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LINEARIZATION METHODS FOR SYSTEMS NOT AT CHEMICAL EQUILIBRIUM

II

EQUILIBRIUM PRESSURES AND PHASE COMPOSITIONS FOR NON-IDEAL MIXTURES

Thesis by

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SUMMARY

In Part I a method for calculating the effect of changes in the variables temperature and pressure on the reaction yields of chemical systems not at equilibrium is developed. The method circumvents the exact solution of the differential rate equation by expanding the time derivative of the progress variable about its equilibrium value and retaining the linear terms. The equations are valid near equilibrium and comparisons with the results obtained by exact solution of the rate equation show good agreement. Much economy of algebraic labour is achieved at small cost in accuracy. The method is extended to systems of competing reactions but the results do not appear to be very useful. In addition the ease with which some other questions may be answered is illustrated.

In Part II an equation for the calculation of equilibrium pressures and phase compositions for non-ideal systems is derived. Conformal solution theory is applied to the liquid phase and a second order virial equation is employed in the description of the gas phase. Calculated and experimental results for binary systems show good agreement in most cases.

I

LINEARIZATION METHODS FOR SYSTEMS NOT AT CHEMICAL EQUILIBRIUM

INTRODUCTION

In investigating the effect of changes in termperature or pressure on chemically reacting systems a state of equilibrium is frequently assumed. Such an assumption allows the use of the relatively simple equilibrium equations in predicting the result. However, the assumption of the equilibrium state for systems not at equilibrium can lead to results which are significantly in error. In fact Rastogi and Denbigh (1) have shown that, even for a system which has attained ninety percent of its equilibrium state, the results can be in error by a factor of ten.

To investigate the effect of a change in temperature or pressure without assuming the equilibrium state generally requires that the rate equation for the system be solved. The rate equation can be solved for the concentration of one of the chemical species and the resulting equation involves the concentration of one or more chemical species and the rate constants for the system. The appropriate derivative of this equation yields the effect of a change in temperature or pressure. Rastogi and Denbigh have utilized this approach in the paper cited above but such a method becomes cumbersome for all but the simplest rate laws.

The assumption of equilibrium can be avoided and the unwieldy equations, which result from direct solution and differentiation of the rate equation, can be replaced by the use of the Kirkwood and Crawford linearization (2).

In this, Section I of the thesis, the Kirkwood and Crawford linearization will be applied in a completely general way to the problem of obtaining the effect of a change in temperature or pressure on a system not at equilibrium. Further, the method will be worked out in detail for several systems and the results compared with results obtained by the exact method of Rastogi and Denbigh. In the second part of this section the methods are extended in a completely general way to a system of competing reactions and in particular to a system of two competing reactions. In the final part some other questions about the system are answered with the aid of the equations developed.

SINGLE CHEMICAL REACTIONS

Essentially the method of this work is the expansion of the time derivative of the progress variable about its equilibrium value of zero and the retention of the linear terms.

The progress variable λ is defined as

$$dn_\alpha = \nu_\alpha \, d\lambda \tag{1}$$

In this definition n_α is the concentration of species N_α in moles per liter and ν_α is the stoichiometric coefficient of N_α in the reaction considered. The sign attached to ν_α is such that $d\lambda$ is always positive. It should be noted that is for convenience defined here in moles per liter but this does not detract from the generality of the methods developed. If we expand the time derivative $d\lambda/dt$ about its equilibrium value and retain only the first derivative term we obtain

$$\frac{d\lambda}{dt} = \frac{d\lambda}{dt}\Big/_e + \Sigma(n_\alpha - n_\alpha^e)\,\frac{d\mathring{\lambda}}{dn_\alpha}\Big/_e$$

Here the subscript indicates evaluation of the derivative at equilibrium. Since dn_α/dt is zero at equilibrium it follows from equation 1 that $(d\lambda/dt)_e$ is zero and we have

$$\frac{d\lambda}{dt} = \dot{\lambda} = \sum_\alpha (n_\alpha - n_\alpha^e)\,\frac{d\mathring{\lambda}}{dn_\alpha}\Big/_e \tag{2}$$

Integration of equation 1 yields $n_\alpha^t - n_\alpha^e = \nu_\alpha\,(\lambda^t - \lambda^e)$ where the superscripts "t and e" indicate evaluation at time t and at equilibrium respectively. Insertion of this last statement into equation 2 gives

$$\dot{\lambda} = (\lambda^t - \lambda^e) \sum_\alpha \nu_\alpha \frac{d\dot{\lambda}}{dn_\alpha} \Big/_e \tag{3}$$

$\sum_\alpha \nu_\alpha \frac{d\dot{\lambda}}{dn_\alpha} \Big/_e$ depends on $\dot{\lambda}$ for the system, a constant for a given system, and is denoted by β. Rewriting equation 3 we have $\frac{d\lambda}{\lambda^t - \lambda^e} = \beta dt$ which has the solution

$$\ln(\lambda^t - \lambda^e) = \beta t + \ln I$$

where I is a constant of integration. Since for t = 0 $\mathring{\lambda} = 0$ then $\ln(-\lambda^e) = \ln I$ so we have $\lambda^t = \lambda^e(1 - e^{\beta t})$. Replacing β by $-1/\tau$ where τ, designated as the relaxation time, is greater than zero we obtain finally

$$\lambda^t = \lambda^e(1 - e^{-t/\tau}) \tag{4}$$

We may use equation 4 to obtain the effect of a change in temperature or pressure. Letting X = P or T and taking the derivative d/dX of equation 4 we have

$$\frac{d\lambda}{dX} = \frac{\lambda}{\lambda^e} \cdot \frac{d\lambda^e}{dX} - \lambda^e(1 - \lambda/\lambda^e)\ln(1 - \lambda/\lambda^e)\frac{d\ln 1/\tau}{dX} \tag{5}$$

Defining f, the fractional attainment of equlibrium as f = λ/λ^e and equation 5 can be rewritten as

$$\frac{d\lambda}{dX} = f\frac{d\lambda^e}{dX} - \lambda^e(1 - f)\ln(1 - f)\frac{d\ln 1/\tau}{dX} \tag{6}$$

From equation 1 we have $dn_\alpha/dX = \nu_\alpha\, d\lambda/dX$ so that we obtain for dn_α/dX the equation

$$\frac{dn_\alpha}{dX} = \nu_\alpha f \frac{d\lambda^e}{dX} - \nu_\alpha \lambda^e(1 - f)\ln(1 - f)\frac{d\ln 1/\tau}{dX} \tag{7}$$

This equation clearly gives the effect of a change in temperature or pressure in terms of the relaxation time τ and the fractional attainment of equilibrium for any reaction near equilibrium.

The effect of a change in temperature or pressure for the equilibrium state is given by equation 1 as

$$\frac{dn_\alpha}{dX} = \nu_\alpha \frac{d\lambda^e}{dX} \tag{8}$$

Defining r as the ratio $r = \frac{dn_\alpha/dX}{dn_\alpha^e/dX}$ one obtains on dividing equation 7 by equation 8

$$r = f - (1 - f) \ln (1 - f) \frac{d \ln 1/\tau /dX}{d \ln \lambda^e/dX} \tag{9}$$

Clearly the ratio r is a measure of the effect of a change in temperature or pressure for a non equilibrium state compared to the effect of a similar change for the equilibrium state. As such, the magnitude of r is a measure of the error which arises from assuming the equilibrium state compared to the result when equilibrium is not assumed.

It is to be emphasized that the equations 4 for λ and 9 for r are completely general and can be formulated for any system near equilibrium for which the relaxation time τ and the fractional attainment of equilibrium f are known.

Application and Numerical Calculations

The magnitude of r is a convenient and significant number by which the results of the linearization methods developed above can be compared to the exact results obtained by the direct solution method used by Rastogi and Denbigh. In order to make the comparison it is necessary to formulate r for the systems considered both by the linearization method and by the direct solution method. For further comparison the system types chosen are of increasing complexity.

The systems considered are:

System A

$$N_1 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} N_2$$

where: N_α is the molecular formula of a chemical species α

System B

$$N_1 + N_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} N_3 + N_4$$

: k_1 and k_2 are respectively the forward and backward rate constants

System C

$$N_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} N_2 + N_3$$

The kinetics for the systems are taken as;

for A: unimolecular opposed by a unimolecular reaction so that the rate law is

$$\frac{dn_2}{dt} = k_1 n_1 - k_2 n_2 \tag{10}$$

for B: bimolecular opposed by a bimolecular reaction so that the rate law is

$$\frac{dn_3}{dt} = k_1 n_1 n_2 - k_2 n_3 n_4 \tag{11}$$

for C: unimolecular opposed by a bimolecular reaction so that the rate law is

$$\frac{dn_3}{dt} = k_1 n_1 - k_2 n_2 n_3 \tag{12}$$

where in each case the n_α for a particular reaction are again mole/liter concentrations of species N_α at time t. For convenience the initial concentrations of the products are taken as zero and the initial concentrations of all reactants are taken the same and equal to "a" moles/l. Thus at any time t the following relations hold:

for System A

$$n_1 = a - n_2 \tag{13}$$

for System B

$$n_1 = n_2 = a - n_3 \,;\; n_3 = n_4 \tag{14}$$

for System C

$$n_1 = a - n_3 \,;\; n_2 = n_3 \tag{15}$$

In each case the equilibrium condition $\frac{dn_\alpha}{dt} = 0$ defines the equilibrium constant K as $K = k_1/k_2$. Writing n_α^e as the equilibrium concentration of species N_α and making use of the equilibrium condition we have;

for System A:

$$n_2^e = \frac{aK}{1 + K} \tag{16}$$

for System B:

$$n_3^e = \frac{aK^{1/2}}{1 + K^{1/2}} \tag{17}$$

for System C:

$$n_3^e = \frac{K(\rho - 1)}{2} \quad \text{where} \quad 1 + \frac{4a}{K} = \rho^2 \tag{18}$$

We may now formulate r for a change in termperature for the systems A, B and C. To obtain r by the method of linearization (i.e. by equation 9) we proceed as outlined below for each system.

For system A we find the relaxation time τ by noting that from equations 1 and 10 that

$$\dot{\lambda} = k_1 n_1 - \frac{k_1}{K} n_2 \quad \text{so that from equation 4}$$

$$\frac{1}{\tau} = \frac{k_1(K + 1)}{K}$$

and thus

$$\frac{d \ln 1/\tau}{dT} = \frac{d \ln k_1}{dT} - \frac{d \ln K}{dT} + \frac{K}{1 + K} \cdot \frac{d \ln K}{dT} \tag{19}$$

The derivatives in equation 19 can be taken from thermodynamics as

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} \tag{20}$$

where ΔH is the enthalpy change of the reaction and

$$\frac{d \ln k_1}{dT} = \frac{E}{RT^2} \tag{21}$$

where E is the activation energy of the forward reaction. Substituting equations 20 and 21 into equation 19 gives

$$\frac{d \ln 1/\tau}{dT} = \frac{\Delta H}{RT^2} \cdot \frac{1}{(1 + K)} \left[(K + 1) \frac{E}{\Delta H} - 1 \right] \tag{22}$$

To find λ^e for system A we make use of equation 1 and the conditions $n_2^o = 0$ and $\lambda^o = 0$ so that $n_2^e = \lambda^e$. Then from equation 16 we have $\lambda^e = \frac{\alpha K}{1 + K}$ which gives

$$\frac{d \ln \lambda^e}{dT} = \frac{d \ln K}{dT} - \frac{K}{1 + K} \cdot \frac{d \ln K}{dT} \tag{23}$$

Substitution of equations 19 and 23 into equation 9 yields the required formulation of r for this system as

$$r = f - (1 - f) \ln (1 - f) \left[\frac{E}{\Delta H} (1 + K) - 1 \right] \tag{24}$$

We proceed in an identical manner for the systems B and C and obtain the formulas summarized in Table I.

To obtain r by the method of exact solution and differentiation requires, for each system, that the differential rate equation be solved for one of the components and then the solution differentiated in order that dn_α/dT in the ratio r can be formulated.

For system A the differential rate equation to be solved is from equations 10 and 13

$$\frac{dn_2}{dt} = k_1 \left[a - n_2 \frac{(1 + K)}{K} \right] \tag{25}$$

Since $n_2^o = 0$ we may write the solution as

$$\ln \left[1 - \frac{(1 + K)}{K} \frac{n_2}{a}\right] = - \frac{1 + K}{K} k_1 t \tag{26}$$

and from equation 16 we may substitute $\frac{n_2^e}{a} = \frac{K}{1 + K}$ and obtain

$$\ln \left[1 - \frac{n_2}{n_2^e}\right] = -k_1 \left(\frac{K + 1}{K}\right) t \tag{27}$$

On solving this explicity for n_2 and differentiating with respect to temperature we have

$$\frac{dn_2}{dT} = n_2^e \left(1 - \frac{n_2}{n_2^e}\right) tk_1 \left\{ \frac{K + 1}{K} \cdot \frac{d \ln k_1}{dT} - \frac{1}{K} \cdot \frac{d \ln K}{dT} \right] + \frac{n_2}{n_2^e} \cdot \frac{dn_2^e}{dT}$$

Substitution for the derivatives from equations 20 and 21 allows one to write

$$\frac{dn_2}{dT} = - \frac{n_2^e(1 - {}^{n_2}/n_2^e)}{1 + K} \ln \left(1 - {}^{n}/n_2^e\right) \left[\frac{E\,(1 + K)}{\Delta H} - 1\right] \frac{\Delta H}{RT^2} + \frac{n_2}{n_2^e} \frac{dn_2^e}{dT}$$

Eliminating t with aid of equation 27 we obtain

$$\frac{dn_2}{dT} = \frac{- n_2^e\,(1 - {}^{n_2}/n_2^e)}{1 + K} \ln \left(1 - {}^{n_2}/n_2^e\right) \left[\frac{E}{\Delta H}(1 + K) - 1 \right] \frac{\Delta H}{RT^2} + \frac{n_2}{n_2^e} \frac{dn_2^e}{dT} \tag{28}$$

For the derivative dn_2^e/dT we differentiate the expression for n_2^e in equation 16 and obtain

$$\frac{dn_2^e}{dT} = \frac{aK}{(1 + K)^2} \cdot \frac{d \ln K}{dT}$$

Substituting for the derivative d ln K/dT from equation 20 we have

$$\frac{dn_2^e}{dT} = \frac{aK}{(1 + K)^2} \frac{\Delta H}{RT^2} \tag{29}$$

Dividing equation 28 by equation 29 and replacing n_2^e/n_2 by f yields the required formulation of r for this system as

$$r_{exact} = f - (1 - f) \left[\frac{E}{\Delta H} (1 + K) - 1 \right] \ln (1 - f) \tag{30}$$

In an exactly similar manner we obtain r_{exact} for the systems B and C. The formulations for r_{exact} are summarized in Table I. It is to

Table I

Summary of Equations for r for a Change in Temperature

System Type	Kinetics	Formulation of r for a change in temperature	
		By the method of Linearization	By exact solution of the rate equation followed by differentiation
$N_1 \underset{}{\overset{k_1}{\rightleftharpoons}} N_2$	unimolecular opposed by a unimolecular	$f-(1-f)\ln(1-f)\left[\frac{E}{\Delta H}(1+K)-1\right]$	$f-(1-f)\ln(1-f)\left[\frac{E}{\Delta H}(1+K)-1\right]$
$N_1 + N_2 \overset{k_1}{\rightleftharpoons} N_3 + N_4$	bimolecular opposed by a bimolecular	$f-2(1-f)\ln(1-f)\left[\frac{E}{\Delta H}-\frac{1}{2}\right](1+K^{1/2})$	$\ln\left[\frac{1-f\,\frac{K^{1/2}-1}{K^{1/2}+1}}{1-f}\right]\cdot\left\{f^2(K-1)-2fK^{1/2}(1+K^{1/2})+(1+K^{1/2})\frac{E}{\Delta H}\right\}$ $+\left\{f\left[1+K^{1/2}(1-f)\right]\right\}$
$N_1 \overset{k_1}{\rightleftharpoons} N_2 + N_3$	unimolecular opposed by a bimolecular	$f-(1-f)\ln(1-f)\left[\frac{\frac{E}{\Delta H}-\frac{2a}{K^2}(\varrho-1)}{\varrho-1-2a/K\varrho}\right]$ where $\varrho^2=(1+\frac{4a}{K})$	$\frac{f(\varrho-1-2a/\varrho K)-\frac{2a}{\varrho^2 K}(1-f)}{\varrho-1-2a/\varrho K}+\frac{2a}{K}\cdot\left\{\frac{[f(\;-1)+1]^2-\varrho^2}{\varrho^2(\varrho^2-1)(\varrho-1-2a/\varrho K)}\right\}$ $+\left\{\frac{[f(\varrho-1)+1]^2-\varrho^2}{2\varrho(\varrho-1-2a/\varrho K)}\right\}\cdot\left\{\frac{E}{\Delta H}-\frac{2a}{K\varrho^2}\right\}\cdot\left\{\ln\frac{(1-f)(1+\varrho)}{\varrho(1+f)+(1-f)}\right\}$

be emphasized that although r and r_{exact} are identical for system A that this is not the case for the systems B and C. This is due of course to the fact that the rate law for system A was linear to begin with while B and C do not have linear rate laws.

For purposes of comparison, numerical calculations of r are carried out here for different values of f for each of the systems of types A, B and C. The chemical systems along with the calculated values of r and r_{exact} are tabulated in Table II. Chemical systems were chosen having the characteristics of A, B and C, and for which the required data were available. In addition the systems were chosen, such that the magnitude of $E/\Delta H$ was in the range 10-20; for as pointed out by Rastogi and Denbigh, r is principally a function of $E/\Delta H$ and is small, unless $E/\Delta H$ is of the order of 10.

We next consider the formulation of r for a change in pressure for a system of the type B. The chemical system chosen was again $HI + HI \rightleftharpoons H_2 + I_2$. The reaction is taken to be in the gaseous phase. The gases are considered non-ideal and the mixture of gases is considered a perfect mixture.

To obtain r, by the linearization method, we first note that it is expedient to express $\dot{\lambda}$ as a function of the fugacities of the chemical species in the system rather than the concentrations. The Taylor expansion of equation 2 now reads

$$\dot{\lambda} = \sum_{\alpha} (f_{\alpha} - f_{\alpha}^{e}) \frac{d\lambda}{df_{\alpha}} \Big/_{e}$$

where f_{α} is the fugacity of species N_{α} in the reaction mixture. The Lewis and Randall approximation is employed to define the f_{α} as

Table II

Effect of a Change in Temperature

Comparison of r computed by present method [r (present)] with r computed by the exact method of Reference (1) [r (exact)]. Numbers in brackets are literature references.

Reaction		$H_2 + I_2 \rightleftharpoons 2HI$		cis $\rightleftharpoons$ trans $CH_3 - CH = CHCH_3$		$CH_3CO_2C_2H_5 \rightleftharpoons (H_2O)$ $CH_3COOH + C_2H_5CH$	
Kinetic Type		Bimolecular-Bimolecular		Unimolecular-Unimolecular		Unimolecular-Bimolecular	[4]
E(Kcal)		44	[3]	18	[8]	14.9	[7]
H(Kcal)		3	[3]	.950	[8]	.890	[6]
K		.0022	[3]	1.12	[8]	.005	[5]
T(°K)		764		620		298	
		(present)	(exact)	(present)	(exact)	(present)	(exact)
	0.99	2.49	2.86	2.8	2.8	2.64	2.88
f	0.95	5.80	7.0	6.8	6.8	6.45	-
	0.90	8.40	10.6	9.9	9.9	9.3	10.8

$$f_\alpha = \frac{n_\alpha}{\sum_i n_i} f'_\alpha$$

where $\sum_i n_i$ is the total number of moles in the mixture and where f'_α is the fugacity of the pure species N_α at a given pressure. If $\Delta n = 0$ and only differential pressure changes are considered, then f'_α can safely be taken constant with respect to time. Since $\Delta n = 0$ then $\sum_i n_i = C$, a constant and f_α can be written as

$$f_\alpha = \frac{n_\alpha f'_\alpha}{C} = n_\alpha d_\alpha \qquad \text{where } d_\alpha \neq f(t)$$

From equation 1 we can obtain $n_\alpha - n_\alpha^e = \nu_\alpha (\lambda - \lambda^e)$ and on substituting for n_α we have

$$f_\alpha - f_\alpha^e = d_\alpha \nu_\alpha (\lambda - \lambda^e)$$

Thus we can now write the expansion as

$$\lambda = \sum_\alpha d_\alpha \nu_\alpha (\lambda - \lambda^e) \frac{d\dot{\lambda}}{df_\alpha}\Big/_e = (\lambda - \lambda^e) \beta_f$$

where

$$\beta_f = \sum_\alpha d_\alpha \nu_\alpha \frac{d\dot{\lambda}}{df_\alpha}\Big/_e$$

and is again constant with respect to time. As before we have the solution

$$\lambda = \lambda^e (1 - e^{-t/\tau}) \quad \text{but where } \frac{1}{\tau} = - \sum_\alpha d_\alpha \nu_\alpha \frac{d\lambda}{df_\alpha}\Big/_e \tag{31}$$

Since equation 31 is identical with equation 4, except for the definition of τ, one can write directly the pressure form of equation 9 as

$$r = f - (1 - f) \ln (1 - f) \frac{d \ln {}^1\!/\tau / dP}{d \ln \lambda^e / dP} \tag{32}$$

To obtain r for system B we note first that the rate law (11) written in terms of fugacities is

$$\dot{\lambda} = \frac{d\lambda}{dt} = \frac{dn_3}{dt} = k_1 f_1 f_2 - k_2 f_3 f_4$$

which gives

$$\frac{1}{\tau} = + k_1 \left[d_1 f_2^e + d_2 f_1^e + \frac{1}{K} (d_3 f_4^e + d_4 f_3^e) \right]$$

Using the conditions of equation 14 and the Lewis and Randall relation of n_α and f_α given above we may obtain the expression for $1/\tau$ as

$$\frac{1}{\tau} = 2k_1 d_1 d_2 \left[a - n_3^e + \frac{d_3 d_4}{d_1 d_2} \cdot \frac{n_3^e}{K} \right] \tag{33}$$

Now $K = \frac{f_3^e f_4^e}{f_1^e f_2^e} = \frac{d_3 d_4}{d_1 d_2} \cdot \frac{(n_3^e)^2}{(a - n_3^e)}$

and for convenience write $\frac{d_1 d_2}{d_3 d_4} K = \sigma K$

so that on solving for n_3^e we have

$$n_3^e = \frac{a\,(\sigma K)^{1/2}}{1 + (\sigma K)^{1/2}} \tag{34}$$

Substituting from equation 34 for n_3^e in equation 33 we have

$$\frac{1}{\tau} = 2k_1 d_1 d_2\, a \left[1 - \frac{(\sigma K)^{1/2}}{1 + (\sigma K)^{1/2}} + \frac{(\sigma K)^{1/2}}{1 + (\sigma K)^{1/2}} \cdot \frac{1}{K} \right]$$

which reduces to

$$\frac{1}{\tau} = 2\, a\, k_1\, d_1\, d_2\, (\sigma K)^{-1/2} \tag{35}$$

Noticing that we can write $\sigma = \frac{f_1' f_2'}{f_3' f_4'}$

and $d_1\, d_2 = \frac{f_1'\, f_2'}{c^2}$

and inserting these last two expressions into equation 35 one obtains finally

$$\ln {}^{1}/_{\tau} = \ln \frac{2a}{c^2} + \ln k_1 + \frac{1}{2} \sum_\alpha \ln f_\alpha' - \frac{1}{2} \ln K$$

Taking the derivative with respect to pressure we have

$$\frac{d \ln {}^{1}/_{\tau}}{dP} = \frac{1}{2} \sum_\alpha \frac{d \ln f_\alpha'}{dP}$$

But $\frac{d \ln f'_\alpha}{dP} = \frac{V_\alpha}{RT}$; where V_α is here the molecular volume of species N_α at temperature and pressure T, P. Thus we can write

$$\frac{d \ln {}^{1}/\tau}{dP} = \frac{1}{2RT} \sum_\alpha V_\alpha \tag{36}$$

To find $d \ln n_3^e/dP$ we note since $n_3^o = 0$ that one has $n_3^e = \nu_\alpha \lambda^e$

So that from equation 34 $\ln \lambda^e = \ln n_3^e = \ln a + \frac{1}{2} \ln \sigma K - \ln [1 + (\sigma K)^{1/2}]$

Differentiating this with respect to pressure gives

$$\frac{d \ln \lambda^e}{dP} = \frac{1}{2} \frac{d \ln \sigma}{dP} + \frac{1}{2} \frac{d \ln K}{dP} - \frac{1}{1 + (\sigma K)^{1/2}} \cdot \frac{d (\sigma K)^{1/2}}{dP}$$

which reduces to

$$\frac{d \ln \lambda^e}{dP} = \frac{1}{2} \frac{1}{1 + (\sigma K)^{1/2}} \frac{\Delta V}{RT} \tag{37}$$

Inserting equations 36 and 37 into 32 we obtain the required expression for r as

$$r = f + (1 - f) [\ln (1 - f)] [1 - (\sigma K)^{1/2}] \frac{\Sigma_\alpha V_\alpha}{V}$$

To obtain r, by exact solution of the rate equation, we note first that the rate equation 11 in terms of fugacities is

$$\frac{dn_3}{dt} = k_1 f_1 f_2 - k_2 f_3 f_4$$

Inserting $f_\alpha = \frac{n_\alpha}{c} f'_\alpha$ from the definition given earlier, the rate law becomes

$$\frac{dn_3}{dt} = \frac{k_1}{c^2} [f'_1 f'_2 n_1 n_2 - \frac{1}{K} n_3 n_4 f'_3 f'_4]$$

Noting that for this chemical system that $f'_1 = f'_2$ and making use of equation 14, we can eliminate n_1, n_2 and n_4 and obtain

$$\frac{dn_3}{dt} = \frac{k_1 (f'_1)^2}{c^2} [a^2 - 2an_3 + (1 - \phi) n_3^2] \quad \text{where} \quad \phi = \frac{f'_3 f'_4}{f'_1 f'_2 K}$$

This differential equation has the solution

$$\ln \frac{2(1 - \phi)n_3 - 2a + 2a\phi^{1/2}}{2(1 - \phi)n_3 - 2a - 2a\phi^{1/2}} = \frac{2k_1 (f'_1)^2}{c^2} a \phi^{1/2} t + \ln I$$

The constant of integration I can be evaluated since for $t = 0$, $n_3 = 0$ then

$$\ln \frac{1 + \phi^{1/2}}{1 - \phi^{1/2}} = \ln I$$

and the solution can be written as

$$\ln \frac{(1 - \phi^{1/2})(1 + \phi^{1/2})n_3 - a(1 + \phi^{1/2})}{(1 - \phi^{1/2})(1 + \phi^{1/2})n_3 - a(1 - \phi^{1/2})} = \ln \frac{1 + \phi^{1/2}}{1 - \phi^{1/2}} + \frac{2k_1(f_1')^2}{c^2} a\phi^{1/2} t$$

which reduces to

$$\ln \frac{(1 - \phi^{1/2})n_3 - a}{(1 + \phi^{1/2})n_3 - a} = \frac{2k_1(f_1')^2}{c^2} a\phi^{1/2} t$$

Taking the derivatives with respect to pressure we obtain after some algebra

$$\frac{\frac{dn_3}{dP} 2n_3\phi^{1/2} - 2(n_3 - a)\frac{dn_3\phi^{1/2}}{dP}}{n_3(1 - \phi) - 2an_3 + a^2} = \frac{2atK}{c^2}\left[2\frac{d \ln f_1'}{dP} + \frac{1}{2}\frac{d \ln \phi}{dP}\right](f')^2\phi^{1/2} \quad (38)$$

But $\phi = \frac{f_3' f_4'}{f_1' f_2' K}$ so that $\frac{d \ln \phi}{dP} = \frac{\Delta V}{RT}$ and $\frac{d \ln f_1'}{dP} = \frac{V_1}{RT}$. Also

$$\frac{dn_3\phi^{1/2}}{dP} = \frac{n_3\phi^{1/2}}{2RT}\Delta V + \phi\frac{dn_3}{dP}$$

Inserting these last three equations into equation 38 and rearranging one can obtain

$$\frac{dn_3}{dP} = \frac{n_3(n_3 - a)}{a}\frac{\Delta V}{2RT} + \frac{\sum_\alpha V_\alpha}{2RT} \cdot \left[\frac{n_3^2(1 - \phi) - 2an_3 + a^2}{2a\phi^{1/2}}\right] \cdot \left[\ln \frac{(1 - \phi^{1/2})n_3 - a}{(1 + \phi^{1/2})n_3 - a}\right] \quad (39)$$

To obtain dn_3^e/dP we note that since $n_3^o = 0$ then from equation 1

$$n_3^e = \lambda^e \text{ and } \frac{dn_3^e}{dP} = n_3^e \frac{d(\ln n_3^e)}{dP}$$

From equation 37 $\frac{dn_3^e}{dP} = -\frac{n_3^e}{2[1 + (\sigma K)^{1/2}]} \cdot \frac{\Delta V}{RT}$

and from equation 34 $n_3^e = \frac{a(\sigma K)^{1/2}}{[1 + (\sigma K)^{1/2}]}$

so that $$\frac{dn_3^e}{dP} = -\frac{a(\sigma K)^{1/2}}{[1 + (\sigma K)^{1/2}]} \cdot \frac{\Delta V}{RT} \quad (40)$$

On dividing equation 39 by equation 40 we can obtain r as

$$r = - \frac{n_3(n_3-a)(1+(\sigma K)^{1/2})}{a^2(\sigma K)^{1/2}} - \frac{\alpha V_\alpha}{V} \cdot \left[\frac{n_3^2(1-\phi)-2an_3+a^2}{2a^2\phi^{1/2}(\sigma K)^{1/2}}\right] \cdot \left[\ln \frac{(1-\phi^{1/2})n_3-a}{(1+\phi^{1/2})n_3-a}\right]$$

from $\phi = \frac{f_3' f_4'}{(f_1')^2 K}$ and $\sigma = \frac{(f_1')^2}{f_3' f_4'}$

we have the identity $\phi = \frac{1}{\sigma K}$. Eliminating n_3 by the relation $n_3 = fn_3^e$ and the use of equation 34 and inserting the identity $\phi = \frac{1}{\sigma K}$ we obtain finally

$$r_{exact} = f \left[(\sigma K)^{1/2}(1-f)-1\right] - \frac{\Sigma_\alpha V_\alpha}{\Delta V}\{f^2(\sigma K-1)-2f(\sigma K)^{1/2}[(\sigma K)^{1/2}+1]+(\sigma K)^{1/2}+1\} \cdot \ln\left[\frac{1-\frac{(\sigma K)^{1/2}-1}{(\sigma K)^{1/2}+1}}{1-f}\right] \qquad (41)$$

For the system chosen, $HI + HI \underset{k_2}{\overset{k_1}{\rightleftharpoons}} H_2 + I_2$, the known data are taken as:

$T = 764°K$, ref. (3)

$K = 2.2 \times 10^{-2}$, ref. (3)

$P \doteq 0.4$ atmos., calculated from reference (3) data

The molecular volume V_α is considered given by the formula

$$V_\alpha = \frac{RT}{P}[1 + \beta_\alpha'(T)P]$$

where β_α' is for the pure gas of species α at a pressure P and temperature T. The $\beta_\alpha'(T)$ were calculated with the aid of Lennard-Jones potential functions and for the species involved were found to be

for HI $\beta_\alpha'(T) = 7.76 \times 10^{-4}$ atmos.$^{-1}$

for H_2 $\beta_\alpha'(T) = 2.26 \times 10^{-4}$ "

for I_2 $\beta_\alpha'(T) = 34.1 \times 10^{-4}$ "

So that

$$\sum_\alpha V_\alpha = \frac{RT}{P}(4\cdot 002)$$

$$\Delta V_\alpha = \frac{RT}{P} \times 10^{-4} \times 20.8$$

Inserting the above data into the equations for r and r_{exact} we obtain the data tabulated and compared in Table III. It should be pointed out that the magnitude of r is largely due to the pressure effectively increasing the concentration.

Table III

Effect of a Change in Pressure

f	r by linearization method	r by exact solution of the rate law followed by differentiation (r_{exact})	% Difference in r by the two methods
1.0	+ 1	+ 1	0
0.999	- 12.2	inaccurate	
0.99	- 87	- 97	10
0.90	- 440	- 500	12

Discussion

In comparing the algebra and manipulations involved, in obtaining r by the exact method and by the method of linearization, it should be quite clear that the method of linearization involves much less labour. Comparing the complexity of the equations summarized in Table I it is also evident that numerical evaluations with the r obtained by linearization will be much less tedious than those required to obtain r_{exact}.

From the percent difference columns of Tables II and III it is clear that the values of r by the two methods are similar (within 10-20%)

and that the difference in,r by the two methods,becomes more significant further from equilibrium. It is also apparent that the difference in r, by the two methods,increases somewhat for an increase in the "order" of the equation that has undergone linearization.

Thus we may say,for systems not far from equilibrium,that it would appear that much saving of labour may be accomplished by the use of linearization methods and without significant loss in accuracy.

SYSTEMS OF COMPETING REACTIONS

We now extend the concept of linearization to a system where we have competing reactions. For the sake of clarity and simplicity a system of two competing reactions has been chosen. The methods of solution and all manipulations are, however, quite general and would apply to a system of n competing reactions.

Let the progress variable of the two reactions be denoted by λ_1 and λ_2, and define the "lag" of a reaction as $X_s = \lambda_s - \lambda_s^e$. If we expand $\dot{\lambda}_s$ as in equation 2 we have

$$\lambda_s = (\dot{\lambda}_s)_e + \sum_\alpha (n_\alpha - n_\alpha^e) \frac{d\lambda_s}{dn_\alpha}\Big/_e \qquad (42)$$

where the subscript on λ refers to the progress variable of a particular reaction s. For a system of reactions we must write

$$dn_\alpha = \sum_s \nu_\alpha^s \, d\lambda_s$$

where the ν_α^s is the stoichiometric coefficient of species N_α in reaction s and for a system of two reactions

$$dn_\alpha = \nu_\alpha^1 \, d\lambda_1 + \nu_\alpha^2 \, d\lambda_2$$

so that

$$n_\alpha - n_\alpha^e = \nu_\alpha^1 (\lambda_1 - \lambda_1^e) + \nu_\alpha^2 (\lambda_2 - \lambda_2^e)$$

This allows equation 42 to be written for a system of two reactions as

$$\lambda_1 = \sum_\alpha [\nu_\alpha^1 (\lambda_1 - \lambda_1^e) + \nu_\alpha^2 (\lambda_2 - \lambda_2^e) \cdot \frac{d\dot{\lambda}_1}{dn_\alpha} \Big/_e$$

Defining β_{rs} as

$$\beta_{rs} = \sum_\alpha \nu_\alpha^s \frac{\partial \lambda_r}{\partial n_\alpha} \Big/_e \qquad (43)$$

we have $\dot{\lambda}_s = \sum_s \beta_{rs} (\lambda_s - \lambda_s^e)$

in general and for a system of two reactions we have

$$\dot{\lambda}_1 = \beta_{11} (\lambda_1 - \lambda_1^e) + \beta_{12} (\lambda_2 - \lambda_2^e). \quad \text{Since} \quad \dot{\lambda}_1^e = 0$$

then

$$\dot{X}_1 = \beta_{11} X_1 + \beta_{12} X_2 \qquad (44)$$

Similarly

$$\dot{X}_2 = \beta_{21} X_1 + \beta_{22} X_2 \qquad (45)$$

Taking the Laplace transforms of equations 44 and 45 we obtain

$$-X_1(0) + P\overline{X}_1 = \beta_{11}\overline{X}_1 + \beta_{12}\overline{X}_2 \quad \text{where} \quad \overline{X}_s = \int_0^\infty X_s e^{-pt}\, dt \qquad (46)$$

$$-X_2(0) + P\overline{X}_2 = \beta_{21}\overline{X}_1 + \beta_{22}\overline{X}_2 \quad \text{and} \quad X_s(0) = \lambda_s^o - \lambda_s^e = -\lambda_s^e \qquad (47)$$

For non trivial solutions we have the determinant

$$\begin{vmatrix} \beta_{11} - P & \beta_{12} \\ \beta_{21} & \beta_{22} - P \end{vmatrix} \qquad \text{with roots } P_+ \text{ and } P_-$$

where

$$P_\pm = \frac{\beta_{11} + B_{22}}{2} \pm [(\beta_{11} - \beta_{22})^2 + 4\beta_{12}\,\beta_{22}]^{1/2} \qquad (48)$$

So we can write

$$\begin{vmatrix} \beta_{11} - P & \beta_{12} \\ \beta_{21} & \beta_{22} - P \end{vmatrix} = \frac{1}{(P-P_+)(P-P_-)} = \frac{1}{(P_+-P_-)(P-P_+)} + \frac{1}{(P_-+P_+)(P-P_-)}$$

For which the inverse Laplace transforms are

$$\frac{e^{P_+ t}}{P_+ - P_-} \quad \text{and} \quad \frac{e^{P_- t}}{P_- - P_+} = - \frac{e^{P_- t}}{P_+ - P_-} \ .$$

For the solution of the "set"(equations 46 and 47)we have

$$\overline{X}_1 = \frac{\begin{vmatrix} -X_1(0) & \beta_{12} \\ -X_2(0) & \beta_{22} - P \end{vmatrix}}{\begin{vmatrix} \beta_{11} - P & \beta_{12} \\ \beta_{21} & \beta_{22} - P \end{vmatrix}} = \frac{\begin{vmatrix} -X_1(0) & \beta_{12} \\ -X_2(0) & \beta_{22} - P_+ \end{vmatrix}}{(P_+ - P_-)(P - P_+)} - \frac{\begin{vmatrix} -X_1(0) & \beta_{12} \\ -X_2(0) & \beta_{22} - P_- \end{vmatrix}}{(P_+ - P_-)(P - P_-)}$$

So that

$$X_1 = \frac{\begin{vmatrix} -X_1(0) & \beta_{12} \\ -X_2(0) & \beta_{22} - P_+ \end{vmatrix}}{(P_+ - P_-)} e^{P_+ t} - \frac{\begin{vmatrix} -X_1(0) & \beta_{12} \\ -X_2(0) & \beta_{22} - P_- \end{vmatrix}}{(P_+ - P_-)} e^{P_- t}$$

Replacing X_1 by $\lambda_1 - \lambda_1^e$ and since $X_1(0) = - \lambda_1^e$ we obtain

$$\lambda_1 = \lambda_1^e + \frac{1}{P_+ - P_-} \left\{ [(\beta_{11} - P_+) \lambda_2^e - \beta_{21} \lambda_1^e] e^{P_+ t} - [(\beta_{11} - P_-) \lambda_2^e - \beta_{21} \lambda_1^e] e^{P_- t} \right\} \quad (49)$$

and in a similar fashion we obtain

$$\lambda_2 = \lambda_2^e + \frac{1}{P_+ - P_-} \left\{ [(\beta_{11} - P_+) \lambda_2^e - \beta_{21} \lambda_1^e] e^{P_+ t} - [(\beta_{11} - P_-) \lambda_2^e - \beta_{21} \lambda_1^e] e^{P_- t} \right\} \quad (50)$$

Equation 48 can be expanded as

$$P_{\pm} = \frac{\beta_{11} + \beta_{22}}{2} \pm \frac{\beta_{11} - \beta_{22}}{2} \left[1 + \frac{\beta_{12} \beta_{21}}{(\beta_{11} - \beta_{22})^2} \right] + \ldots .$$

So that

$$P_+ \simeq \beta_{11} + \frac{\beta_{12} \ \beta_{21}}{2(\beta_{11} - \beta_{22})}$$

$$P_- \simeq \beta_{22} - \frac{\beta_{12} \ \beta_{21}}{2(\beta_{11} - \beta_{22})}$$

And we can then write, by making use of these approximations for P_+ and P_-,

$$\frac{1}{P_+ - P_-} \simeq \frac{1}{\beta_{11} - \beta_{22}} \left[1 - \frac{\beta_{12} \beta_{21}}{(\beta_{11} - \beta_{22})^2} \right] \quad (51)$$

And if we take $\frac{\beta_{12}\,\beta_{21}}{(\beta_{11} - \beta_{22})^2} << 1$

then equation 51 becomes

$$\frac{1}{P_+ - P_-} \simeq \frac{1}{\beta_{11} - \beta_{22}} \tag{52}$$

On substituting for P_+, P_- and $(P_+ - P_-)$ into equation 49 we have

$$\lambda_1 = \lambda_1^e(1-e^{P_+t}) - \frac{\lambda_2^e\ \beta_{12}}{\beta_{11}-\beta_{22}}\,(e^{P_+t}-e^{P_-t}) + \frac{\lambda_1^e\beta_{12}\beta_{21}}{2(\beta_{11}-\beta_{22})^2}(e^{P_+t}-e^{P_-t}) \tag{53}$$

If $\frac{\beta_{12}\,\beta_{21}}{(\beta_{11} - \beta_{22})^2}$ is taken as small,compared to the first two terms,we have

$$\lambda_1 = \lambda_1^e\ (1 - e^{P_+t}) - \frac{\lambda_2^e\ \beta_{12}}{\beta_{11} - \beta_{22}}\ (e^{P_+t} - e^{P_-t}) \tag{54}$$

and similarly for λ_2 we have

$$\lambda_2 = \lambda_2^e\ (1 - e^{P_-t}) - \frac{\lambda_1^e\ \beta_{21}}{\beta_{11} - \beta_{22}}\ (e^{P_+t} - e^{P_-t}) \tag{55}$$

Equations 54 and 55 give the extent of each reaction and could be used to determine the concentration of any component in the system at any time t not far from equilibrium. For any chemical species N_α we may write

$$dn_\alpha = \nu_\alpha^1\, d\,\lambda_1 + \nu_\alpha^2\, d\,\lambda_2$$

so that

$$n_\alpha = n_\alpha^o + \nu_\alpha^1\,\lambda_1 + \nu_\alpha^2\ \lambda_2 \tag{56}$$

Suppose we were interested in knowing the effect of a change in temperature on the yield at time t. We insert equations 54 and 55 into equation 56 and on differentiating one obtains

$$\frac{dn_\alpha}{dT} = \nu_\alpha^1\,\frac{d\lambda_1}{dT} + \nu_\alpha^2\ \frac{d\,\lambda_2}{dT}$$

$$= (1-e^{P_+t})\frac{d\lambda_1^e}{dT} - te^{P_+t}\lambda_1^e\frac{dP_+}{dT} - \frac{\lambda_2^e\ \beta_{12}}{\beta_{11}-\beta_{22}}\left[te^{P_+t}\frac{dP_+}{dT} - te^{P_-t}\frac{dP_-}{dT}\right]$$

$$+(e^{P_+t}-e^{P_-t})\left[\lambda_2^e\frac{\beta_{11}-\beta_{22}}{(\beta_{11}-\beta_{22})^2}\frac{d\beta_{12}}{dT} - \frac{\lambda_2^e\ \beta_{12}}{(\beta_{11}-\beta_{22})^2}\left(\frac{d\beta_{11}}{dT} - \frac{d\beta_{22}}{dT}\right) + \frac{\beta_{12}}{\beta_{11}-\beta_{22}}\frac{d\lambda_2^e}{dT}\right] \quad (57)$$

Equation 57 appears rather awkward and further substitutions and manipulations have failed to improve it. Thus it appears that even with the approximations made in leading up to equations 54 and 55, that their use in calculating the effect of a change in a parameter, such as temperature, leads to rather unwieldy equations such as equation 57. The equations are workable but still so cumbersome that the extension of linearization methods, to the problem of a change in a variable for a system of competing reactions, has not led to readily applicable equations.

OTHER ASPECTS

In this section we point out that certain other questions, not considered in the first two sections, may be answered about the system with the aid of the methods already developed.

Suppose we are interested in knowing the effect a change in temperature would have on the time required for a system to reach ninety percent of its equilibrium state. From equation 4 we have $t = -\tau \ln(1-\lambda/\lambda^e)$ but for these considerations we have fixed $\lambda/\lambda^e = 0.9$ as a constant. Taking the derivative we have the answer sought as

$$\frac{dt}{dT} = -\ln(1-\lambda/\lambda^e)\frac{d\tau}{dT} = -\ln(1-\lambda/\lambda^e)\quad\frac{d\ln\tau}{dT}$$

For the reaction $N_1 + N_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} N_3$ in a closed vessel, we can quite easily obtain the effect that a change in initial concentration of $N_1 = N_2 = a$ would have on the yield, near for example ninety percent of equilibrium, compared to the effect of a similar change on the equilibrium yield. In a manner similar to that employed for equation 19, one can obtain $\frac{1}{\tau} = \frac{k_1 \rho}{K}$ for this reaction, where $\rho^2 = 1 + 4aK$, and subsequently $\frac{d \ln {}^1/\tau}{da} = \frac{2K}{\rho}$. Similarly we can obtain $\frac{d \ln \lambda^e}{da} = \frac{1 - {}^1/\rho}{a + \frac{K}{2} - \frac{\rho}{2K}}$ and on insertion of these equations into equation 9 we obtain

$$\frac{dn_\zeta/da}{dn_\zeta^e/da} = f - (1 - f) \cdot [\ln (1 - f)] \cdot \left[\frac{\frac{2Ka}{\rho} + \frac{1}{\rho} - 1}{1 - \frac{1}{\rho}} \right]$$

These two examples should demonstrate the ease with which various other questions concerning a chemical system may be answered when linearization methods are employed.

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II

EQUILIBRIUM PRESSURES AND PHASE COMPOSITIONS FOR NON-IDEAL MIXTURES

INTRODUCTION

A good deal of effort has been expended in the past few years in developing equations equal to the task of describing the equilibrium pressure, temperature and composition relations for non-ideal mixtures. Contributors prominent in this field have been Clark, whose equations relate liquid and vapour composition; Hirata, whose equations express the liquid-vapour relation as three straight line segments; and Redlich and Kister, whose equations describe the ratios of activity coefficients. Such equations have been successful in the sense that they predict correct results with varying degrees of accuracy. However, all have involved the determination of a number of empirical constants and consequently have required much experimental data on the mixtures.

Since the necessity for determining much experimental data in part nullifies the usefulness of these equations it would be worthwhile to develop a method employing only the readily available pure component data and fewer empirical parameters. Such an equation will not be expected to be as exact but since all the required data are available or readily determined analytically it should prove useful.

In this section an expression is derived for the equilibrium total pressure over a liquid mixture. In addition partial pressures and phase compositions may be calculated from the equation. To obtain the equation, conformal solution theory is applied to the liquid phase and a second order virial equation is employed in the description of the gas phase.

DEVELOPMENT AND METHOD

We let the equation of state for the gas phase be given by

$$\frac{PV}{RT} = 1 + \frac{P}{RT}\left[\sum_i \sum_j y_i \; y_j \; B_{ij}\right] \tag{1}$$

where: P is the total pressure over the liquid phase; y_i, i ... n, is the mole fraction of species N_i in the gas phase.

: B_{ij} is the second virial coefficient for the interaction of chemical species N_i and N_j in the gas phase.

From equation 1 we have the partial molar volume $\overline{V}_k$ of species N_k given by

$$\overline{V}_k = RT + \sum_i \sum_j y_i y_j \left[B_{ik} - B_{ij} + B_{jk}\right] \tag{2}$$

Taking

$$\frac{\partial \ln f_k}{\partial P} = \frac{\overline{V}_k}{RT} \tag{3}$$

one obtains

$$f_k^{(g)P} = y_k \; P \exp\left[\frac{P}{RT} \sum_i \sum_j y_i y_j \left(B_{ik} - B_{ij} + B_{jk}\right)\right] \tag{4}$$

in which $f_k^{(g)P}$ is the fugacity of species N_k in the mixture of gases at a total pressure of P and mole fraction y_k.

For the liquid phase, we express the fugacity f_k (l) of species N_k in the liquid mixture by the relation

$$f_k^{(l)} = x_k \; \gamma_k \; f_k^{(l)ref.} \tag{5}$$

where; x_k = mole fraction of N_k in the liquid phase.

: $f_k^{(l)ref.}$ = the fugacity of species N_k in some reference state.

: γ_k = is the activity coefficient.

For the vapour and liquid in equilibrium, at the same temperature and pressure, we may equate the fugacities as

$$f_k^{(l)} = f_k^{(g)} \tag{6}$$

Substituting equations 4 and 5 into equation 6 we have

$$\ln x_k + \ln \gamma_k + \ln f_k^{(l)\mathrm{ref.}} = \ln P y_k + \frac{P}{RT} \sum_i \sum_j y_i y_j \left(B_{ik} - B_{ij} + B_{jk}\right) \tag{7}$$

We select as the reference state, for $f_k^{(l)\mathrm{ref.}}$, the pure liquid of species N_k at the same temperature and pressure as the mixture so that

$$f_k^{(l)\mathrm{ref.}} \equiv f_k^{o(l)P} \tag{8}$$

And

$$\ln f_k^{o(l)P} = \ln f_k^{o(l)P''_k} + \frac{V_k^{o(l)}}{RT} \cdot \int_{P''_k}^{P} dP$$

in which $f_k^{o(l)P''_k}$ represents the fugacity of species N_k at a pressure P''_k, where P''_k is the vapour pressure of pure species at the same temperature as the mixture. $V_k^{o(l)}$ is the average molar volume of N_k over the interval P to P''_k. Since we know

$$f_k^{o(l)P''_k} = f_k^{o(g)P''_k}$$

and

$$f_k^{o(g)P''_k} = P''_k \exp\left(\frac{P''_k}{RT} B_k\right)$$

$$\ln f_k^{(l)\mathrm{ref.}} = \ln P''_k + \frac{P''_k B_k}{RT} + \frac{V_k^{o(l)}}{RT}\left(P - P''_k\right) \tag{9}$$

To obtain an expression for γ_k we resort to conformal solution theory (1,2), and use the expression from reference 2

$$\ln \gamma_k = \frac{E_o}{RT}\left[\sum_i x_i d_{ik} - \sum_{i<j} x_i x_j d_{ij} \right] \tag{10}$$

Insertion of equations 9 and 10 into equation 7 leads to the required equation

$$Py_k = P_k'' x_k \left[e^{-\frac{P}{RT} \sum_i \sum_j y_i y_j D_{ijk}} \right] \cdot \left[e^{\frac{-(P-P_k'')(B_k - V_k^{o(l)})}{RT}} \right] \cdot$$

$$\left[e^{\frac{E_o}{RT} \left(\sum_i x_i d_{ik} - \sum_{i<j} x_i x_j d_{ij} \right)} \right] \quad (11)$$

In equation 11 we have used the following notation:

$$\Delta_{ij} = B_{ij} - \frac{B_{ii} + B_{jj}}{2} \quad (12)$$

$$D_{ijk} = \Delta_{ik} - \Delta_{ij} + \Delta_{jk} = B_{ik} - B_{ij} + B_{jk} - B_{kk} \quad (13)$$

$$d_{ij} = 2f_{ij} - (f_{ii} + f_{jj}) \quad (14)$$

$$d_{ik} = 2f_{ik} - (f_{ii} + f_{jj}) \quad (15)$$

The significance of the first two parameters, which are defined by equations 12 and 13, is clear and we see that the term in D_{ijk} attempts to correct for the mixing imperfections of the gas phase. Although a more complete description of the significance of the parameter d_{12} is available (1,2) we can, for the purposes of this section, consider d_{ij} as performing the same function for the liquid phase as D_{ijk} did for the gas. E_o is the configurational energy of the reference species used in defining d_{ij}. For convenience, we may think of the first and last exponential terms as accounting for imperfections due to mixing of the liquid and gas phases respectively. The middle term is not due to mixing but rather to the pure components.

For binary systems equation 11 simplifies considerably to

$$P = P_k'' \frac{x_k}{y_k} \left[e^{\frac{-2P(1-y_k)^2}{RT} \Delta_{12}} \right] \cdot \left[e^{\frac{-(P-P_k'')(B_k - V_k^{o(1)})}{RT}} \right] \cdot \left[e^{\frac{E_o}{RT} (1-x_k)^2 d_{12}} \right] \quad (16)$$

To apply equation 16 to any system we require values for Δ_{12}, P_k'', B_k,

$\overset{o}{V}{}_k^{(1)}$, E_o and d_{12} and in line with the ideas stated earlier, we have tried to obtain the required data primarily from the more readily available pure component data. The proposed sources and methods for obtaining the data are outlined below.

The vapour pressure P_k'' of most compounds is tabulated at various temperatures in appropriate handbooks or in reference tables such as Jordan's tables (3). In order to obtain the average molar volume $V_k^{o(1)}$ we follow the procedure outlined by Fried and Vilim (7). This procedure, based on theory of corresponding states as modified by Watson (5,6), is valid for $T_r < 0.8$ and is reasonably accurate. The virial coefficients B_k may be obtained from the literature. However, since this limits the applicability of equation 16 to the temperature ranges covered by the experiment, we have used a Lennard-Jones potential and the force constants tabulated in Tables IA and IB, pp. 1110 in reference (8). Similarly in calculating the B_{12} for Δ_{12}, we have used the Lennard-Jones potentials and have assumed applicability of the combining rules (8)

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)$$

$$\epsilon_{ij} = (\epsilon_i \cdot \epsilon_j)^{1/2}$$

The conformal solution interaction parameter d_{ij} may be found tabulated in the literature (1,2) or calculated from experimental data as described by reference (1). In the calculations herein, only systems for which d_{ij} is tabulated are considered. The configurational energy E_o may be obtained by the equation (4)

$$E_o = \frac{-1}{V_o^{(g)}} RT^2 \frac{\partial B_0(T)}{\partial T} - \Delta H_o + P\,(V_o^{(g)} - V_o^{(1)}) \qquad (17)$$

where the Δ refers to the change of the reference species from liquid to vapour. This equation can easily be derived (4) with the aid of thermodynamics and the statements

$$E_o = E_o^{(l)} = E_o^{(g)} - \Delta E_o$$

$$\Delta E_o = \Delta H_o - P \Delta V_o$$

and the virial equation of state for the pure gas given earlier.

The data so obtained is given in Tables I and II.

APPLICATIONS AND DISCUSSION

In equation 16 we have already pointed out that the exponential is the sum of three different terms namely the corrections to the liquid, to the gas and to the pure components. At lower temperatures and pressures (i.e. at the boiling temperatures near one atmosphere) the terms in Δ_{12} and for the pure components may be small in comparison with the term in d_{12}. In such a case equation 16 can be approximated by

$$P \simeq P_k'' \frac{x_k}{y_k} \cdot \exp \left[\frac{E_o}{RT} (1 - x_k)^2 d_{12} \right] \tag{18}$$

This equation, which corrects only for the liquid imperfections, is readily solved (i.e. it is not a transcendental equation when x_k and T are the independent variables). A less drastic approximation is valid when Δ_{12} is much smaller than either d_{12} or the Poynting term for the pure components. In this case we may write

$$P \simeq P_k'' \frac{x_k}{y_k} \cdot \exp \left[\frac{E_o}{RT} (1 - x_k)^2 d_{12} - \frac{(P - P_k'')(B_k - \overset{\circ(l)}{V_k})}{RT} \right] \tag{19}$$

This latter approximation is valid for certain systems at higher temperatures and pressures and we may consider it as adequately correcting for both the gas and liquid imperfections.

The systems indicated in Table II have been selected to test the accuracy of the results predicted by equations 18 and 19. The selection of these systems is based on the availability of experimental data with which to compare the calculated results. The choice is limited at higher temperatures and pressures because of the lack of experimental data. Calculated and experimental values are tabulated and compared in the Tables III through VII and the figures I through VI.

From the Tables III and IV it is seen that the maximum deviation of the calculated from the experimental is about 5%. Also it is evident that of the order of 85% of the deviation from ideality is predicted by equation 18. Although it was known that conformal solution theory is not too satisfactory for the Benzene-Cyclohexane system,the system was nevertheless selected since experimental data was available. Table V thus only bears out the known fact that the conformal solution parameter $d_{12} = - 0.065$ does not give satisfactory results. If d_{12} is adjusted to give a best fit of the experimental data,as in Table VI,then one can use this adjusted d_{12} at other temperatures and pressures. In Table VII we have the pressures calculated by equations 18 and 19 using the different values of d_{12}. It is clear from Table VII and the accompanying figures V and VI that if the conformal solution is adjusted at a given temperature then the parameter applies equally well at another temperature. It is also evident that the vapour phase contributions are significant being about 25% of the total correction. Again experimental and calculated results agree to within about 5%.

Pure Substance Data Table I

Symbol	T °K	P'' atmos.	Δ H Kcal/ mole	$-E_0$ Kcal/ mole	-B l/mole	T_c °K	P_c atmos.	$\overset{\circ}{V}(1)$ liters
CS_2	308.4	0.674						
$(CH_3)_2CO$	308.4	0.453	7.41	6.80				
$CHCl_3$	293.2	0.215	7.498	6.917				
CS_2	293.2	0.399						
$C_yC_6H_{12}$	313.0	0.243			0.770	554.2	40.4	0.115
ØH	313.0	0.239	7.86	7.14	0.850	561.7	41.7	0.095
$C_yC_6H_{12}$	475.5	13.4			0.355	554.2	40.4	0.143
ØH	475.5	14.4	5.325	4.754	0.408	561.7	47.7	0.115

System Data Table II

Numbers in parentheses are literature references

System	Temp °K	$-B_{12}$ l/mole	Δ_{12} l/mole	$-d_{12}$ (are from lit.)	$-d_{12}$ adjusted for fit at (T_1)	T_1 °K
$CS_2/(CH_3)_2CO$	308.4			0.130 (2)		
$CS_2/CHCl_3$	293.2			0.054 (2)		
ØH/$C_yC_6H_{12}$	313.0			0.065 (1)	0.0426	313
ØH/$C_yC_6H_{12}$	475.5	0.388	0.007	0.065 (1)	0.0426	313

Calculated Results Compared to Experimental Results

System: Carbon disulphide/Acetone

Table III

Temp: 308.4°K

d_{12}: - 0.130

Exptl. data: Ref. (14)

Mole fraction CS_2 in liquid	Total Pressure atmos.		Partial Pressures (atmos.)				Vapour Composition, Mole Fraction CS_2	
			CS_2		Acetone			
	Exptl.	Calc.	Exptl.	Calc.	Exptl.	Calc.	Exptl.	Calc.
0	0.453	0.453	0	0	0.453	0.453	0	0
0.2	0.750	0.725	0.368	0.341	0.382	0.384	0.50	0.469
0.4	0.833	0.797	0.497	0.454	0.335	0.343	0.59	0.569
0.5	0.862	0.809	0.55	0.484		0.325		0.598
0.6	0.862	0.815	0.559	0.510	0.303	0.305	0.62	0.625
0.8	0.857	0.800	0.605	0.571	0.250	0.229	0.70	0.714
1.0	0.674	0.674	0.674	0.674	0	0	1.0	1.0

System: Carbon disulphide/Chloroform

Table IV

Temp: 293.2°K

d_{12}: -0.054

Exptl. Data: Ref. (15)

Mole fraction CS_2 in liquid	Total Pressure atmos.		Partial Pressures (atmos.)				Vapour Composition, Mole Fraction CS_2	
	Exptl.	Calc.	$CHCl_3$		CS_2		Exptl.	Calc.
			Exptl.	Calc.	Exptl.	Calc.		
0	0.215	0.215	0.215	0.215	0	0	0	0
0.2	0.285	0.297	0.180	0.176	0.103	0.120	0.42	0.41
0.4	0.332	0.344	0.143	0.143	0.190	0.201	0.60	0.59
0.5	0.350	0.361	0.125	0.126	0.225	0.234	0.66	0.65
0.6	0.365	0.371	0.103	0.108	0.260	0.265	0.072	0.71
0.7	0.375	0.384	0.083	0.088	0.293	0.296	0.78	0.77
0.8	0.385	0.392	0.060	0.065	0.325	0.327	0.83	0.83
1.0	0.399	0.399	0	0	0.399	0.399	1	1

System: Benzene/Cyclohexane Table V

Temp: 313°

d_{12}: - 0.065

Exptl. Data: Ref. (13)

Mole fraction Benzene in liquid	Total Pressure (atmos.)		Partial Pressures (atmos.)				Vapour Composition, Mole Fraction CS_2	
			Benzene		Cyclohexane			
	Exptl.	Calc.	Exptl.	Calc.	Exptl.	Calc.	Exptl.	Calc.
0	0.243	0.243		0		0.243	0	0
0.2	0.262	0.277		0.077		0.200	0.245	0.277
0.4	0.271	0.290		0.125		0.164	0.430	0.432
0.5	0.272	0.291		0.144		0.146	0.500	0.497
0.6	0.271	0.298		0.162		0.127	0.570	0.560
0.8	0.262	0.276		0.197		0.078	0.740	0.715
1.0	0.239	0.239		0.239		0	1.0	1.0

System: Benzene/Cyclohexane

Table VI

Temp: 313°

d_{12}: - 0.0426

Exptl. Data: Ref. (13)

Mole fraction Benzene in liquid	Total Pressure (atmos.)		Partial Pressures (atmos.)				Vapour Composition, Mole Fraction Benzene	
			Benzene		Cyclohexane			
	Exptl.	Calc.	Exptl.	Calc.	Exptl.	Calc.	Exptl.	Calc.
0	0.243	0.243		0		0.243	0	0
0.2	0.262	0.262		0.067		0.196	0.245	0.250
0.4	0.271	0.272		0.114		0.158	0.430	0.420
0.5	0.272	0.273		0.135		0.137	0.500	0.496
0.6	0.271	0.2715		0.155		0.116	0.570	0.572
0.8	0.262	0.262		0.193		0.066	0.740	0.744
1.0	0.239	0.239				0	1.0	1

System: Benzene/Cyclohexane

Table VII

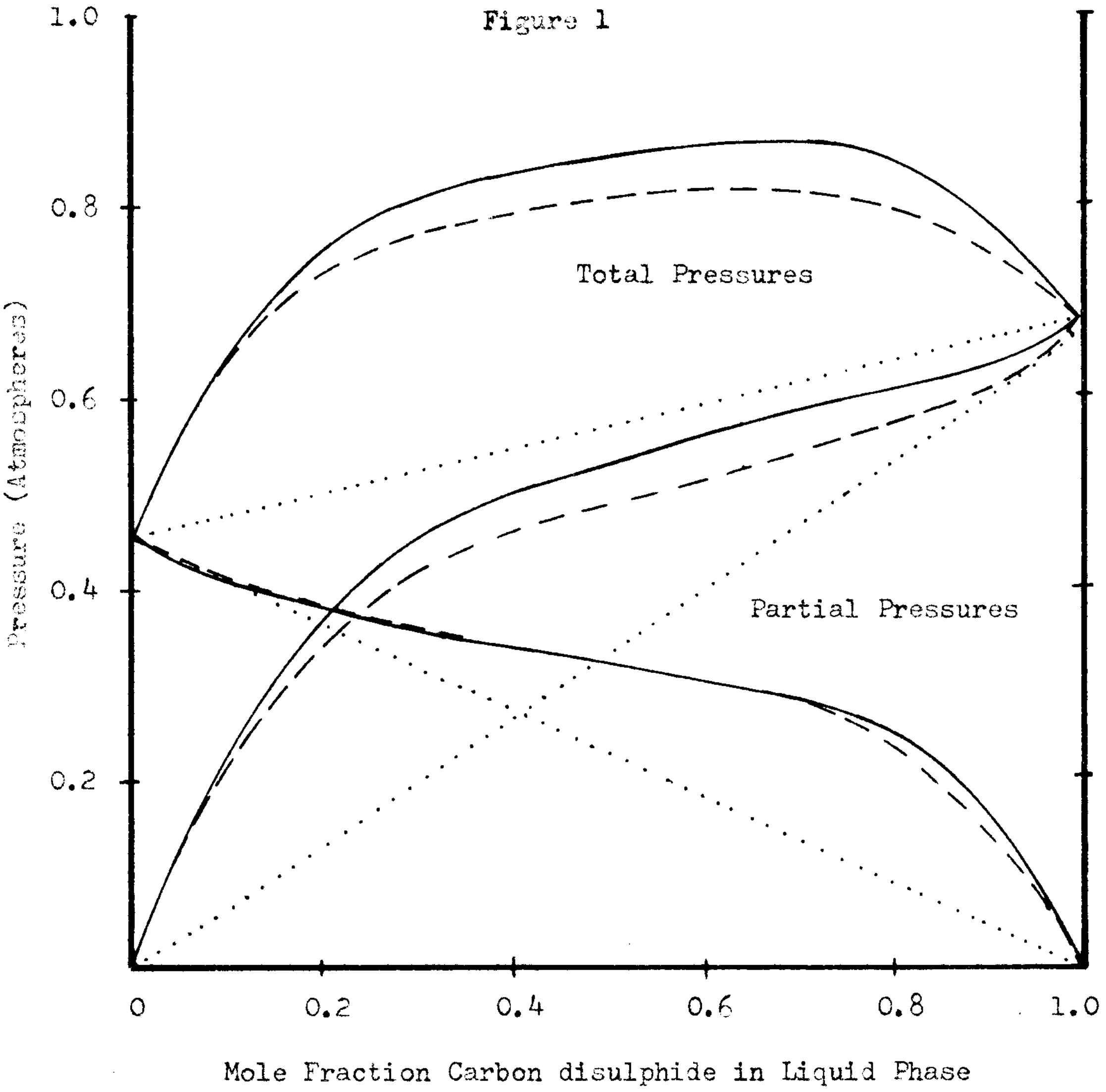
Temp: 475.5°K

d_{12}: - 0.065 (literature ave.) and d_{12} = - 0.0426 (adjusted)

Exptl. Data: Ref. (12)

Mole Fraction Benzene in Liquid	Exptl. Total Pressure (atmos.)	Calculated Total Pressure for d_{12} = - 0.065 (atmos.)		Calculated Total Pressure for d_{12} = - 0.0426 (atmos.)	
		Corrected for liquid imperfections	Corrected for gas and liquid imperfections	Corrected for liquid imperfections	Corrected for gas and liquid imperfections
0	13.40	13.40	13.40	13.40	13.40
0.2	14.20	14.41	14.59	14.12	14.22
0.4	14.70	14.91	15.17	14.545	14.71
0.5	14.80	15.04		14.67	14.85
0.6	14.96	15.14	15.42	14.73	14.90
0.7	15.00	15.10		14.745	14.90
0.8	14.97	14.98	15.18	14.70	14.82
1.0	14.40	14.40	14.40	14.40	14.40

Figure 1



Total Pressure and Partial Pressures over a Liquid Mixture of Carbon disulphide and Acetone

Legend

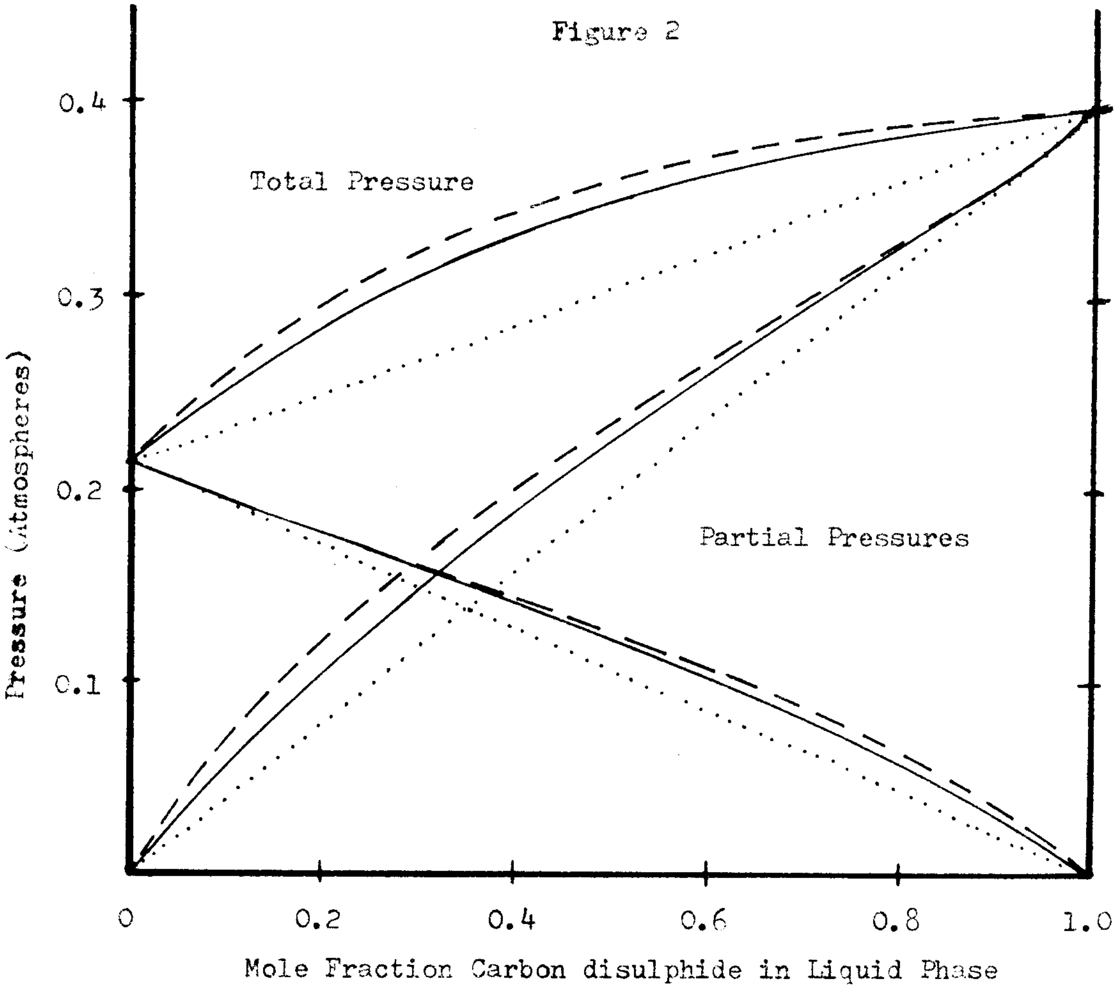
Temperature 308°K

Experimental Pressures ————————

Calculated Pressures — — — — —

Raoults Law (ideal) Pressure ....

Figure 2



Total Pressure and Partial Pressures over a Liquid Mixture of Carbon disulphide and Chloroform

Legend

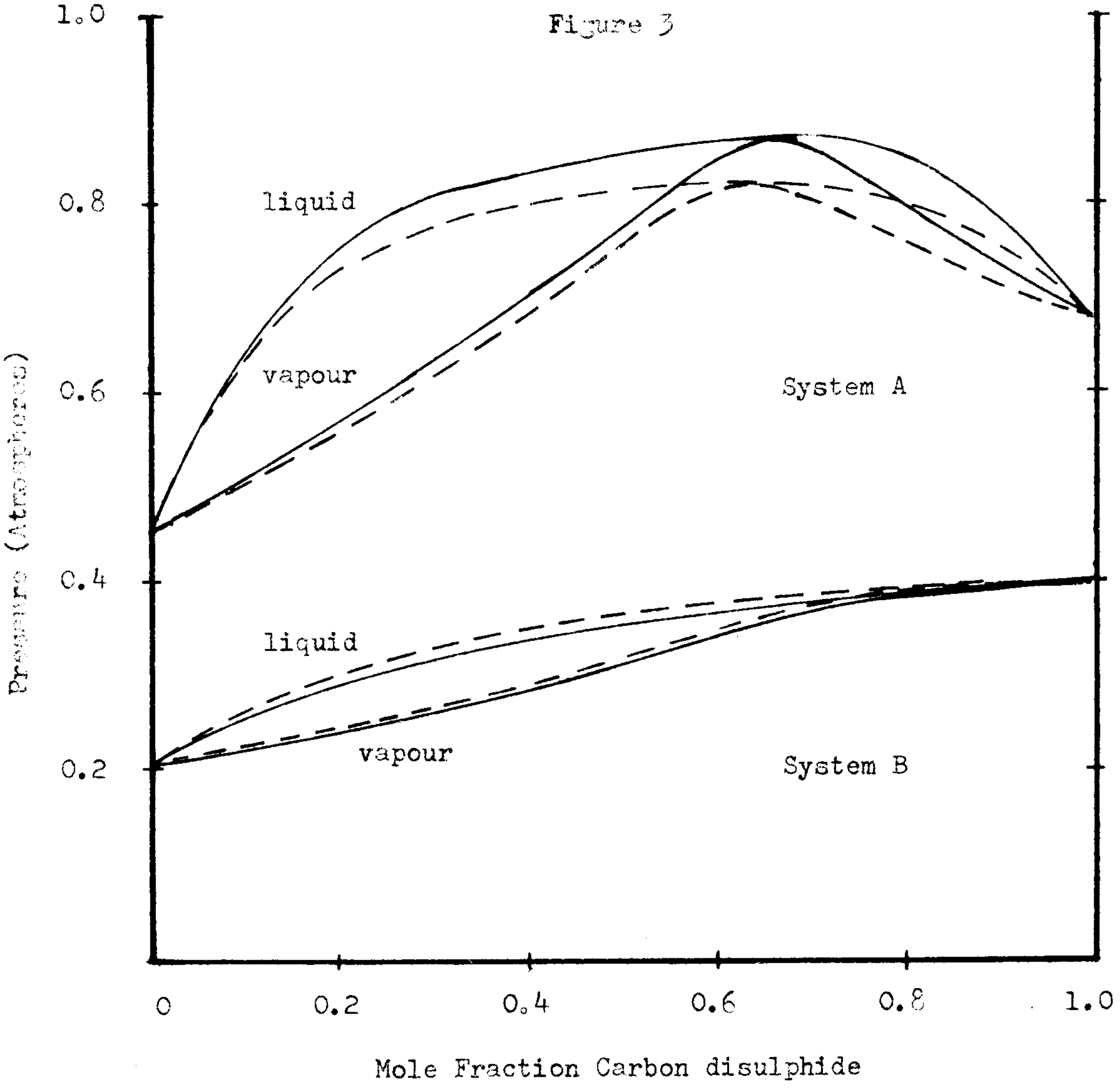
Temperature 293.2°K

Experimental Pressures ————————

Calculated Pressures — — — — — — — —

Raoults Law (ideal) Pressures · · · · · · · · · · · · · ·

Figure 3



Composition of Liquid and Vapour Phases for a Given Temperature and Pressure

Legend

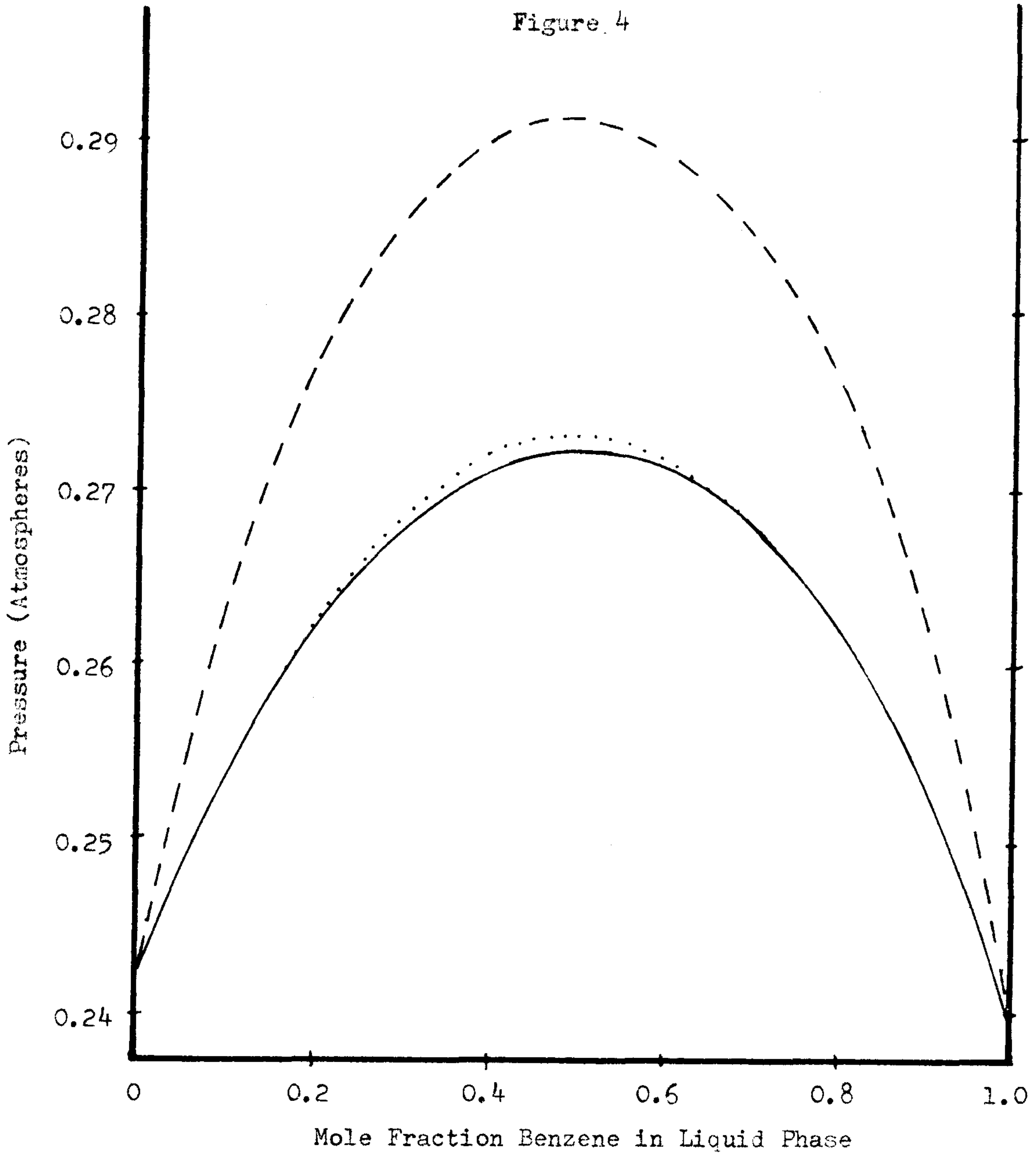
System A (upper)
    Carbon disulphide and Acetone
    Temperature 308.4°K

System B (lower)
    Carbon disulphide and Chloroform
    Temperature 293.2°K

Experimental Pressure ————————

Calculated Pressure — — — — — —

Figure 4



<u>Total Pressure over a Liquid Mixture of Benzene and Cyclohexane</u>

<u>Legend</u>

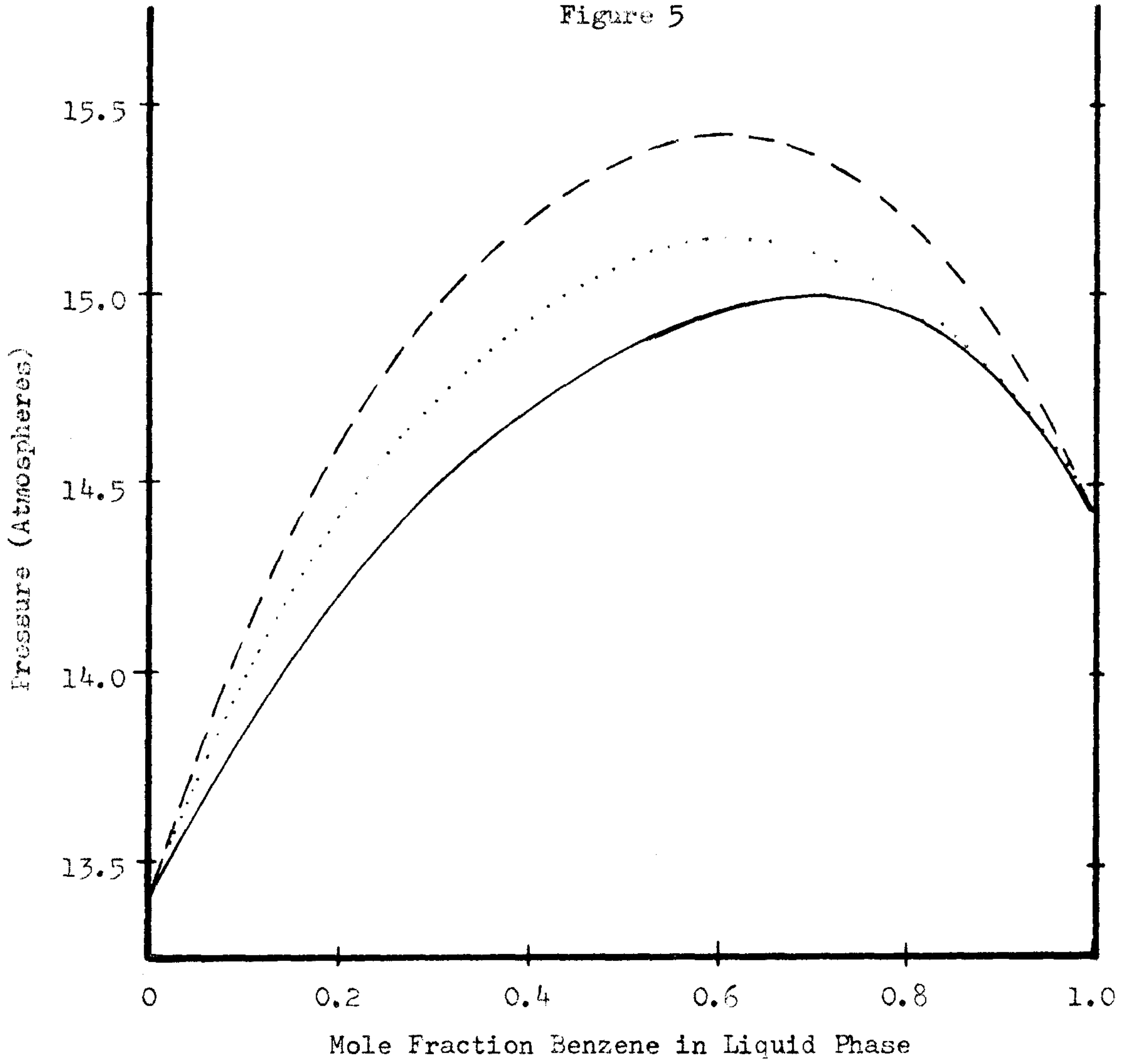
Temperature 313°K

Experimental results ————————

Corrections for liquid with d_{12} = - 0.065 — — — — — — —

Corrections for liquid with d_{12} = - 0.0426 . . . .

Figure 5



<u>Total Pressure over a Liquid Mixture of Benzene and Cyclohexane</u>

Legend

Temperature 475.5°K

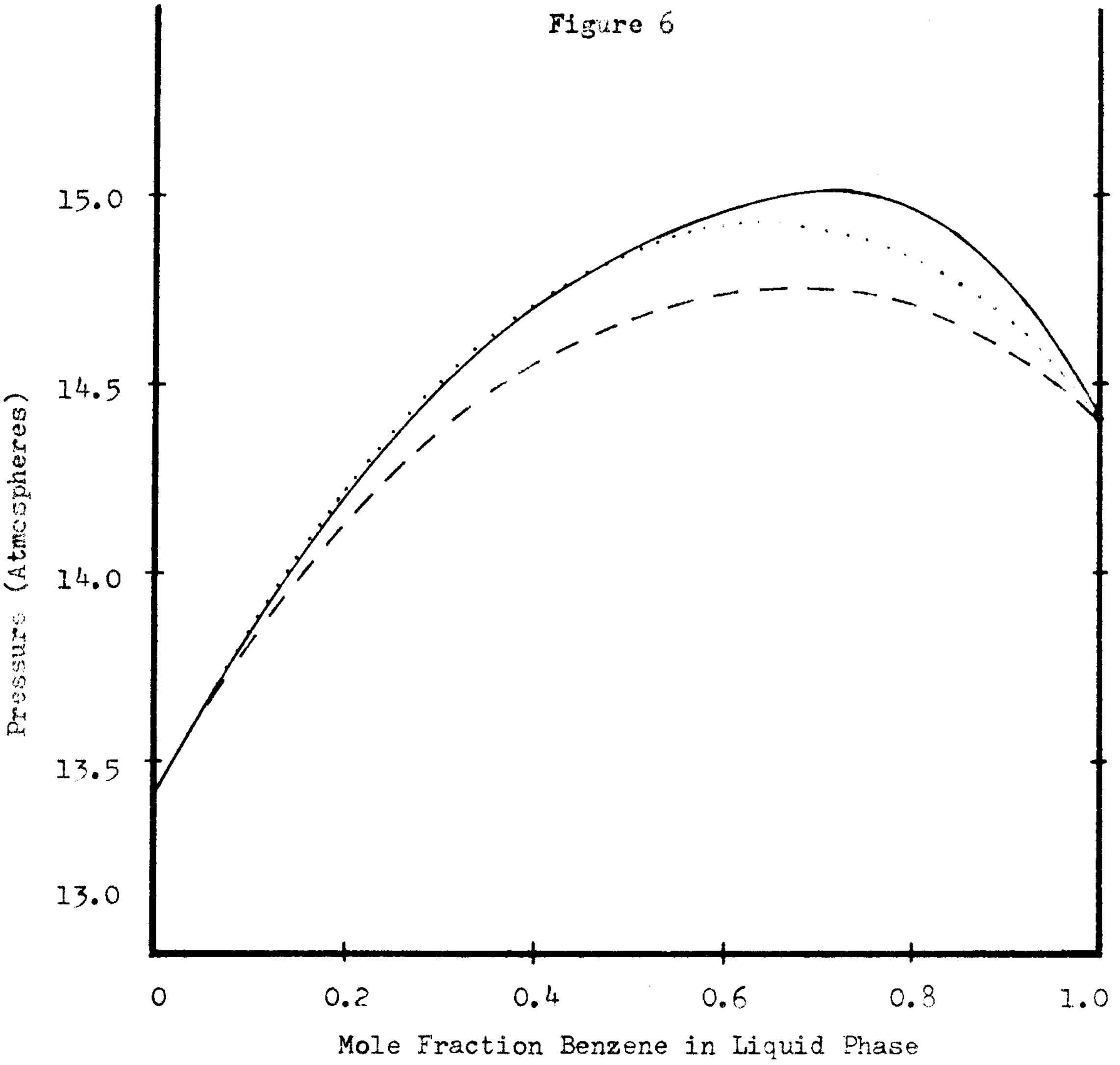
$d_{12} = -0.065$

Experimental ————————

Corrections for liquid only · · · · · · · · · · · · · ·

Corrections for both gas and liquid — — — — — —

Figure 6



Total Pressure over a Liquid Mixture of Benzene and Cyclohexane

Legend

Temperature 475.5°K

$d_{12} = - 0.0426$

Experimental results ————————

Corrections for liquid only — — — — — —

Corrections for both gas and liquid ....

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