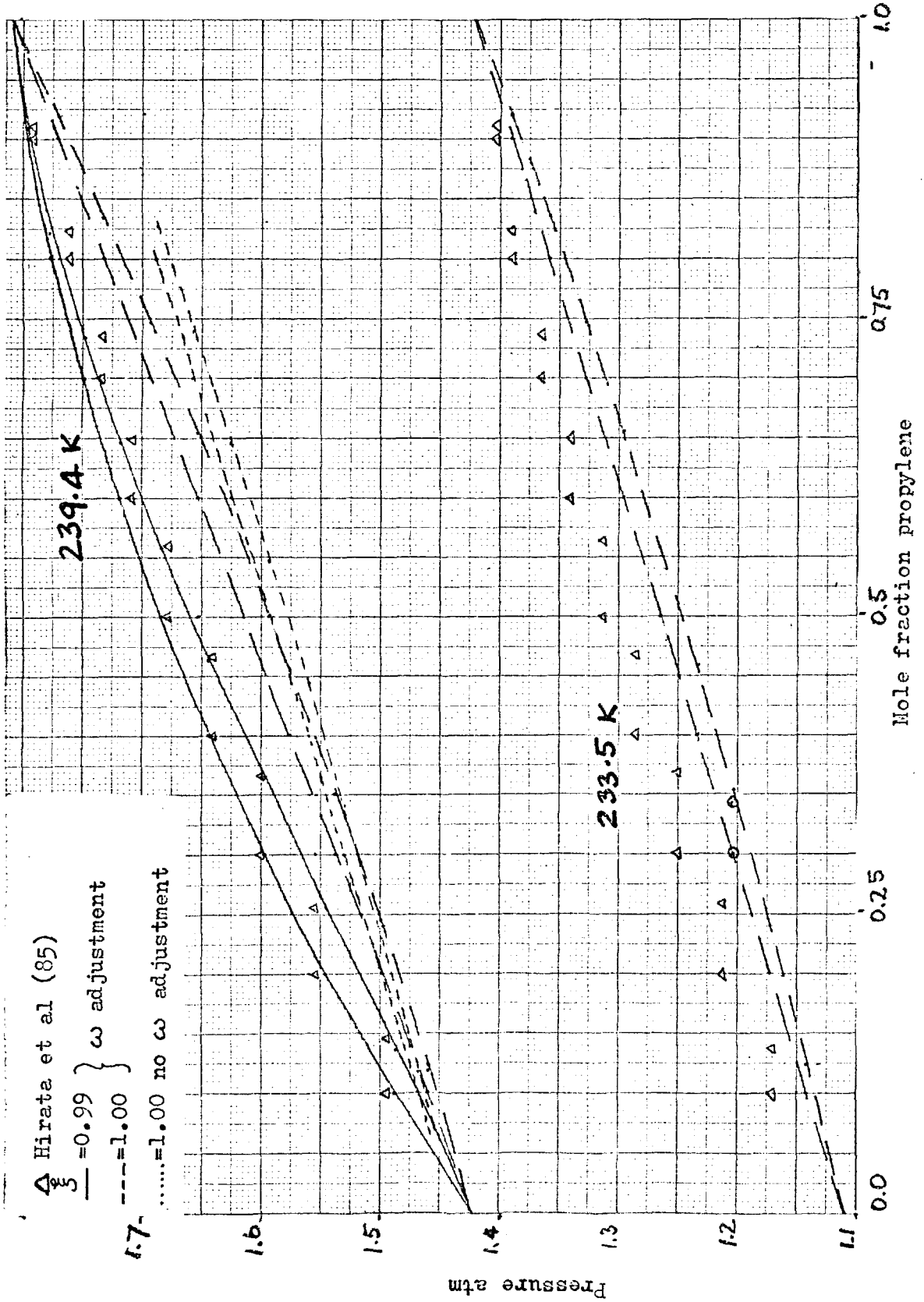


Fig 57. Propane-propylene system, bubble pressure calculation at 239.4 K and 233.5 K.



They chose this region because hydrocarbons with similar properties are difficult to separate. However relative volatilities increase with decreasing temperatures and experimental work at low temperature is not as abundant as at room temperature or higher. The similarity of the properties of propane and propylene makes the prediction of their two-phase equilibrium a more difficult proposition too.

Hirata et al give compositions for four isotherms - and at these four temperatures, bubble pressures were computed. Two of these are shown in Fig 57, with Hirata's experimental results - at 233.5 and 239.4K. At 239.4K, computations were made with $\xi = 1.0$ and 0.99, and with adjustment to the acentric factor in both cases. With no adjustment to the acentric factor, ξ was taken as 1.0. The change in predicted pressures (from $\xi = 1$ to $\xi = 0.99$) is considerable. Agreement with experiment is good especially at high propane concentrations but it falls off towards higher propylene concentration.

18. Butane-Heptane

Butane-heptane vapour-liquid equilibria has been measured experimentally by Kay (87). He measured pressures and temperatures for six compositions and tabulated interpolations for dew and bubble points for seven pressures (6.8 - 39)atm at regular composition intervals.

At three of these pressures, the computation of bubble points were attempted. At 6.8 atm a bubble point line for the complete composition range was successful - shown in Fig 58; ξ_{12} was 1.0. The vapour pressures for adjustment to the acentric factors were taken from the extrapolation in Kay's paper.

Fig 58. Butane-heptane system, bubble point calculation at 6.8 atm.

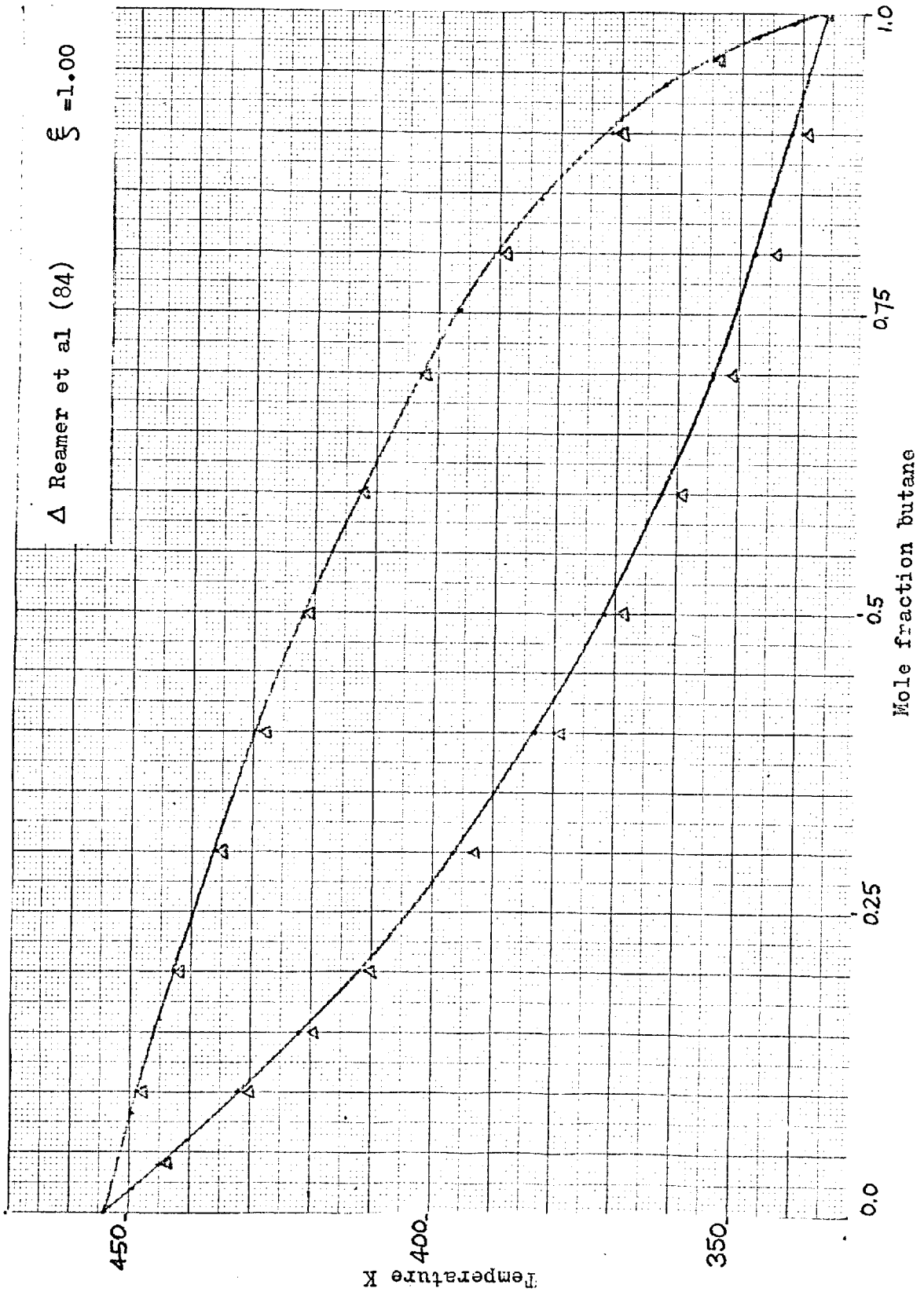
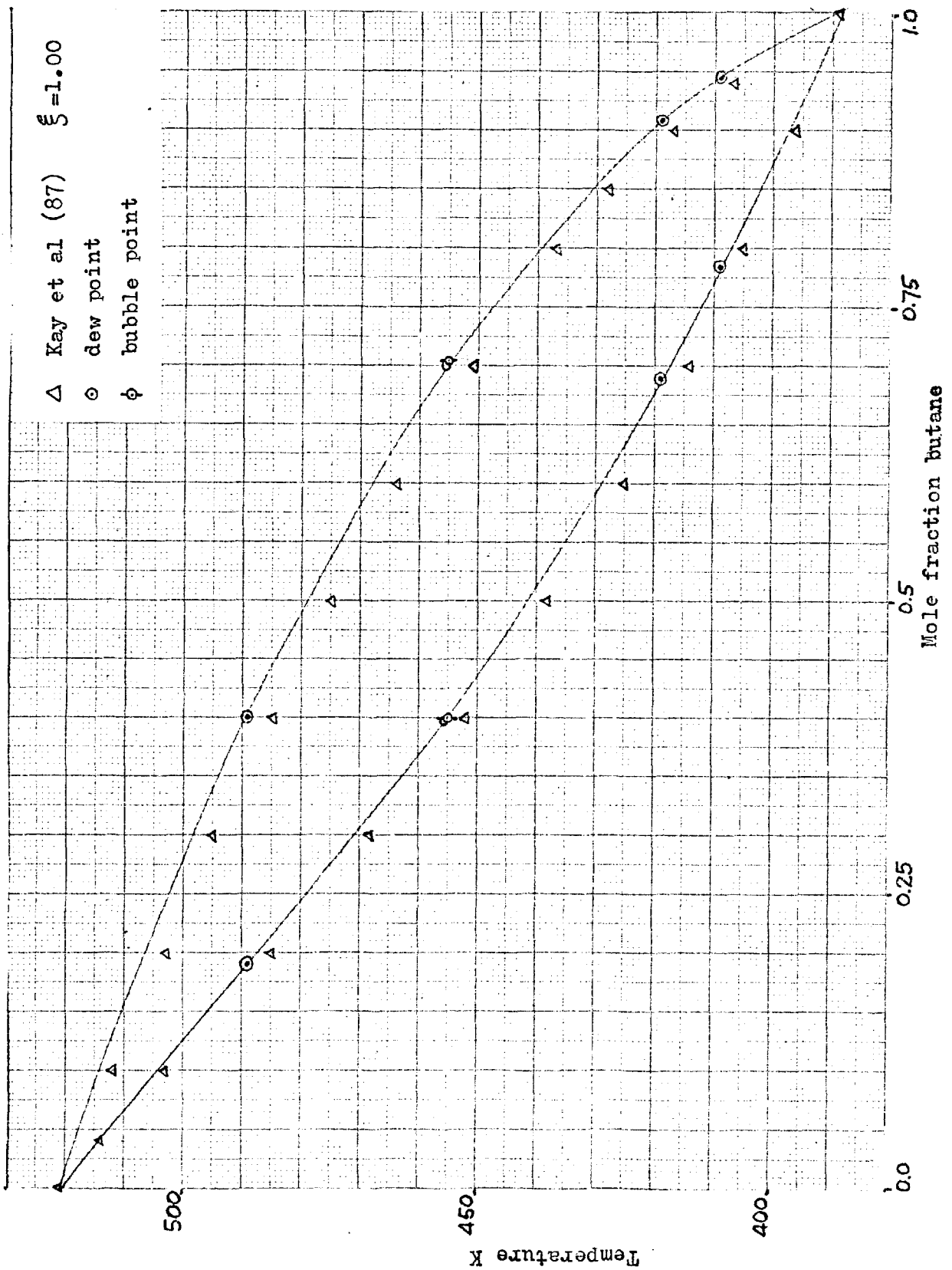


Fig 59. Butane-heptane system, dew and bubble point calculations at 20.4 atm.



Agreement of the computations with experiment is good.

At 20.4 atm computation of dew points were more difficult, possibly due to the value assigned to the initial guesses. In Fig 59 the four successfully computed dew points are shown and the experimental points of Kay. A bubble point at 0.4 butane was computed without difficulty, and is also shown in Fig 59.

19. Butane Decane

Shelton (88) has developed a computer program for the prediction of vapour liquid equilibrium. He uses the Redlich-Kwong equation of state and a flash procedure for dew and bubble points. For comparison of computations with experiment he gives bubble pressures for butane-decane mictures at four temperatures. The experimental work is that of Reamer et al (89). This experimental work is in good agreement with muct later work of Reamer and Sage (in 1964) on the same system. Agreement of Shelton's computations with experiment is good except at higher pressures and higher mole fractions of butane.

Bubble pressures were computed in this work at the same four temperatures. Figs 60, 61 show the results with both sets of experimental work. The values of ξ used at 311.0 and 344.3K were both 0.94 and 0.97. The latter gave much better agreement, although the bubble pressures were still not as close to experiment as those predicted by Shelton. However, at high mole fractions of butane at 377.6 and 411.0K, bubble pressures computed in this work were much closer to experiment than those of Shelton.

Fig 60. Butane-decane system, bubble pressure calculations at 344.3 K and 311.0 K.

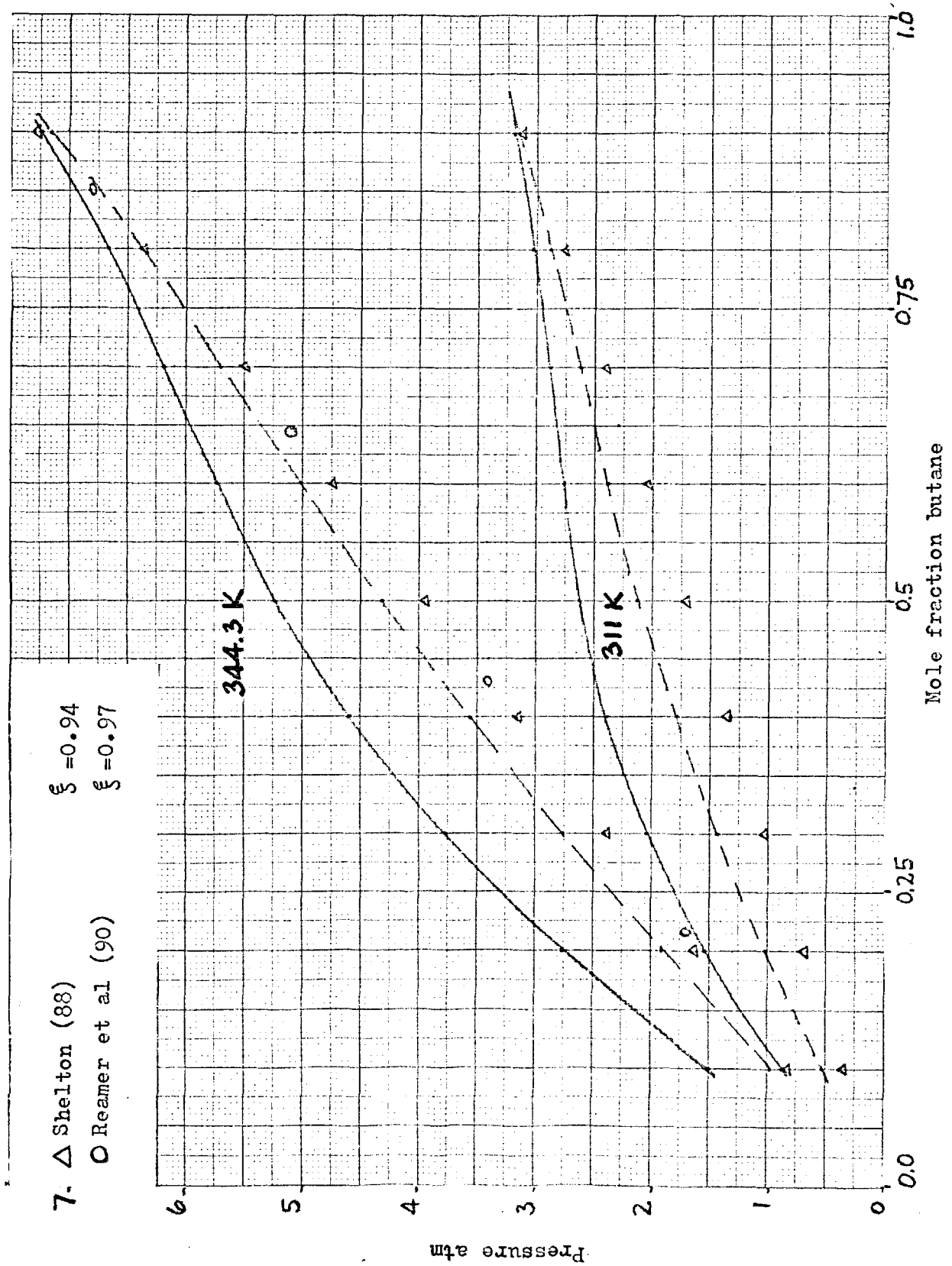
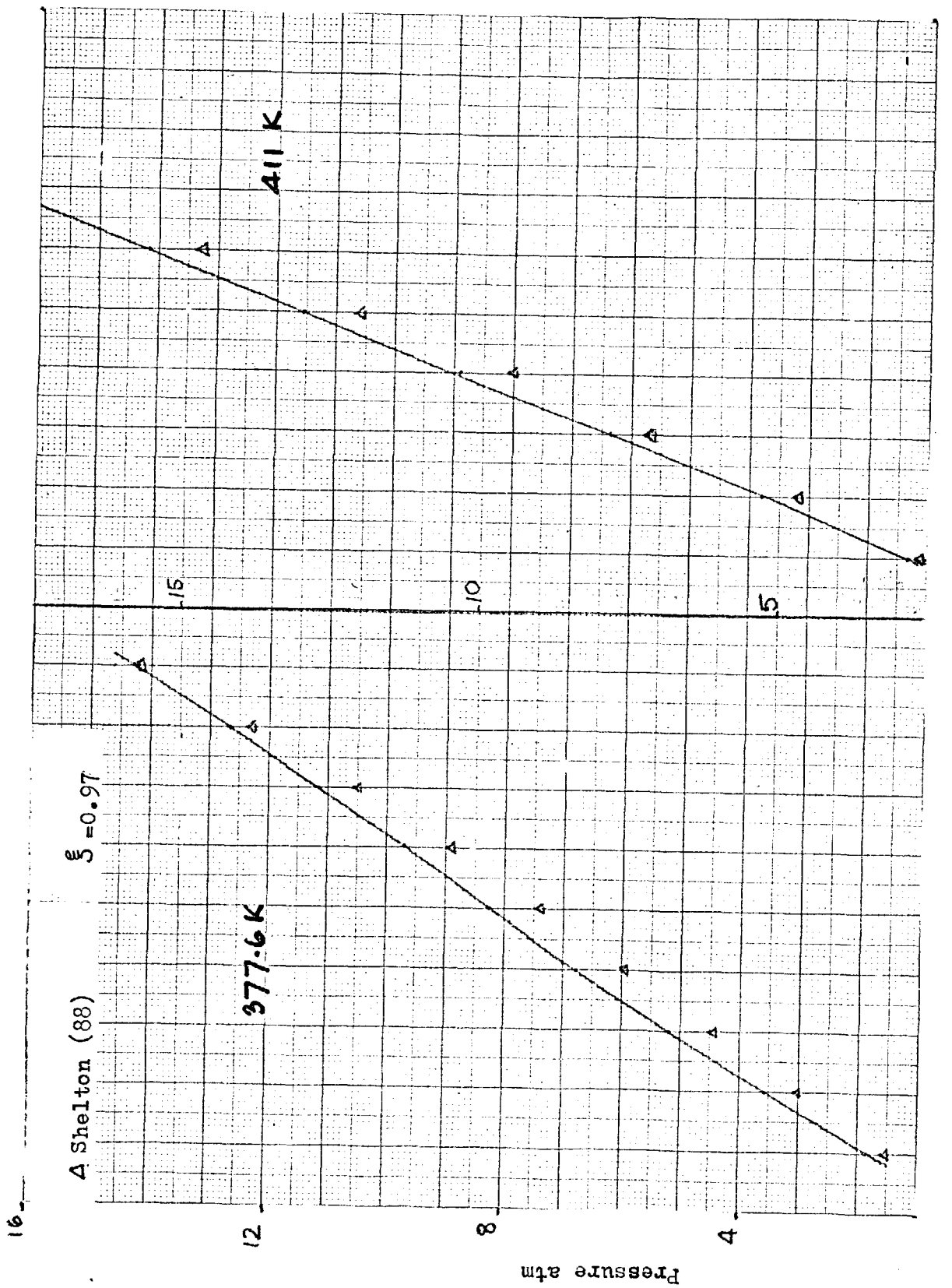


Fig 61. Butane-decane system, bubble pressure calculation at 377.6 K and 411.0 K. No ω adjustment at 411.0 K.



Multi-component Mixtures

Published experimental work on multi-component mixtures under two phase conditions is not so widespread as work on binary mixtures; generally the more the components, the less the published work. As the number of components increases, generally only the thermodynamic properties very much bound up in industrial practice are of interest.

The theory developed in this thesis shows that multi-component phase behaviour can be treated in terms of binary interactions. To test this, the phase compositions and temperature or pressure have been computed for three, four and five component mixtures and various natural gases.

A binary system is the limit for showing easily on a graph two-phase behaviour as a function of composition. Hence higher component mixtures suffer the disadvantage that comparison of computations with experiment is limited to tables of figures, or else pressure-temperature graphs which eliminate composition variation.

Three Component Mixtures

In their book, Prausnitz et al (92) describe in detail their method for predicting vapour-liquid equilibrium. They give facsimiles of their computer output, for several three component mixtures of hydrocarbons. These mixtures were used in computations here to compare Prausnitz's method with this one. He uses equality of fugacities in each phase as the criterion of equilibrium.

The vapour fugacity is expressed in terms of the fugacity coefficient, vapour mole fraction and total pressure, and the liquid fugacity in terms of activity coefficient, liquid mole fraction and standard state fugacity. He uses a virial equation of state and various mixing rules for the interaction terms of the mixture critical volume, compressibility and temperature.

Prausnitz (91) has also published computed results for the vapour-liquid equilibrium of ternary systems, using the Redlich-Kwong equation of state, and compares them with the experimental work of several workers (63, 93, 94, 95, 96). The method of Zudkevitch and Joffe (64) for vapour liquid equilibrium prediction is very similar to that of Prausnitz, differing only by the former's flash procedure for saturation conditions and the latter's method similar to that used in the work here. Zudkevitch and Joffe compare computations for a ternary system with experimental work (97).

Chang and Lu (61) have made measurements in the subcritical region of dew and bubble points for the system nitrogen-methane ethane. A computation was made, for this system, of each type of saturation condition.

The tables given following give the results of computation in this work, with corresponding experimental work or computations by other methods. Values for ξ used on these computations are given at the end of the tables.

Bubble Pressure

	Ref	T K	P expt (atm)	P calc *	Component	x(expt) or given	y(calc) ξ all 1.0	y(expt)	y(calc) ξ≠ 1.0
1	91	311.0	40.8	42.2	H_2S	0.810	0.594	0.660	0.533
				52.3	CO_2	0.170	0.254	0.220	0.325
				51.7[a]	CH_4	0.020	0.152	0.118	0.142
2	91	311.0	8.16	73.56	H_2S	0.843	0.470	0.470	0.438
				90.31	CO_2	0.042	0.044	0.095	0.060
				86.66[b]	CH_4	0.115	0.486	0.435	0.501
3	61	122.0	5.62	6.05	N_2	0.095	0.812	0.845	0.864
				9.6	CH_4	0.341	0.187	0.152	0.135
					C_2H_6	0.564	0.001	0.003	0.001
4	92	344.3	68.7**	55.69	N_2	0.012	0.115	0.116**	
					CH_4	0.223	0.883	0.881	
					C_{10}	0.765	0.002	0.003	
5	91, 63	227.6	68.0	68.63	C_3H_8	0.145	0.030	0.047	0.035
				71.0	C_2H_6	0.089	0.043	0.050	0.041
					CH_4	0.766	0.932	0.903	0.924
6	91	311.0	34.0	31.69	C_5H_{12}	0.678	0.042	0.049	0.037
				42.26	C_3H_8	0.170	0.080	0.085	0.071
					CH_4	0.152	0.878	0.866	0.892
7	91	344.3[c]	102.0	100.5	C_5H_{12}	0.501	0.078	0.206	0.085
				123.7	C_3H_8	0.125	0.064	0.099	0.065
					CH_4	0.374	0.858	0.695	0.850
8	92	344.3	26.8**	24.94	CH_4	0.104	0.867	0.849**	
					C_4H_{10}	0.358	0.131	0.149	
					C_{10}	0.538	0.002	0.002	
9	91, 95	235.0	13.6	11.95	C_2H_2	0.187	0.152	0.202	0.216
				13.45	C_2H_6	0.330	0.249	0.260	0.239
					C_2H_4	0.483	0.599	0.538	0.545
10	91, 95	255.4	21.8	20.81	C_2H_2	0.025	0.022	0.034	0.034
				21.20	C_2H_6	0.437	0.350	0.347	0.347
					C_2H_4	0.538	0.628	0.619	0.619

* Upper figure is pressure at $\xi = 1$ and lower figure is $\xi \neq 1.0$

** From (92) not experimental.

Bubble Temperature

	Ref	P atm	T K expt	T* calc	Component	x(expt) or given	y calc Σ all 1.0	y(expt)	y cal $\Sigma \neq$ 1.0
11	61	13.81	122.0	128.4	CH_4	0.487	0.155	0.111	0.117
				123.0	N_2	0.307	0.844	0.888	0.882
					C_2H_6	0.206	0.001	0.001	0.001
12	92	68.0	339.0	412.0	N_2	0.015	0.120	0.147	
					CH_4	0.216	0.868	0.850	
					C_{10}	0.769	0.012	0.003	
13	91	34.0	344.3	347.0	C_5H_{12}	0.533	0.081	0.091	0.042
				218.0	C_3H_8	0.355	0.272	0.297	0.193
					CH_4	0.112	0.647	0.612	0.765
14	91	34.0	377.6	378.9	C_5H_{12}	0.384	0.392	0.153	0.393
				376.6	C_3H_8	0.577	0.571	0.680	0.570
					CH_4	0.039	0.037	0.167	0.037
15	91	102.0	311.0	300.0	C_5H_{12}	0.213	0.021	0.046	0.015
				379.0	C_3H_8	0.320	0.118	0.160	0.090
					CH_4	0.467	0.861	0.794	0.895
16	91	102.0	377.6[c]	348.0	C_5H_{12}	0.501	0.085	0.206	
					C_3H_8	0.125	0.067	0.099	
					CH_4	0.374	0.848	0.695	
17	92	27.2	311.0	378.0	CH_4	0.109	0.894	0.960	
					C_4H_{10}	0.178	0.100	0.039	
					C_{10}	0.713	0.006	0.001	

Dew Pressure

	Ref	T K	P expt atm	P* calc	Component	y(expt) or given	x calc	x(expt)	x cal
18	61	171.5	13.6	12.4	N_2	0.624	0.045	0.049	0.029
				12.8	CH_4	0.333	0.150	0.187	0.139
					C_2H_6	0.043	0.805	0.764	0.832
19	92	344.3			CH_4	0.827			
					C_4H_{10}	0.172	no convergence		
					C_{10}	0.001			

Dew Temperature

	Ref	P atm	T K ex t	T* calc	Comp-onent	y(expt) or iven	x calc all 1.0	x ex t	x calc 1.0
20	61	27.26	171.4	172.2	N_2	0.380	0.097	0.075	0.079
				171.2	CH_4	0.603	0.616	0.632	0.624
					C_2H_6	0.017	0.287	0.293	0.297
21	92	68.0	321.0		N_2	0.632			
					CH_4	0.367	no convergence		
					C_{10}	0.001			

Values of ξ used in the above computations

Methane - H_2S	: 0.95	CO_2 - H_2S	: 0.92
CO_2	: 0.95	C_2H_6- C_3H_8	: 1.0
C_2H_6	: 0.99	C_2H_6- N_2	: 0.95
C_3H_8	: 0.98	C_3H_8-C_5H_{12}	: 0.99
N_2	: 0.97		
C_5H_{12}	: 0.94		

a. Also computed with slight changes in ξ (H_2S - CO_2: 0.92, H_2S - CH_4: 0.96, CO_2 - H_4 : 0.96) but this have negligible changes in vapour compositions: 0.537, 0.328, 0.135.

b. As for 'a' above, the vapour composition was 0.445, 0.062, 0.493.

c. Possibly an error in (91), see discussion further on.

The computations on the nitrogen-methane-ethane system are in good agreement with experiment, except the bubble pressure (No 3). This is a strange result. Comparing with the Set No.11, the experimental vapour compositions are very similar and the temperatures are the same. This suggests that the liquid composition and the pressure might also be very similar.

Maybe there is a misprint in the results published by Chang and Lu.

Comparison of results using ξ all equal to 1.0 and ξ equal to more appropriate values, shows quite marked differences. The effect of adjustment to ξ in the computation of equilibrium of binary mixtures is not nearly so great, and using the possible values of ξ obtained from work on binary systems in computations on multi-component mixtures does not seem to produce a comparable improvement in accuracy. This suggests that these parameters cannot completely reflect binary interactions in multi-component mixtures. In sets 1 and 2, a third computation was made using modified ξ ; an improvement in predicted pressure was obtained and very slight improvement in vapour composition.

Particularly poor results occurred in mixtures containing pentane (Nos. 6, 7, 13-16). Prausnitz gives ξ for methane-pentane as 0.94 and this value was used here, but Teja (109) gives 0.90 as a best value. However a recalculation of No.16 using this latter value of ξ gives quite unacceptable values for the temperature and vapour composition. A discrepancy comes to light by comparing Nos.7 and 16. By mistake, No.7 was given a fixed temperature of 344.3K instead of 377.6K, and this is why the vapour compositions (experiment and computation) differ. A bubble point computation at the same pressure (102 atm) on the same liquid gave a temperature of 348K and a very similar vapour composition. This suggests that there is a misprint in Prausnitz's paper (91).

Successful use of $\xi \neq 1.0$ for the system acetylene-ethane where excellent agreement for both bubble pressures and vapour compositions have been obtained.

For dew computations for methane-butane-decane no results could be obtained at all. Prausnitz (93) could not achieve any convergence for a dew pressure calculation either. There are some conditions for which there is no solution for a dew calculation at which $\Sigma x = 1.0$ This usually occurs when the mixture consists of components having widely separated volatilities.

For two other ternary systems, more detailed computations were made. They were oxygen-nitrogen-argon and nitrogen-argon-methane.

Oxygen-Nitrogen-Argon

Watson and Rowlinson (10) compare experimental compositions for this mixture at 6 and 18 atm with their own computed results. They use both one - and two fluid models. Computations were made in this work at the same conditions, using adjustment of the acentric factor. At 6 atm the difference between the two computed sets of bubble points was negligible. This is probably due to the fact that the component vapour pressures are close together and approximately equal to a reduced temperature of 0.7. At 18 atm this work was an improvement on that of Watson and Rowlinson. The tables of bubble temperatures below show the two sets of computed results and experimental points. Compositions computed in this work did not agree as closely with experiment as those of Watson did. All the computations in this work at 18 atm were made using the Vennix equation for both phases, because the reduced temperature was close to 1.0.

Bubble temperatures at 6 atm and 18 atm in K

6 atm			18 atm		
Expt'l bub.pt.	Watson & Rowlinson	this work	Expt'l bub.pt.	Watson & Rowlinson	this work
97.1	97.0	96.9	114.8	114.5	114.8
97.6	97.5	97.5	115.4	115.0	115.3
97.6	97.4	97.4	116.5	116.1	116.3
98.7	99.5	99.5	116.5	115.9	116.2
99.8	99.6	99.6	119.3	118.6	118.8
99.8	99.5	99.5	119.3	118.6	118.8
101.5	101.2	101.2	122.1	121.7	121.3
101.5	101.1	101.0	124.8	123.7	123.9
103.7	103.2	103.2	124.8	123.7	123.9
103.7	103.1	103.1	127.6	126.8	127.1
105.9	105.4	105.3	127.6	126.5	126.9
105.9	105.3	105.2	129.8	129.2	129.6
108.2	107.6	107.7			
110.4	110.1	110.1			

Latimer (98) has experimentally determined bubble temperatures for many different mixtures of oxygen-nitrogen-argon, at 1.316 atm (1000mm Hg). The average deviation of bubble temperatures computed in this work - using Latimer's liquid compositions as fixed conditions - is 0.3%, whereas his own computations deviate by 0.25%. He computates bubble temperatures using a method developed by Weishaupt (122) as well as his own method.

That of Weishaupt is not actually given as equations, and Latimer's method is based on Raoult's Law and uses relative volatilities. He gives a special chart by which one can determine two constants for use in an Antoine-type equation for vapour temperatures. He compares his own predictions with Weishaupt's by using relative volatilities. In the table below, a sample of various mixtures is given with relative volatilities for both these two authors' computations and for this work. ξ was taken from Watson and Rowlinson (10).

Relative Volatilities at 1.316 atm for the system

Oxygen-argon-nitrogen

Run No. (98)	Components	α expt (98)	α calc (122)	α calc (98)	α this work
10	N_2-O_2	3.25	3.57	3.61	3.31
15	Ar-O_2	1.39	1.34	1.37	1.23
18	N_2-Ar	2.57	2.62	2.66	2.90
21	N_2-O_2	3.46	3.65	3.69	3.60
23	Ar-O_2	1.43	1.44	1.42	1.24
26	N_2-Ar	2.34	2.60	2.39	2.62
30	N_2-O_2	3.75	3.72	3.77	3.46
34	Ar-O_2	1.56*	1.19	1.22	1.23
42	N_2-Ar	1.75*	2.56	2.53	2.56

* not actually quoted as α in (98).

There seems to be no significant difference between Latimer's relative volatilities and those computed here.

Nitrogen-Argon-Methane

Interest in the system nitrogen-argon-methane grew from a communication (106) from the British Oxygen Company (BOC), who were developing a computer program using BWR equation of state, and wished to compare their results with those from other well established procedures. Sprow and Prausnitz (99) have measured bubble pressures at 90.67K (the triple point of methane) for this system. Their temperatures were accurate to within ± .06K. Bubble points at each experimental pressure were computed by both methods(BWR and this work). In the table below are the results from this work, and experimental work of Sprow and Prausnitz.

Average percent deviation of the fifteen bubble points from 90.67K computed by BOC was 0.08% and in this work was 0.14%. These deviations are almost within experimental error.
Also computed in this work were the bubble pressures at 90.67K. There was excellent agreement with experimental measurements.

The trend of the disagreements between computed bubble temperature and 90.67K and between computed bubble pressure and the experimental pressures showed that the values of ξ were probably a little high. At constant composition, where the bubble pressure was too high, the bubble temperature was too low, and vice versa. Use of ξ raises the vapour pressure.

Bubble temperatures (ξ from (12))

P expt	T calc	Liquid composition (99)			Vapour composition (99)			Calc'd vapour composition		
atm	K	N_2	Ar	CH_4	N_2	Ar	CH_4	N_2	Ar	CH_4
1.488	90.57	0.049	0.904	0.047	0.139	0.855	0.006	0.138	0.856	0.0006
0.782	91.26	0.081	0.108	0.811	0.631	0.240	0.129	0.606	0.242	0.151
1.361	90.61	0.093	0.628	0.279	0.304	0.669	0.027	0.300	0.668	0.032
1.015	91.03	0.108	0.203	0.689	0.587	0.330	0.083	0.570	0.332	0.098
1.529	90.76	0.204	0.350	0.446	0.610	0.350	0.040	0.607	0.349	0.044
1.937	90.54	0.236	0.677	0.087	0.488	0.504	0.008	0.487	0.505	0.008
1.911	90.57	0.313	0.367	0.320	0.685	0.287	0.028	0.689	0.286	0.025
1.773	90.89	0.328	0.101	0.571	0.865	0.090	0.045	0.859	0.091	0.050
1.989	90.63	0.382	0.174	0.444	0.830	0.135	0.035	0.832	0.135	0.033
2.461	90.59	0.459	0.453	0.088	0.717	0.275	0.008	0.712	0.281	0.007
2.903	90.67	0.685	0.186	0.129	0.888	0.101	0.011	0.886	0.104	0.010
3.139	90.64	0.732	0.248	0.020	0.869	0.127	0.004	0.865	0.133	0.002
3.263	90.69	0.823	0.101	0.076	0.942	0.050	0.008	0.941	0.053	0.006
3.591	90.71	0.952	0.004	0.044	0.995	0.002	0.003	0.995	0.002	0.003

Four and Five Component Mixtures

The published results of experimental work on mixtures with greater numbers of components tend to be work on natural gases and mixtures of industrial significance. For example, the four component mixture for which Solomons (100) measured vapour liquid equilibrium was light hydrocarbons in several types of absorbing oil. The results using hexadecane are of interest here, and were used for comparison with computations. Solomons gives six sets of equilibria, two at 311.0K, and four at 377.6K. An unusual feature of these phase equilibria is that there is no absorber oil (hexadecane) in the vapour phase. For this reason the dew computations were unsuccessful - as explained in the previous section on ternary mixtures.

Tabulated below are the three bubble computations. All $\xi = 1.0$

Bubble Pressure

T K	P(expt)	P calc	Component	x (given)	y calc	y (expt)
311.0	34.0	27.5	CH_4	0.0495	0.3885	0.3225
			C_2H_4	0.3065	0.5365	0.6170
			i-C_4	0.2320	0.0750	0.0600
			C_{16}	0.4120	0.0	0.0
377.6	34.0	21.7	CH_4	0.0950	0.7930	0.7590
			C_2H_4	0.0745	0.1907	0.2310
			i-C_4	0.0190	0.0162	0.0009
			C_{16}	0.8115	0.0001	0.0

Bubble Temperature

P atm	T K(expt)	T(calc)				
68.04	377.6	396.0	CH_4	0.1320	0.5699	0.5235
			C_2H_4	0.2125	0.3408	0.4000
			i-C_4	0.1525	0.0889	0.0765
			C_{16}	0.5030	0.0004	0.0

Agreement with experiment is not too bad - the compositions are good, with no hexadecane in the vapour phase. But the computed pressures are low and temperatures are high. Introduction of $\xi \neq 1.0$ should have made an improvement to the temperature or pressure in the right direction, but no success was had. The reduced temperatures became too high and liquid phase computations broke down. Various different starting conditions were tried for temperature in the bubble point computations but to no avail. Neither 370K nor 390K as a guess for temperature would produce a complete bubble point computation.

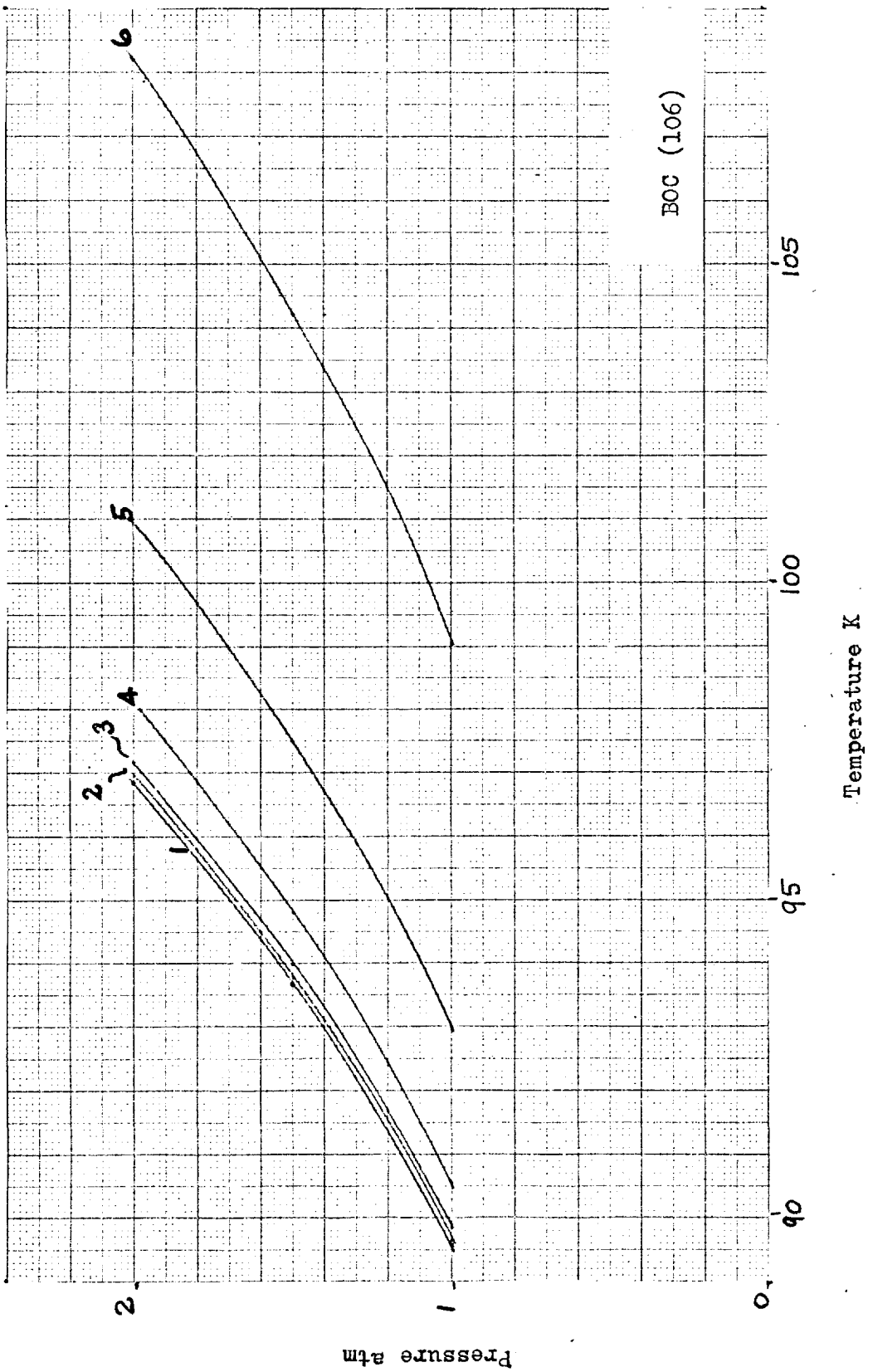
The bubble point for a four component mixture essentially of ethylene and ethane was computed to compare with the computed bubble point from a program developed by British Petroleum (BP) (105). Below are the phase compositions.

Bubble temperature

P atm	T K (this work)	T(105)	Component	x given	y calc (this work)
22.52	254.0	253.0	CH_4	.0002	.0008
			C_2H_4	.7753	.8321
			i-C_4	.2220	.1664
			C_3H_6	.0025	.0007

The BP method uses the Redlich Kwong equation of state, and balances fugacities as a criterion for equilibrium. The BP method yielded a bubble point of 253K, and this work gave 254K.

Fig 62. Krypton, methane, xenon, oxygen system. Bubble point calculations at 1.0, 1.5 and 2.0 atm. for six compositions.



Another four component mixture of industrial interest was a mixture of rare gases containing traces of light hydrocarbons. These traces of hydrocarbons become detectable - and hence significant - after extensive distillation of air. A series of bubble temperatures were computed for this mixture. For six different compositions at three pressures (1.0, 1.5, 2.0 atm). The compositions of the liquid phases are given below.

	Mixture Number					
Component	1	2	3	4	5	6
Kr	0.0010	0.0100	0.0300	0.1000	0.3000	0.6000
CH_4	0.0001	0.0002	0.0004	0.0008	0.0020	0.0040
Xe	0.0001	0.0008	0.0020	0.0080	0.0200	0.0400
O_2	0.9988	0.9890	0.9676	0.8912	0.6780	0.3560

The results of the computations are shown in Fig 62 - bubble temperature plotted against pressure. The interaction parameters were taken as follows :

Kr - CH_4	:	0.995	CH_4 - Xe	:	0.99
- Xe	:	1.0	- O_2	:	0.99
- O_2	:	0.99	Xe - O_2	:	0.99

The results could be a little in error as some of the bubble temperatures are below the triple points of methane (90.67K), Krypton (116.0K) and Xenon (161.3K), and thus some solid material would be present. These liquid compositions were supplied by BOC (106).

The computed vapour compositions for all six mixtures show oxygen as the dominant component - but with the mole fraction dropping with temperature.

Prausnitz (91) compares his own computed bubble pressures with some experimental data (101) for some five component mixtures. The same conditions were used as data for three bubble pressure computations in this work. The results are tabulated below.

Bubble Pressures

	T K	P expt(atm)	P calc $\xi = 1$	P calc $\xi \neq 1$	P calc (91)
1	311.0	19.65	18.65	22.88	19.65
2	311.0	6.52	5.18	6.51	5.78
3	366.7	53.20	53.69	60.26	52.50

Compositions computed for vapour phases in the bubble pressure computations above :

	Component	x given	y calc $\xi = 1$	y calc $\xi \neq 1$	y expt
1	C_5	0.488	0.042	0.037	0.033
	C_4	0.213	0.052	0.044	0.044
	C_3	0.120	0.085	0.075	0.091
	C_2	0.115	0.224	0.209	0.233
	C_1	0.064	0.597	0.635	0.599
2	C_5	0.802	0.184	0.149	0.129
	C_4	0.114	0.078	0.062	0.068
	C_3	0.045	0.093	0.083	0.089
	C_2	0.023	0.137	0.130	0.144
	C_1	0.016	0.508	0.576	0.570
3	C_5	0.356	0.085	0.084	0.068
	C_4	0.222	0.097	0.092	0.097
	C_3	0.160	0.129	0.124	0.130
	C_2	0.126	0.186	0.181	0.194
	C_1	0.136	0.503	0.519	0.511

The vapour compositions are closer to experiment than those predicted by Prausnitz, although the pressures are not. Once again the effect of using $\xi \neq 1.0$ seems to overdo the correction for bubble pressure, except at the low pressure (No.2 above). Examining the tables of results for ternary mixtures, the same effect occurs - at low pressures use of ξ gives better predictions than with ξ all 1.0 whereas at high pressures results are definitely worse. The general effect of decreasing ξ (i.e. from 1.0) is to decrease the concentration of the least volatile component and increase that of the most volatile component in the vapour phase and just such an effect is obtained in the computations here for the five component mixtures. The change in distribution of intermediate components cannot be surmised so easily.

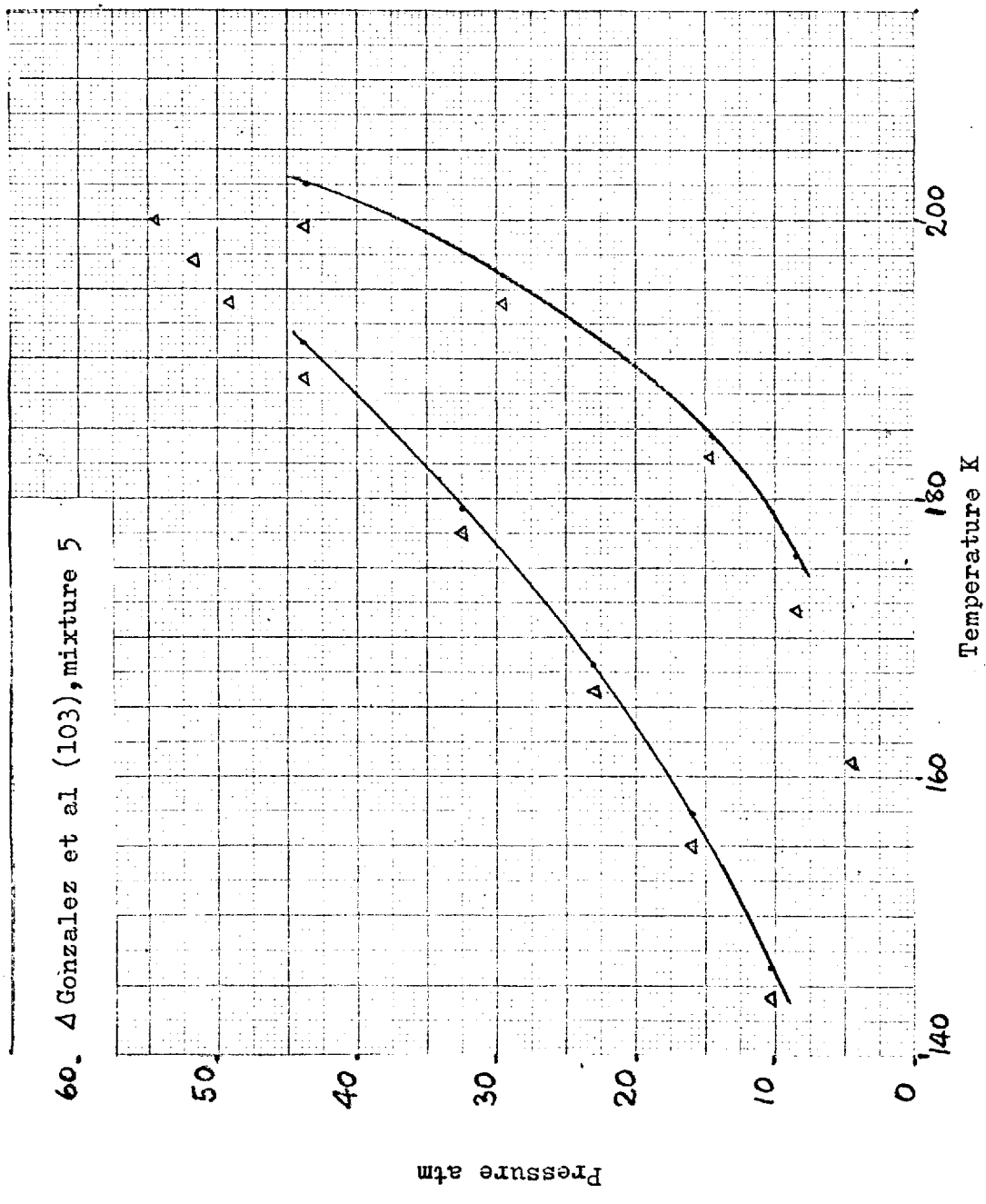
Natural Gases

The growth in the transmission of liquefied natural gases by pipeline has lead to an increasing interest in their behaviour under various conditions of pressure and temperature. The dew and bubble points of several types of natural gases have been computed here, and in the following section the phase compositions after flashing have been also computed. Some of the gas compositions and working conditions have been obtained from industry, and others from published experimental work on real and synthetic natural gases.

Yarborough and Vogel (102) composed their own gas mixture, containing six hydrocarbons, nitrogen and carbon dioxide. At 366.7K they measured many equilibrium compositions and pressures. In the tables of results following, two sets of Yarborough and Vogel's experimental work are compared with computations at the same conditions - a bubble point and a bubble pressure. Both computations were made with $\xi = 1.0$ and the bubble pressure was repeated using $\xi \neq 1.0$. In this last case, the resulting pressure increased in the right direction but by a little too much. The vapour compositions show small changes - the most volatile, nitrogen, does increase its mole fraction, but methane mole fraction is virtually unchanged.

The bubble point computed at 7.48 atm with all ξ equal to 1.0 gave a temperature which was too high. Use of $\xi \neq 1.0$ would have reduced this, but it is uncertain how far.

Fig 63. Natural gas, calculated dew and bubble points.



Gonzalez and Lee (103) measured dew and bubble points for a series of natural gas mixtures. Two of these were selected as suitable data for computing dew and bubble points. The first had four components and the second had six. Their compositions are given below.

Natural gas compositions (103)

	No.5	No.6*
N_2	0.0330	0.0310
CH_4	0.9098	0.8144
C_2	0.0560	0.1110
C_3	0.0012	0.0180
C_4	-	0.0026
C_6	-	0.0230

* these numbers correspond to those in Gonzalez's paper.

Fig 63 shows bubble and dew temperatures plotted against pressure for mixture 5. The bubble calculations broke down at 45 atm and approximately 191K, and the reduced temperature was 1.0. The conditions are not surprising in a mixture nearly all methane. Rough calculations show that the critical point of mixture 5 is 195K, 47.6 atm. The dew pressure calculations broke down at the maximum temperature point. At the lower end of the diagram, no calculations could be persuaded to work below 5 atm, 162K.

All the foregoing computations on mixture 5 were made with no adjustment to the acentric factor. Several points were repeated making an adjustment.

The results were almost indistinguishable from those with no adjustment to the acentric factor. The table below shows three such points.

Bubble Point for mixture 5

P atm	T K (no adjustment to ω)	T K (ω adjusted)
15.89	191.10	191.12
10.37	157.32	157.38
Dew Point		
14.69	184.54	184.34

With mixture 6 computations were not very successful - only two bubble points were obtained. These are shown in Fig 64.
Dew and bubble points at many different conditions, with and without adjustment to the acentric factor, with ξ all 1.0 and $\xi \neq 1.0$ would not work. The reason for this is not clear, but the reduced temperatures were very close to 1.0; possibly the phase boundary is very close to the dew line.

The British Oxygen Company (BOC)(106) suggested some interesting natural gases as data for dew and bubble point computations. In the table of results are four bubble pressures for some eight component mixtures computed in this work and for comparison, the results computed by BOC using their BWR based method. Both methods give very similar results, except in No.4. Here the nitrogen vapour mole fraction is higher in this work, while other compositions are only changed very slightly. The bubble pressure for No.4 is higher than the BOC pressure too. The computed bubble point for a six-component mixture given by BOC (No.7) was in good agreement with their bubble temperature, but the vapour compositions did not agree so well.

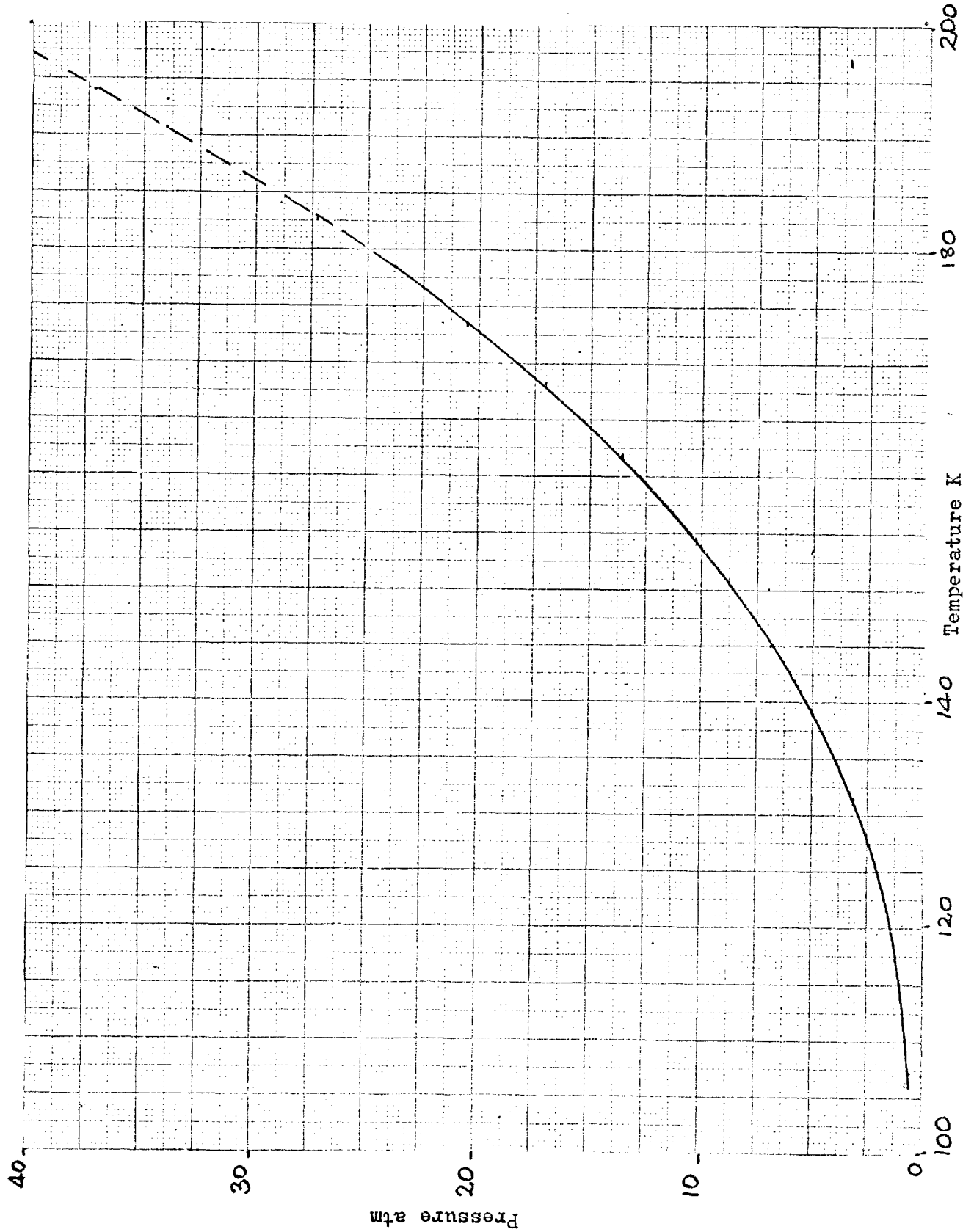
One dew point computation was made to compare with the BOC method, at 36.49 atm. The temperatures agreed well although the compositions were a little different - but not significantly so. The results are in the table following this section.

A natural gas with thirteen components was suggested by BOC for a bubble point computation. This had to be tailored into a ten component mixture as the program developed in this work will only accommodate up to ten components. The bubble point was computed twice - with ξ all 1.0 and $\xi \neq 1.0$. The results were good - omitting heavy components in a bubble point computation makes little difference to the answer (both composition and temperature). A similar alteration for a dew point calculation would have a drastic effect on both temperature and liquid composition,

Two dew pressures were computed for a natural gas (108) containing no heavy hydrocarbons. Unfortunately there are no comparable experimental two phase equilibria to include here for comparison. This is because this gas is a synthetic natural gas and was made for a study on gas compressibility. It was necessary to know approximately the dew points at various pressures to enable minimum working conditions to be established for determinations of compressibilities on a Burnett apparatus. These two sets of results are in the tables following.

A bubble pressure line was computed for yet another gas, again twice, with and without ξ all equal to 1.0. The effect of this change in ξ was again insignificant. An interesting point is that while computations with ξ all 1.0 continued to (42 atm, 200K), a point close to where the critical point of the mixture must be, computations with ξ 1.0 broke down at 25 atm, 180K.

Fig 65. Natural gas, (107), calculated bubble point line.



These results are shown in Fig 65. This could be due to the increased reduced temperature (due to using $\xi \neq 1.0$) going prematurely above 1.0. Alternative starting conditions (guesses) might well overcome this difficulty, but unfortunately not tried in this work. A sample is given below of results showing the effect of changing ξ from all 1.0 to $\xi \neq 1.0$ on bubble temperature and vapour composition.

Bubble temperatures at 17.01 atm

Temperatures : all $\xi = 1.0$ 167.92K, $\xi \neq 1.0$ 168.13K

Liquid Composition		Vapour, all $\xi = 1.0$	$\xi \neq 1.0$
N_2	0.001	0.00535	0.00668
CH_4	0.810	0.98653	0.98393
C_2	0.130	0.00787	0.00899
C_3	0.040	0.00024	0.00035
i-C_4	0.003	0.00001	0.00002
C_4	0.010	0.00001	0.00002
i-C_5	0.002	0.00000	0.00001

Introduction of $\xi \neq 1.0$ does not have the same effect on bubble temperature as in binary mixtures - probably due to a more complex P-V-T surface, where the vapour pressure of the mixture is not directly dependent on its methane content.

Tables of results for computed dew and bubble conditions for natural gases.

Table of compositions of various liquefied natural gases

Component	No 1 (102)	No 2 (102)	No 3 (106)	No 4 (106)	No 5 (106)	No 6 (106)	No 7 (106)	No 8 (106)
N_2	0.0003	0.00005	0.0019	0.0022	0.0020	0.0019	0.0128	0.00018
CO_2	0.0003	0.00005						
C_1	0.1349	0.0251	0.6136	0.5850	0.4669	0.4398	0.1049	0.26906
C_2	0.0290	0.0065	0.1442	0.1317	0.1454	0.1278		0.21911
C_3	0.0312	0.0082	0.1976	0.2205	0.2642	0.1357	0.1207	0.22119
C_4			0.0120	0.0168	0.0386	0.0583	0.1769	0.08819
iC_4			0.0165	0.0217	0.0333	0.0317	0.0974	0.07202
C_5	0.1714	0.0690	0.0114	0.0176	0.0416	0.1240		0.05636
C_6								0.02310
C_7	0.2783	0.2275						0.02241
C_{10}	0.3546	0.6635						
benzene			0.0028	0.0045	0.0080	0.0808		0.02778
ethylene							0.4873	

Computed results

Bubble Pressure (data from (102))

Liquid composition:	1	1
Fixed temperature	: 366.7K	366.7K
Expt'l pressure	: 37.55atm	37.55
Pressure calc.	: 36.17	39.41
	(ξ all 1.0)	($\xi \neq 1.0$)

Bubble Temperature

2	
Fixed pressure:	7.48atm
Expt. temp.	: 366K
Temp. calc.	: 403.8K

Vapour compositions

	this work	expt.	this work	expt.	this work	expt.
N_2	0.0043	0.0051	0.0076	as for	0.0030	0.0050
CO_2	0.0003	0.0020	0.0010	ξ all 1.0	0.00025	0.0015
C_1	0.8690	0.8495	0.8659		0.7120	0.8261
C_2	0.0515	0.0619	0.0465		0.0564	0.0598
C_3	0.0271	0.0302	0.0271		0.0378	0.0302
C_5	0.0334	0.0355	0.0337		0.08385	0.0432
C_7	0.0126	0.0137	0.0160		0.0755	0.0275
C_{10}	0.0018	0.0021	0.0022		0.0312	0.0067

Bubble Pressures (data from 106)

Liquid composition:	3	4	5
Fixed temperature	200.4K	209.4K	221K
P calc (106)	34.4 atm	40.0	40.0
P calc (this work)	34.49	40.6	41.3

Vapour compositions

	this work	(106)calc	this work	(106)calc	this work	106(calc)
N_2	0.0099	0.0105	0.0109	0.0103	0.0124	0.0103
C_1	0.9618	0.9587	0.9537	0.9507	0.9371	0.0327
C_2	0.0224	0.0244	0.02565	0.0281	0.0350	0.0387
C_3	0.0057	0.0065	0.00928	0.0106	0.01434	0.0161
C_4	0.00006	<0.0001	0.00015	0.0001	0.00045	0.0005
iC_4	0.00013	0.0001	0.00029	0.0003	0.00059	0.0007
C_5	0.00001	.0	0.00003	<0.0001	0.00011	0.0001
Benzene	0.00000	4 ppm	0.00000	8 ppm	0.00001	1.7 x 10-6

Bubble Pressure (data (106))

Liquid composition : 6
Fixed temperature : 220.8K
Pressure calc(106) : 40 atm
Pressure(this work) : 45.67

Bubble Point (data (106))

Liquid composition : 7
Fixed pressure : 32.12 atm
Temperature calc(106) : 260K
Temperature(this work) : 259.9K

Vapour composition

	this work	106 calc		this work	106 calc
N_2	0.0137	0.0100	N_2	0.1256	0.1159
C_1	0.9482	0.9473	C_1	0.3904	0.3673
C_2	0.02956	0.0330	C_3	0.0214	0.0237
C_3	0.00707	0.0076	C_4	0.00856	0.0107
C_4	0.00064	0.0007	iC_4	0.00674	0.0084
iC_4	0.00051	0.0006	ethylene	0.4473	0.4736
C_5	0.00029	0.0005			
Benzene	0.00005	0.00005			

Bubble Temperature (data (106))

Liquid composition	: 8	8
Fixed pressure	: 26 atm	26 atm
Temperature calc (106)	: 248K	248K
Temperature (this work)	: 245K	247.5
	(ξ all 1.0)	($\xi \neq 1.0$)

Vapour compositions

	this work	(106) calc	this work	(106) calc
N_2	0.00773	0.00581	0.00845	as for
C_1	0.87225	0.85119	0.76618	ξ all 1.0
C_2	0.09154	0.10744	0.17116	
C_3	0.02315	0.02783	0.04178	
C_4	0.00217	0.00294	0.00468	
iC_4	0.00274	0.00365	0.00656	
C_5	0.00034	0.00114	0.00083	
C_6	0.00003)		0.00008	
C_7+	0.00001}	10 ppm	0.00005	
Benzene	0.00005)		0.00022	

Dew Pressure (data (108)

Fixed temperature	: 180K	200K
Pressure(this work)	: 10.51 atm	33.72

Dew temperature (data (106)

Fixed pressure	: 36.49 atm
Temperature (106)	: 190K
Temperature(this work)	: 190K

	Vap.comp'n	Liquid Composition		Vap.comp'n	Liquid Composition	
		180K	200K		(106)	(this work)
N_2	0.1508	0.0062	0.0252	0.0327	0.0081	0.0056
C_1	0.7697	0.2315	0.4927	0.9570	0.8562	0.8340
C_2	0.0743	0.7425	0.4739	0.0188	0.1026	0.1000
C_3	0.0002	0.0176	0.0054	0.0015	0.0331	0.0288
CO_2	0.0001	0.0006	0.0003			
ethylene	0.0002	0.0009	0.0008			
oxygen	0.0047	0.0007	0.0017			

Flash separations

Twelve isothermal flash separations were computed in this work. The feed mixtures contained from three to six components, and flash conditions ranged between (153 - 298)K and (5 - 71)atm. In some cases experimentally determined phase compositions were not available (123, 128), but for all mixtures the ratio V was available (as a computed quantity). The methods used by the various workers were forms of either the BWR method (127) or the Redlich Kwong equation of state method (126, 123, 128, 127).

The table following shows the computed ratios V for this work, and those from the various other sources.

Partial molal enthalpies were available for two mixtures (128) and it was possible to compare the phase enthalpies computed by this method and those computed by the Redlich Kwong equation of state. It was also possible to show the consistency of enthalpies calculated in this program by comparing the residual enthalpy of the phase calculated from equation (2.87) and the sum $\Sigma x\bar{h}^{resid}$ (2.119), where $\bar{h}_i^{resid} = (\bar{h}_i - \bar{h}_i^{pg})$. Below are shown the enthalpy comparisons. It was not possible to ascertain the value for the total enthalpy for a perfect gas used in (128) so the comparison of total phase enthalpies was made by using the difference between the phase enthalpies - which is independant of the perfect gas enthalpy.

Mixture number	Difference* between liquid and vapour enthalpies	
	Shelton (128)	This work
7	3936.9	4339.05
8	3415.1	3843.00

* in cals/mol

Consistency of computed residual enthalpies

Mixture number		$\Sigma x\bar{h}_i^{resid}$	$(H_{mix}-1)RT$
7	liquid	- 4550.0	- 4540.8
	vapour	- 201.7	- 201.75
8	liquid	- 4130.0	- 4121.7
	vapour	- 278.8	- 278.7

Results of Computed Flash Separation

	Flash Conditions		N_2	CH_4	C_2H_6	C_3H_8	iC_4H_{10}	V(this work)	V calc (ref)	V(expt) (ref)
1	172.0K 33.2 atm	Feed m.f. K products	0.26347 2.804	0.71358 0.848	0.02295 0.105			0.796	0.807[a] (123)	
2	161.1K 33.2 atm	Feed m.f. K products	0.26347 2.260	0.71358 0.677	0.02295 0.079			0.182	0.258[a] (123)	
3	177.61K 27.4 atm	Feed m.f. K products	0.0394 3.901	0.9074 1.066	0.0384 0.115	0.0111 0.022	0.0037 0.007	0.568	0.846[a] (126)	0.632
4	179.37K 27.6 atm	Feed m.f. K products	0.0393 4.226	0.9072 1.111	0.0386 0.114	0.0112 0.021	0.0037 0.007	0.688	0.861[a] (126)	0.731
5	181.33K 28.1 atm	Feed m.f. K products	0.0381 4.511	0.9056 1.156	0.0405 0.114	0.0121 0.021	0.0037 0.007	0.745	0.863[a] (126)	0.756
6	153.0K 10.9 atm	Feed m.f. K products	0.101 1.162	0.716 0.025	0.151 0.001	0.032 10.245		0.415	0.585[a] 0.406[b]	0.530 (127)
7	243.0K 71.2 atm	Feed m.f. K products	0.092 1.609	0.550 0.390	0.197 0.147	0.161 3.980		0.439	0.416[a] 0.358[b]	0.438 (127)
8	244.0K 40.9 atm	Feed m.f. K products	0.128	0.646	0.132	0.094		no convergence	0.877[a] 0.891[b]	0.848 (127)
9	153.0K 12.2 atm	Feed m.f. K products	0.061 1.008	0.769 0.028	0.143 0.002	0.027 7.659		0.167	0.506[a] 0.176[b]	0.320 (127)

a: calculated using the Redlich-Kwong method. b: calculated using the BWR method.

Results of Computed Flash Separations, continued.

	Flash Conditions		CH_4	C_2H_6	C_3H_8	iC_4H_{10}	C_4H_{10}	C_5H_{12}	V(this work)	V calc[a] (128)
11	288.7K 5.035 atm	Feed m.f. K products	0.00537 30.625	0.15580 4.569	0.44522 1.310	0.20074 0.615	0.17379 0.425	0.01909 0.181	0.637	0.562
12	298.7K 10.207 atm	Feed m.f. K products	0.00537 15.492	0.15580 2.806	0.44522 0.906	0.20074 0.437	0.17379 0.319	0.01909 0.141	0.055	0.054

Section 5

Discussion of results

Discussion of Results

In the presentation of results, comments have been made on the individual characteristics of each system. Some general trends have emerged from the computed work as a whole and these are discussed here. It was also felt advisable to check some aspects of the Vennix equation of state as a preliminary to the main work.

1. Vennix equation of state

A small program was written to compute solutions to equation (2.6) at a reduced temperature of 1.0 for a range of reduced volume (0.82 - 1.10). The results are tabulated below. The reduced pressure was computed from

$$P^R = Z.T^R/Z_o^c/V^R$$

Z is from equation (2.6) and Z_o^c is 0.28793.

Computed reduced pressures at $T^R = 1.0$

V^R	P^R
0.82	1.00436
0.86	1.00061
0.90	0.99948
0.94	0.99950
0.98	0.99993
1.00	1.00017
1.02	1.00039
1.06	1.00069
1.10	1.00073

This curve does show a slight minimum and maximum in the critical region which, if equation (2.6) were completely accurate it would not do. This means that it is slightly unreliable for use in conditions where the reduced volume is between 0.86 and 1.0 when the reduced temperature is 1.0. However this very slight disadvantage does not affect the work here.

2. Vapour pressure of methane

Several equations are available for the vapour pressure of methane. Some are in terms of temperature and others in terms of reduced temperature. Leach (8) gives the following :

$$P^{RL} = \exp(4.77726-4.782895/T^{R} + (\ln T^{R}).\ 0.73611) \qquad (5.1)$$

Vennix (16) gives another correlation for the vapour pressure of methane (5.2) which is based on a correlation developed by Armstrong, Brickwedde and Scott (113).

$$P^{SV} = \exp(18.0288-1264.51/T - 0.550663T + 0.196832.10^{-3}.T^{2} - 0.223451.\ 10^{-6}.T^{3}) \qquad (5.2)$$

where P^{SV} is in psi.

The correlation of Armstrong et al is :

$$\log_{10}P^{SA} = (10.68631-595.546/T-0.0348066.T + 0.13338.10^{-3}.T^{2} - 1.7869.10^{-7}.T^{3}) \qquad (5.3)$$

where P^{SA} is in mm Hg.

Leach also gives a correlation for the reduced saturated volume of methane as a function of reduced temperature only - equation (5.4) below.

$$V^{RL} = 1.0/(1.0 + \exp(0.83531 + 0.4175105.(\ln(1.-T^{R})) + 0.214866.\exp(50.908(T^{R} - 1.0)))$$

(5.4)

In order to compare volumes computed from equation (5.4), saturated volumes for methane were calculated from Vennix's equation of state - using the version which expresses pressure as a function of volume and temperature - equation (5.5).

$$P^{V} = \rho^2(A_1+A_2\rho+A_3\rho^2+A_4\rho^3+A_5\rho^4)+T.\rho(75.175+B_1\rho+B_2\rho^2+B_3\rho^3+B_4\rho^4+B_5\rho^5)+\rho^2.(\rho+\rho_0).((\rho+\rho_0)^3-(\alpha+\rho_0)^3).((\beta+\rho_0)^3-(\rho+\rho_0)^3).\exp(G_1+(E_1+E_2(\rho+\rho_0)^3)(T-t_0))+\rho^2(D_1+D_2\rho+D_3\rho^2+D_4\rho^3+D_5\rho^4).\exp(k-(F_1+F_2.\rho)/T)$$

(5.5)

The constants (A_1.....F_2) are listed in Appendix A.

In the table below, the following computed results are compared :

(i) saturation pressures from equations (5.3) and (5.2)

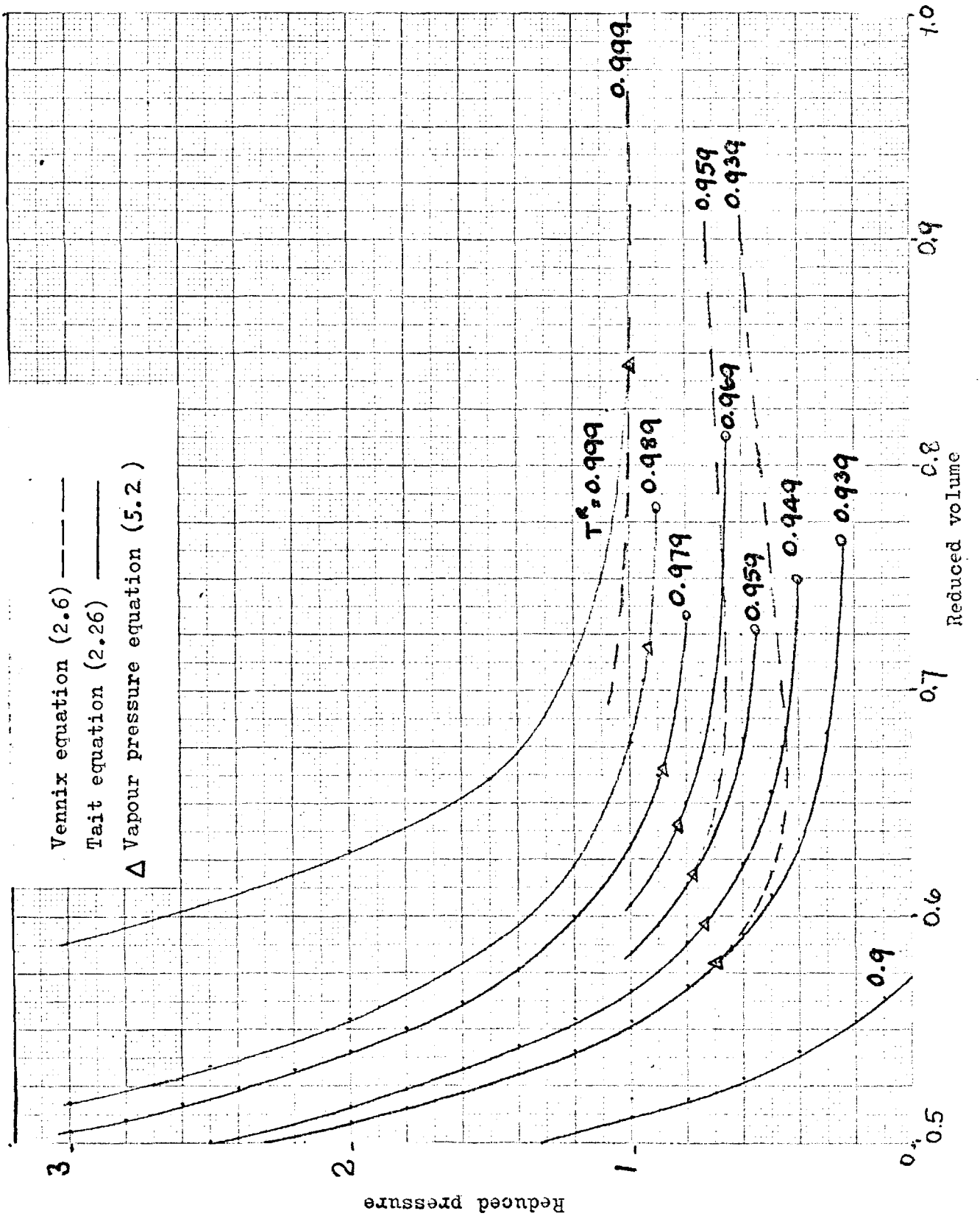
(ii) pressure from (5.3) reduced by a critical pressure of 671.0 psi and reduced pressure from equation (5.1)

(iii) the reduced volumes from (5.4) and the solution to (5.5) are compared at temperatures from 100K to 190K. In computing a reduced saturated volume from (5.5) a critical density of 0.1625 gm/cc for methane was assumed.

T K	Vapour Pressures psi		Reduced Pressures		Reduced Volumes	
	P^{SA}(5.3)	P^{SV}(5.2)	$P^{SA}/671.0$	P^{RL}(5.1)	V^{R}(5.5)	V^{RL}(5.4)
100	4.917	5.063	0.00733	0.00805	-	0.3716
120	27.857	27.980	0.04152	0.04210	-	0.3962
140	93.286	92.949	0.13903	0.13975	0.4294	0.4298
160	231.268	230.131	0.34466	0.34822	0.4809	0.4816
180	476.803	376.277	0.71059	0.71563	0.5865	0.5872
190	652.231	654.500	0.97239	0.97240	0.8078	0.7844

The vapour pressure equation of Vennix (P^{SV}) gives critical points used in this work - 190.77K and 671.0psi, so naturally this was the correlation adopted for the prediction of vapour pressures. The correlation of Leach(P^{RL}) was also used in program, for computing saturation pressures for use with the Tait equation.

Fig 66. Reduced volume and pressure for reduced temperatures approaching 1.0, for methane, using Vennix equation of state, Tait equation of state and the vapour pressure equation.



He used slightly different critical constants (191.06K and 671.2psi) for his correlations for the constants in the Tait equation and hence P^{RL} must be used to be consistent with the rest of the Tait correlations. Reduced saturated volumes from Leach's correlation V^{RL} are very close to those obtained from Vennix's pressure equation of state (5.5) - the slight differences are due to the two sets of critical constants.

3. Reduced temperatures close to 1.0

Where the phase conditions are such that the reduced temperature is very close to 1.0, there are some computation difficulties. It has been found that there are limiting values for the reduced temperature below 1.0, beyond which the Tait equation (2.26) has no solution. In the vapour-liquid equilibrium programs developed in this work, the Vennix equation (2.6) has been used to take over the computation of liquid phase compressibility when the Tait equation becomes unusable. This procedure is satisfactory up to a reduced temperature of 1.0.

In Fig 66 are shown a few of the isotherms computed using both the Vennix and Tait equations, and the saturated vapour pressure curve for methane using equation (5.2). Too much significance should not be attached to the value of V_R where the isothermal calculation by Tait equation breaks down. The apparent irregularity of these points is due to the incremental approach used to find the value of P_R at which the term $(P_A^R + H)/(P_0^R + H)$ becomes negative. H is a function of reduced temperature (2.29), correlated by Leach (8) for the Tait equation. Reduced pressure (P_A^R) was decreased at intervals of 0.05, and the points shown ⊙ in Fig 62 are the last possible computation of the reduced volume using the Tait equation, at that particular T^R.

The isotherms computed by both equations coincide at the vapour pressure curve calculated from (5.2), showing the very reasonable consistency of the three equations used to describe phase equilibrium in this work.

4. Consistency check

Some tests were made to check the thermodynamic consistency of the shape factor correlations derived by Leach (8).
The tests showed that these correlations (1.17 and 1.18) were satisfactorily consistent within the principle of corresponding states. That is, the right-hand side and left-hand side of equation (5.6) are equal (or very nearly so).

$$\frac{U_o}{RT_o}\cdot\left(\frac{\partial f_{ii,o}}{\partial V}\right)_T \cdot \frac{1}{f_{ii,o}} = \frac{-(Z_o - 1)}{h_{ii,o}}\cdot\left(\frac{\partial h_{ii,o}}{\partial V}\right)_T \qquad (5.6)$$

The derivatives of f and h with respect to volume can be computed in the same way as the derivations of f and h with respect to temperature. Equation (5.6) was derived in Section 1. However it is not necessary to compute these derivatives if the following simplifications are made.

$\frac{1}{f_{ii,o}}\cdot\left(\frac{\partial f_{ii,o}}{\partial V}\right)_T$ can be transformed to $\frac{1}{\Theta_{ii,o}}\cdot\frac{\partial \Theta_{ii,o}}{\partial V_i^R}$

and $\frac{1}{h_{ii,o}}\cdot\left(\frac{\partial h_{ii,o}}{\partial V}\right)_T$ to $\frac{1}{\Phi_{ii,o}}\cdot\frac{\partial \Phi_{ii,o}}{\partial V_i^R}$ using the definition

of $f_{ii,o}$ and $h_{ii,o}$ in equations (1.12, 13 and 1.14, 15)

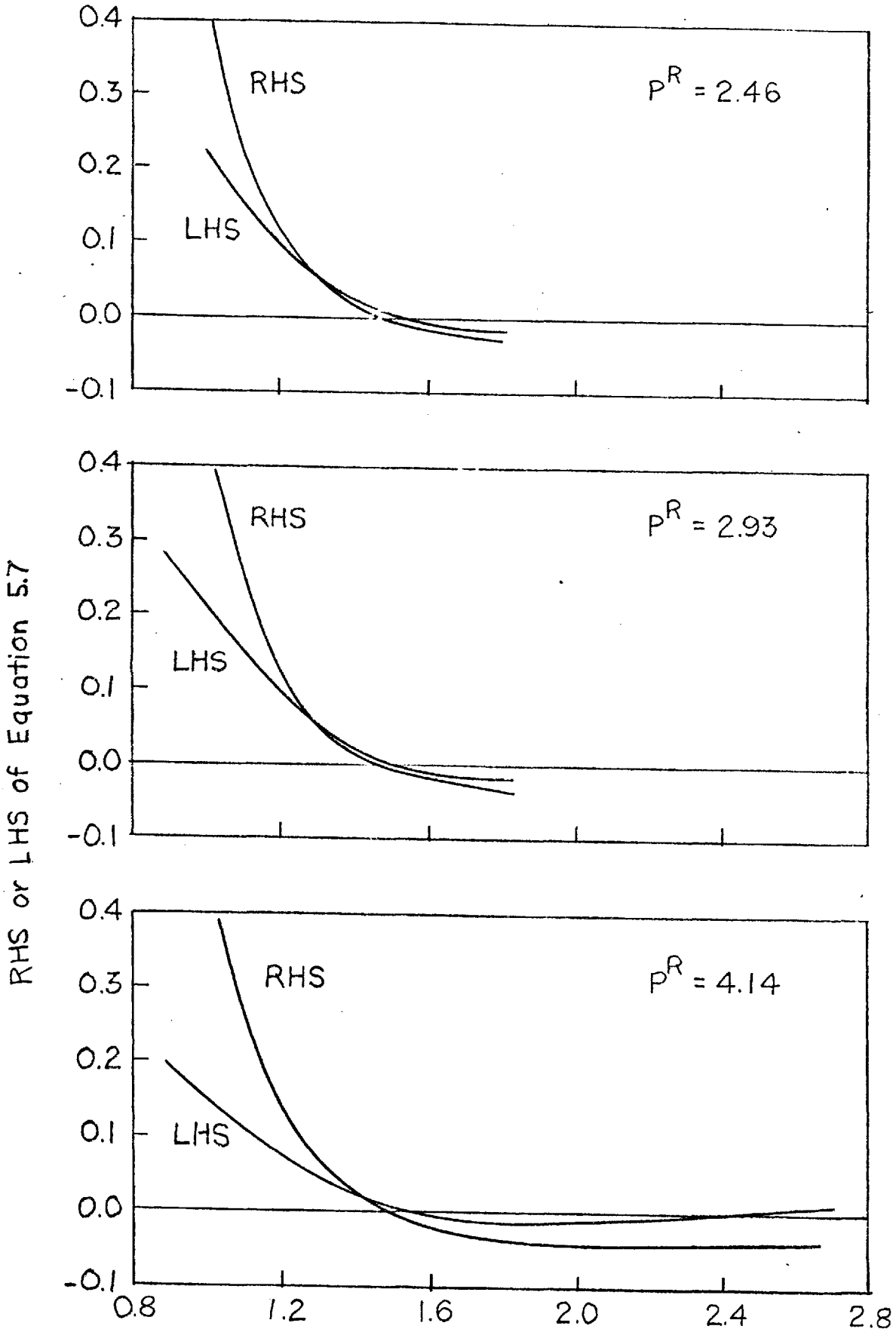


Fig 68. Application of Consistency Test

From the defining equations of Θ and ϕ (1.17 and 1.18) we have

$$\left(\frac{\partial \Theta_{ii,o}}{\partial V_i^R}\right)_{T_i^R} = (\omega_i - \omega_o)\ (0.3063 - 0.4506/T_i^R) \tag{5.7}$$

$$\left(\frac{\partial \phi_{ii,o}}{\partial V_i^R}\right)_{T_i^R} = (\omega_i - \omega_o)\ \frac{Z_o^c}{Z_i^c}\ (0.3903 - 0.9462 \ln T_i^R) \tag{5.8}$$

Actually T_i^R and V_i^R are functions of Θ and ϕ (1.15, 1.16) and i and although this means $(\partial \phi_{ii,o}/\partial V_i^R)T_i^R$ and $(\partial \Theta_{ii,o}/\partial V_i^R)\ T_i^R$ are dependent on Θ and ϕ, this interdependency is ignored as Θ and ϕ are very close to unity for the range of V_i^R and T_i^R examined here. They are assumed equal to unity. Substituting equations (5.7) and (5.8) into (5.6) the test equation for consistency is

$$(Z_o - 1).\frac{Z_o^c}{Z_i^c}.\ (0.3903 - 0.9463 \ln T_i^R) = -\frac{U_o}{RT_o}\ (0.3603 - 0.4506/T_i^R) \tag{5.7}$$

Oxygen, nitrogen, argon data were used for the calculations. Fig 68 shows either side of equation (5.7) plotted against reduced temperature for several reduced pressures. Two specific cases below show both sides of (5.7), and how errors in prediction of thermodynamic properties cannot be deduced from the small inequalities of the sides of (5.7). A full discussion of this consistency test is described by Canfield and Gunning in (110).

Nitrogen	Argon
140K, 98.7atm	203K, 200atm
LHS of (5.7) = 0.15207	0.03273
RHS of (5.7) = 0.24264	0.04505
calculated H/RT = 2.008	- 0.8368
experimental (37) H/RT = 2.030	- 0.8320 (35)
calculated Z = 0.4732	0.7006
experimental Z = 0.4797	0.7024

5. Compressibility factors

The computed compressibility factors agreed, as a whole, very well with experimental work. Errors are almost all a fraction of a percentage, no matter whether temperature or pressure are high or low. There is a slight tendency for higher errors to be at low temperature and high pressure, and the greatest errors are in the critical region - up to about 5%. For mixtures most errors occur at equimolar mixtures, or with increasing concentration of the component with lesser similarity to methane. Equimolar mixtures will be least accurate in their predictions because the mixing rules are least adequate at this concentration.

Good results for predicted compressibility factors are not entirely unexpected since compressibility is one of the two dimensionless configurational properties used in the pair of equations (2.1, 2.82) defining the principle of corresponding states.

The excellent correlations for shape factors, Θ and Φ, have helped to make these very accurate predictions of Z. If it were not possible to evaluate Θ and Φ, and they were taken as 1.0, the principle of corresponding states would revert to its simpler form $Z_i = F(T/T_i^c, V/V_i^c)$. This latter definition is used in the well-known "compressibility charts", where Z is plotted as a function of T^R and V^R.

The work on computed Z for mixtures was used to evaluate the worth of using the 2-fluid model for mixtures. The results for air showed that it is not really worth the effort. Watson and Rowlinson (10) found that their 2-fluid model bubble point computations gave better results for vapour-liquid equilibrium for oxygen-nitrogen-argon mixture. Their work was at 6 and 18atm, and temperatures up to 129K (i.e. comparatively low), and they used the Leach equation of state. Their results bear out what was noted in the discussion on Z in this work for air - that Leach's equation of state incorporated with the 2-fluid model is best at low temperatures and pressures.

The reason for the 2-fluid model being only the best at low pressures may be due to the fact that it is based on the concept of an ideal mixture of hypothetical components. As pressure drops in the gas phase ideality is approached, and this model therefore becomes appropriate at low pressures. In addition, at higher temperatures and pressures, the mixing rules will contribute increasing inaccuracies which must accumulate more quickly in the 2-fluid model.

The computation of Z for natural gases has been made very successfully by Roe (108). His results are in the approximate range (294-218)K and (3-100)atm. He uses the extended principle of corresponding states (as described in this work) and the Vennix equation of state in his computer program. The three natural gases which he uses as data are of two types - two with fifteen components and very high methane content, and the third with four components and only 74% methane with 15% nitrogen. He estimates a maximum error of 0.1% in the experimental compressibility factors, and his computed Z are generally within experimental error.

6. Joule-Thomson coefficients

Computations of Joule-Thomson coefficients, both isothermal and adiabatic, were less accurate than for compressibility factors or enthalpies. Comparison of computed adiabatic coefficients with older experimental work shows very great differences - particularly for hydrocarbons. There is good reason to believe - as described earlier - that these early data are unreliable. Various methods of predicting Joule-Thomson coefficients all give similar answers for η and φ. Comparison of computed φ (both this work and others) for mixtures (for example nitrogen, methane and ethane) with recent experimental work shows very much better agreement.

A source of error in predicted coefficients in this work is probably due to the use of finite differences in equations (2.123, 2.130), instead of using analytical expressions for the derivatives of enthalpy with respect to pressure.

ΔT and ΔP were varied in computations of η for hydrocarbons and the results for η showed very little change. Computed and experimental η were so different in this case that it is difficult to say whether or not smaller finite differences brought computed η nearer the true η. In the case of for the three component mixture (N_2,CH_4,C_2H_6) mentioned above, it is more likely that smaller ΔT and ΔP would improve predictions for φ. The use of analytical derivatives of enthalpy could be avoided by using an alternative definition for φ:

$$\varphi = V + T\left(\partial P/\partial T\right)_V / \left(\partial P/\partial V\right)_T$$

or

$$\varphi = \frac{-RT^2}{P} \cdot \left(\frac{\partial Z}{\partial T}\right)_P$$

These give a more accurate method, but much more time-consuming. However it does seem that it might be worthwhile since there is evidence (117) that it gives better answers.

7. Vapour-liquid equilibrium

The computed results described for the vapour-liquid equilibrium are generally very close to experiment. A wide range of representative mixtures and components have shown the adequacy as well as the limitations of the method described here. K values have only been used sparingly as a means for comparison with experiment, since they mask actual compositions computed.

The great drawback of using a pure substance for the reference component for mixtures, is that pure substances do not exhibit retrograde behaviour.

Thus, vapour-liquid equilibrium at conditions where the reduced properties are greater than 1.0 cannot be computed. This is because configurational interal energy, U is defined :

$$\frac{U}{RT} = -\int_0^{\rho^R} \left\{ \frac{T_o^R}{\rho_o^R} \left(\frac{\partial Z_o}{\partial T_o^R} \right)_{\rho^R} \right\} d\rho^R \qquad (2.53)$$

and in the liquid phase the limits of this integral are V^R and V_S^R (plus the saturation value of U_o/RT). Since the limit of ρ_s is at $T^R = 1$, for T^R greater than 1.0, ρ_s is inaccessible.

Usually retrograde behaviour is associated with the dew line, thus it should be possible to calculate vapour-liquid equilibria by bubble calculations to very near the critical point. This is exactly borne out by the work here; for almost all computations the bubble temperatures or pressures proceed to within about 5% of the critical point. Dew calculations in this work always fail at the point of maximum concentration - which is the point of maximum temperature for fixed temperature calculations and the point of maximum pressure for fixed pressure calculations.

For dew pressure calculations there are conditions where the equations of state will not yield any solution for which the vapour phase is at the dew point - that is the sum of the liquid mole fractions cannot be converged to 1.0 for any value of pressure. Vapour-liquid equilibrium calculations are relatively more sensitive to temperature than pressure, so it is possible that the chemical potential for the vapour phase of a dew pressure computed at pressures above the maximum temperature point is not very different to that calculated for a similar composition below the maximum temperature point.

The program is able to find a solution for the lower dew pressure but not another higher one at the same composition.

The maximum pressure line rarely departs far from the critical locus, so this means that dew temperature calculations should proceed to near the critical point, in theory. Unfortunately the dew lines at constant pressure are often almost coincident with the critical locus and this makes computations difficult - for example butane-heptane at 20.4atm. It is possible to calculate these saturation lines by bubble calculation where a dew calculation has failed. Two specific examples of this are : the system methane-carbon dioxide at 223K - Fig 37 and the system butane heptane at 20.4atm - Fig 59.

Closer investigation shows that this phenomenon is due to the generation of intermediate conditions (in the dew calculations) which are single phase. These the liquid phase computations cannot deal with - for reasons given above. The actual figures for butane heptane at 20.4atm show how this happens.

Bubble point

Liquid composition		Vapour composition calc'd
C_4	0.400	0.704
C_7	0.600	0.296

Calculated temperature 455.2K.

Dew point

Vapour composition		Liquid composition calc'd
C_4	0.700	not found
C_7	0.300	

Guess for temperature 452K.

For the bubble point calculation the vapour mole fractions began at C_4 0.681 and C_7 0.289, and these gradually progressed to the answer without oscillation. It may be noted in passing that the bubble point computed without adjustment to ω was 454.5K, although the vapour composition was unchanged.

For the dew point, the reduced temperature went immediately very close to 1.0 and the mole fractions were first C_4 0.411 and C_7 0.624. The sum of these oscillated wildly about 1.0 without converging to a constant value, after the temperature had been adjusted to 467K.

Another attempt at calculating the dew point was made with the guess for temperature at 445K. This resulted in a complete calculation. The final result was :

Dew point 455.7K

Liquid composition : C_4 0.397

C_7 0.603

Exactly what happens can now be seen. In the first calculation for dew point, T_g (the guessed temperature) equal to 455.0K was below the correct dew point (because Σ x was greater than 1.0), but the temperature adjustment gave far too high a temperature for the next iteration. This meant the liquid phase could not cope with the high reduced temperature. In the second calculation with a lower T_g (445K), although even further from the dew point to begin with (Σ x was even greater than 1.0) the correction to temperature brings it towards the dew point without going into the one phase region.

However, in conditions where some components are supercritical, raising or lowering the starting temperature, T_g does not facilitate dew computations, once the point of maximum concentration has been passed.

It has been concluded from experience in this work of systems such as the butane-heptane one above, that conditions specified as guesses for computations of vapour-liquid equilibrium influence the path of the iterations to quite a large extent. Misleading compositions can cause havoc. A reasonably successful method (if experimental work is not available) is to use vapour pressure curves and Raoult's law. It has also been found advisable to have the guess for temperature or pressure within the two phase region. This generally ensures critical points less than 1.0 for the fixed phase.

8. Unlike Pair interaction parameter ξ

Introduction of the unlike pair interaction parameter ξ makes a considerable difference to the accuracy of the prediction of vapour-liquid equilibria for binary mixtures. Prausnitz (12) gives a long list of values for ξ (he calls it $(1-K_{12})$) for common hydrocarbons and gases. Rowlinson et al (11) give values for rare gases and a few other compounds. Prausnitz determined his values for excess volumes, and Rowlinson et al from excess Gibbs free energies. Where they have a binary pair in common, the values of ξ and $(1-K_{12})$ agree. Generally it is assumed that ξ is independant of temperature and pressure, and in this work is always treated as such, However some workers - Gravelle and Lu (73) found some variation of ξ with temperature.

Variation between the experimental work of different workers is not considered here to be small enough to justify attempts to correlate ξ with temperature, or to assign values to ξ with more than two significant figures. It is thought that improvement to predictions should come from better equations of state and mixing rules, and not from empirical "constants".

In some cases the value of ξ given by Prausnitz is disputed. Work on critical points by Teja (109) has shown some of Prausnitz's values to be unsuitable for the accurate prediction of critical points using the principle of corresponding states. The best possible values found by Teja were tried for vapour-liquid equilibrium computations, and found - only in some cases - to give an improved prediction. In others the predictions were very much worse. This finding seems to bear out the supposition that ξ does vary with temperature.

Use of these parameters in multicomponent mixtures does not seem to reflect the same accuracy of prediction as they do for binary mixtures - for example in work on the four-component mixtures of Solomon (100), and natural gases. Just as pure component behaviour is modified by the interaction of unlike pairs in a binary mixture, so these binary interactions could well be modified by the presence of a third, fourth etc species. The mixing rule for unlike pairs using ξ modifies each f_{12}, but when there are more than two components, the simple geometric mean seems to be an increasingly more suitable description.

9. The acentric factor

The acentric factor is defined by Pitzer at a reduced temperature of 0.7. Hence in vapour-liquid equilibrium calculations at mole fractions of 1.0, the predicted pressure or temperature will not be exactly equal to the experimental saturation values except at $T^R = 0.7$. Thus, modification to the acentric factor was thought necessary. The method developed here has produced excellent results. The only drawback is that if vapour pressure data are unknown, then adjustment to ω is not possible. This is very unlikely - if the vapour pressure data are unknown, then application of the principle of corresponding states using methane as the reference compound will hardly be valid.

The method here of reproducing correct saturation data breaks down almost invariably at about 10K from the critical point. Due to the method of adjusting ω and the fact that it increases with temperature, supercritical conditions can easily be reached when the saturation temperature is close to the critical point. The acentric factor varies inversely with vapour pressure (see Fig 4) so that this fault is less likely to occur at pressures close to the critical point. Such conditions have not actually been used in this work.

Although the effect of adjusting ω is noticeable for binary mixtures, adjustment in a natural gas (103) with four components produced a negligible effect on the bubble temperature. This may be due to the fact that the effect of adjustment to the acentric factor is only really marked (and most important) at high mole fractions of a particular component - i.e. near the vapour pressure line.

It was originally found that ω varied with the starting value of the temperature or pressure for the adjustment calculations. This value was originally the guessed parameter for the vapour-liquid equilibrium calculations - no other number being available at the time. The variation was small but consistent, probably due to round-off errors. This was eliminated by setting the starting value of temperature or pressure for adjustment computations equal to the saturation data supplied.

10. Isothermal Flash Separations

The relatively low number of computed flash separations is due to the fact that for each mixture, three or four different methods for making an initial guess for V were tried, two different methods for the starting guess for the K values and two different methods for converging the K values were tried. The nett result of all these combinations of methods was that the answers were virtually identical. What the variety of methods did show was how they affect the number of iterations needed to converge on the answer.

The four methods used for guessing V were :

1. $V = 0.5$ or some other similar number.
2. $V = ((T - T_{dew})/(T_{bubble} - T_{dew}))^{0.25}$
3. $V = (T - T_{dew})/(T_{bubble} - T_{dew})$
4. $V = 1 - \sum (q_i/(1 + K_i))$

Method 3 was very poor, but also for some cases (No. 12 for example) method 1 produced a false answer. Method 4 was only tested for two mixtures (No 8 and a mixture quoted by Banks and Haseldin (126)). For neither of these could any convergence be obtained and all four methods of initialising V were tried-in vain. Elsewhere (130) method 4 has been quite successful.

However choice of initial V is not the only factor involved - control of V between 0.0 and 1.0 during the iterative procedure also affects the final answer.

The methods for obtaining initial values for K were either all K equal to 1.0, or $K = p_i/P$. The vapour pressure p_i was determined by generating Antoine constants from the critical data and a vapour temperature at the flash pressure . This method was also developed independently by Liddle (129). In this work, this method of finding a rough value of the vapour pressure was used to calculate an estimate of the bubble point. This is necessary since, as it will be remembered, calculation of saturation data requires an initial guess of the unknown phase composition. The flash feed composition and temperature are not good enough. A similar procedure was used for the dew point. However it was found that accurate dew point calculations did not always go to conclusion, and since this held up the flash calculations, dew calculations were dropped from the program and the estimate used instead. The estimate is only 5-10 degrees from the real dew point so it was felt to be adequate for the check on the feed temperature.

This second method of initialising K values was favoured partly because it was necessary anyway for dew and bubble point calculations, and partly because it seemed to slightly reduce the number of iterations.

Two methods were tried for adjusting K-values between consecutive iterations - direct substitution and replacing each K with the square root of the product of the K assumed for the calculations and the K resulting from them. It was found that the former method was very much faster. For example for No. 11, 15 iterations compared with 45, and both had four iterations on V. Another example, for No. 12, 19 iterations compared with 31, but this time with 6 and 4 iterations on V respectively. It is appreciated though, that for control of oscillating K values, the square root method is the more suitable one.

Of the twelve computations of V, some were close to experimental V, (No. 5, 7) and others were further away. Computed V by other methods are no closer although in several cases, V computed here was less inaccurate - for example (No. 3, 4). There seems to be no definite trend to the deviations, but from only twelve results no significant conclusions can be drawn.

The consistency of the enthalpy calculations is good. The differences between the phase enthalpy differences in this work and Shelton (128) could be due to the slight differences in the final V ratios and hence phase compositions. Shelton calculates his total enthalpies from his partial enthalpies using the phase compositions.

Conclusions and recommendations

The results obtained here in this work for the prediction of thermodynamic properties show that the principle of corresponding states is a most suitable method, provided that the components of the mixtures are not too different from the reference substance - methane in this case. The mixing rules used are adequate, even for mixtures containing molecules of very different sizes, but they are not perfect and further work on these rules should be worthwhile. The temperature and pressure ranges of the predictions is very wide but the limits of the ranges have not been established. In the ranges studied, the computed properties are all close to experimental data. These data were determined during approximately an 40-year period, and there are no significant differences between deviations of computations from recent and early data. Nor does there seem to be any fall off in the accuracy of the predictions towards the limits of the temperature and pressure ranges except in the case of compressibility factors in the critical region.

Work has shown that the 2-fluid model has no great advantages over the 1-fluid model, except perhaps at very low temperatures.

In vapour-liquid equilibrium computations, the dew point calculations at super critical conditions were not possible beyond the point of maximum concentration. This difficulty could be further investigated. It has also been shown that successful computation of equilibrium does depend to some extent on the starting values for the compositions of the unknown phase.

This is a slight disadvantage of this method. Flash separations are successful as far as could be tested but again the initial value for the molar vapour-feed ratio V affects the convergence path quite considerably. How to choose an initial value for V is a point which needs closer investigation, and even more important, how to control the oscillating values of V between the limits 0.0 and 1.0, during the convergence iterations.

References

1 Rowlinson J.S., "Liquids and Liquid Mixtures", Butterworths, London, 1969.

2 Leland T.W., Rowlinson J.S., Sather G.A., Watson I.D., Trans.Farad. Soc., 65 (8), 2034, (1969).

3 Pitzer K.S., Lippmann D.Z., Curl R.F., Huggins C.M., Petersen D.E., J.Am.Chem.Soc., 77 (13), 3433, (1955).

4 Reid R.C., Sherwood T.K., "The properties of Gases and Liquids: their estimation and correlation", McGraw Hill, 1966.

5 Hakala R.W., J.Phys. Chem., 71, 1880, (1967).

6 Leland T.W., Chappelear P.S., Ind.Eng.Chem., 60 (7),15, (1968).

7 Stiel L.I., Ind.Eng.Chem., 60, 50, (1968).

8 Leach J.W., Ph.D. Thesis, Rice Univ., Houston, Texas, 1967.

9 Leach J.W., Chappelear P.S., Leland T.W., A.I.Ch.E.J., 14 (4), 568, (1968).

10 Rowlinson J.S., Watson I.D., Chem.Eng.Sci., 24, 1565, 1575, (1969).

11 Leland T.W., Rowlinson J.S., Sather G.A., Trans.Farad.Soc., 64 (6), 1447, (1968).

12 Prausnitz J.M., "Molecular Thermodynamics of Fluid-Phase Equilibria", Prentice Hall, 1969.

13 Joffe J., Zudkevitch D., Ind.Eng.Chem.(Fund), 9 (4) 545, (1970).

14 Barner H.E., Adler S.B., Ind.Eng.Chem.(Fund), 9 (4), 521, (1970).

15 Vennix A.J., Kobayashi R., A.I.C.E.J., 15, 926, (1969).

16 Vennix A.J., Ph.D. Thesis, Rice Univ., Houston, Texas, 1966.

17 Chappelear P.S., Leach J.W., Leland T.W., "Computer program PROPERTY for thermodynamic calculations on Natural Gas Systems", Dept. of Chem. Eng., Rice Univ., Houston, Texas.

18 Margenau H., Murphy G.M., "The Mathematics of Physics and Chemistry", van Nostrand, New York, 1943.

19 Rohl J.S., Sudall N., Symposium "Efficient Computer Methods for the Practising Chemical Engineer", Page Y38, Inst. Chem. Eng., April (1967).

20 Smith J.M., van Ness H.C., "Introduction to Chemical Engineering thermodynamics" 2nd Edition, McGraw Hill, 1959.

21 Shelton R.J., Wood R.M., Chem.Engr. London, No.187, CE68, (1965).

22 Joffe J., Ind.Eng.Chem., 40 (9), 1738, (1948).

23 Roebuck J.R., Murrell T.A., Miller E.E., J.Am.Chem.Soc., 64, 400, (1942).

24 Charnley A., Rowlinson J.S., Sutton J.R., Townley J.R., Proc.Roy.Soc. A, 230, 354, (1955).

25 National Bureau of Standards, Circular 564,

26 Manning F.S., Canjar L.N., J.Ch.Eng. data, 6 (3), 365, (1961).

27 Kennedy E.R., Sage B.H., Lacey W.N., Ind.Eng.Chem., 28 718, (1936).

28 Sage B.H., Kennedy E.R., Ind.Eng.Chem., 28, 601, (1936).

29 Yesavage V.F., Katz D.L., Powers J.E.,Proc. 4th Symp on Thermophysical Properties, 1968, Am. Soc. Mech. Eng.

30 McGlashan M.L., Potter D.J.B., Proc. Joint Conf. on Thermodynamic and Transport props. of Fluids., Inst. Mech. Engrs., London, 1958.

31 Brown G.G., Pattee E.C., Ind.Eng.Chem., 26, 511, (1934).

32 Michels A., Wassenaar T., Wolkers G.J., App.Sci.Res. (A), 5, 121, (1954).

33 Crain R.W., Sonntag R.E., Adv. in Cryo. Eng., 11, 379, (1965).

34 Michels A., Lunbeck R.J., Wolkers G.J., Appl. Sci. Res., A2, 345, (1951).

35 Michels A., Levelt J.M., Wolkers G.J., Physica XXIV, 769, (1958).

36 Michels A., Levelt J.M., De Graaf W., Physica XXIV, 659, (1958).

37 Wasserman A.A., Kavachinskii Y.Z., Rabinovitch V.A., "Thermodynamic Properties of Air and its Components", Nauk, Moscow (1966).

38 Kate F.H., Robinson R.L., Chao K.C., Chem. Eng. Prog. Sym. Series, No.88 64, 91, (1968).

39 Reamer H.H., Sage B.H., Lacey W.N., Ind.Eng.Chem., 43, 976, (1951).

40 Kohn J.P., Kurata F., J.Ch.Eng.Data, 4, 33, (1959).

41 Yudovitch A., Robinson R.L., Chao K.C., Chem.Eng.Prog.Sym. Series, No.88, 64, 85, (1968).

42 Reamer H.H., Olds R.H., Sage B.H., Lacey W.N., Ind.Eng.Chem., 36, 88, (1944).

43 Lunbeck R.J., Michels A., Wolkers G.J., Appl.Sci.Res., A3 197, (1952).

44 Beattie J.A., Kay W.C., Kaminsky J., J.Am.Ch.Soc., 59, 1589, (1937).

45 Reamer H.H., Sage B.H., Lacey W.N., Ind.Eng.Chem., 41, 482, (1949).

46 Watson L.M., Dodge B.F., Chem.Eng.Prog.Sym. Series, No.3, 48, 76, (1952).

47 Sage B.H., Lacey W.N., Ind.Eng.Chem., 34, 730, (1942).

48 Kelso E.A., Felsing W.A., Ind.Eng.Chem., 34, 161, (1942).

49 Stewart D.E., Sage B.H., Lacey W.N., Ind.Eng.Chem., 46, 2529, (1954).

50 Beattie J.A., Simard G.L., Su G.J., J.Am.Ch.Soc., 61, 24, (1939).

51 Sage B.H., Webster D.C., Lacey W.N., Ind.Eng.Chem., 29, 1188, (1937).

52 Marchman H., Prengle H.N., Motard R.L., Ind.Eng.Chem., 41, 2658, (1949).

53 Beattie J.A., Su G.J., Simard G.L., J.Am.Ch.Soc., 61, 926, (1939).

54 Reamer H.H., Olds R.H., Sage B.H., Lacey W.N., Ind.Eng.Chem., 36, 956, (1944).

55 Beattie J.A., Hadlock C., Poffenberger N., J.Chem.Phys., 3, 93, (1935).

56 Smith L.B., Beattie J.A., Kay W.C., J.Am.Chem.Soc., 59, 1589, (1937).

57 Michels A., Schamp H.N., De Graaf W., Physica XX, 1209, (1954).

58 Michels A., Wassenaar J., Wolkers G.J., Appl.Sci.Res., A5, 121, (1954).

59 Bloomer O.T., Parent J.D., Chem.Eng.Prog.Sym.Series., No.6, 49, 18, (1953).

60 Cines M.R., Roach J.T., Hogan R.J., Roland C.H., Chem.Eng.Prog.Sym. Series, No.6, 49, 4, (1953).

61 Chang S.D., Lu B.C., Chem.Eng.Prog.Sym.Series, No.81, 63, 21, (1967).

62 Ruhemann M., Proc.Roy.Soc., 171A, 121, (1939).

63 Price A.R., Kobayashi R., J.Ch.Eng.Data, 4, 40, (1959).

64 Zudkevitch D., Joffe J., A.I.C.E.J., 16, 112, (1970).

65 Donnelly H.G., Katz D.L., Ind.Eng.Chem., 46, 511, (1954).

66 Sage B.H., Lacey W.N., Reamer H.H., Olds R.H., Ind.Eng.Chem., 36, 88, (1944).

67 Sage B.H., Hicks B.L., Lacey W.N., Ind.Eng.Chem., 32, 1085, (1940).

68 Roberts L.R., Wang R.H., Azarnoosh A., McKetta J.J., J.Ch.Eng.Data, 7, 484, (1962).

69 Hsi C., Lu B.C.Y., Can.J.Ch.Eng., 49, 134, (1971).

70 Olds R.H., Sage B.H., Lacey W.N., Ind.Eng.Chem., 34, 1008, (1942).

71 Amick E.H., Johnson W.B., Dodge B.F., Chem.Eng.Prog.Sym. Series, 48, 70, (1952).

72 Reamer H.H., Olds R.H., Sage B.H., Lacey W.N., Ind.Eng.Chem., 34, 1526, (1942).

73 Gravelle D., Lu B.C.Y., Can.J.Chem.Eng., 49, 147, (1971).

74 Duncan A.G., Hiza M.J., Adv. in Cryo.Eng., 15, 45, (1970).

75 Wilson G.M., Silverberg P.M., Zellner N.G., Adv. in Cryo.Eng., 11, 192, (1965).

76 Poettmann F.H., Katz D.L., Ind.Eng.Chem., 37, 847, (1945).

77 Akers W.W., Kelley R.E., Libscomb T.G., Ind.Eng.Chem., 46, 2535, (1954).

78 Reamer H.H., Sage B.H., Lacey W.N., Ind.Eng.Chem., 43, 2515, (1951).

79 Olds R.H., Reamer H.H., Sage B.H., Lacey W.N., Ind.Eng.Chem., 41, 475, (1949).

80 McKay R.A., Reamer H.H., Sage B.H., Lacey W.N., Ind.Eng.Chem., 43, 2112, (1952).

81 Lu H., Newitt D.M., Ruhemann M., Proc.Roy.Soc. A, No.975, 178, 506, (1941).

82 Kay W.B., Nevens T.D., Chem.Eng.Prog.Sym. Series, No.3, 48, 108, (1952).

83 Kay W.B., J.Ch.Eng.Data, 15, 48, (1970).

84 Reamer H.H. Sage B.H., Ind.Eng.Chem., 43, 1628, (1951).

85 Hirata M., Hakuta T., Onoda T., Int. Chem. Eng., 8, No.1, 176, (1968).

86 Hanson G.H., Hogan R.J., Cines M.R., Ind.Eng.Chem., 44, 604, (1952).

87 Kay W.B., Ind.Eng.Chem., 33, 590, (1941).

88 Shelton R.J., The Chem.Eng'r., Nov. 1968, p CE 385.

89 Reamer H.H., Sage B.H., Lacey W.N., Ind.Eng.Chem., 38, 986, (1946).

90 Reamer H.H., Sage B.H., J.Ch.Eng.Data, 9, 24, (1964).

91 Prausnitz J.M., Ind.Eng.Chem., 60, 48, (1968).

92 Prausnitz J.M., Eckert C.A., Orye R.V., O'Connell J.P., "Computer Calculations for Multicomponent Vapour-Liquid Equilibria", Prentice-Hall (1967).

93 Couter R.T., Sage B.H., Lacey W.N., Trans.Am.Inst.Mining Met. Engrs., 142, 170, (1941).

94 Dourson R.H., Sage B.H., Lacey W.N., ibid, 151, 206, (1943).

95 McCurdy J.L., Katz D.L., Ind.Eng.Chem., 36, 678, (1944).

96 Robinson D.B., Bailey J.A., Can.J.Ch.E., 34, 151, (1957).

97 Reamer H.H., Fiskin J.M., Sage B.H., Ind.Eng.Chem., 41, 2871, (1949).

98 Latimer R.E., A.I.C.E.J., 3, 75, (1957).

99 Sprow F.B., Prausnitz J.M., Cryogenics, 338, Dec., (1966).

100 Solomons E., Chem.Eng.Prog.Sym.Series, No.3, 48, 95, (1952).

101 DePriester C.L., Chem.Eng.Prog.Sym.Series, No.7, 49, 1, (1953).

102 Yarborough L., Vogel J.L., Chem.Eng.Prog.Sym.Series No.81, 63, 5, (1967).

103 Gonzalez M.A., Lee A.L., J.Ch.Eng.Data, 13, 172, (1968).

104 Lee J.I.,Mather A.E., J.Chem.Thermodynamics, 2, 881, (1970).

105 British Petroleum Company, Private Communication.

106 British Oxygen Company, Private Communication.

107 Gas Council, Private Communication.

108 Roe D.R., Gas Council, London Research Station, Report LRST91, July 1971.

109 Teja A., Ph.D. Thesis, University of London, 1971.

110 Canfield F., Gunning A.J., Chem.Eng.Sci., 26, 1139, (1971),

111 Benedict M., Webb G.E., Rubin L.C., Chem.Eng.Prog., 47, 419, (1951).

112 Chao K.C., Seader J.D., A.I.C.E.J., 7, 598, (1961).

113 Armstrong G.T., Brickwedde F.G., Scott R.L., J.Res.Nat.Bur. Stand., 55, 39, (1955).

114 Sage B.H., Webster D.C., Lacey W.N., Ind.Eng.Chem., 29, 658, (1937).

115 British Oxygen Company, Report 3775, 1967.

116 Keesom W.H., Bijl A., Monte L.A.J., Bull.Inst.int. du Froid, Annexe D.4 (1942).

117 Alkasab K.A., Shah J.M., Laverman R.J., Budenholzer R.A., Ind.Eng.Chem.(Fund.), 10 (2), 237, (1971).

118 Budenholzer R.A., Sage B.H., Lacey W.N., Ind.Eng.Chem., 31, 369, (1939).

119 Wenzel L.A., A.I.C.E.J., 15, 256, (1969).

120 Hipkin H, A.I.C.E.J, 12, 486, (1966).

121 Leland T.W., Rowlinson J.S., Sather G.A., Watson I.D., Trans.Farad.Soc., 65 (8), 2034, (1969).

122 Weishaupt J., Agnew.Chem., B20, 321, (1948).

123 Zellner M.G., Claitor L.C., Prausnitz J.M., Ind.Eng.Chem. (Fund.), No. 4, 9, 549, (1970).

124 Reid R.C., Leland T.W., A.I.C.E.J., 11, 228, (1965).

125 Fisher G.D., Leland T.W., Ind.Eng.Chem.(Fund.), No. 4, 9, 537, (1970).

126 Banks R., Haselden G.G., Proc. of Int. Conf. on Liquefied Natural Gas, London, 1969, p.117.

127 Banks R., Haselden G.G., Sym. on Phys. Props. of Liquids and Gases for Plant and Process Design, NEL/Scottish Branch of Inst. Ch. Eng., March 1968.

128 British Petroleum Co. Ltd., Private Communication.

129 Liddle C.J., Brit. Chem. Eng., 16, 193, (1971).

130 Gunning A.,European Fed. of Chem. Eng.,Working party on Distillation,Brussels,April 1968.

APPENDIX A.

Constants for Vennix Equations of State (2.6) and (5.5)

	T^c = 190.77K, ρ^c = 0.1625 g/cc	T^c = 190.77K, ρ^c = 0.1625 g/cc
	Compressibility equation	Pressure equation
a_1	- 1.9079137	- 168379.37
a_2	0.1859404	100983.52
a_3	0.6206085	2074154.8
a_4	- 0.6050965	- 12444994.0
a_5	0.1390605	17600314.0
b_1	0.7986446	369.46526
b_2	0.1947895	554.53908
b_3	- 0.4916982	- 8614.1411
b_4	0.4110596	44316.430
b_5	- 0.0650830	- 43179.188
d_1	- 0.8398430	- 174.18776
d_2	- 0.5167966	- 2806.7029
d_3	2.4138572	80674.262
d_4	- 1.6793539	- 345392.00
d_5	0.3022386	382530.92
e_1	8.7758015	0.046002000
e_2	0.1733543	0.21177000
f_1	7.2275164	1378.7933
f_2	- 1.1449913	- 1344.1846
G	8.423558	34.348141
t_o	- 0.774286	- 147.71055
k	1.394830	6.00000
α	0.868917	0.141199
β	2.226390	0.361788
ρ_o	0.697342	0.113318

APPENDIX B

1. Methane
2. Nitrogen
3. Carbon dioxide
4. Hydrogen sulphide
5. Ethane
6. Propane
7. iso-Butane
8. n-Butane
9. iso-Pentane
10. n-Pentane
11. Hexane
12. Heptane
13. Octane
14. Nonane
15. Decane
16. Undecane
17. Dodecane
18. $C_{13}H_{28}$
19. $C_{14}H_{30}$
20. $C_{15}H_{32}$
21. $C_{16}H_{34}$
22. Argon
23. Ethylene
24. Oxygen
25.
26. Propylene
27. Benzene
28. Krypton
29. Acetylene
30. Xenon

Appendix C

Critical constants used in computations in this work.

Component number (see Appendix B)	T^c K	V^c cc/gmol	Z^c	ω	P^c atm
1	190.77	98.72	0.28793	0.0050	45.80
2	126.20	90.10	0.29100	0.0400	33.54
3	304.20	94.00	0.27500	0.2250	72.80
4	373.60	98.00	0.28400	0.1000	88.90
5	305.50	141.72	0.27418	0.1000	48.20
6	370.00	195.70	0.27137	0.1519	42.01
7	407.94	255.80	0.28000	0.1780	36.00
8	425.13	251.62	0.26864	0.2010	37.47
9	460.90	308.31	0.26800	0.2080	32.86
10	469.78	310.65	0.26846	0.2524	33.308
11	507.90	368.0	0.26420	0.3033	29.90
12	540.16	426.0	0.25950	0.3499	27.00
13	569.40	486.0	0.25600	0.3945	24.60
14	595.00	543.0	0.25000	0.4398	22.52
15	619.0	602.0	0.24600	0.4801	20.14
16	640.0	660.0	0.24200	0.5208	19.18
17	659.0	718.0	0.23700	0.5390	17.89
18	677.0	780.0	0.23000	0.5280	17.01
19	695.0	830.0	0.23000	0.6160	15.65
20	710.0	890.0	0.23000	0.6792	14.97
21	725.0	950.0	0.22000	0.7000	13.60
22	150.86	74.57	0.29100	0.0000	48.00
23	283.10	124.00	0.27000	0.0730	50.50
24	154.77	75.00	0.30792	0.0210	50.14

Component number (see Appendix B)	T^c K	V^c cc/gmol	Z^c	ω	P^c atm
26	365.10	181.00	0.26837	0.1451	45.38
27	562.00	260.10	0.27412	0.2110	48.60
28	209.20	92.20	0.29110	0.0	54.20
29	308.50	112.90	0.27498	0.1900	61.66
30	289.75	119.50	0.28971	0.0020	57.64

```
      PROGRAM VENNIX (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
      DIMENSION TE(10,10),VE(10,10),W(10),Z1(10),T(50),P(50),V(50),TS(10
     1),ZPT(50),X(10),EF(10,10),GE(10,10),ACH(10,10),ETA1(10,10),EF1(10,
     110),CRITT(10),CRITV(10),ETA(45),THMF(10,10),PHMF(10,10),DHA(10),DF
     1A(10),PARTLY(10),ALMOST(10),HL(10),DL(10),UF(10,10),TH(10,10),PH(1
     10,10)
      INTEGER REGION,PDIM,VDIM
      REAL M
      LOGICAL ZONLY,UANDZ,DONE,MODEL1,PHASE
      COMMON X,W,Z1,EF1,ACH,TE,VE,DXV,HXV,WR,ZC,NCOMP,M,TC,TRL,MODEL1,TS
     1,HL,DL
      READ (5,16) NUMSET
   16 FORMAT(I3)
      DO 23 NNN=1,NUMSET
      READ (5,30) PDIM,VDIM,AMW,NDATA,NCOMP,MODEL1,ZONLY
   30 FORMAT (2I3,F10.5,2I4,2L5)
      MODEL1=.NOT.MODEL1
      IF(.NOT.MODEL1.AND.(NCOMP.EQ.1))GO TO 474
      READ(5,50)(T(I),P(I),V(I),I=1,NDATA)
   50 FORMAT(3F15.6)
      READ(5,51)(CRITT(I),CRITV(I),W(I),Z1(I),I=1,NCOMP)
   51 FORMAT (4F15.6)
      DO 205 I=1,NDATA
      IF((PDIM.EQ.5).AND.(VDIM.EQ.5))GO TO 24
      IF((PDIM.EQ.5).AND.(VDIM.NE.3))GO TO 25
      IF(PDIM.EQ.1)P(I)=P(I)/14.696
      IF(PDIM.EQ.3)P(I)=P(I)/1.01325
      IF(PDIM.EQ.4)P(I)=P(I)*0.967841
   65 IF(PDIM.EQ.5)P(I)=P(I)*V(I)
      IF(VDIM.EQ.0)GO TO 205
      IF(VDIM.EQ.1)V(I)=AMW/V(I)
      IF(VDIM.EQ.2)V(I)=1000./V(I)
      IF(VDIM.EQ.3)V(I)=100000./(V(I)*4.4647)
      IF(VDIM.EQ.4)V(I)=V(I)*AMW
```

```
      IF(VDIM.EQ.5)V(I)=100000.*V(I)/(4.4647*P(I))
      IF(VDIM.EQ.6)V(I)=1./V(I)
      IF(VDIM.EQ.7)V(I)=V(I)*62.42*AMW
      GO TO 76
   24 WRITE (6,67)
   67 FORMAT(48H UNITS OF PRESSURE AND VOLUME ARE BOTH PV AMAGAT)
      GO TO 34
   25 IF(VDIM.EQ.1)V(I)=V(I)*100000./(AMW*4.4647)
      IF(VDIM.EQ.4)V(I)=V(I)*AMW*4.4647/100000.
      IF(VDIM.EQ.2)V(I)=V(I)*100000./4.4647*1000.
      IF(VDIM.EQ.6)V(I)=V(I)*100000./4.4647
      VDIM=3
      GO TO 65
   76 ZPT(I)=P(I)*V(I)/(82.0567*T(I))
  205 CONTINUE
      IF(NCOMP.EQ.1)GO TO 8
      NC=(NCOMP-1)*NCOMP /2
      READ(5,217)(ETA(I),I=1,NC)
  217 FORMAT( F10.6)
  196 READ(5,10)
      WRITE(6,10)
   10 FORMAT(80H
     1                                )
      DO 498 I=1,NCOMP
      READ(5,217) X(I)
  498 CONTINUE
      PC=45.8
       VC=98.72
      TC=190.77
      ZC=.288382
      WR=0.005
    8 DO9 I=1,NCOMP
      EF(I,I)=CRITT(I)/TC
    9 GE(I,I)=CRITV(I)/VC
      I=1
```

```
      IF(NCOMP.EQ.1)NC=0
      DO420 K=1,NCOMP
      ETA1(K,K)=1.
      IF(I.GT.NC)GO TO 196
      K1=K+1
      DO 420 J=K1,NCOMP
      ETA1(K,J)=ETA(I)
      ETA1(J,K)=ETA1(K,J)
      I=I+1
  420 CONTINUE
  196 DX=0.
      HX=0.
      DO 520  I=1,NCOMP
      DO 520  J=1,NCOMP
      UF(I,J)=1.
      ACHONE=(GE(I,I)**0.3333+GE(J,J)**0.3333)/2.
      ACH(I,J)=ACHONE*ACHONE*ACHONE
      EF1(I,J)=ETA1(I,J)*(EF(I,I)*EF(J,J))**0.5
      IF(.NOT.MODEL1)GO TO 520
      HX=HX+X(I)*X(J)*ACH(I,J)
      DX=DX+X(I)*X(J)*ACH(I,J)*EF1(I,J)
  520 CONTINUE
      IF(MODEL1)GO TO 12
      CALL EQFL(X,UF,ACH,NCOMP,HL)
      CALL EQFL(X,EF1,ACH,NCOMP,DL)
   12 WRITE(6,1761)
 1761 FORMAT (119H TEMPERATURE,K     PRESSURE,ATMS      VOLUME,CC/GM.MOLE       990
     1    VOLUME,CALC,D     Z EXPT     Z CALC    REGION       UMIX       HMIX)
      WRITE(6,19)
   19 FORMAT (18H 1=LIQUID,2=VAPOUR)
 1003 CONTINUE
      DO 1763 I=1,NDATA
      VR=82.0567*T(I)/(P(I)*VC)
      NUMBER=0
      IF(.NOT.MODEL1)GO TO 13
```

```
      TRL=T(I)*HX/(TC*DX)
   13 DO 826 K=1,NCOMP
      IF(.NOT.MODEL1)GO TO 1
      TE(K,K)=TRL
      VE(K,K)=2.
      IF(VR.LT.2.0)VE(K,K)=VR
      IF(VR.LT.0.5)VE(K,K)=0.5
      GO TO 826
    1 TS(K)=T(I)/TC*HL(K)/DL(K)
      DO 2 J=1,NCOMP
      TE(J,K)=TS(K)
      VE(J,K)=2.
      IF(VR.LT.2.)VE(J,K)=VR
      IF(VR.LT.0.5)VE(J,K)=0.5
    2 CONTINUE
  826 CONTINUE
      M=T(I)
      DONE=.FALSE.
      UANDZ=.FALSE.
    6 CALL THEPHI(TH,PH,THMF,PHMF)
      NUMBER=NUMBER+1
      NN=NCOMP
      IF(MODEL1)NN=1
   73 Z=0.
      ENTH=0.
      VOL=0.
      DO 17 N=1,NN
      IF(MODEL1)GO TO 21
      HXV=HL(N)
      DXV=DL(N)
   21 TR=T(I)*HXV/DXV/TC
      PCP=82.0567*ZC/VC*DXV/HXV*TC/HXV
      IF(NUMBER.EQ.1)VR=82.*T(I)/(P(I)*VC*HXV)
      PRA=P(I)/PCP
      NO=1
```

```
  827 IF((TR.LT.1.).AND.(VR.LT.1.))GO TO 22
    5 IF(N.EQ.1)PHASE=.FALSE.
      REGION=2
   28 IF(PHASE.AND.(REGION.EQ.1))GO TO 29
      IF(.NOT.PHASE.AND.(REGION.EQ.2))GO TO 31
      WRITE(6,33)
   33 FORMAT (41H MULTIFLUID MIXTURE CONTAINS MIXED PHASES)
      GO TO 1763
   31 CALL ZEDU(UANDZ,TR,PRA,U,VR,ZC,DONE,COMP,DZR)
   38 IF(DONE)GO TO 27
 2154 PR=COMP*TR/(ZC*VR)
      DPR=TR*(DZR/VR+COMP)/ZC
      ERR=(PR/PRA-1.)*100.
      ERR=ABS(ERR)
      IF(NO.GT.5000)GO TO 34
      IF(ERR.GT.0.001)GO TO 1784
      GO TO 1764
 1784 DELR=(PRA-PR)/DPR
      VR=1./(1./VR+DELR)
      VR=ABS(VR)
      NO=NO+1
      GO TO 827
   22 TEMP=T(I)*HXV/DXV
      PRE=18.0288-1264.51/TEMP-0.0550663*TEMP+0.196832E-3*TEMP*TEMP-0.22
     13451E-6*TEMP*TEMP*TEMP
      PRS=EXP(PRE)/PC/14.696
      IF(PRA.LT.PRS)GO TO 5
      IF(N.EQ.1)PHASE=.TRUE.
      REGION=1
      GO TO 28
   29 PRA=PRA*0.99691
      TR=TR*0.99848
      CALL LIQ(TR,PRA,COMP,U,ZC,VR)
      IF(DONE)GO TO 27
 1764 VRE=VR
```

```
      IF ((VR.LT.2.).AND.(VR.GT.0.5))GO TO 26
      IF(VR.LT.0.5)VRE=0.5
      IF(VR.GT.2.)VRE=2.
   26 IF(MODEL1)GO TO 14
      VE(N,N)=VRE
      GO TO 27
   14 DO 32 L=1,NCOMP
   32 VE(L,L)=VRE
   27 EXTRA=1.
      IF(MODEL1)GO TO 18
      IF(.NOT.DONE)GO TO 66
   69 ENTH=ENTH+X(N)*U
      PARTLY(N)=X(N)*U/DL(N)*HL(N)
      ALMOST(N)=X(N)*(COMP-1.)/HL(N)
   66 EXTRA=X(N)
      Z=Z+X(N)*COMP
   18 VOL=VOL+COMP*82.0567*T(I)/P(I)*EXTRA
   17 CONTINUE
      IF(DONE)GO TO 68
      IF (NUMBER.LE.3)GO TO 6
      IF(ZONLY)GO TO 72
      UANDZ=.TRUE.
   72 DONE=.TRUE.
      GO TO 73
   68 IF(.NOT.MODEL1)COMP=Z
 1039 IF(ZONLY)GO TO 39
      TITC=T(I)/TC
      VIVC=VOL/VC
      IF(.NOT.MODEL1)GO TO 7
      CONST1=HXV/DXV*TITC
      CONST2=VIVC/HXV
    7 DO 35 K=1,NCOMP
      IF(.NOT.MODEL1)GO TO 3
      TE(K,K)=CONST1*TH(K,K)
      VE(K,K)=CONST2*PH(K,K)
```

```
      GO TO 35
    3 CONST3=HL(K)/DL(K)*TITC
      CONST4=VIVC/HL(K)
      DO 4 J=1,NCOMP
      TE(K,J)=CONST3*THMF(K,J)
      VE(K,J)=CONST4*PHMF(K,J)
    4 CONTINUE
   35 CONTINUE
      CALL DIFFER (TH,PH,DFX,DHX,THMF,PHMF,DHA,DFA)
      IF(MODEL1)GO TO 20
      SUM=0.
      TOT=0.
      DO 11 N=1,NCOMP
      SUM=PARTLY(N)*DFA(N)+SUM
   11 TOT=TOT+ALMOST(N)*DHA(N)
      UMIX=ENTH-T(I)*(SUM+TOT)
      GO TO 15
   20 UMIX=U*(1.-T(I)*DFX/DXV*HXV)-(COMP-1.)*T(I)*DHX/HXV
      WRITE(6,3000) U,T(I),DFX,DXV,HXV,COMP,VOL
 3000 FORMAT (7F10.5)
   15 HMIX=UMIX+COMP
   39 CONTINUE
      IF(VDIM.EQ.0)ZPT(I)=0.
  174 WRITE(6,1760)T(I),P(I),V(I),VOL,ZPT(I),COMP,REGION,UMIX,HMIX
 1760 FORMAT (2F16.6,6X,F15.6,2X,F15.6,3X,F8.6,2X,F8.6,4X,I1,3X,2F10.5)
 1763 CONTINUE
   23 CONTINUE
   34 STOP
  474 WRITE(6,40 )
   40 FORMAT(56H ERROR IN DATA-CANT BE MULTIFLUID FOR ONE COMPONENT ONLY    40
     1)
      GO TO 34
      END
```

```
 PROGRAM EQUOM(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
 DIMENSION IDENT(10),Z(10),Q(10),ETA(10),TC(30),VC(30),ZC(30),W(30)
1,X(10),FSTAR(10,10),HSTAR(10,10),ETA1(10,10),TE(10,10),VE(10,10),T
1H(10,10),PH(10,10),MUZ(10),MUQ(10),DELF(10),DELH(10),PART(10),Y(10
1),PC(30),OMEGA(10),VP(10)
 DIMENSION TEM(10)
 DIMENSION X1(10,10),X2(10,10),ANSWER(10,6),QDATA(10),SUPER(10)
 DATA TC/190.77,126.2,304.2,373.6,305.5,370.,407.94,425.13,460.9,46
19.78,507.9,540.16,569.4,595.,619.,640.,659.,677.,695.,710.,725.,15
10.86,283.1,154.77,33.44,365.1,562.0,209.2,308.5,289.75/
 DATA VC/98.72,90.1,94.,98.,141.72,195.7,255.8,251.62,308.31,310.65
1,368.,426.,486.,543.,602.,660.,718.,780.,830.,890.,950.,74.57,124.
1,75.,64.5,181.,260.1,92.2,112.9,119.5/
 DATA ZC/0.28793,.291,.275,.284,.27418,.27137,.28,.26864,.268,.2684
16,.2642,.2595,.256,.25,.246,.242,.237,.23,.23,.23,.22,.291,.27,.30
17916,0.30557,0.26837,0.24712,0.2911,0.27498,0.28971/
 DATA W/0.005,.04,.225,.1,.1,.1519,.178,.201,.208,.2524,.3033,.3499
1,.3945,.4398,.4801,.5208,.539,.528,.616,.6792,.7,0.,.073,.021,0.,
10.1451,.211,0.,0.19,0.002/
 DATA PC/45.8,33.54,72.8,88.9,48.2,42.01,36.0,37.47,32.86,33.308,29
1.9,27.0,24.6,22.52,20.14,19.18,17.89,17.01,15.65,14.97,13.60,48.0,
150.5,50.14,12.99,45.38,48.6,54.2,61.66,57.64/
 LOGICAL LIQUID,SUPER
 LOGICAL SETW
 LOGICAL FIRST,DONE,UANDZ
 INTEGER WHSTOR
 INTEGER WHICH,PDIM
 REAL MUZ,MUQ
 COMMON/TAIT/LIQUID,VRO
 COMMON/PHITHE/TE,VE,X,HSTAR,FSTAR,T    ,NCOMP,HX,HXFX,TH,PH
 COMMON/DATE/TC,VC,ZC,IDENT,PC
 COMMON/REFS/TCREF,VCREF,WREF,PCREF
 COMMON/UZ/          UANDZ,DONE,PRA,VR
 COMMON/REFTEM/TR,ZCREF
```

```
      COMMON/OM/OMEGA,VP
C 1 METHANE          2 NITROGEN          3 CARBON DIOXIDE    4 HYDROGEN SULPHIDE
C 5 ETHANE           6 PROPANE           7 ISO BUTANE        8 N BUTANE
C 9 ISO PENTANE     10 N PENTANE        11 HEXANE           12 HEPTANE
C13 OCTANE          14 NONANE           15 DECANE           16 UNDECANE
C17 DUODECANE       18 C13H28           19 C14H30           20 C15H32
C21 C16H34          22 ARGON            23 ETHYLENE         24 OXYGEN
C25 HYDROGEN        26 PROPYLENE        27 BENZENE          28KRYPTON
C29ACETYLENE        30 XENON
      READ (5,2) NSAT
    2 FORMAT (I3)
      NSET=1
   54 READ (5,1)
    1 FORMAT (80H
     1                              )
      READ(5,3)NCOMP,SET,GUESS,WHICH,PDIM
    3 FORMAT(I3,2F15.4,2I5)
      READ(5,4)(IDENT(I),Z(I),QDATA(I),I=1,NCOMP)
    4 FORMAT(I2,10X,F7.5,8X,F7.5)
      IF(NCOMP.EQ.1)GO TO 21
      NC=(NCOMP-1)*NCOMP/2
      READ(5,8) (ETA(I),I=1,NC)
    8 FORMAT (F8.4)
      IF((WHICH.EQ.1).OR.(WHICH.EQ.3))READ(5,30)(TEM(N),N=1,NCOMP)
      IF((WHICH.EQ.2).OR.(WHICH.EQ.4))READ(5,30)(VP(N),N=1,NCOMP)
   30 FORMAT(F10.5)
   21 NCONV=0
      NT=0
      T=SET
      P=GUESS
      IF((WHICH.EQ.2).OR.(WHICH.EQ.4))GO TO 5
      P=SET
      TGUESS=GUESS
    5 IF(PDIM.EQ.2)GO TO 6
      IF(PDIM.EQ.1)P=P/14.696
```

```
      IF(PDIM.EQ.3)P=P/1.01325
      IF(PDIM.EQ.4)P=P*0.967741
      IF(PDIM.EQ.5)P=P/760.
    6 PGUESS=P
      PCREF=45.8
      TCREF=TC(1)
      VCREF=VC(1)
      ZCREF=ZC(1)
      WREF=W(1)
      WHSTOR=WHICH
      M=1
      IF(NCOMP.EQ.1)NC=0
      DO 11 K=1,NCOMP
      ETA1(K,K)=1.
      IF(M.GT.NC)GO TO 10
      K1=K+1
      DO 11 J=K1,NCOMP
      ETA1(K,J)=ETA(M)
      ETA1(J,K)=ETA1(K,J)
      M=M+1
   11 CONTINUE
   10 DO 9 I=1,NCOMP
      N=IDENT(I)
      SUPER(I)=.FALSE.
      IF(((WHICH.EQ.1).OR.(WHICH.EQ.3)).AND.(P.GT.PC(N)))SUPER(I)=.TRUE.
      IF(((WHICH.EQ.2).OR.(WHICH.EQ.4)).AND.(T.GT.TC(N)))SUPER(I)=.TRUE.
      OMEGA(I)=W(N)
      IF(OMEGA(I).EQ.0.)SUPER(I)=.TRUE.
      FSTAR(I,I)=TC(N)/TCREF
    9 HSTAR(I,I)=VC(N)/VCREF
      DO 12 I=1,NCOMP
      DO 12 J=1,NCOMP
      IF(I.EQ.J)GO TO 12
      H=(HSTAR(I,I)**0.33333+HSTAR(J,J)**0.33333)/2.
      HSTAR(I,J)=H*H*H
```

```
      FSTAR(I,J)=ETA1(I,J)*(FSTAR(I,I)*FSTAR(J,J))**0.5
   12 CONTINUE
      SETW=.FALSE.
      A=0.95
      B=0.05/FLOAT(NCOMP-1)
      C=0.975
      D=B/2.
      DO 200 N=1,NCOMP
      DO 200 M=1,NCOMP
      X1(N,M)=D
      IF(N.EQ.M)X1(N,M)=C
      X2(N,M)=B
      IF(N.EQ.M)X2(N,M)=A
  200 CONTINUE
      IF(WHICH.EQ.3)WHICH=1
      IF(WHICH.EQ.4)WHICH=2
      J=1
  206 DO 202 I=1,NCOMP
      IF(SUPER(I))GO TO 202
      IF(WHICH.EQ.1)GO TO 100
      IF(WHICH.EQ.2)P=VP(I)
      GUESS=P
      GO TO 101
  100 T=TEM(I)
      GUESS=T
  101 CONTINUE
      DO 201 N=1,NCOMP
      IF((J.EQ.1).OR.(J.EQ.3))X(N)=X1(I,N)
      IF((J.EQ.4).OR.(J.EQ.2))X(N)=X2(I,N)
      Q(N)=X(N)
  201 CONTINUE
      GO TO 7
   99 DO 43 K=1,NCOMP
   43 X(K)=Z(K)
      TOTALS=1.
```

```
      FIRST=.TRUE.
      CALL HF
   55 TR=T/TCREF*HX/HXFX
      IF(TR.LT.1.)GO TO 13
      IF((WHICH.EQ.3).OR.(WHICH.EQ.4))GO TO 33
      IF(WHICH.EQ.2)GO TO 27
      T=T-10.
      GO TO 55
   27 WRITE (6,28)
   28 FORMAT (78H BUBBLE PRESSURE.TEMPERATURE IS TOO HIGH FOR LIQUID.PLE
     1ASE ADJUST AND RESUBMIT)
      STOP
   13 A=T*HX/HXFX
      PRE=18.0288-1264.51/A-0.0550663*A+0.196832E-3*A*A-0.223451E-6*A*A*
     1A
      PRS=EXP(PRE)/PCREF/14.696
      PCP=82.054*ZCREF/VCREF*HXFX/HX*TCREF/HX
      PRA=P/PCP
      IF(WHICH.EQ.1)GO TO 66
      IF(WHICH.EQ.2)GO TO 67
      IF(WHICH.EQ.3)GO TO 68
      IF(PRA.LT.PRS)GO TO 33
      PRA=PRS
      P=PRA*PCP
      GUESS=P
      WRITE(6,60) GUESS
   60 FORMAT(72H DEW PRESSURE.INITIAL GUESS FOR PRESSURE TOO HIGH.IT HAS
     1BEEN ADJUSTED TO,F10.5,6H ATMS.)
      GO TO 14
   66 IF(PRA.GE.PRS)GO TO 17
      T=T-10.
      GO TO 13
   17 IF(T.EQ.GUESS)GO TO 33
      GUESS=T
      WRITE(6,61)GUESS
```

```
61 FORMAT(76H BUBBLE POINT.INITIAL GUESS FOR TEMPERATURE TOO HIGH.IT
  1HAS BEEN ADJUSTED TO,F10.5,6H DEG.K)
   GO TO 14
67 IF(PRA.GE.PRS)GO TO 33
   PRA=PRS
   P=PRA*PCP
   GUESS=P
   WRITE(6,62) GUESS
62 FORMAT(75H BUBBLE PRESSURE.INITIAL GUESS FOR PRESSURE TOO LOW.IT H
  1AS BEEN ADJUSTED TO,F10.5,6H ATMS.)
   GO TO 14
68 IF(PRA.LT.PRS)GO TO 20
   T=T+10.
   GO TO 13
20 IF(T.EQ.GUESS)GO TO 33
   GUESS=T
   WRITE(6,63)GUESS
63 FORMAT(72H DEW POINT.INITIAL GUESS FOR TEMPERATURE TOO LOW.IT HAS
  1BEEN ADJUSTED TO,F10.5,6H DEG.K)
33 CONTINUE
   GO TO 14
 7 FIRST=.TRUE.
   IF(NCONV.EQ.1)TOTAL1=TOTAL
   DO 64 L=1,NCOMP
   X(L)=Z(L)
   IF((.NOT.SETW).AND.((J.EQ.1).OR.(J.EQ.3)))X(L)=X1(I,L)
   IF((.NOT.SETW).AND.((J.EQ.2).OR.(J.EQ.4)))X(L)=X2(I,L)
64 CONTINUE
16 CALL HF
14 VR=82.054*T/P/VCREF
   TR=T*HX/(TCREF*HXFX)
   NUMBER=0
   DO 15 K=1,NCOMP
   TE(K,K)=TR
   VE(K,K)=2.
```

```
      IF(VR.LT.2.)VE(K,K)=VR
      IF(VR.LT.0.5)VE(K,K)=0.5
   15 CONTINUE
      DONE=.FALSE.
      UANDZ=.FALSE.
   18 CALL THEPHI
      NUMBER=NUMBER+1
   36 TR=T*HX/HXFX/TCREF
      IF((.NOT.SETW).AND.((TR.GT.1.).OR.(TR.LT.0.6)))GO TO 130
      PCP=82.054*ZCREF/VCREF*HXFX/HX*TCREF/HX
      PRA=P/PCP
      NO=1
      IF((WHICH.EQ.1).OR.(WHICH.EQ.2))GO TO 29
      IF(.NOT.FIRST)GO TO 65
   26 LIQUID=.FALSE.
   69 CALL ZEDU(U,COMP,DZR,FCOEFF)
      IF(DONE)GO TO 23
   74 PR=COMP*TR/(ZCREF*VR)
      DPR=TR*(DZR/VR+COMP)/ZCREF
      ERR=(PR/PRA-1.)*100.
      ERR=ABS(ERR)
      IF(NO.GT.5000)GO TO 24
      IF(ERR.LT.0.001)GO TO 25
      DELR=(PRA-PR)/DPR
      VR=1./(1./VR+DELR)
      VR=ABS(VR)
      NO=NO+1
      IF(NEXIT.EQ.1)GO TO 69
      GO TO 26
   25 VRE=VR
      IF((VR.LT.2).AND.(VR.GT.0.5))GO TO 57
      IF(VR.LT.0.5)VRE=0.5
      IF(VR.GT.2.)VRE=2.
   57 DO 34 L=1,NCOMP
   34 VE(L,L)=VRE
```

```
23 VOL=COMP*82.054*T/P
   IF(DONE)GO TO 35
   IF(NUMBER.LE.3)GO TO 18
   UANDZ=.TRUE.
   DONE=.TRUE.
   GO TO 36
35 CONST1=T/TCREF*HX/HXFX
   V=VOL
   CONST2=V/VCREF/HX
   DO 37 K=1,NCOMP
   TE(K,K)=CONST1*TH(K,K)
37 VE(K,K)=CONST2*PH(K,K)
   CALL DIFFER(DFX,DHX)
   UMIX=U*(1.-T*DFX/HXFX*HX)-(COMP-1.)*T*DHX/HX
   HMIX=UMIX+COMP
   VR=VOL/VCREF/HX
   IF(.NOT.FIRST)GO TO 19
   CALL DELTA(DELH,DELF,VR)
   PINKY=U*HX/HXFX
   PERKY=(COMP-1.)/HX
   DO 38 K=1,NCOMP
   MUZ(K)=FCOEFF+PINKY*DELF(K)+PERKY*DELH(K)+ALOG(X(K))
   X(K)=Q(K)
   MUQ(K)=MUZ(K)
38 CONTINUE
   FIRST=.FALSE.
   GO TO 16
29 IF(.NOT.FIRST)GO TO 26
65 PRA=PRA*0.99691
   NEXIT=0
   TR=TR*0.99848
   CALL LIQ(COMP,U,FCOEFF,NEXIT)
   IF(NEXIT.EQ.1)GO TO 74
   IF(DONE)GO TO 23
   GO TO 25
```

```
19 CALL DELTA(DELH,DELF,VR)
   BLOB=U    *HX/HXFX
   PIP=(COMP-1.)/HX
   TOTAL=0.
   DO 40 K=1,NCOMP
   PART(K)=FCOEFF+BLOB*DELF(K)+PIP*DELH(K)
   Y(K)=EXP(MUQ(K)-PART(K))
   IF(.NOT.SETW)GO TO 40
40 TOTAL=TOTAL+Y(K)
   ERROR=ABS(TOTAL-TOTALS)
   IF(ERROR.LT.0.0001)GO TO 32
   DO 39 K=1,NCOMP
   Q(K)=Y(K)
39 X(K)=Q(K)
   TOTALS=TOTAL
   GO TO 16
32 IF(ABS(TOTAL-1.).LT.0.0001)GO TO 41
   NCONV=NCONV+1
   IF(NCONV.EQ.1)GO TO 22
   IF(NCONV.GT.50)GO TO 44
   TOTDIF=TOTAL1-TOTAL
   IF(NCONV.GT.2)GO TO 31
   IF(TOTDIF.LT.0.0001)TOTDIF=TOTDIF*100.
31 IF((WHICH.EQ.1).OR.(WHICH.EQ.3))GO TO 42
   P1=P-(GUESS-P)*(TOTAL-1.)/TOTDIF
   IF(P1.LT.0.)P1=P*0.5
   TOTAL1=TOTAL
   GUESS=P
   P=P1
   GO TO 7
42 T1=T-(GUESS-T)*(TOTAL-1.)/TOTDIF
   IF(T1.LT.0.)T1=T-20.
   TOTAL1=TOTAL
   GUESS=T
   T=T1
```

```
      GO TO 7
  130 SUPER(I)=.TRUE.
      N=IDENT(I)
      OMEGA(I)=W(N)
      NCONV=0
      GO TO 202
   41 IF(SETW)GO TO 80
      IF(WHICH.EQ.1)ANSWER(I,J)=T
      IF(WHICH.EQ.2)ANSWER(I,J)=P
      NCONV=0
  202 CONTINUE
      J=J+1
      IF(J.LE.2)GO TO 206
      IF(J.EQ.4)GO TO 206
      IF(J.EQ.5)GO TO 208
      DO 203 K=1,NCOMP
      IF(SUPER(K))GO TO 203
      OMEGA(K)=OMEGA(K)*1.1
  203 CONTINUE
      GO TO 206
  208 DO 209 N=1,NCOMP
      IF(SUPER(N))GO TO 209
      ANSWER(N,5)=2. *ANSWER(N,1)-ANSWER(N,2)
      ANSWER(N,6)=2. *ANSWER(N,3)-ANSWER(N,4)
      IF((WHICH.EQ.1).OR.(WHICH.EQ.3))VPORT=TEM(N)
      IF((WHICH.EQ.2).OR.(WHICH.EQ.4))VPORT=VP(N)
      WNEW=(VPORT-ANSWER(N,6))*OMEGA(N)/11./(ANSWER(N,6)-ANSWER(N,5))+OM
     1EGA(N)
      OMEGA(N)=WNEW
  209 CONTINUE
      DO 207 I=1,NCOMP
  207 Q(I)=QDATA(I)
      IF(WHICH.EQ.1)GO TO 81
      P=PGUESS
      GUESS=P
```

```
      SETW=.TRUE.
      WHICH=WHSTOR
      GO TO 99
   81 T=TGUESS
      GUESS=T
      SETW=.TRUE.
      WHICH=WHSTOR
      GO TO 99
   80 WRITE(6,1)
      GO TO (46,47,48,49)WHICH
   46 WRITE(6,45)NSET,P,T,(IDENT(I),Z(I),Y(I),I=1,NCOMP)
   45 FORMAT(15H MIXTURE NUMBER,I3,/20X,12HBUBBLE POINT//17H PRESSURE GI
     1VEN =,F10.4,6H ATMS.//25H TEMPERATURE CALCULATED =,F10.4,6H DEG.K/
     1/10X,83H COMPONENT NUMBER      LIQUID COMPOSITION GIVEN       VAPO
     1UR COMPOSITION CALCULATED//(18X,I2,25X,F7.5,24X,F7.5,/))
      GO TO 53
   47 WRITE(6,50)NSET,T,P,(IDENT(I),Z(I),Y(I),I=1,NCOMP)
   50 FORMAT(15H MIXTURE NUMBER,I3,/20X,15HBUBBLE PRESSURE//20H TEMPERAT
     1URE GIVEN =,F10.4,6H DEG.K//22H PRESSURE CALCULATED =,F10.4,6H ATM
     1S.//10X,83H COMPONENT NUMBER      LIQUID COMPOSITION GIVEN       V
     1APOUR COMPOSITION CALCULATED//(18X,I2,25X,F7.5,24X,F7.5,/))
      GO TO 53
   48 WRITE(6,51)NSET,P,T,(IDENT(I),Z(I),Y(I),I=1,NCOMP)
   51 FORMAT(15H MIXTURE NUMBER,I3,/20X,10H DEW POINT//17H PRESSURE GIVE
     1N =,F10.4,6H ATMS.//25H TEMPERATURE CALCULATED =,F10.4,6H DEG.K//1
     10X,83H COMPONENT NUMBER      VAPOUR COMPOSITION GIVEN       LIQUID
     1COMPOSITION CALCULATED//(18X,I2,25X,F7.5,24X,F7.5,/))
      GO TO 53
   49 WRITE(6,52)NSET,T,P,(IDENT(I),Z(I),Y(I),I=1,NCOMP)
   52 FORMAT(15H MIXTURE NUMBER,I3,/20X,13H DEW PRESSURE//20H TEMPERATUR
     1E GIVEN =,F10.4,6H DEG.K//22H PRESSURE CALCULATED =,F10.4,6H ATMS.
     1//10X,83H COMPONENT NUMBER      VAPOUR COMPOSITION GIVEN       LIQ
     1UID COMPOSITION CALCULATED//(18X,I2,25X,F7.5,24X,F7.5,/))
   53 NSAT=NSAT-1
      NSET=NSET+1
```

```
      IF(NSAT.GT.0)GO TO 54
   56 STOP
   24 WRITE(6,58) PR,PRA
   58 FORMAT(41H MORE THAN 5000 ITERATIONS TO CONVERGE PR,2F10.5)
      GO TO 56
   44 WRITE(6,59)
   59 FORMAT(63H MORE THAN 150 ITERATIONS TO CONVERGE T OR P,RESULTS SO
     1FAR ARE)
      GO TO 41
   22 IF(ABS(1.-TOTAL).LT.0.05)GO TO 76
      IF(WHICH.EQ.1)GO TO 77
      IF(WHICH.EQ.2)GO TO 78
      IF(WHICH.EQ.3)GO TO 79
      IF(P.LT.1.)GO TO 120
      IF(TOTAL.GE.1.)P=P-0.1
      IF(TOTAL.LT.1.)P=P+0.1
      GO TO 7
  120 IF(TOTAL.GE.1.)P=P*0.95
      IF(TOTAL.LT.1.)P=P*1.05
      GO TO 7
   77 IF(TOTAL.GE.1.)T=T-0.5
      IF(TOTAL.LT.1.)T=T+0.5
      GO TO 7
   78 IF(P.LT.1.)GO TO 121
      IF(TOTAL.GE.1.)P=P+0.1
      IF(TOTAL.LT.1.)P=P-0.1
      GO TO 7
  121 IF(TOTAL.GE.1.)P=P*1.05
      IF(TOTAL.LT.1.)P=P*0.95
      GO TO 7
   79 IF(TOTAL.GE.1.)T=T+0.5
      IF(TOTAL.LT.1.)T=T-0.5
      GO TO 7
   76 IF(WHICH.EQ.1)T=T/TOTAL
      IF(WHICH.EQ.3)T=T*TOTAL
```

```
      IF(WHICH.EQ.2)P=P*TOTAL
      IF(WHICH.EQ.4)P=P/TOTAL
      GO TO 7
      END



      SUBROUTINE RICHMD(RATIO,KCALC,COMP,VNEW,OK,NCOMP)
      DIMENSION KCALC(10),COMP(10)
      REAL KCALC
      LOGICAL OK
      FV=0.
      FDASH=0.
      FDDASH=0.
      OK=.FALSE.
      DO 1 N=1,NCOMP
      TERM=KCALC(N)-1.
      X=TERM/(TERM*RATIO+1.)
      FV=FV+X*COMP(N)
      FDASH=FDASH+X*X*COMP(N)
      FDDASH=FDDASH+X*X*X*COMP(N)
    1 CONTINUE
      FDASH=-FDASH
      VNEW=RATIO-FV*FDASH/(FDASH*FDASH-FV*FDDASH)
      IF(VNEW.LT.0.)VNEW=ABS(VNEW+RATIO)/2.
      IF(VNEW.GT.1.)VNEW=(1.+RATIO)/2.
      IF(ABS(1.-VNEW/RATIO).LT.0.001)OK=.TRUE.
      RATIO=VNEW
      RETURN
      END
```

```
 PROGRAM EQFL (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
 DIMENSION K(10),KCALC(10),XX(10),YASS(10)
 DIMENSION PARTNL(10),PARTNV(10)
 DIMENSION LM(10),VM(10),VT(10)
 DIMENSION TREF(10),PREF(10),PC(30)
 DIMENSION IDENT(10),Z(10),Q(10),ETA(10),TC(30),VC(30),ZC(30),W(30)
1,X(10),FSTAR(10,10),HSTAR(10,10),ETAL(10,10),TE(10,10),VE(10,10),T
1H(10,10),PH(10,10),MUZ(10),MUQ(10),DELF(10),DELH(10),PART(10),Y(10
1),COMP(10),VAPMOL(10),LIQMOL(10)
 DIMENSION A (10),B(10)
 DATA TC/190.77,126.2,304.2,373.6,305.5,370.,407.94,425.13,460.9,46
19.78,507.9,540.16,569.4,595.,619.,640.,659.,677.,695.,710.,725.,15
10.86,283.1,154.77,33.44,365.1,562.0,209.2,308.5,289.75/
 DATA VC/98.72,90.1,94.,98.,141.72,195.7,255.8,251.62,308.31,310.65
1,368.,426.,486.,543.,602.,660.,718.,780.,830.,890.,950.,74.57,124.
1,75.,64.5,181.0,260.1,92.2,112.9,119.5/
 DATA ZC/0.28793,.291,.275,.284,.27418,.27137,.28,.26864,.268,.2684
16,.2642,.2595,.256,.25,.246,.242,.237,.23,.23,.23,.22,.291,.27,.30
17916,0.30557,0.26837,0.27412,0.2911,0.27498,0.28971/
 DATA W/0.005,.04,.225,.1,.1,.1519,.178,.201,.208,.2524,.3033,.3499
1,.3945,.4398,.4801,.5208,.539,.528,.616,.6792,.7,0.,.073,.021,0.,
10.1451,0.211,0.,0.19,0.002/
 DATA PC/45.8,33.54,72.8,88.9,48.2,42.01,36.,37.47,32.86,33.308,29
1.9,27.,24.6,22.52,20.14,19.18,17.89,17.01,15.65,14.97,13.6,48.,50.
15,50.14,12.99,45.38,48.6,54.2,61.66,57.64/
 LOGICAL LIQUID,FLASH,OK
 LOGICAL FIRST,DONE,UANDZ
 LOGICAL HBAR
 INTEGER WHICH,PDIM
 REAL K,KCALC,MUZ,MUQ,LM,LIQFLO,LIQMOL
  REAL LIQEN
 COMMON/TAIT/LIQUID,VRO
 COMMON/PHITHE/TE,VE,X,HSTAR,FSTAR,T    ,NCOMP,HX,HXFX,TH,PH
 COMMON/DATE/TC,VC,ZC,W,IDENT
```

```
      COMMON/REFS/TCREF,VCREF,WREF,PCREF
      COMMON/UZ/          UANDZ,DONE,PRA,VR
      COMMON/REFTEM/TR,ZCREF
      COMMON/AB/A,B
C  1 METHANE          2 NITROGEN          3 CARBON DIOXIDE    4 HYDROGEN SULPHIDE
C  5 ETHANE           6 PROPANE           7 ISO BUTANE        8 N BUTANE
C  9 ISO PENTANE     10 N PENTANE        11 HEXANE           12 HEPTANE
C 13 OCTANE          14 NONANE           15 DECANE           16 UNDECANE
C 17 DUODECANE       18 C13H28           19 C14H30           20 C15H32
C 21 C16H34          22 ARGON            23 ETHYLENE         24 OXYGEN
C 25 HYDROGEN        26 PROPYLENE        27 BENZENE          28KRYPTON
C 29 ACETYLENE       30
      READ(5,2) NFLASH
    2 FORMAT (I3)
      NSET=1
   54 READ (5,1)
    1 FORMAT (80H
     1                              )
      READ(5,3) NCOMP,T,P,PDIM
    3 FORMAT (I3,2F15.4,I5)
      READ(5,4) (IDENT(I),COMP(I),I=1,NCOMP)
    4 FORMAT (I2,10X,F7.5)
      READ(5,51) RATE
   51 FORMAT(F11.3)
      READ(5,88) (VT(I),I=1,NCOMP)
   88 FORMAT(F10.5)
      IF(NCOMP.EQ.1)GO TO 21
      NC=(NCOMP-1)*NCOMP/2
      READ(5,8) (ETA(I),I=1,NC)
    8 FORMAT (F8.4)
   21 NCONV=0
      NT=0
      HBAR=.FALSE.
      LCOUNT=0
      TSTORE=T
```

```
      IF(PDIM.EQ.2)GO TO 6
      IF(PDIM.EQ.1)P=P/14.696
      IF(PDIM.EQ.3)P=P/1.01325
      IF(PDIM.EQ.4)P=P*0.967741
      IF(PDIM.EQ.5)P=P/760.
    6 PCREF=45.8
      PSTORE=P
      TCREF=TC(1)
      VCREF=VC(1)
      ZCREF=ZC(1)
      WREF=W(1)
      M=1
      IF(NCOMP.EQ.1)NC=0
      DO 11 I=1,NCOMP
      ETA1(I,I)=1.
      IF(M.GT.NC)GO TO 10
      K1=I+1
      DO 11 J=K1,NCOMP
      ETA1(I,J)=ETA(M)
      ETA1(J,I)=ETA1(I,J)
      M=M+1
   11 CONTINUE
   10 DO 9 I=1,NCOMP
      N=IDENT(I)
      TREF(I)=TC(N)
      PREF(I)=PC(N)
      FSTAR(I,I)=TC(N)/TCREF
    9 HSTAR(I,I)=VC(N)/VCREF
      DO 12 I=1,NCOMP
      DO 12 J=1,NCOMP
      IF(I.EQ.J)GO TO 12
      H=(HSTAR(I,I)**0.33333+HSTAR(J,J)**0.33333)/2.
      HSTAR(I,J)=H*H*H
      FSTAR(I,J)=ETA1(I,J)*(FSTAR(I,I)*FSTAR(J,J))**0.5
   12 CONTINUE
```

```
 90 WHICH=1
    FLASH=.FALSE.
 53 DO 43 I=1,NCOMP
    Q(I)=COMP(I)
 43 X(I)=COMP(I)
    CALL FIXIT(T,WHICH,NCOMP,Q,VT,TREF, PREF,P)
    IF(WHICH.EQ.3)GO TO 41
 80 NCONV=0
    IF(.NOT.FLASH)GO TO 75
    DO 73 N=1,NCOMP
    XX(N)=COMP(N)/(1.-RATIO+K(N)*RATIO)
    YASS(N)=XX(N)*K(N)
    X(N)=XX(N)
    Q(N)=YASS(N)
    IF(WHICH.EQ.1)GO TO 85
    X(N)=YASS(N)
    Q(N)=XX(N)
    GO TO 73
 85 CONTINUE
 73 CONTINUE
 75 TOTALS=1.
  7 FIRST=.TRUE.
    IF(NCONV.EQ.1)TOTAL1=TOTAL
    IF(FLASH)GO TO 16
160 DO 64 I=1,NCOMP
 64 X(I)=COMP(I)
 16 CALL HF
 14 VR=82.054*T/P/VCREF
    TR=T*HX/(TCREF*HXFX)
    NUMBER=0
    DO 15 M=1,NCOMP
    TE(M,M)=TR
    VE(M,M)=2.
    IF(VR.LT.2.)VE(M,M)=VR
    IF(VR.LT.0.5)VE(M,M)=0.5
```

```
15 CONTINUE
   DONE=.FALSE.
   UANDZ=.FALSE.
18 CALL THEPHI
   NUMBER=NUMBER+1
36 TR=T*HX/HXFX/TCREF
   PCP=82.054*ZCREF/VCREF*HXFX/HX*TCREF/HX
   PRA=P/PCP
   NO=1
91 IF(WHICH.EQ.1)GO TO 29
   IF(.NOT.FIRST)GO TO 65
26 LIQUID=.FALSE.
69 CALL ZEDU(U,ZCOM,DZR,FCOEFF)
   IF(DONE)GO TO 23
74 PR=ZCOM*TR/(ZCREF*VR)
   DPR=TR*(DZR/VR+ZCOM)/ZCREF
   ERR=(PR/PRA-1.)*100.
   ERR=ABS(ERR)
   IF(NO.GT.5000)GO TO 24
   IF(ERR.LT.0.001)GO TO 25
   DELR=(PRA-PR)/DPR
   VR=1./(1./VR+DELR)
   VR=ABS(VR)
   NO=NO+1
   IF(NEXIT.EQ.1)GO TO 69
   GO TO 26
25 VRE=VR
   IF((VR.LT.2).AND.(VR.GT.0.5))GO TO 57
   IF(VR.LT.0.5)VRE=0.5
   IF(VR.GT.2.)VRE=2.
57 DO 34 L=1,NCOMP
34 VE(L,L)=VRE
23 VOL=ZCOM*82.054*T/P
   IF(DONE)GO TO 35
   IF(NUMBER.LE.3)GO TO 18
```

```
      UANDZ=.TRUE.
      DONE=.TRUE.
      GO TO 36
   35 CONST1=T/TCREF*HX/HXFX
      V=VOL
      CONST2=V/VCREF/HX
      DO 37 M=1,NCOMP
      TE(M,M)=CONST1*TH(M,M)
   37 VE(M,M)=CONST2*PH(M,M)
      CALL DIFFER(DFX,DHX)
      UMIX=U*(1.-T*DFX/HXFX*HX)-(ZCOM-1.)*T*DHX/HX
      HMIX=UMIX+ZCOM
   92 VR=VOL/VCREF/HX
      IF((.NOT.FIRST).AND.(.NOT.HBAR))GO TO 19
      CALL DELTA(DELH,DELF,VR)
      PINKY=U*HX/HXFX
      PERKY=(ZCOM-1.)/HX
      LIQEN=(HMIX-1.)*1.9867*T
      IF(.NOT.HBAR)STORLN=LIQEN
      DO 38 I=1,NCOMP
      MUZ(I)=FCOEFF+PINKY*DELF(I)+PERKY*DELH(I)+ALOG(X(I))
      IF(.NOT.HBAR)GO TO 121
      IF(LCOUNT.EQ.2)GO TO 122
      PARTNL(I)=+1.9867*(T-1.0)*(T-1.0)/1.0*(MUQ(I)-MUZ(I))
      X(I)=Y(I)
      GO TO 38
  122 PARTNV(I)=+1.9867*(T-1.0)*(T-1.0)/1.0*(MUQ(I)-MUZ(I))
      GO TO 38
  121 X(I)=Q(I)
      MUQ(I)=MUZ(I)
   38 CONTINUE
      IF(LCOUNT.EQ.2)GO TO 123
      IF(HBAR)LCOUNT=2
      FIRST=.FALSE.
      GO TO 16
```

```
29 IF(.NOT.FIRST)GO TO 26
65 PRA=PRA*0.99691
   NEXIT=0
   TR=TR*0.99848
   CALL LIQ(ZCOM,U,FCOEFF,NEXIT)
   IF(NEXIT.EQ.1)GO TO 74
   IF(DONE)GO TO 23
   GO TO 25
19 CALL DELTA(DELH,DELF,VR)
   BLOB=U    *HX/HXFX
   PIP=(ZCOM-1.)/HX
   VAPEN=(HMIX-1.)*1.9867*T
   TOTAL=0.
   DO 40 I=1,NCOMP
   PART(I)=FCOEFF+BLOB*DELF(I)+PIP*DELH(I)
   Y(I)=EXP(MUQ(I)-PART(I))
40 TOTAL=TOTAL+Y(I)
   ERROR=ABS(TOTAL-TOTALS)
   IF(ERROR.LT.0.0001)GO TO 32
   DO 39 I=1,NCOMP
   Q(I)=Y(I)
39 X(I)=Q(I)
   TOTALS=TOTAL
   GO TO 16
32 IF(FLASH)GO TO 5
   IF(ABS(TOTAL-1.).LT.0.0001)GO TO 41
   NCONV=NCONV+1
   IF(NCONV.EQ.1)GO TO 22
   IF(NCONV.GT.150)GO TO 44
   TOTDIF=TOTAL1-TOTAL
   IF(NCONV.GT.5)GO TO 31
   IF(TOTDIF.LT.0.0001)TOTDIF=TOTDIF*100.
31 T1=T-(GUESS-T)*(TOTAL-1.)/TOTDIF
   IF(T1.LT.0.)T1=T-20.
   TOTAL1=TOTAL
```

```
      GUESS=T
      T=T1
      GO TO 7
   41 IF(WHICH.EQ.1)TBUB=T
      IF(WHICH.EQ.3)TDEW=T
      IF(WHICH.EQ.3)GO TO 30
      WHICH=3
      GO TO 53
   30 IF((TSTORE.GE.TBUB).AND.(TSTORE.LE.TDEW))GO TO 70
      WRITE(6,71)  TBUB,TDEW
   71 FORMAT( 43H TEMPERATURE IS OUT OF RANGE .BUBBLE POINT=,F10.6,18H D
     1EG K,DEW POINT =,F10.6,29H DEG K,TEMPERATUTE IN DATA IS,F10.6,6H D
     1EG K)
      STOP
   70 DO 72 N=1,NCOMP
   72 K(N)=EXP(A(N)+B(N)/TSTORE)/PSTORE
      RATIO=0.5
      FLASH=.TRUE.
      WHICH =1
      T=TSTORE
      P=PSTORE
      GO TO 80
    5 TOT=0.
      DO 81 N=1,NCOMP
      KCALC(N)=Y(N)/XX(N)
      IF(WHICH.EQ.3) KCALC(N)=YASS(N)/Y(N)
      DIFF=ABS(KCALC(N)-K(N))
   81 TOT=TOT+DIFF*DIFF
      TOT=SQRT(TOT/NCOMP)
      IF(TOT.LT.0.001)GO TO 82
      DO 83 N=1,NCOMP
   83 K(N)=SQRT(KCALC(N)*K(N))
      GO TO 80
   82 CALL RICHMD(RATIO,KCALC,COMP,VNEW,OK,NCOMP)
      IF(OK)GO TO 84
```

```
      GO TO 80
   84 WRITE(6,1)
      FIRST=.TRUE.
      HBAR=.TRUE.
      T=T+1.0
      LCOUNT=1
      DO 120 N=1,NCOMP
  120 X(N)=XX(N)
      GO TO 16
  123 VAPFLO=RATIO*RATE
      LIQFLO=RATE-VAPFLO
      DO 52N=1,NCOMP
      IF(WHICH.EQ.1)GO TO 86
      LM(N)=Y(N)
      VM(N)=YASS(N)
      GO TO 87
   86 LM(N)=XX(N)
      VM(N)=Y(N)
   87 LIQMOL(N)=LM(N)*LIQFLO
      VAPMOL(N)=VM(N)*VAPFLO
   52 CONTINUE
      LIQEN=STORLN
      ENTH=RATIO*(VAPEN-LIQEN)+LIQEN
      WRITE(6,46) (IDENT(I),COMP(I),I=1,NCOMP)
      WRITE(6,93)TSTORE,PSTORE,RATE,ENTH,RATIO,LIQFLO,LIQEN,VAPFLO,VAPEN
     1,(IDENT(I),XX(I),Y(I),LIQMOL(I),VAPMOL(I),K(I),PARTNL(I),PARTNV(I)
     1,I=1,NCOMP)
   46 FORMAT(21H SUMMARY OF FEED DATA//,6X,41HCOMPONENT IDENTIFICATION
     1  MOLE FRACTION/(17X,I2,19X,F7.5/))
   93 FORMAT(19H FEED TEMPERATURE =,F10.4,8H    DEGK/19H FEED PRESSURE
     1  =,F10.4,9H    ATMS./19H FEED RATE         =,F11.3,10H   MOLS/HR/1
     19H FEED ENTHALPY    =,F11.3,13H   CALS/GMOLE///14H FLASH RESULTS/3
     11H FRACTION OF VAPOUR VAPOURISED=,F7.4/,13H LIQUID FLOW=,F10.3,5H
     1MOLS/18H LIQUID ENTHALPY =,F11.3,11H CALS/GMOLE/13H VAPOUR FLOW=,F
     110.3,5H MOLS/18H VAPOUR ENTHALPY =,F11.3,11H CALS/GMOLE/101H   COMP
```

```
     1PONENT    LIQUID MOLE   VAPOUR MOLE  LIQUID MOLES  VAPOUR MOLES
     1KVALUES   PARTIAL MOLAL ENTHS/40H   IDENTIFIER     FRACTION      F
     1RACTION,45X,15HLIQUID   VAPOUR/(7X,I2,11X,F7.5,7X,F7.5,3X,F9.4,5X,
     1F9.4,5X,F8.5,F10.3,F13.3))
      NSAT=NSAT-1
      NSET=NSET+1
      IF(NFLASH.GT.0)GO TO 54
   56 STOP
   24 WRITE(6,58)
   58 FORMAT(41H MORE THAN 5000 ITERATIONS TO CONVERGE PR)
      GO TO 56
   44 WRITE(6,59)
   59 FORMAT(63H MORE THAN 150 ITERATIONS TO CONVERGE T OR P,RESULTS SO
     1FAR ARE)
      GO TO 41
   22 IF(ABS(1.-TOTAL).LT.0.05)GO TO 76
      GUESS=T
      IF(WHICH.EQ.1)GO TO 77
      IF(TOTAL.GE.1)T=T+0.5
      IF(TOTAL.LT.1.)T=T-0.5
      GO TO 7
   77 IF(TOTAL.GE.1.)T=T-0.5
      IF(TOTAL.LT.1.)T=T+0.5
      GO TO 7
   76 IF(WHICH.EQ.1)T=T/TOTAL
      IF(WHICH.EQ.3)T=T*TOTAL
      GO TO 7
      END
```

```
      SUBROUTINE DELTA(DELH,DELF,VR)
      COMMON/DEL/DTHDVR,DTHDTR,DPHDTR,DPHDVR,F,H
      COMMON/PHITHE/TE,VE,X,HSTAR,FSTAR,T    ,NCOMP,HX,HXFX,TH,PH
      COMMON/REFTEM/TR,ZCREF
      DIMENSION FHSPH(10),HSPH(10),PH(10,10),TH(10,10),H(10,10),HSTAR(10
     1,10),DTHDTR(10,10),DTHDVR(10,10),DPHDTR(10,10),DPHDVR(10,10),X(10)
     1,F(10,10),TE(10,10),VE(10,10),DELTH(10,10),DELPH(10,10),DELF1(10),
     1DELH1(10),DELF(10),DELH(10),DELTR(10,10),DELVR(10,10),FSTAR(10,10)
      DO 1 I=1,NCOMP
      FHSPH(I)=0.
      HSPH(I)=0.
      DO 2J=1,NCOMP
      PH(I,J)=H(I,J)/HSTAR(I,J)
      TH(I,J)=SQRT(TH(I,I)*TH(J,J))
      THIJ=0.5/TH(I,J)
      DTHDTR(I,J)=THIJ*(TH(J,J)*DTHDTR(I,I)+TH(I,I)*DTHDTR(J,J))
      DTHDVR(I,J)=THIJ*(TH(J,J)*DTHDVR(I,I)+TH(I,I)*DTHDVR(J,J))
      DPHDTR(I,J)=0.5/HSTAR(I,J)*(HSTAR(J,J)*DPHDTR(J,J)+HSTAR(I,I)*DPHD
     1TR(I,I))
      DPHDVR(I,J)=0.5/HSTAR(I,J)*(HSTAR(J,J)*DPHDVR(J,J)+HSTAR(I,I)*DPHD
     1VR(I,I))
      FHSPH(I)=FHSPH(I)+      X(J)*H(I,J)*F(I,J)
      HSPH(I)=HSPH(I)+      X(J)*H(I,J)
      TE(I,J)=TR*TH(I,J)
      VE(I,J)=VR*PH(I,J)
      DELTH(I,J)=0.
      DELPH(I,J)=0.
    2 CONTINUE
      DELF1(I)=2.*HXFX/HX*(FHSPH(I)/HXFX-HSPH(I)/HX)
      DELH1(I)=2.*HX*(HSPH(I)/HX-1.)
      DELF(I)=DELF1(I)
      DELH(I)=DELH1(I)
    1 CONTINUE
      DO 4 K=1,NCOMP
```

```
      BEFORE=0.
    5 SUM1=0.
      SUM2=0.
      SUM3=0.
      TERM1=HX/HXFX*DELF(K)
      TERM2=DELH(K)/HX
      DO 3 I=1,NCOMP
      DO 3 J=1,NCOMP
      DELTR(I,J)=TE(I,J)*(DELTH(I,J)/TH(I,J)-TERM1)
      DELVR(I,J)=VE(I,J)*(DELPH(I,J)/PH(I,J)-TERM2)
      DELTH(I,J)=DTHDTR(I,J)*DELTR(I,J)+DTHDVR(I,J)*DELVR(I,J)
      DELPH(I,J)=DPHDTR(I,J)*DELTR(I,J)+DPHDVR(I,J)*DELVR(I,J)
      SUM1=SUM1+X(I)*X(J)*DELTH(I,J)*FSTAR(I,J)*H(I,J)
      SUM2=SUM2+X(I)*X(J)*DELPH(I,J)*HSTAR(I,J)*(F(I,J)-HXFX/HX)
      SUM3=SUM3+X(I)*X(J)*HSTAR(I,J)*DELPH(I,J)
    3 CONTINUE
      TOTAL=(SUM1+SUM2)/HX
      DELF(K)=DELF1(K)+TOTAL
      DELH(K)=DELH1(K)+SUM3
      IF(ABS(BEFORE-TOTAL).LT.0.0001)GO TO 4
      BEFORE=TOTAL
      GO TO 5
    4 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE DIFFER(DFX,DHX)
      COMMON/DEL/DTHDVR,DTHDTR,DPHDTR,DPHDVR,F,H
      COMMON/PHITHE/TE,VE,X,HSTAR,FSTAR,T    ,NCOMP,HX,HXFX,TH,PH
      COMMON/REFTEM/TR,ZCREF
      COMMON/OM/W,VP
      COMMON/DATE/TC,VC,ZC,IDENT
      COMMON/REFS/TCREF,VCREF,WREF,PCREF
      DIMENSION W(10),TC(30),VC(30),ZC(30),IDENT(10),TE(10,10),VE(10,10)
     1,X(10),HSTAR(10,10),FSTAR(10,10),TH(10,10),PH(10,10),DTHDVR(10,10)
     1,DTHDTR(10,10),DPHDTR(10,10),DPHDVR(10,10),F(10,10),H(10,10),G(10)
     1,DVRDTA(10),DTRDTA(10),DTHDT(10),DPHDT(10),DH(10,10),DF(10,10),DTR
     1DTC(10),DVRDTC(10),VP(10)
      DO 1 I=1,NCOMP
      F(I,I)=FSTAR(I,I)*TH(I,I)
      H(I,I)=HSTAR(I,I)*PH(I,I)
      G(I)=H(I,I)**0.33333
      VRED=VE(I,I)
      IF(VRED.GT.2.)VRED=2.
      IF(VRED.LT.0.5)VRED=0.5
      TRED=TE(I,I)
      II=IDENT(I)
      ZI=ZC(II)
      WI=W(I)
      DTHDTR(I,I)=(WI-WREF)*(-0.8493/TRED+0.4506/(TRED*TRED)*(VRED-0.5))
      DPHDTR(I,I)=ZCREF/ZI*(WI-WREF)*(0.3903*(VRED-1.0177)-0.9462*(VRED-
     10.7603)/TRED)
      IF((VE(I,I).LT.0.5).OR.(VE(I,I).GT.2.))GO TO 12
      DTHDVR(I,I)=(0.3063-0.4506/TRED)*(WI-WREF)
      DPHDVR(I,I)=ZCREF/ZI*(WI-WREF)*(0.3903-0.9462*ALOG(TRED))
   13 DVRDTA(I)=0.1
      DTRDTA(I)=0.1
    1 CONTINUE
      NCOUNT=1
    8 DO 2 I=1,NCOMP
```

```
      DTHDT(I)=DTHDTR(I,I)*DTRDTA(I)+DTHDVR(I,I)*DVRDTA(I)
      DPHDT (I)=DPHDTR(I,I)*DTRDTA(I)+DPHDVR(I,I)*DVRDTA(I)
      DH(I,I)=HSTAR(I,I)*DPHDT(I)
      DF(I,I)=FSTAR(I,I)*DTHDT(I)
    2 CONTINUE
      DFX=0.
      DHX=0.
      DO 3 I=1,NCOMP
      DO 4 J=1,NCOMP
      IF(I.EQ.J)GO TO 5
      DH(I,J)=0.5*(DH(I,I)+DH(J,J))
      GIJ=0.5*(G(I)+G(J))
      F(I,J)=FSTAR(I,J)*SQRT(TH(I,I)*TH(J,J))
      H(I,J)=GIJ*GIJ*GIJ
      DF(I,J)=FSTAR(I,J)*0.5/SQRT(TH(I,I)*TH(J,J))*(TH(I,I)*DTHDT(J)+TH(
     1J,J)*DTHDT(I))
    5 DFX=DFX+X(I)*X(J)*(H(I,J)*DF(I,J)+DH(I,J)*F(I,J))
      DHX=DHX+X(I)*X(J)*DH(I,J)
    4 CONTINUE
    3 CONTINUE
      DFX=DFX/HX-HXFX/HX*DHX/HX
      TOT=0.
      DO 6 I=1,NCOMP
      DTRDTC(I)=TE(I,I)*(DTHDT(I)/TH(I,I)+1./T-HX/HXFX*DFX)
      DVRDTC(I)=VE(I,I)*(DPHDT(I)/PH(I,I)-DHX/HX)
      DIFF=DTRDTC(I)-DTRDTA(I)
      TOT=TOT+DIFF*DIFF
    6 CONTINUE
      COMPN=NCOMP
      ERROR=SQRT(TOT)/COMPN
      IF(ERROR.LE.0.00001)GO TO 7
      DO 9 I=1,NCOMP
      DTRDTA(I)=DTRDTC(I)
      DVRDTA(I)=DVRDTC(I)
    9 CONTINUE
```

```
      IF(NCOUNT.GT.40)GO TO 10
      NCOUNT=NCOUNT+1
      GO TO 8
   12 DTHDVR(I,I)=0.
      DPHDVR(I,I)=0.
      GO TO 13
   10 WRITE(6,11)
   11 FORMAT(43H MORE THAN 40 ITERATIONS TO CONVERGE DTR/TR)
    7 RETURN
      END
```



```
      SUBROUTINE LIQ(COMP,U,FCOEFF,NEXIT)
      COMMON/UZ/          UANDZ,DONE,PRA,VR
      COMMON/TAIT/LIQUID,VRO
      COMMON/REFTEM/TR,ZCREF
      LOGICAL UANDZ,DONE,LIQUID
      H=-17.4897+15.9008/TR+EXP(10.5083*TR-11.0064)
      C2=EXP(5.94009-2.105715/TR-0.986772/(TR*TR))
      PRO=EXP(4.77726-4.782895/TR+0.73611*ALOG(TR))
      LIQUID=.TRUE.
      C=C2/PRO
      C3=EXP(50.908*(TR-1.))
      IF(TR.GT.1.)GO TO 3
      XT4=EXP(0.83531+0.4175105*ALOG(1.-TR)+0.214866*C3)
      VRO=1./(1.+XT4)
      ZC=ZCREF
```

```
      TERM=(PRA+H)/(PRO+H)
      IF(TERM)3,3,4
    4 VR=VRO-ALOG(TERM)/C
      COMP=ZCREF*PRA/TR*VR
      IF(.NOT.DONE)GO TO 1
      DPRO=PRO*(4.782895/TR+.73611)/TR
      DC=C2*((2.105715+1.973544/TR)/(TR*TR)-DPRO/PRO)/PRO
      X4=VRO*VRO*XT4
      DVRO=-X4 *(0.4175105/(TR-1.)+10.938398*C3)
      DH=-15.9008/(TR*TR)+10.5083*EXP(10.5083*TR-11.0064)
    5 UO=(-0.29152279+1.934121/TR-(0.2531244-0.3800509/TR)*EXP(15.*(1.00
     1238*TR-1.)))/VRO*(-1.)
      FM=-EXP(3.5197242-4.4195532/TR-1.2808837*ALOG(TR))
      ZM=ZCREF*PRO*VRO/TR
      IF(NEXIT.EQ.1) GO TO 6
      U=UO+ZC*((VR-VRO)*(H/TR-DH+(PRA+H)/C*DC)+(PRA-PRO)/C*(1./TR-(DPRO+
     1DH)/(PRO+H)-C*DVRO+DC/C))
      FCOEFF=FM+COMP-ZM-ALOG(PRA/PRO)+ZCREF*((VR-VRO)*H+(PRA-PRO)/C)/TR
    1 RETURN
    3 NEXIT=1
      PRA=PRA/0.99691
      TR=TR/0.99848
      CALL ZEDU(U,COMP,DZR,FCOEFF)
      WRITE(6,75)TR,VR,PRA
   75 FORMAT (76H HAD TO CALCULATE LIQUID PHASE WITH VENNIX EQUATION AS
     1TAIT WAS UNUSABLE TR=,F10.4,4H VR=,F10.4,4H PR=,F10.4)
      IF(.NOT.DONE)RETURN
      TR=TR*0.99848
      PRA=PRA*0.99691
      GO TO 5
    6 U=U+UO
      FCOEFF=FCOEFF+FM-ZM+ALOG(ZM)-1.
      RETURN
      END
```

```
      SUBROUTINE ZEDU(U,COMP,DZR,FCOEFF)
      DIMENSION A(5),B(5),D(5),S(8),F(2),E(2),U5(8)
      LOGICAL UANDZ,DONE,LIQUID
      REAL K
      COMMON/TAIT/LIQUID,VRO
      COMMON/UZ/          UANDZ,DONE,PRA,VR
      COMMON/REFTEM/TR,ZCREF
      DATAU5/0.09171732,-0.09171732,0.2627662,-0.2627662,0.39833324,-0.3
     19833324,0.48014493,-0.48014493/,
     1S/0.18134189,0.18134189,0.15685333,0.15685333,0.11119052,0.1111905
     12,0.05061427,0.05061427/
      DATA A/-1.9079137,0.1859404,0.6206085,-0.6050965,0.1390605/
      DATA B/0.7986446,0.1947895,-0.4916982,0.4110596,-0.0650830/
      DATA D/-0.8398430,-0.5167966,2.4138572,-1.6793539,0.3022386/
      DATA E/8.7758015,0.1733543/,F/7.2275164,-1.1449913/,G,TO,K,ALPHA,B
     1ETA,RHO /8.423558,-0.774286,1.394830,0.868917,2.226390,0.697342/
      FCOEFF=0.
      U=0.
      RBET3=(BETA+RHO)**3
      RALF3=(ALPHA+RHO)**3
      IF(.NOT.UANDZ)GO TO 26
      DO 27 I=1,8
      R=(U5(I)+0.5)/VR
      IF(LIQUID)R=0.5*(1./VRO+1./VR)+U5(I)*(1./VR-1./VRO)
   26 IF(.NOT.UANDZ)R=1./VR
      R2=R*R
      R3=R2*R
      R4=R3*R
      R5=R4*R
      CB=B(1)*R+B(2)*R2+B(3)*R3+B(4)*R4+B(5)*R5
      CA=A(1)*R+A(2)*R2+A(3)*R3+A(4)*R4+A(5)*R5
      RPLUSR=RHO+R
      RSQ=RPLUSR*RPLUSR
      RCUBE=RSQ*RPLUSR
```

```
      CC=R*RSQ*(RCUBE-RALF3)*(RBET3-RCUBE)
      CD=D(1)*R+D(2)*R2+D(3)*R3+D(4)*R4+D(5)*R5
      CE=E(1)+E(2)*RCUBE
      CF=F(1)+F(2)*R
      TT=1./TR
      EXP1=EXP(G-CE*(TR-TO))
      EXP2=EXP(K-CF*TT)
      Q=CC*EXP1
      QQ=CD*EXP2
      ZM=CB+CA*TT+(Q+QQ)*TT
      IF(UANDZ)GO TO 36
      IF(DONE)GO TO 1
      DCA=A(1)+2.*A(2)*R+3.*A(3)*R2+4.*R3*A(4)+5.*A(5)*R4
      DCB=B(1)+2.*B(2)*R+3.*B(3)*R2+4.*B(4)*R3+5.*B(5)*R4
      DCD=D(1)+2.*D(2)*R+3.*D(3)*R3+4.*D(4)*R3+5.*D(5)*R4
      DZR=DCB+TT*DCA+Q*TT*(1./R+2./RPLUSR+3.*RSQ*(1./(RCUBE-RALF3)-1./(R
     1BET3-RCUBE)-E(2)*(TR-TO)))+EXP2*(DCD-CD*F(2)*TT)*TT
      IF(.NOT.UANDZ)GO TO 37
   36 DZT=(-TT*(CA*TT+Q*(CE+TT)+QQ*TT*(1.-TT*CF)))/R
      U=S(I)*DZT+U
      FCOEFF=FCOEFF+S(I)*ZM/R
   27 CONTINUE
      IF(LIQUID)FVRO=FCOEFF/VRO
      IF(.NOT.LIQUID)FVRO=0.
      IF(LIQUID)GO TO 2
      U=U*TR/VR*(-1.)
    3 CONTINUE
      UANDZ=.FALSE.
      GO TO 26
    1 FCOEFF=ZM-ALOG(ZM+1.)+FCOEFF*R
      FCOEFF=FCOEFF+FVRO
   37 COMP=ZM+1.
      IF(DONE)UANDZ=.TRUE.
      RETURN
    2 U=U*TR*(1./VRO-1./VR)
```

```
      GO TO 3
      END
```

```
      SUBROUTINE FIXIT(T,WHICH,NCOMP,Q,VT,TC,PC,P)
C  THIS IS THE FOURTH VERSION OF FIXIT
      DIMENSION PC(10),TC(10)
      DIMENSION Q(10),VT(10),PT(10)
      DIMENSION A (10),B(10)
      INTEGER WHICH
      COMMON/AB/A,B
      IF(WHICH.EQ.3)GO TO 5
      TOLD=200.
      PSTORE=P
      DO 9 N=1,NCOMP
      IF(PSTORE.GT.PC(N))P=0.9*PC(N)
      A(N)=ALOG(PC(N))-VT(N)/(TC(N)-VT(N))*ALOG(P/PC(N))
      B(N)=ALOG(P/PC(N))*TC(N)*VT(N)/(TC(N)-VT(N))
      P=PSTORE
    9 CONTINUE
    7 FUNC=0.
      DERIV=0.
      DO 1N=1,NCOMP
      VAP=EXP(A(N)+B(N)/TOLD)
      FUNC=FUNC+Q(N)*VAP
      DERIV=DERIV+Q(N)*VAP*B(N)/TOLD/TOLD
    1 CONTINUE
      TNEW=TOLD-(P-FUNC)/DERIV
```

```
      IF(ABS(TNEW-TOLD).LT.1.5)GO TO 3
      TOLD=TNEW
      GO TO 7
    3 T=TNEW
      DO 2 N=1,NCOMP
      VAP=EXP(A(N)+B(N)/T)
      Q(N)=Q(N)*VAP/P
    2 CONTINUE
      RETURN
    5 FUNC=0.
      DERIV=0.
      DO 10 N=1,NCOMP
      VAP=EXP(A(N)+B(N)/TOLD)
      FUNC=FUNC+Q(N)/VAP
      DERIV=B(N)/TOLD/TOLD/VAP*Q(N)+DERIV
   10 CONTINUE
      TNEW=TOLD-(P*FUNC-1.)/P/DERIV
      IF(ABS(TNEW-TOLD).LT.1.5)GO TO 4
      TOLD=TNEW
      GO TO 5
    4 T=TNEW
      DO 6 N=1,NCOMP
      VAP=EXP(A(N)+B(N)/T)
   12 Q(N)=Q(N)*P/VAP
    6 CONTINUE
      P=PSTORE
      RETURN
      END
```

```
      SUBROUTINE THEPHI
      DIMENSION TE(10,10),VE(10,10),X(10),HSTAR(10,10),FSTAR(10,10),PH(1
     10,10),TH(10,10),H(10,10),F(10,10),G(10),VP(10),W(10)
      COMMON/PHITHE/TE,VE,X,HSTAR,FSTAR,T    ,NCOMP,HX,HXFX,TH,PH
      COMMON/DATE/TC(30),VC(30),ZC(30),IDENT(10)
      COMMON/OM/W,VP
      COMMON/REFS/TCREF,VCREF,WREF,PCREF
      COMMON/REFTEM/TR,ZCREF
    7 DO 1 I=1,NCOMP
      TEI=TE(I,I)
      VEI=VE(I,I)
      TH(I,I)=1.+(W(I)-WREF)*(0.0892-0.8493*ALOG(TEI) +(0.3063-0.4506/TE
     1I)*(VEI-0.5))
      N=IDENT(I)
      PH(I,I)=ZCREF/ZC(N)*(1.+(W(I)-WREF)*(0.3903*(VEI-1.0177)-0.9462*(V
     1EI-0.7663)*ALOG(TEI)))
      TE(I,I)=TR*TH(I,I)
      F(I,I)=FSTAR(I,I)*TH(I,I)
      H(I,I)=HSTAR(I,I)*PH(I,I)
    1 G(I)=H(I,I)**0.33333
      KOUNT=1
      HX=0.
      HXFX=0.
      DO 2 I=1,NCOMP
      DO 3 J=1,NCOMP
      IF(I.EQ.J)GO TO 4
      GIJ=0.5*(G(I)+G(J))
      H(I,J)=GIJ*GIJ*GIJ
      F(I,J)=FSTAR(I,J)*(TH(I,I)*TH(J,J))**0.5
    4 HX=HX+X(J)*X(I)*H(I,J)
      HXFX=HXFX+X(I)*X(J)*H(I,J)*F(I,J)
    3 CONTINUE
    2 CONTINUE
      TR2=T/TCREF*HX/HXFX
```

```
      IF(ABS(TR2-TR).GT.0.0001)GO TO 5
      TR=TR2
      RETURN
    5 IF(KOUNT.GT.10)GO TO 6
      KOUNT=KOUNT+1
      TR=TR2
      GO TO 7
    6 WRITE(6,8)
    8 FORMAT(39H MORE THAN 10 ITERATIONS TO CONVERGE TR)
      STOP
      END
```



```
      SUBROUTINE HF
      COMMON/PHITHE/TE,VE,X,HSTAR,FSTAR,T,NCOMP,HX,HXFX,TH,PH
      DIMENSION TE(10,10),VE(10,10),X(10),HSTAR(10,10),FSTAR(10,10),TH(1
     10,10),PH(10,10)
      HX=0.
      HXFX=0.
      DO1 I=1,NCOMP
      DO1 J=1,NCOMP
      HX=HX+X(I)*X(J)*HSTAR(I,J)
      HXFX=HXFX+X(I)*X(J)*HSTAR(I,J)*FSTAR(I,J)
    1 CONTINUE
      RETURN
      END
```