

CHAPTER 4DISCUSSION4.1 THERMODYNAMIC RELATIONSHIPS

Of interest are the changes in the thermodynamic functions (for example, the Gibbs free energy, enthalpy, entropy and volume), which occur on mixing two components. These thermodynamic functions of mixing are given by the following equations:

$$\Delta G^m = G(P, T, x_2) - x_1 G_1^o(P, T) - x_2 G_2^o(P, T)$$

$$\Delta S^m = S - x_1 S_1^o - x_2 S_2^o$$

$$\Delta H^m = H - x_1 H_1^o - x_2 H_2^o$$

$$\Delta V^m = V - x_1 V_1^o - x_2 V_2^o$$

The temperature and pressure are considered constant and the index "o" refers to the pure components. The meaning of the symbols and the subscripts are given in the glossary. From a practical point of view it is more convenient to consider the thermodynamic excess functions of mixing which are defined as the differences between the thermodynamic functions of mixing for an actual solution and the values calculated for an ideal solution.

An ideal solution is one where the Gibbs free energy of mixing is given by,

$$\Delta G^m = RTx_1 \ln x_1 + RTx_2 \ln x_2 \quad \dots \quad (4.1.1)$$

As the mixing functions are related by the following equations,

$$\Delta S^m = - \partial \Delta G^m / \partial T \quad \dots \quad (4.1.2)$$

$$\Delta H^m = - T^2 \partial \left(\frac{\Delta G^m}{T} \right) / \partial T \quad \dots \quad (4.1.3)$$

$$\Delta V^m = \partial \Delta G^m / \partial p \quad \dots \quad (4.1.4)$$

it follows that the enthalpy and volume of mixing are zero for an ideal solution but the entropy of mixing is given by,

$$\Delta S^m = - R x_1 \ln x_1 - R x_2 \ln x_2 \quad \dots \quad (4.1.5)$$

For a real solution, the mixing functions are given in terms of the activity coefficients of the two species, f_1 and f_2 respectively,

$$\Delta G^m = RT x_1 \ln f_1 x_1 + RT x_2 \ln f_2 x_2 \quad \dots \quad (4.1.6)$$

$$\begin{aligned} \Delta S^m = & - R x_1 \ln f_1 x_1 - R x_2 \ln f_2 x_2 - x_1 RT \partial \ln f_1 / \partial T \\ & - x_2 RT \partial \ln f_2 / \partial T \quad \dots \quad (4.1.7) \end{aligned}$$

$$\Delta H^m = - x_1 RT^2 \partial \ln f_1 / \partial T - x_2 RT^2 \partial \ln f_2 / \partial T \quad \dots \quad (4.1.8)$$

$$\Delta V^m = - x_1 RT \partial \ln f_1 / \partial p - x_2 RT \partial \ln f_2 / \partial p \quad \dots \quad (4.1.9)$$

The excess thermodynamic functions then become,

$$G^E = RT x_1 \ln f_1 + RT x_2 \ln f_2 \quad \dots \quad (4.1.10)$$

$$\begin{aligned} S^E = & - R x_1 \ln f_1 - R x_2 \ln f_2 - x_1 RT \partial \ln f_1 / \partial T \\ & - x_2 RT \partial \ln f_2 / \partial T \quad \dots \quad (4.1.11) \end{aligned}$$

$$H^E = \Delta H^m \quad \dots \quad (4.1.12)$$

$$V^E = \Delta V^m \quad \dots \quad (4.1.13)$$

$$G^E = H^E - TS^E \quad \dots \quad (4.1.14)$$

It is convenient to define partial molar excess thermodynamic quantities and these are given, for component one, by,

$$\bar{G}_1^E = RT \ln f_1 \quad \dots \quad (4.1.15)$$

$$\begin{aligned} \bar{H}_1^E &= -RT^2 \partial \ln f_1 / \partial T \quad \dots \quad (4.1.16) \\ &= -R \partial \ln f_1 / \partial (1/T) \end{aligned}$$

$$\bar{S}_1^E = -R \ln f_1 - RT \partial \ln f_1 / \partial T \quad \dots \quad (4.1.17)$$

and are related to the excess functions by the general equation

$$X^E = x_1 \bar{X}_1^E + x_2 \bar{X}_2^E \quad \dots \quad (4.1.18)$$

Further, for a two component mixture the activity coefficients and the partial molar excess functions for one component are related to those of the other component by the Gibbs-Duhem equation having the general form,

$$x_1 (\partial \bar{X}_1^E / \partial x_2) + x_2 (\partial \bar{X}_2^E / \partial x_2) = 0 \quad \dots \quad (4.1.19)$$

$$x_1 (\partial \ln f_1 / \partial x_2) + x_2 (\partial \ln f_2 / \partial x_2) = 0 \quad \dots \quad (4.1.20)$$

The following relationships between the total and partial excess functions hold:

$$\bar{X}_1^E = X^E - x_2 (\partial X^E / \partial x_2) \quad \dots \quad (4.1.21)$$

$$\bar{X}_2^E = X^E + x_1 (\partial X^E / \partial x_2) \quad \dots \quad (4.1.22)$$

100.

$$\bar{x}_1^E = - \int_0^{x_2} (x_2/x_1) d(\bar{x}_2^E) \quad \dots (4.1.23)$$

and

$$\ln f_1 = - \int_0^{x_2} (x_2/x_1) d(\ln f_2) \quad \dots (4.1.24)$$

Experimentally, the variation of the activity coefficient of the volatile component (component 2) with temperature was measured at various mole fractions. By applying equations (4.1.15) - (4.1.24) to these results all the partial molar excess and total excess thermodynamic quantities previously described, with the exception of the excess volume, may be calculated.

OMCTS - benzene

For this system plots of $\ln f_2$ against $1/T$, at rounded mole fractions, were found to be linear, within experimental error, indicating that the excess enthalpy and excess entropy were independent of temperature.

The excess functions derived from the experimental measurements are given in the following tables. It should be noted that the nearly ideal behaviour of this system is a result of a cancellation of relatively large enthalpy and entropy terms. The excess Gibbs free energy calculated from equation (4.1.10) and equation (4.1.14) agree, (compare Tables 4.1.1 and 4.1.3), indicating that the derived quantities are consistent. Both the excess Gibbs free energy and the excess enthalpy are positive for this system.

OMCTS - carbon tetrachloride

Plots of $\ln f_2$ against $1/T$ were not linear, indicating that either the excess enthalpy is slightly temperature dependent or the results are not accurate enough to warrant close analysis. The enthalpy term is small compared with the benzene system so that the large negative activity coefficients result from a predominating entropy term. The activity data at 45°, 55° and 60°C, being almost linear with $1/T$, has been analysed to derive the excess thermodynamic functions but it should be noted that these may be in error. Any conclusions made for this system must be tentative until enthalpy of mixing results become available. For this system, the excess enthalpy and entropy are positive, with a maximum at $x_1 = .4$, and the excess Gibbs free energy is negative. The variation of the excess functions with concentration are shown in Figs. 4.1.1 - 4.1.6.

Note that in all the tables in this chapter the entropy is expressed in the dimensionless units of S/R and the enthalpy and energy are expressed in calories mole⁻¹.

TABLE 4.1.1

Activity Coefficients and Excess Gibbs Free EnergyOMCTS (1) - C₆H₆ (2)

	x_1	$\ln f_1$	$\ln f_2$	G^E
<u>25°C</u>	.1	.254	.015	23
	.2	.121	.037	31
	.3	.050	.059	33
	.4	.018	.077	31
	.5	.005	.088	28
	.6	-.001	.094	21
	.7	-.003	.098	16
	.8	-.002	.095	11
	.9	-.001	.087	6
<u>60°C</u>	.1	.106	.010	13.0
	.2	.048	.022	18.0
	.3	.003	.034	16.3
	.4	-.010	.041	13.6
	.5	-.010	.041	10.3
	.6	-.008	.039	7.1
	.7	-.005	.033	4.2
	.8	-.002	.023	1.9
	.9	-.001	.013	.3

G^E - cal mole⁻¹

TABLE 4.1.2

Excess Entropy and Partial Molar Excess EntropyOMCTS (1) - C₆H₆ (2)

x_1	\bar{S}_1^E/R	\bar{S}_2^E/R	S^E/R
.1	.998	.040	.136
.2	.663	.102	.215
.3	.416	.181	.252
.4	.265	.263	.264
.5	.157	.352	.255
.6	.085	.441	.227
.7	.036	.524	.182
.8	.010	.598	.128
.9	.004	.660	.070

TABLE 4.1.3

Excess Enthalpy and Partial Molar Excess EnthalpyOMCTS (1) - C₆H₆ (2)

x_1	\bar{H}_1^E	\bar{H}_2^E	H^E	$G^E(25^\circ\text{C})$	$G^E(60^\circ\text{C})$
.1	700	36	102	21	12
.2	441	87	158	31	16
.3	284	141	184	35	17
.4	174	198	189	33	14
.5	99	256	178	27	9
.6	49	315	155	21	5
.7	17	367	122	14	3
.8	6	409	87	11	2
.9	2	450	47	6	1

H^E, G^E - cal mole⁻¹

Fig. 4. 1.1

Excess Entropy OMCTS(1) - C₆H₆(2)

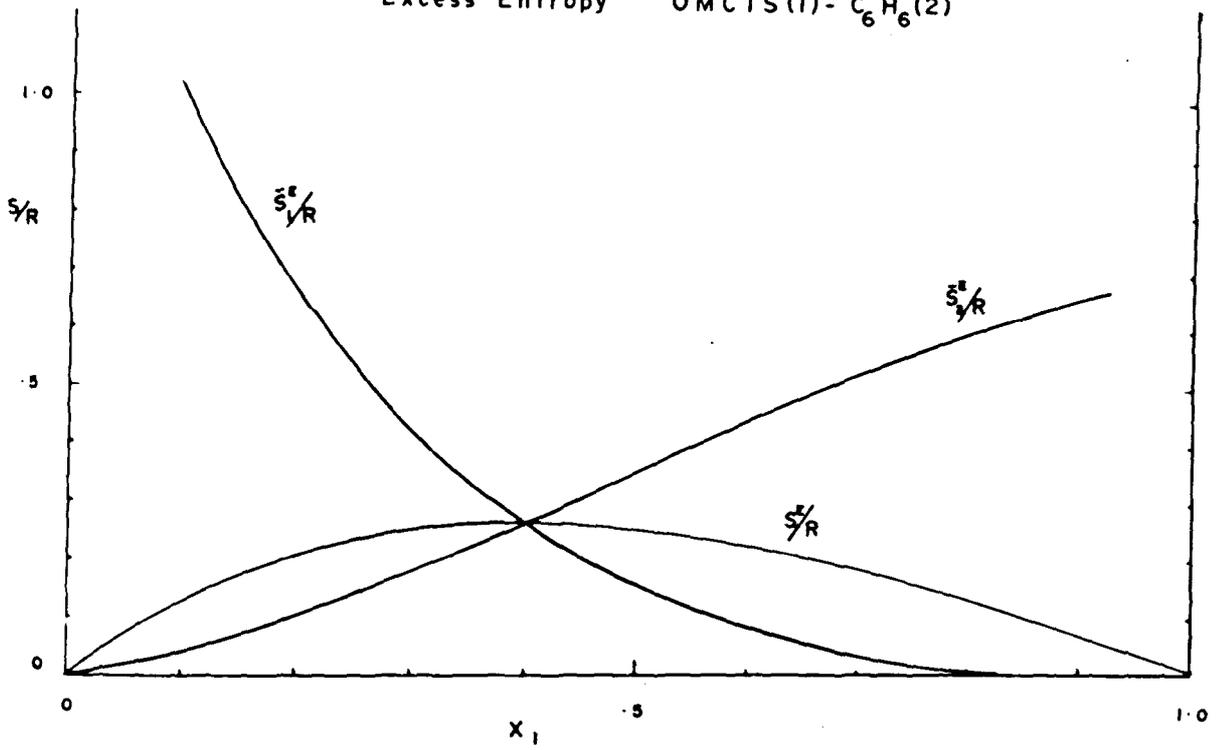


Fig. 4.1.2

Partial Molar Excess Enthalpy

OMCTS(1) C_6H_6 (2)

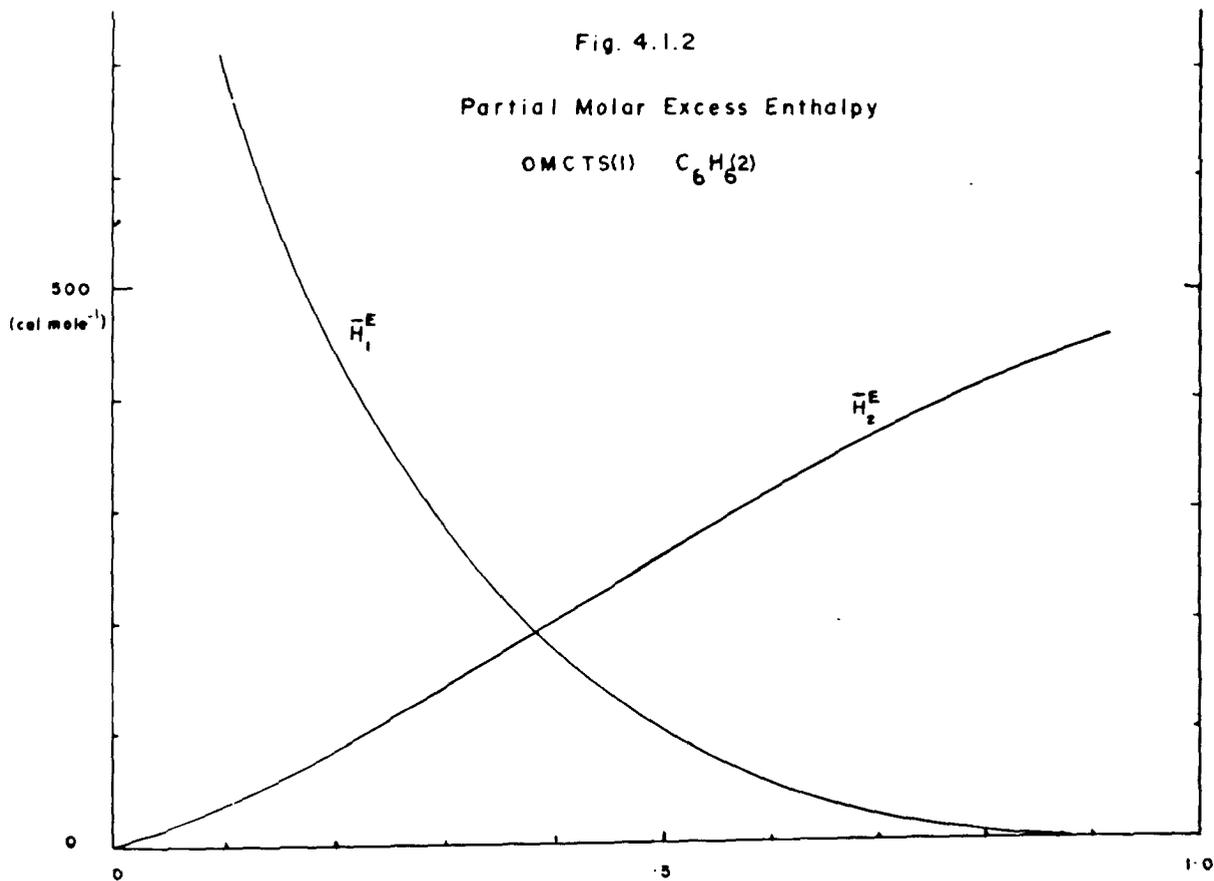


Fig. 4.1.3

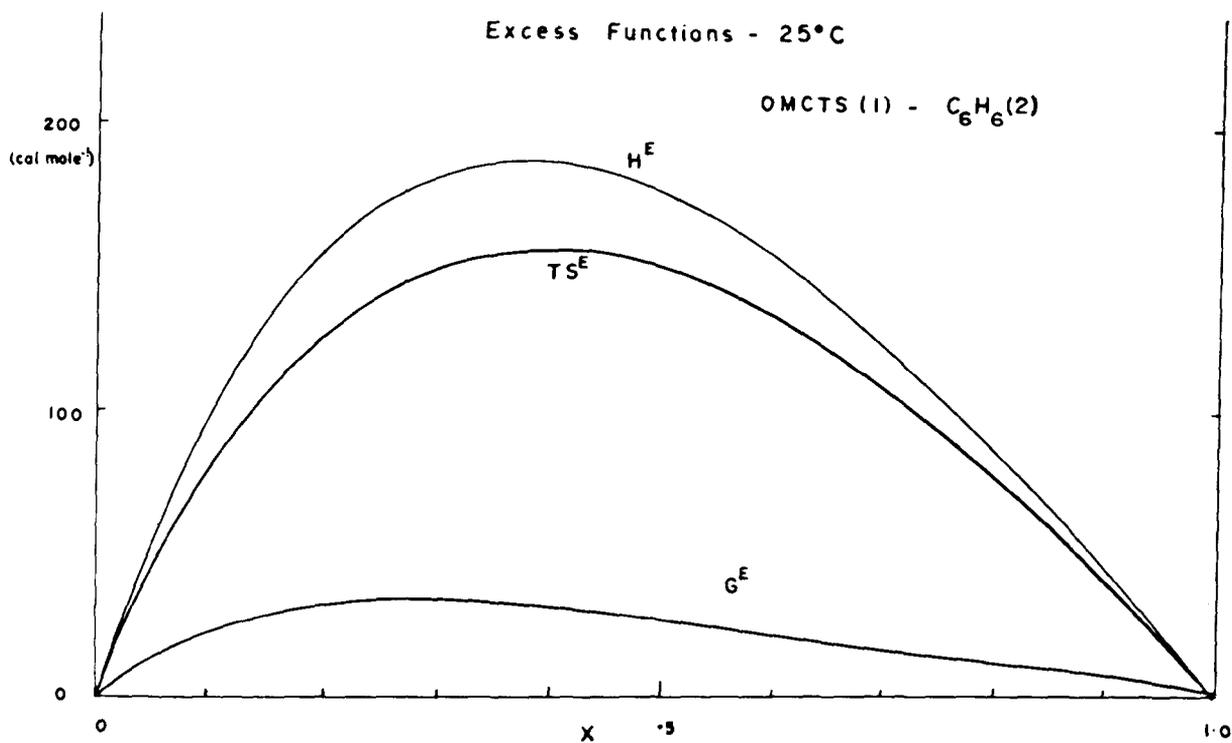


TABLE 4.1.4Activity Coefficients and Excess Gibbs Free EnergyOMCTS (1) - CCl₄ (2)

	x_1	$\ln f_1$	$\ln f_2$	G^E
<u>25°C</u>	.1	-.178	-.001	-11
	.2	-.145	-.008	-20
	.3	-.105	-.022	-28
	.4	-.073	-.038	-31
	.5	-.048	-.057	-31
	.6	-.028	-.083	-30
	.7	-.014	-.108	-25
	.8	-.004	-.131	-17
	.9	.000	-.155	-10
<u>60°C</u>	.1	-.200	-.003	-15
	.2	-.156	-.012	-27
	.3	-.110	-.027	-34
	.4	-.076	-.046	-38
	.5	-.050	-.068	-39
	.6	-.030	-.093	-36
	.7	-.014	-.120	-30
	.8	-.004	-.146	-21
	.9	-.000	-.169	-11

G^E - cal mole⁻¹

TABLE 4.1.5

Excess Entropy and Partial Molar Excess EntropyOMCTS (1) - CCl₄ (2)

x_1	\bar{S}_1^E/R	\bar{S}_2^E/R	S^E/R
.1	.464	.016	.060
.2	.299	.044	.095
.3	.194	.076	.111
.4	.118	.118	.118
.5	.075	.156	.116
.6	.044	.196	.104
.7	.022	.235	.086
.8	.008	.274	.061
.9	.002	.314	.033

TABLE 4.1.6

Excess Enthalpy and Partial Molar Excess EnthalpyOMCTS (1) - CCl₄ (2)

x_1	\bar{H}_1^E	\bar{H}_2^E	H^E	$G^E(60^\circ\text{C})$
.1	170	10	26	-14
.2	90	25	38	-25
.3	53	35	40	-33
.4	30	45	39	-39
.5	17	55	36	-41
.6	10	70	34	-35
.7	4	80	26	-31
.8	1	90	19	-22
.9	0	92	9	-12

H^E, G^E - cal mole⁻¹

Fig. 4.1.4

Excess Entropy OMCTS(1) - $\text{CCl}_4(2)$

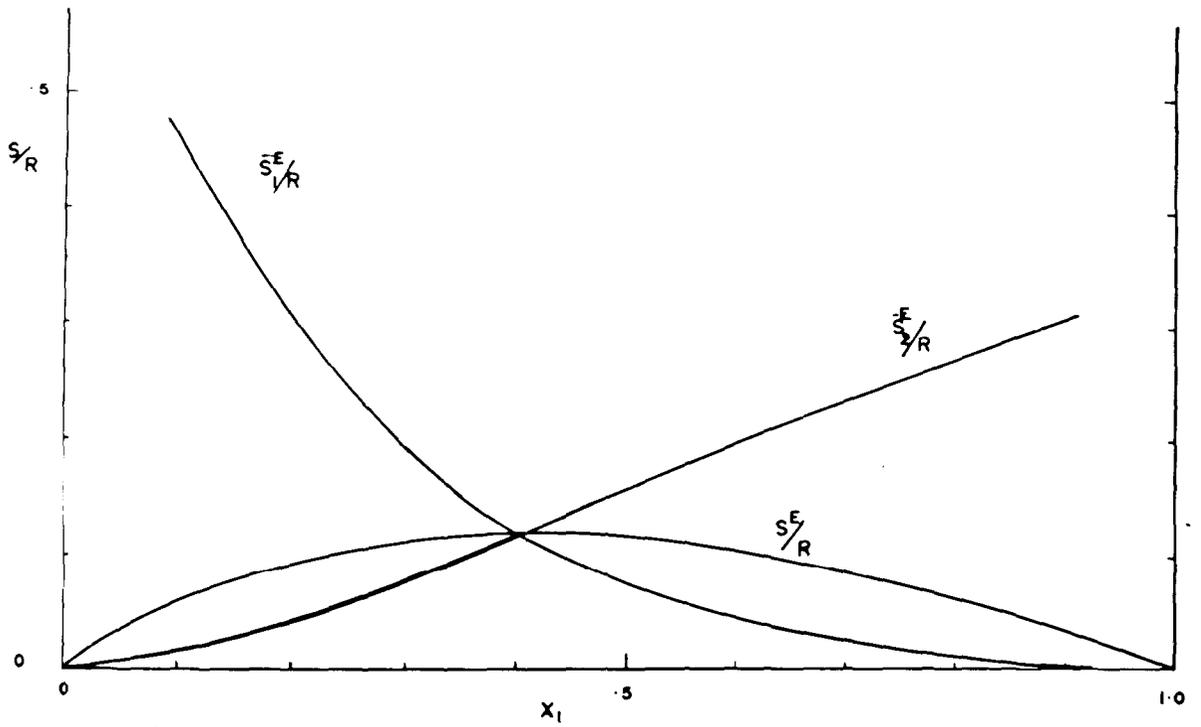


Fig. 4.1.5

Partial Molar Excess Enthalpy

OMCTS (1) - CCl_4 (2)

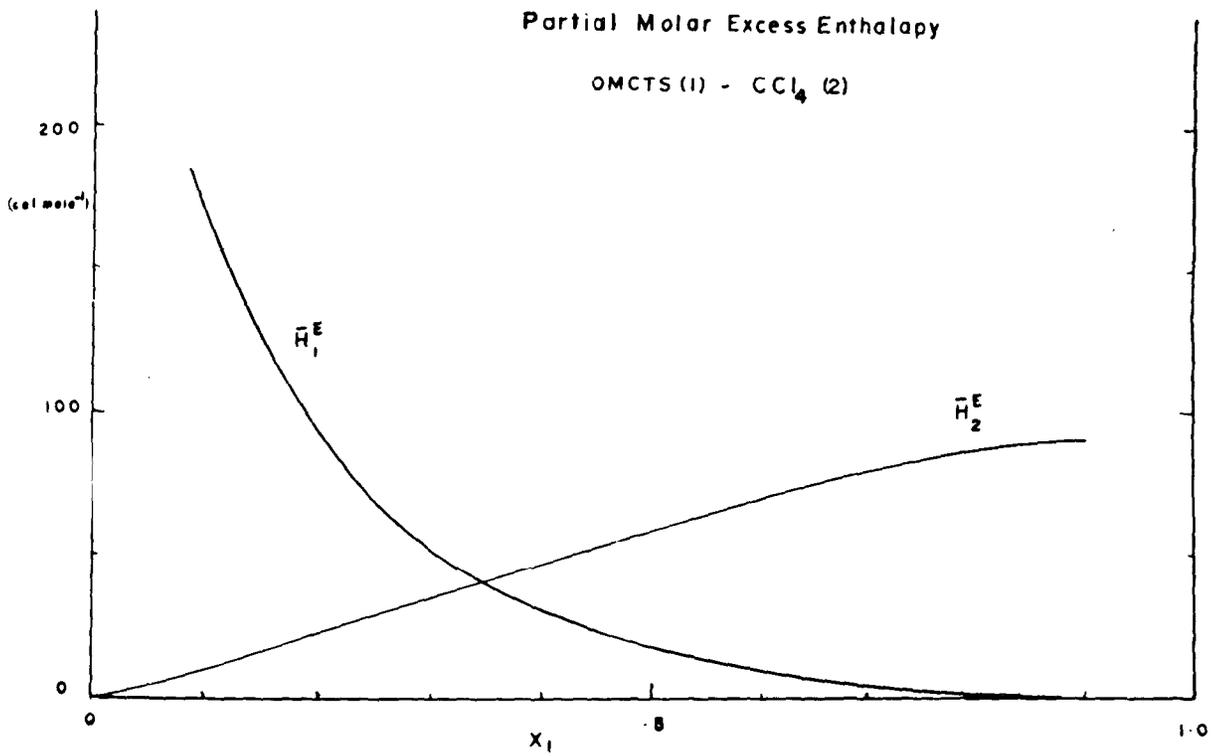
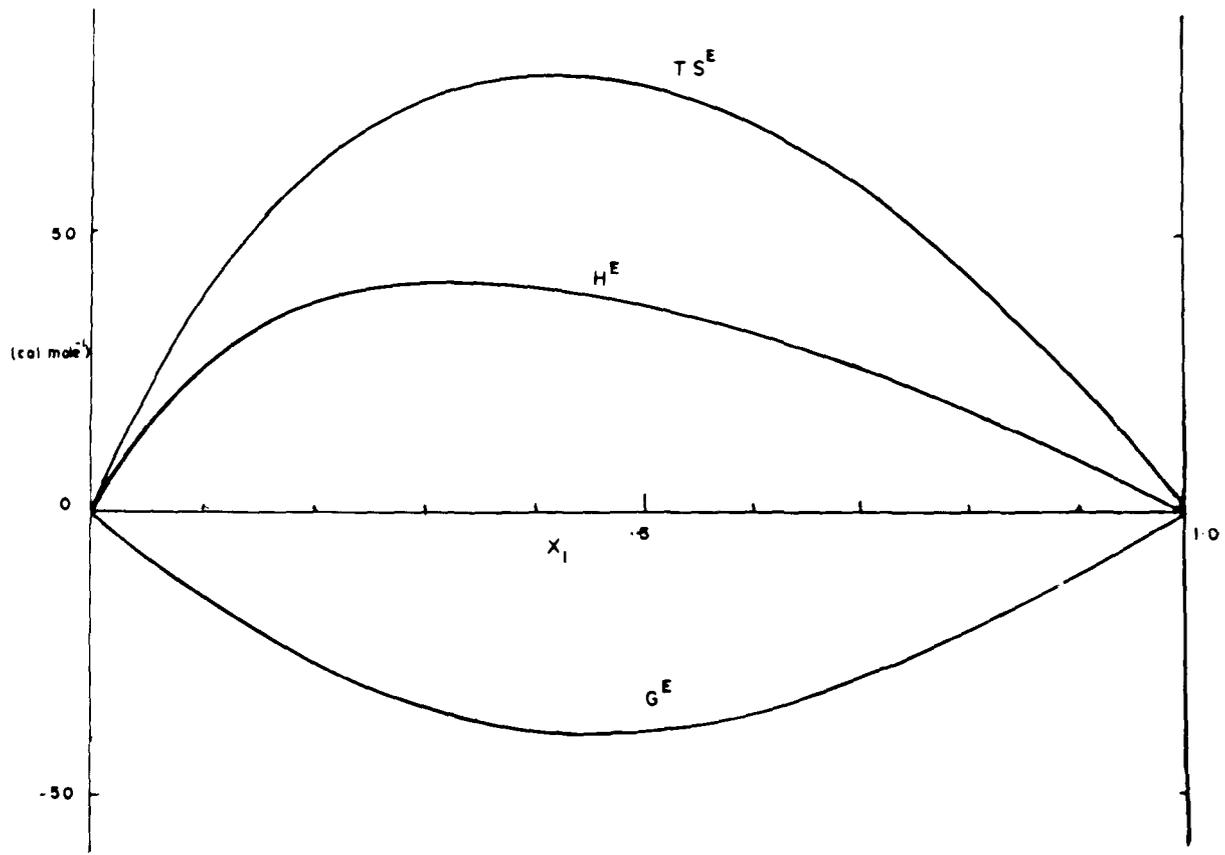


Fig. 4.1.6
Excess Functions OMCTS - CCl₄ 25°C



4.2 EXCESS FUNCTIONS AT CONSTANT VOLUME

Most theories of solutions calculate thermodynamic properties corresponding to a constant volume process, hence it is necessary to transform experimental results if they are measured under conditions of constant pressure. Scott¹⁰⁵ has discussed two constant volume processes corresponding to (a) a constant volume-equal initial pressure process and (b) a constant molecular composition process. He concluded that the latter process should apply to lattice theories but that difficulties arise in the interpretation of computed results.

Equally valid is the process of compressing the mixture to the volume given by the sum of the volumes of the two pure components. Alternatively there is no reason why the pressure applied to the pure components must be the same - one could consider a whole range of pressures applied to each component, the pressures being such that on mixing the volume remains constant. Since there are so many processes which can be considered and as all are of approximately equal validity the correction to constant volume remains controversial.

Fortunately the excess volume for the system OMCTS - benzene is very small so that the problem of the correct process becomes insignificant. For the other system the exact form of the correction will be important. In this thesis the constant volume-equal initial pressure process has been considered. The argument which follows was used to establish the required corrections.

It is necessary to establish equations for (1) the excess Helmholtz free energy at constant volume A^E , (2) the excess energy at constant volume U^E and (3) the excess entropy at constant volume S_v^E .

Excess Helmholtz Free Energy

Consider n_1 moles of component 1 and n_2 moles of component 2 at an initial pressure p^0 and both being compressed to a pressure p such that on mixing there is no change in volume. The change in volume of the pure components on compression is

$$\begin{aligned}\Delta V &= V_p - V_{p^0} \\ &= \int_{p^0}^p (n_1 \partial V_1^0 / \partial p + n_2 \partial V_2^0 / \partial p) dp \quad \dots (4.2.1)\end{aligned}$$

Now $(\partial V / \partial p)_T = -\beta V$ and if the volume change is small relative to the total volume and if the compressibilities of the pure components β_1 and β_2 are independent of pressure

$$\Delta V = (p - p^0)(-n_1 \beta_1 V_1^0 - n_2 \beta_2 V_2^0) \quad \dots (4.2.2)$$

The change in the Helmholtz free energy on compressing the pure components from pressure p^0 to p can be calculated from

$$\begin{aligned}(\partial A / \partial V)_T &= -p \\ A_p - A_{p^0} &= \int_{p^0}^p -pdV \quad \dots (4.2.3)\end{aligned}$$

$$= \frac{(p^2 - p^{02})}{2} B \quad \dots (4.2.4)$$

where $B = n_1 V_1^0 \beta_1 + n_2 V_2^0 \beta_2$.

$$\therefore A_p - A_p^\circ = - \frac{(p + p^\circ)}{2} \Delta V \quad \dots (4.2.5)$$

Since $p = p^\circ - \Delta V/B \quad \dots (4.2.6)$

$$A_p - A_p^\circ = - p^\circ \Delta V + (\Delta V)^2/2B \quad \dots (4.2.7)$$

As the Helmholtz free energy refers to a constant volume process the Helmholtz free energy of mixing is given by

$$\begin{aligned} \Delta A^m &= A_{p^\circ}^m - A_p \quad (\text{pure components}) \\ &= (A_{p^\circ}^m - A_{p^\circ}) + p^\circ \Delta V - (\Delta V)^2/2B \end{aligned}$$

where $A_{p^\circ}^m$ is the Helmholtz free energy of the mixture at pressure p° .

Since $A = G - pV.$

$$\Delta A^m = \Delta G_{p^\circ}^m - p^\circ \Delta V + p^\circ \Delta V - (\Delta V)^2/2B$$

For one mole of mixture

$$\Delta A^m = \Delta G_{p^\circ}^m - (V^E)/2B \quad \dots (4.2.8)$$

As the volume change for an ideal solution is zero the excess Helmholtz free energy, A^E , is

$$A^E = G_{p^\circ}^E - (V^E)^2/2B \quad \dots (4.2.9)$$

Thus the excess free energy for the two processes are almost identical as only a second order term in the excess volume needs to be considered.

Excess Entropy

The following thermodynamic relationships hold

$$(\partial S/\partial V)_T = (\partial p/\partial T)_V = \alpha/B \quad \dots (4.2.10)$$

where α is the coefficient of thermal expansion and

$$\Delta S_v^m = S_{p^o}^m - S_p \quad (\text{pure components}) \quad \dots (4.2.11)$$

The change in entropy on compressing the pure components to a pressure p is

$$S_p - S_{p^o} = \int_{p^o}^p (\alpha/\beta) dV$$

Since

$$\begin{aligned} dV &= \frac{1}{V} (\partial V / \partial p) V dp \\ &= -\beta V dp \end{aligned}$$

$$S_p - S_{p^o} = - \int_{p^o}^p \alpha V dp$$

Assuming the coefficients of thermal expansion of the components α_1 and α_2 to be independent of pressure

$$S_p - S_{p^o} = - (p - p^o) (n_1 \alpha_1 V_1^o + n_2 \alpha_2 V_2^o)$$

From equation (4.2.11)

$$\begin{aligned} \Delta S_v^m &= S_{p^o}^m - S_p + (p - p^o) (n_1 \alpha_1 V_1^o + n_2 \alpha_2 V_2^o) \\ &= \Delta S_{p^o}^m + (p - p^o) (n_1 \alpha_1 V_1^o + n_2 \alpha_2 V_2^o) \end{aligned}$$

Again, as the volume change for an ideal solution is zero the excess entropy at constant volume, S_v^E , is

$$S_v^E = S^E + (p - p^o) (n_1 \alpha_1 V_1^o + n_2 \alpha_2 V_2^o)$$

For one mole of mixture

$$S_v^E = S^E - V^E \frac{(x_1 \alpha_1 V_1^o + x_2 \alpha_2 V_2^o)}{(x_1 \beta_1 V_1^o + x_2 \beta_2 V_2^o)} \quad \dots (4.2.12)$$

Excess Energy

From the relationships, $H = G + TS$ and $U = A + TS_v$ it can readily

be shown that

$$U^E = H^E - TV^E \frac{(x_1 V_{1\alpha_1}^{\circ} + x_2 V_{2\alpha_2}^{\circ})}{(x_1 V_{1\beta_1}^{\circ} + x_2 V_{2\beta_2}^{\circ})} \quad \dots (4.2.13)$$

where U^E is the excess energy for a constant volume process.

Partial Molar Excess Energy and Entropy

$$\bar{H}_1^E = H^E - n_2 \partial H^E / \partial n_2 \quad \dots (4.2.14)$$

$$\bar{U}_1^E = U^E - n_2 \partial U^E / \partial n_2 \quad \dots (4.2.15)$$

Substituting equation (4.2.13) and equation (4.2.15)

$$\begin{aligned} \bar{U}_1^E = & U^E - n_2 \partial H^E / \partial n_2 + n_2 T (\partial V^E / \partial n_2) \frac{(n_1 V_{1\alpha_1}^{\circ} + n_2 V_{2\alpha_2}^{\circ})}{(n_1 V_{1\beta_1}^{\circ} + n_2 V_{2\beta_2}^{\circ})} \\ & + \frac{n_2 TV^E V_{2\alpha_2}^{\circ}}{(n_1 V_{1\beta_1}^{\circ} + n_2 V_{2\beta_2}^{\circ})} - n_2 TV^E V_{2\beta_2}^{\circ} \frac{(n_1 V_{1\alpha_1}^{\circ} + n_2 V_{2\alpha_2}^{\circ})}{(n_1 V_{1\beta_1}^{\circ} + n_2 V_{2\beta_2}^{\circ})^2} \end{aligned}$$

Since $\bar{V}_1^E = V^E - n_2 \partial V^E / \partial n_2$, then by applying equation (4.2.14) the partial molar excess energy for one mole of mixture becomes,

$$\begin{aligned} \bar{U}_1^E = & \bar{H}_1^E - T\bar{V}_1^E \frac{(x_1 V_{1\alpha_1}^{\circ} + x_2 V_{2\alpha_2}^{\circ})}{(x_1 V_{1\beta_1}^{\circ} + x_2 V_{2\beta_2}^{\circ})} + \frac{x_2 TV^E V_{2\alpha_2}^{\circ}}{(x_1 V_{1\beta_1}^{\circ} + x_2 V_{2\beta_2}^{\circ})} \\ & - x_2 TV^E V_{2\beta_2}^{\circ} \frac{(x_1 V_{1\alpha_1}^{\circ} + x_2 V_{2\alpha_2}^{\circ})}{(x_1 V_{1\beta_1}^{\circ} + x_2 V_{2\beta_2}^{\circ})^2} \quad \dots (4.2.16) \end{aligned}$$

By a similar argument, the partial molar excess entropy at constant volume for one mole of mixture is given by,

$$\begin{aligned} \bar{S}_{V1}^E &= \bar{S}_1^E - \bar{V}_1^E \frac{(x_1 V_{1\alpha_1}^{\circ} + x_2 V_{2\alpha_2}^{\circ})}{(x_1 V_{1\beta_1}^{\circ} + x_2 V_{2\beta_2}^{\circ})} + \frac{x_2 V_{2\alpha_2}^E V_{2\alpha_2}^{\circ}}{(x_1 V_{1\beta_1}^{\circ} + x_2 V_{2\beta_2}^{\circ})} \\ &- x_2 V_{2\beta_2}^E V_{2\beta_2}^{\circ} \frac{(x_1 V_{1\alpha_1}^{\circ} + x_2 V_{2\alpha_2}^{\circ})}{(x_1 V_{1\beta_1}^{\circ} + x_2 V_{2\beta_2}^{\circ})^2} \quad \dots (4.2.17) \end{aligned}$$

Similar equations hold for the partial molar quantities at constant volume for component two. It should be noted that the assumption that the compressibilities and thermal expansion coefficients are independent of pressure will hold only when the pressures required are small, i.e. the excess volume is small. Coefficients of thermal expansion and compressibilities are listed in Table 4.2.1. In Tables 4.2.2 and 4.2.3 the excess functions at constant volume at 25°C only are listed. Partial molar excess volumes were determined graphically as suggested by Hildebrand and Scott¹⁰⁶.

The above considerations have been neglected by some authors¹⁰⁷, even though the correction is significant when the excess volumes are large. It will be shown in the next chapter that if constant volume excess functions are used, closer agreement with theoretical equations results.

TABLE 4.2.1

Coefficients of Thermal Expansion and Compressibility
for the Pure Components - 25°C

	$\alpha \times 10^3$ (deg ⁻¹)	Ref.	$\beta \times 10^3$ (ml cal ⁻¹)	Ref.
C ₆ H ₆	1.218	32	4.09	117
CCl ₄	1.217	93	4.48	118
OMCTS	1.202	a	6.30	119
a from experimental data				

TABLE 4.2.2Excess Functions at Constant Volume

OMCTS (1) - C ₆ H ₆ (2)						
x_1	U^E	\bar{U}_1^E	\bar{U}_2^E	S_v^E/R	\bar{S}_{v1}^E/R	\bar{S}_{v2}^E/R
.1	103	710	37	.140	1.033	.042
.2	160	444	89	.222	.674	.108
.3	186	284	144	.258	.416	.189
.4	190	172	202	.268	.257	.275
.5	178	96	260	.256	.148	.364
.6	155	47	318	.227	.079	.450
.7	122	16	368	.181	.033	.526
.8	87	6	408	.127	.010	.593
.9	47	2	448	.069	.004	.653

TABLE 4.2.3Excess Functions at Constant Volume

OMCTS (1) - CCl ₄ (2)						
x_1	U^E	\bar{U}_1^E	\bar{U}_2^E	S_v^E/R	\bar{S}_{v1}^E/R	\bar{S}_{v2}^E/R
.1	36	257	12	.094	.755	.023
.2	53	126	36	.147	.420	.082
.3	57	79	48	.167	.283	.121
.4	56	46	63	.175	.172	.178
.5	52	21	82	.169	.090	.247
.6	47	11	100	.146	.048	.296
.7	36	4	111	.119	.023	.339
.8	25	1	122	.082	.008	.381
.9	12	0	124	.043	.002	.420

U^E - cal mole⁻¹

4.3 REGULAR SOLUTION THEORY

In the regular solution or solubility parameter concept⁹ it is assumed that the entropy and the energy terms can be treated separately. Hildebrand has reached the following general conclusions:

- (i) The entropy of mixing is ideal, resulting in a zero excess entropy.
- (ii) The excess energy is a function of volume fractions.
- (iii) The excess volume is related to the energy of mixing and again, is a function of volume fractions. In the following discussion the excess entropy, energy and volume will be treated separately.

Entropy of Mixing

Three factors need to be considered when discussing the entropy, namely random mixing, the effect of differences in molecular size and the contribution from expansion (the correction to constant volume). Concerning the first: most evidence points to the fact that, except in the region near the critical point, mixtures of non-polar molecules, even when they have very different attractive fields, are randomly mixed¹⁰⁸. It is necessary, if any of the conclusions reached in the following sections are to be valid, for this assumption concerning random mixing to be correct. Effects due to molecular size differences and expansion should be considered together, since it appears clear that the entropy which must be considered is the one calculated after

allowing for expansion¹⁰⁵. Reference to Tables 4.2.1 and 4.2.2 indicates that the excess entropies at constant volume are not zero, as would be expected from regular solution theory. A number of formulations have been given for the excess entropy.

The Flory-Huggins theory,^{3,4} based on a lattice model for the liquid state, predicts that if molar volumes, rather than chain lengths are used, the entropy of mixing is given by,

$$\Delta S^m = -R(x_1 \ln \phi_1 + x_2 \ln \phi_2) \quad \dots \quad (4.3.1)$$

or the excess entropy is given by,

$$S^E = -R(x_1 \ln \phi_1 + x_2 \ln \phi_2) + R(x_1 \ln x_1 + x_2 \ln x_2) \dots (4.3.2)$$

the latter term representing the ideal entropy of mixing. The partial molar excess entropy for components 1 and 2 are given by,

$$\bar{S}_1^E = -R(\ln \phi_1 + \phi_2(1 - V_1/V_2)) + R \ln x_1 \quad \dots \quad (4.3.3)$$

$$\bar{S}_2^E = -R(\ln \phi_2 + \phi_1(1 - V_2/V_1)) + R \ln x_2 \quad \dots \quad (4.3.3a)$$

where the second term in each equation represents the ideal partial molar entropy of mixing.

The free volume theory¹⁰⁹ predicts that the entropy of mixing is given by,

$$\Delta S^m = -R \left[x_1 \ln \frac{x_1 V_1^f}{x_1 V_1^f + x_2 V_2^f} + x_2 \ln \frac{x_2 V_2^f}{x_1 V_1^f + x_2 V_2^f} \right] \quad \dots \quad (4.3.4)$$

but difficulties arise in determining the free volume, V^f . Bondi¹¹⁰

has discussed three types of free volume and he distinguishes them by the terms (i) "empty volume" - referring to the excess of the volume occupied by one mole of the substance over the sum of the volumes occupied by all the individual molecules, (ii) "expansion volume" - which is the excess of the molar volume over the volume at 0°K, (iii) "fluctuation volume" - calculated from the entropy of vaporisation equation,

$$\Delta S^{\text{vap}} = R \ln[V^g/V^f] \quad \dots (4.3.5)$$

where V^g is the volume of the gas. The free volumes calculated from the three methods give discordant results. Scatchard¹¹¹ has suggested that a reasonable assumption is to take the free volume as proportional to the surface area, rather than the volume, of the molecules so the entropy of mixing becomes,

$$\Delta S^m = -R (x_1 \ln A_1 + x_2 \ln A_2) \quad \dots (4.3.6)$$

where A is the surface fraction which for spherical molecules is given by,

$$A_1 = \frac{x_1 V_1^{2/3}}{x_1 V_1^{2/3} + x_2 V_2^{2/3}} \quad \dots (4.3.7)$$

The excess entropy and the partial molar excess entropy are given by equations similar to equations(4.3.2) and(4.3.3) with A substituted for ϕ . In Tables 4.3.1 and 4.3.2 the entropies of mixing calculated from the equations for ideal mixing, mixing according to volume fraction statistics and mixing according to surface fraction statistics, are listed. In Tables 4.3.3 and 4.3.4 the excess entropies

calculated for volume fraction and surface fraction statistics are compared with the experimental excess entropies after allowing for expansion.

For both systems studied, the surface area fraction statistics underestimate the excess entropy, while for the system OMCTS - CCl_4 volume fraction statistics give a remarkably good account of both the total and partial excess entropy. For the system OMCTS - C_6H_6 the latter statistics still underestimates. One is tempted to suggest that the lack of agreement is due to the fact that the benzene molecule cannot be treated as a truly spherical molecule. The other possibility is that the entropy of mixing should include a term involving the energy of mixing, but this can only be justified if the excess enthalpy is much greater than RT .

The theory of Flory to be discussed later, includes a residual entropy term which depends on the excess volume which in turn depends on the excess enthalpy.

It should be noted that surface area fraction statistics underestimate the excess entropy for both systems, even when corrections for expansion are not made.

TABLE 4.3.1Entropy of Mixing - According to Various StatisticsOMCTS (1) - C₆H₆ (2)

x_1	Mole fract.	Area fract.	Vol. fract.	Expt. (const.vol.)
.1	.325	.364	.422	.465
.2	.500	.565	.655	.722
.3	.611	.691	.794	.869
.4	.673	.759	.864	.941
.5	.693	.778	.877	.949
.6	.673	.750	.837	.900
.7	.611	.675	.745	.792
.8	.500	.547	.596	.627
.9	.325	.350	.376	.394

TABLE 4.3.2Entropy of Mixing - According to Various StatisticsOMCTS (1) - CCl₄ (2)

x_1	Mole fract.	Area fract.	Vol. fract.	Expt. (const.vol.)
.1	.325	.358	.408	.419
.2	.500	.556	.633	.647
.3	.611	.680	.770	.778
.4	.673	.748	.840	.848
.5	.693	.767	.855	.862
.6	.673	.741	.818	.819
.7	.611	.667	.730	.729
.8	.500	.542	.586	.582
.9	.325	.347	.370	.368

Entropy Units - S/R

TABLE 4.3.3

Excess Entropy According to Various StatisticsOMCTS (1) - C₆H₆ (2)

x_1	<u>Vol. Fract.</u>			<u>Surface Area Fract.</u>			<u>Experimental (const. vol.)</u>		
	S^E/R	\bar{S}_1^E/R	\bar{S}_2^E/R	S^E/R	\bar{S}_1^E/R	\bar{S}_2^E/R	S_v^E/R	\bar{S}_{v1}^E/R	\bar{S}_{v2}^E/R
.1	.097	.767	.023	.039	.326	.007	.140	1.033	.042
.2	.154	.484	.072	.065	.224	.025	.222	.674	.108
.3	.183	.306	.130	.079	.151	.049	.258	.416	.190
.4	.191	.190	.192	.086	.099	.077	.268	.257	.275
.5	.184	.113	.254	.085	.062	.107	.256	.148	.364
.6	.164	.063	.315	.077	.036	.139	.227	.079	.450
.7	.134	.031	.374	.064	.018	.171	.181	.033	.526
.8	.096	.012	.430	.047	.008	.204	.127	.010	.593
.9	.051	.003	.485	.025	.002	.236	.069	.004	.653

TABLE 4.3.4

Excess Entropy According to Various StatisticsOMCTS (1) - CCl₄ (2)

x_1	<u>Volume Fract.</u>			<u>Surface Area Fract.</u>			<u>Experimental (const. vol.)</u>		
	S^E/R	\bar{S}_1^E/R	\bar{S}_2^E/R	S^E/R	\bar{S}_1^E/R	\bar{S}_2^E/R	S_v^E/R	\bar{S}_{v1}^E/R	\bar{S}_{v2}^E/R
.1	.083	.664	.019	.033	.282	.006	.094	.755	.023
.2	.133	.427	.060	.056	.196	.021	.147	.420	.082
.3	.159	.273	.110	.069	.134	.042	.167	.283	.121
.4	.167	.171	.165	.075	.088	.066	.175	.172	.178
.5	.162	.103	.220	.074	.055	.092	.169	.089	.247
.6	.145	.058	.275	.068	.032	.121	.146	.047	.296
.7	.119	.029	.328	.057	.017	.149	.118	.023	.339
.8	.085	.012	.380	.041	.007	.179	.082	.007	.381
.9	.045	.003	.430	.022	.002	.208	.043	.002	.420

Excess Energy

Van Laar¹¹² attempted to explain the energy of mixing in terms of van der Waals equation of state and derived the expression

$$\Delta U^m = \frac{x_1 x_2 b_1 b_2}{x_1 b_1 + x_2 b_2} \left(a_1^{1/2}/b_1 - a_2^{1/2}/b_2 \right)^2 \quad \dots (4.3.8)$$

where a and b are constants given by the van der Waals equation. He later modified the equation to the form

$$\Delta U^m = \frac{x_1 x_2 V_1^0 V_2^0}{x_1 V_1^0 + x_2 V_2^0} \left(a_1^{1/2}/V_1^0 - a_2^{1/2}/V_2^0 \right)^2 \quad \dots (4.3.9)$$

by substituting molar volumes V_1^0 , V_2^0 for the constants b_1 , b_2 .

Scatchard¹¹³ extended the van Laar equation and derived:

$$\Delta U^m = (x_1 V_1^0 + x_2 V_2^0) A_{12} \phi_1 \phi_2$$

Hildebrand and Wood,¹¹⁴ by assuming a continuous distribution function and integrating the intermolecular potentials between pairs of molecules throughout the liquid, derived a similar equation. The coefficient A_{12} , a constant for a particular system, has the form,

$$A_{12} = C_{11} - 2C_{12} + C_{22} \quad \dots (4.3.10)$$

where, in general form, C_{ii} is the cohesive energy density for a particular component and is related to the energy of vaporization. The three terms in the above equation characterize the interaction between the pairs of molecules 11, 12, and 22. To determine C_{12}

it is necessary to use the Berthelot relationship,

$$C_{12}^2 = C_{11}C_{22}$$

so that,

$$A_{12} = (C_{11}^{\frac{1}{2}} - C_{22}^{\frac{1}{2}})^2 \quad \dots \quad (4.3.11)$$

Hildebrand has called $C_{ii}^{\frac{1}{2}}$ the solubility parameter (δ_i), so that the energy of mixing equation known as the Scatchard - Hildebrand equation becomes,

$$U^E = \Delta U^m = (x_1 V_1^o + x_2 V_2^o)(\delta_1 - \delta_2)^2 \phi_1 \phi_2 \quad \dots \quad (4.3.12)$$

and the partial molar excess energies are given by,

$$\bar{U}_1^E = V_1^o (\delta_1 - \delta_2)^2 \phi_2^2 \quad \dots \quad (4.3.13a)$$

$$\bar{U}_2^E = V_2^o (\delta_1 - \delta_2)^2 \phi_1^2 \quad \dots \quad (4.3.13b)$$

Other assumptions made in deriving these equations have been discussed in detail by Hildebrand and Scott¹¹⁵.

To calculate the partial and total excess energies it is necessary to know the solubility parameter for each component.

Hildebrand and Scott give a number of equations, including,

$$(i) \quad \delta = [(\Delta H_{app}^V - RT)Z/V]^{\frac{1}{2}} \quad \dots \quad (4.3.14)$$

where ΔH_{app}^V , the apparent latent heat of vaporization, is given by,

$$d(\ln p)/dT = \Delta H_{app}^V / RT^2 \quad \dots \quad (4.3.15)$$

and Z is a compressibility factor which, for systems where the temperature and pressure are sufficiently below the critical values, is very

close to unity¹¹⁶.

$$(ii) \quad \delta = (T\alpha/\beta n)^{\frac{1}{2}} \\ = \left[\frac{T(\partial p/\partial T)_v}{n} \right]^{\frac{1}{2}} \quad \dots (4.3.16)$$

and for normal liquids n is a constant approximately equal to one. Hildebrand prefers the values calculated from the heat of vaporization equation.

Solubility parameters were calculated from equation (4.3.14) using the experimental vapour pressure data, and from equation (4.3.16) employing literature internal pressure data^{117,118,119} and assuming n equal to one. Ross and Hildebrand have determined $n = 2.3$ from the slope of $\log(\partial E/\partial V)_T$ versus $\log V$. Using this value of n in equation (4.3.16) gives a solubility parameter for OMCTS equal to 4.9. This value is much too low. The other value of n suggested, 1.38, has been determined by adjusting the compressibility equation to fit the heat of vaporization value for δ . The values calculated from the above equations are listed in Table 4.3.5.

TABLE 4.3.5

Solubility Parameters - 25°C

	(4.3.14) (cal ^{1/2} cm ^{-3/2})	(4.3.16) $n = 1$ (cal ^{1/2} cm ^{-3/2})
Benzene	9.117	9.40
Carbon tetrachloride	8.627	8.99
OMCTS	6.01	7.54

Solubility parameters determined from compressibility data were found to underestimate the excess energy for the system C_6H_6 - OMCTS and to overestimate in the system CCl_4 - OMCTS, while solubility parameters calculated from heats of vaporization overestimated in both cases, as shown in Tables 4.3.6.

It was felt that most of the problems with solubility parameter theory resided in the difficulty in determining unambiguous values of the solubility parameter. A better test of the Hildebrand - Scatchard equation can be made by considering the triad OMCTS - CCl_4 , OMCTS - C_6H_6 , and CCl_4 - C_6H_6 . Total and partial excess energies for the system CCl_4 - C_6H_6 were determined from the enthalpy data of van Ness¹²⁰ and the excess volume data of Wood and Brusie¹²¹. If the solubility parameters for the three components are denoted by, OMCTS - δ_1 , CCl_4 - δ_2 and C_6H_6 - δ_3 then the differences $(\delta_1 - \delta_3)$ and $(\delta_2 - \delta_3)$ were adjusted to fit the experimental data at $x_1 = .4$ for the system OMCTS (1) - C_6H_6 (3) and CCl_4 (2) - C_6H_6 (3) respectively. The total and partial excess energies for these systems are given in Tables 4.3.7 and 4.3.8. From these two systems a value of $(\delta_1 - \delta_2)$ corresponding to the system OMCTS (1) - CCl_4 (2) was derived and used to predict the total and partial excess energies for this system. These values are listed in Table 4.3.9. This method of dealing with the excess energy equation gave good agreement with experiment for the three systems for both the total and partial excess energies.

TABLE 4.3.6

Excess Energy from Solubility Parameter Theory

x_1	U^E (4.3.16)	U^E (4.3.14)	U^E (expt.)
<u>OMCTS (1) - C₆H₆ (2)</u>			
.1	77	217	103
.2	115	322	160
.3	129	362	186
.4	129	362	190
.5	119	335	178
.6	101	285	155
.7	82	231	122
.8	57	161	87
.9	30	84	47
<u>OMCTS (1) - CCl₄ (2)</u>			
.1	49	157	36
.2	74	237	53
.3	84	269	57
.4	85	272	56
.5	79	253	52
.6	68	220	47
.7	55	176	36
.8	38	123	25
.9	20	64	12

U^E - cal. mole.⁻¹

TABLE 4.3.7

Total and Partial Excess EnergiesOMCTS (1) - C₆H₆ (2) $(\delta_1 - \delta_3) = 2.25$ adjusted to fit total energy data at $x_1 = .4$

x_1	U^E (calc.)	U^E (exp.)	\bar{U}_1^E (calc.)	\bar{U}_1^E (exp.)	\bar{U}_2^E (calc.)	\bar{U}_2^E (exp.)
.1	114	103	820	710	35	37
.2	169	160	450	444	98	89
.3	190	186	254	284	163	144
.4	190	190	143	172	221	202
.5	178	178	78	96	273	260
.6	152	155	41	47	319	318
.7	121	122	19	16	359	368
.8	84	87	7	6	394	408
.9	44	47	2	2	425	448

TABLE 4.3.8

Total and Partial Excess EnergiesCCl₄ (2) - C₆H₆ (3) $(\delta_2 - \delta_3) = 1.065$

x_1	U^E (calc.)	U^E (exp.)	\bar{U}_1^E (calc.)	\bar{U}_1^E (exp.)	\bar{U}_2^E (calc.)	\bar{U}_2^E (exp.)
.1	9.8	9.3	87.6	85.1	1.1	.6
.2	17.3	16.5	68.1	64.0	4.6	3.2
.3	22.5	21.7	51.2	48.2	10.2	8.0
.4	25.5	24.7	37.0	36.1	17.8	15.4
.5	26.3	25.5	25.3	25.2	27.4	24.8
.6	25.1	24.3	15.9	16.6	38.9	36.7
.7	21.8	21.1	8.8	9.6	52.1	49.2
.8	16.4	16.3	3.8	4.3	67.0	64.9
.9	9.1	8.6	.9	1.0	83.4	83.5

 $\delta - \text{cal}^{\frac{1}{2}} \text{cm}^{-3/2}$ $U - \text{cal mole}^{-1}$

TABLE 4.3.9Total and Partial Excess EnergiesOMCTS (1) - CCl₄ (2)

$$(\delta_1 - \delta_2) = (2.250 - 1.065) = 1.185$$

x_1	U^E (calc.)	U^E (exp.)	\bar{U}_1^E (calc.)	\bar{U}_1^E (exp.)	\bar{U}_2^E (calc.)	\bar{U}_2^E (exp.)
.1	32	36	238	257	9	12
.2	49	53	135	126	27	36
.3	55	57	78	79	46	48
.4	56	56	44	46	63	63
.5	52	52	25	21	79	82
.6	45	47	13	11	94	100
.7	36	36	6	4	106	111
.8	25	25	2	1	117	122
.9	13	12	0	0	127	124

$$\delta - \text{cal.} \cdot \frac{1}{2} \text{cm.}^{-3/2}$$

$$U - \text{cal. mole.}^{-1}$$

Excess Volumes

The original equation given by regular solution theory for the excess volume¹²²

$$V^E = (\delta_1 - \delta_2)^2 (x_1 V_1^0 + x_2 V_2^0) (\phi_1 \beta_1 + \phi_2 \beta_2) \phi_1 \phi_2 \quad \dots (4.3.17)$$

can only predict positive excess volumes and is therefore of little use.

A second equation,

$$V^E = n \beta_m A^E \quad \dots (4.3.18)$$

has been suggested, but this equation is only a modification of the previous equation, as an implicit assumption in the derivation is $S_v^E = 0$ making $U^E = A^E$. Scott¹²³ has derived a more exact equation

free from the approximations required to derive the previous equations

$$\begin{aligned} V^E &= n_m \beta_m G^E - T \left(\frac{\partial S_v^E}{\partial p} \right)_T \\ &+ n_m \beta_m U_m - x_1 n_1 \beta_1 U_1 - x_2 n_2 \beta_2 U_2 \\ &+ n_m \beta_m T S_v^E \quad \dots (4.3.19) \end{aligned}$$

where n_1 , n_2 and n_m are the ratio of internal pressure to cohesive energy density for the two pure components and the mixture, U_1 and U_2 are the total energies of the two pure components and U_m is the energy of the resultant mixture at a volume V , given by

$$V = x_1 V_1^0 + x_2 V_2^0$$

and
$$\beta_m = \phi_1 \beta_1 + \phi_2 \beta_2$$

Unfortunately it is impossible to test this equation because of the lack of data on a number of terms, especially $(\partial S_V^E/\partial p)_T$. For many systems this term appears to be far from zero and can give rise to a negative term in the excess volume. The excess volume for the system OMCTS - CCl_4 can be fitted to an equation of the form,

$$V^E = A(x_1 V_1^0 + x_2 V_2^0)(\phi_1 \beta_1 + \phi_2 \beta_2) \phi_1 \phi_2$$

The data for the system OMCTS - C_6H_6 do not appear to be accurate enough to warrant this close analysis. It is therefore tentatively suggested that the excess volume is given by equations using the volume fraction rather than the mole fraction.

Summary

For the two systems studied the entropy of mixing, after allowing for expansion, is not ideal and is best represented by volume fraction statistics; while the excess energy can be well represented by the Hildebrand - Scatchard equation if the solubility parameters are suitably adjusted. Adjustment is necessary because of the mutually inconsistent results obtained for the solubility parameter from the various equations. The excess volume still defies explanation, particularly for the system OMCTS - C_6H_6 , where the excess free energy is positive and the excess volume negative.

4.4 FLORY'S THEORY OF SOLUTIONS

Flory^{15,124} has recently formulated several theoretical expressions for the excess enthalpy, entropy and volume in terms of parameters characterizing the pure components, namely the density, the thermal expansion coefficient and the compressibility. A brief outline of his theory is given.

By considering a one dimensional system composed of N particles each of length l^* distributed over a total length, L a configuration integral or partition function of the form

$$Z = \Omega \exp(-U_0/kT)$$

can be derived. The totality of configuration space Ω available to the system is

$$\Omega \approx [(1 - l^*)e]^N$$

where $l = L/N$ and U_0 is the "mean" intermolecular energy. Extension to a three dimensional system comprised of spheres gives

$$Z = [\gamma e^3 (v^{1/3} - v^{*1/3})^3]^N \exp(-U_0/kT) \dots (4.4.1)$$

where γ is a geometric factor used to establish the relationships

$$(\gamma v^*)^{1/3} = l^* \text{ and } (\gamma v)^{1/3} = 1$$

By defining an element or segment such that there are r segments in a molecule and, by allowing each such one to have $3C$ degrees of freedom, the partition function reduces to,

$$Z = Z_{\text{comb}} [\gamma(v^{1/3} - v^*^{1/3})^3]^{rNC} \exp(-U_0/kT) \dots (4.4.2)$$

where Z_{comb} is a term accounting for the number of ways of dispersing the rN segments among one another, without regard to the precise location of each segment relative to the other segments.

The mean intermolecular energy, U_0 , can be calculated from the cell model for liquids, but Scott¹²⁵ has shown that this model leads to an energy which is too dependent on the volume. Alternatively, U_0 can be determined from considerations of the radial distribution function¹²⁶. Frank¹²⁷ has suggested

$$U_0 = A/V^n$$

where A is a constant, V the volume and n the ratio of internal pressure to the cohesive energy density. To develop the theory further Flory equates $n = 1$ and finds,

$$U_0 = -Nrs\eta/2v \dots (4.4.3)$$

where s is the number of intermolecular contact sites per segment, η is an energy of interaction term and v is the volume of a segment. In the above equation, the intermolecular energy is implicitly related to the area of contact. By defining the reduced volume, temperature and pressure by the following equations,

$$\bar{v} = v/V^*$$

$$\bar{T} = T/T^* = 2V^*CRT/sn \dots (4.4.4)$$

$$\bar{p} = p/p^* = 2pV^{*2}/sn \dots (4.4.5)$$

where T and p are the temperature and pressure of the system, a reduced partition function (in molar units) is obtained:

$$Z = Z_{\text{comb}} (\gamma V^*)^{r_{\text{NC}}} (\bar{v}^{-1/3} - 1)^{3r_{\text{NC}}} \exp(r_{\text{NC}}/\bar{v}\bar{T}) \quad \dots (4.4.6)$$

The reduced equation of state obtained from this function

$$\bar{p}\bar{v}/\bar{T} = [\bar{v}^{-1/3}/(\bar{v}^{-1/3} - 1)] - 1/\bar{v}\bar{T} \quad \dots (4.4.7)$$

gives at zero pressure,

$$\bar{T} = (\bar{v}^{-1/3} - 1)/\bar{v}^{-4/3} \quad \dots (4.4.8)$$

In a previous paper Flory¹²⁹ related the reduced variables to the experimentally measured coefficients of thermal expansion and compressibility. They take the form,

$$\bar{v}^{-1/3} - 1 = \frac{\alpha T}{3(1 + \alpha T)}$$

$$\bar{T} = (\bar{v}^{-1/3} - 1)/\bar{v}^{-4/3}$$

$$\bar{p} = p/p^*$$

where $p^* = (\partial p/\partial T)_V \bar{T} \bar{v}^2$ is termed the characteristic pressure.

Binary Mixtures

The molecular elements or segments of the two species r_1 and r_2 are defined such that their ratio is equal to the ratio of their respective molar core volumes v_1^* and v_2^* . The molar core volume or characteristic volume is given in terms of the reduced volume by,

$$v^* = V/\bar{v} = rV^*$$

where V is the molar volume. Similarly, the ratio of s_1 to s_2 is given by the ratio of the molecular surface areas of contact per segment.

If A_{11} , A_{22} and A_{12} represent the number of contact pairs between the respective species, then

$$2A_{11} + A_{12} = s_1 r_1 N_1$$

$$2A_{22} + A_{12} = s_2 r_2 N_2$$

and, by defining a site fraction θ_2 by

$$\theta_2 = 1 - \theta_1 = s_2 r_2 N_2 / s \bar{r} N \quad \dots (4.4.9)$$

where

$$\bar{r} = (r_1 N_1 + r_2 N_2) / N$$

$$s = (s_1 r_1 N_1 + s_2 r_2 N_2) / \bar{r} N \quad \dots (4.4.10)$$

$$N = N_1 + N_2 = \text{total number of moles.}$$

A_{12} can be calculated from

$$A_{12} = s_1 r_1 N_1 \theta_2 \quad \dots (4.4.11)$$

If η_{11}/v , η_{12}/v and η_{22}/v represents the energies associated with each contact pair then the mean intermolecular energy is given by,

$$-U_o = (A_{11} \eta_{11} + A_{12} \eta_{12} + A_{22} \eta_{22}) / v$$

From the preceding equations,

$$-U_o = (s_1 r_1 N_1 \eta_{11} + s_2 r_2 N_2 \eta_{22} - s_2 r_2 N_2 \theta_1 \Delta \eta) / 2v \quad \dots (4.4.12)$$

where

$$\Delta\eta = \eta_{11} + \eta_{22} - 2\eta_{12}$$

Further simplification gives

$$-U_o = (\bar{r}Ns/2v)(\theta_1\eta_{11} + \theta_2\eta_{22} - \theta_1\theta_2\Delta\eta) \quad \dots (4.4.13)$$

To obtain the interaction terms η_{11} , etc., in terms of the characteristic parameters it is necessary to define the segment fraction

$$\begin{aligned} \phi_2' &= 1 - \phi_1' = r_2N_2/(r_1N_1 + r_2N_2) \\ &= N_2v_2^*/(N_1v_1^* + N_2v_2^*) \quad \dots (4.4.14) \end{aligned}$$

and the site fraction is given in terms of the segment fraction by

$$\theta_2 = (s_2/s)\phi_2'$$

From equation (4.4.5)

$$p_1^* = s_1\eta_{11}/2v_1^{*2}, \quad p_2^* = s_2\eta_{22}/2v_2^{*2} \quad \dots (4.4.15)$$

and to avoid the use of the suspect Berthelot relationship,

$$\begin{aligned} \eta_{12} &= (\eta_{11}\eta_{22})^{1/2}, \text{ a term } X_{21} \text{ is defined by,} \\ X_{21} &= s_2\Delta\eta/2v_1^{*2} \quad \dots (4.4.16) \end{aligned}$$

By ignoring the difference between the energy and the enthalpy, and using the relationship $v^* = rV^*$, Flory obtains for the enthalpy of mixing

$$\begin{aligned} \Delta H^m &= U_o(\text{mixture}) - U_o(1) - U_o(2) \\ &= x_1 p_{11}^* v_1^* (1/\bar{v}_1 - 1/\bar{v}) + x_2 p_{22}^* v_2^* (1/\bar{v}_2 - 1/\bar{v}) \\ &\quad + x_2 v_2^* \theta_1 X_{21} / \bar{v} \quad \dots (4.4.17) \end{aligned}$$

where \bar{v}_1 and \bar{v}_2 are the reduced volumes of the pure components and \bar{v} is the reduced volume of the mixture - \bar{v} depends on the X_{21} term, as can be seen from the following relationships,

$$\bar{v} = \bar{v}^E + \bar{v}^O \quad \dots (4.4.18)$$

where

$$\bar{v}^O = \phi_1' \bar{v}_1 + \phi_2' \bar{v}_2 \quad \dots (4.4.19)$$

$$\bar{v}^E = (\bar{v}^O)^{7/3} [4/3 - \bar{v}^{O1/3}]^{-1} (\bar{T} - \bar{T}^O) \dots (4.4.20)$$

and

$$\bar{T}^O = (\bar{v}^{O1/3} - 1) / \bar{v}^{O4/3} \quad \dots (4.4.21)$$

$$\bar{T} = \left[\frac{\phi_1' p_1^* \bar{T}_1 + \phi_2' p_2^* \bar{T}_2}{\phi_1' p_1^* + \phi_2' p_2^*} \right] \left[\frac{\phi_2' \theta_1 X_{21}}{1 - \phi_1' p_1^* + \phi_2' p_2^*} \right]^{-1} \quad \dots (4.4.22)$$

The partial molar excess enthalpy is given by,

$$\begin{aligned} \bar{H}_2^E &= p_2^* v_2^* \left\{ 1/\bar{v}_2 - 1/\bar{v} \right\} + \alpha' T (\bar{T}_2 - \bar{T}) / \bar{T} \bar{v} \\ &\quad + v_2^* X_{21} (1 + \alpha' T) \theta_1^2 / \bar{v} \quad \dots (4.4.23) \end{aligned}$$

$$\text{where } \alpha' = \frac{3(\bar{v}^{1/3} - 1)}{T[1 - 3(\bar{v}^{1/3} - 1)]} \quad \dots (4.4.24)$$

The excess volume is given by,

$$V^E = (x_1 v_1^* + x_2 v_2^*) \bar{v}^E \quad \dots (4.4.25)$$

The excess entropy is given by

$$\begin{aligned}
S^E &= -3(x_1 p_1^* v_1^* \bar{T}_1 / T) \ln [(\bar{v}_1^{1/3} - 1) / (\bar{v}^{1/3} - 1)] \\
&\quad - 3(x_2 p_2^* v_2^* \bar{T}_2 / T) \ln [(\bar{v}_2^{1/3} - 1) / (\bar{v}^{1/3} - 1)] \\
&\quad - R(x_1 \ln \phi_1' + x_2 \ln \phi_2') + R(x_1 \ln x_1 + x_2 \ln x_2) \quad \dots (4.4.26)
\end{aligned}$$

and

$$\begin{aligned}
\bar{S}_2^E &= -\frac{3p_2^* v_2^* \bar{T}_2}{T} \ln [(\bar{v}_2^{1/3} - 1) / (\bar{v}^{1/3} - 1)] \\
&\quad + p_2^* v_2^* \alpha' (\bar{T}_2 - \bar{T}) / \bar{T} \bar{v} + \alpha' v_2^* x_{21} \theta_1^2 / \bar{v} \\
&\quad - R[\ln \phi_2' + \phi_1'(1 - v_2^* / v_1^*)] + R \ln x_2 \quad \dots (4.4.27)
\end{aligned}$$

The terms used in the above equations for the excess thermodynamic functions are summarized for convenience.

Pure Components

$$\bar{v} = \left[\frac{\alpha T}{3(1 + \alpha T)} + 1 \right]^3$$

$$\bar{T} = (\bar{v}^{1/3} - 1) / \bar{v}^{4/3}$$

$$p^* = (\partial p / \partial T)_{\bar{v}} \bar{T} \bar{v}^{-2}$$

Mixtures

\bar{v} is defined by equations (4.4.18) to (4.4.22).

$$\phi_2' = x_2 v_2^* / (x_1 v_1^* + x_2 v_2^*)$$

$$\theta_2 = s_2 \phi_2' / (s_1 \phi_1' + s_2 \phi_2')$$

For spherical molecules Flory equates

$$s_1/s_2 = (v_1^*/v_2^*)^{-1/3}$$

$$\theta_2 = \frac{\phi_2'}{\phi_1'(s_1/s_2) + \phi_2'}$$

From Flory's equations it is not clear whether one should consider

- (i) the enthalpy or the energy of mixing,
- (ii) the entropy determined for the constant volume or constant pressure process. From the introduction, one suspects that the constant pressure process is under consideration but in the derivation of his equation (33) he states "Ignoring the difference between the energy and the enthalpy of a condensed system at low pressure ...". It is not explicitly defined whether the term energy refers to the constant volume or constant pressure process. For the system OMCTS - C₆H₆ this question is unimportant because of the small excess volume. For the system OMCTS - CCl₄ this distinction is important.

For the former system, the excess energy at $x_1 = .4$ was used to fix a value for X_{21} as required by the theory. From this value of X_{21} the partial and total excess energies and entropies were calculated over the concentration range and compared with the constant volume experimental results. The excess volumes were also calculated. Flory gives an alternative method where the experimental excess volumes, rather than the theoretical values, are used. Excess functions calculated from both methods are listed in Tables 4.4.1 and 4.4.2.

Flory's theory gives a remarkably good account of the excess entropy,

a reasonably good account of the partial molar excess entropy and the partial molar excess energy and predicts the approximate shape of the variation of the excess energy with concentration when the calculated excess volumes are used. Much poorer agreement between theory and experiment results when experimental excess volumes are used.

The theory fails to give any account of the excess volumes. Calculations at 60°C gave the following results at $x_1 = .4$:

$$V^E = 0.984 \text{ ml mole}^{-1}$$

$$S^E/R = 0.278$$

$$\bar{S}_2^E/R = 0.249$$

The theory therefore predicts that there is an increase in the excess volume with temperature (at variance with experiment) and that the excess entropy is temperature independent.

For the system OMCTS - CCl_4 , the theory again gives a good account of the total and partial excess entropy, provided the calculated values of the excess volume are used, and the excess energy not the excess enthalpy, is used to establish the X_{21} term. By using the experimental excess volumes, negative partial molar excess functions are predicted at low x_1 . Furthermore, the theory predicts for this system an increase in the excess volume with temperature, again at variance with experiment, and that the excess entropy is independent of temperature. The results calculated using the excess energy are given in Tables 4.4.3 and 4.4.4.

Calculations were carried out using the excess enthalpy rather than the excess energy. The calculated and experimental entropy values are listed in Table 4.4.5. A much poorer fit was obtained.

Summary

By including a term in the entropy (\bar{v}) which depends on the energy (or enthalpy) of mixing, a remarkably good agreement between experiment and theory results. The theory does not give a good account of the partial molar excess functions and totally fails to predict the excess volume. From the foregoing analysis, it appears that the calculated excess volume should be used and that better agreement results if the excess energy rather than the excess enthalpy is used to establish X_{21} . Flory¹²⁸ has observed that in some systems a better agreement is achieved by using the observed excess volumes. The computer program is listed in Appendix III.

TABLE 4.4.1

Flory Calculations using Calculated Excess VolumesOMCTS (1) - C₆H₆ (2) - 25°C

x_1	V^E (calc.)	V^E (exp.)	U^E (calc.)	U^E (exp.)	\bar{U}_2^E (calc.)	\bar{U}_2^E (exp.)
.1	.343	-.017	95	103	14	36
.2	.588	-.028	152	160	46	88
.3	.739	-.027	180	186	84	144
.4	.806	-.017	189	190	126	202
.5	.800	-.007	181	178	166	260
.6	.731	.001	161	155	206	320
.7	.610	.006	131	122	244	367
.8	.443	.006	94	87	279	408
.9	.238	.004	50	47	312	448

x_1	S^E/R (calc.)	S^E/R (exp.)	\bar{S}_2^E/R (calc.)	\bar{S}_2^E/R (exp.)
.1	.141	.140	.029	.042
.2	.223	.222	.092	.107
.3	.265	.258	.169	.189
.4	.277	.268	.249	.275
.5	.265	.257	.330	.364
.6	.237	.227	.409	.450
.7	.193	.181	.485	.526
.8	.138	.127	.557	.593
.9	.073	.069	.626	.653

V^E Units - ml mole⁻¹

U^E Units - cal mole⁻¹

TABLE 4.4.2

Flory Calculations using Experimental Excess Volumes

OMCTS (1) - C₆H₆ (2)

x_1	U^E (calc.)	U^E (exp.)	\bar{U}_2^E (calc.)	\bar{U}_2^E (exp.)
.1	94	103	-14	36
.2	150	160	15	89
.3	180	186	65	144
.4	189	190	126	202
.5	182	178	188	260
.6	163	155	251	318
.7	133	122	311	368
.8	95	87	369	408
.9	50	47	424	448

x_1	S^E/R (calc.)	S_V^E/R (exp.)	\bar{S}_2^E/R (calc.)	\bar{S}_{v2}^E/R (exp.)
.1	.093	.140	-.026	.042
.2	.147	.222	.019	.108
.3	.176	.258	.096	.189
.4	.185	.268	.188	.275
.5	.179	.256	.286	.364
.6	.161	.227	.384	.450
.7	.132	.181	.481	.526
.8	.095	.127	.574	.593
.9	.050	.069	.664	.653

U^E Units - cal mole⁻¹

TABLE 4.4.3

Flory Calculations using Calculated Excess Volumes

OMCTS (1) - CCl₄ (2) - 25°C

x_1	v^E (calc.)	v^E (exp.)	U^E (calc.)	U^E (exp.)	\bar{U}_2^E (calc.)	\bar{U}_2^E (exp.)
.1	.115	-.138	27	36	4	12
.2	.195	-.226	44	53	13	36
.3	.243	-.257	53	57	25	48
.4	.263	-.269	56	56	37	63
.5	.260	-.258	54	52	50	82
.6	.237	-.210	48	47	62	100
.7	.198	-.165	39	36	74	110
.8	.144	-.108	28	25	86	122
.9	.077	-.054	15	12	96	124

x_1	S^E/R (calc.)	S^E/R (exp.)	\bar{S}_2^E/R (calc.)	\bar{S}_2^E/R (exp.)
.1	.096	.094	.021	.023
.2	.154	.147	.066	.082
.3	.183	.167	.122	.121
.4	.193	.175	.182	.178
.5	.186	.169	.243	.247
.6	.167	.146	.304	.296
.7	.137	.119	.363	.339
.8	.098	.082	.420	.381
.9	.052	.043	.475	.420

v^E units - ml mole⁻¹
 U^E units - cal mole⁻¹

TABLE 4.4.4

Flory Calculations using Experimental Excess VolumesOMCTS (1) - CCl₄ (2) - 25°C

x_1	U^E (calc.)	U^E (exp.)	\bar{U}_2^E (calc.)	\bar{U}_2^E (exp.)
.1	26	36	-15	12
.2	42	53	- 7	36
.3	53	57	13	48
.4	56	56	33	63
.5	55	52	64	82
.6	51	47	93	100
.7	42	36	120	111
.8	31	25	147	122
.9	17	12	172	124
x_1	S^E/R (calc.)	S^E/R (exp.)	\bar{S}_2^E/R (calc.)	\bar{S}_2^E/R (exp.)
.1	.064	.094	-.015	.023
.2	.104	.147	.018	.082
.3	.127	.167	.075	.121
.4	.135	.175	.143	.178
.5	.131	.169	.215	.247
.6	.121	.146	.290	.296
.7	.100	.119	.363	.340
.8	.073	.082	.434	.381
.9	.039	.043	.502	.420

U^E units - cal mole⁻¹

TABLE 4.4.5Flory Calculations using Calculated Excess Volumes and ExcessEnthalpy at $x_1 = .4$ to calculate X_{21} OMCTS (1) - CCl₄ (2) -25°C

x_1	S^E/R (calc.)	S_P^E/R (exp.)	\bar{S}_2^E/R (calc.)	\bar{S}_{p2}^E/R (exp.)
.1	.092	.060	.020	.016
.2	.147	.095	.064	.044
.3	.176	.111	.119	.076
.4	.184	.118	.177	.118
.5	.179	.116	.237	.156
.6	.160	.104	.295	.196
.7	.131	.086	.353	.235
.8	.094	.061	.408	.274
.9	.050	.033	.462	.314

4.5 QUASI-LATTICE THEORY

Barker's quasi-lattice theory¹¹ has been extensively used by a number of authors to correlate the thermodynamic properties of associated solutions^{130,131,132}. By fixing certain contact energies for the various types of interactions these authors have been able to correlate the variation of the excess energy with the concentration. In the quasi-lattice model it is assumed that the molecules in the solution are distributed over a fixed lattice which is usually assumed to have a coordination number Z equal to four. To allow for different molecular sizes, the molecules are allowed to occupy a number of lattice sites proportional to their volumes. The excess energy is determined by considering the number of contact areas or sites on each molecular species and assigning an energy u_{ij} to represent the energy of interaction (per mole) between a contact area of type i and type j .

The excess energy for interactions occurring between two types of sites is given by,

$$U^E = -2RTX_1X_2\eta_{12}\ln\eta_{12} \quad \dots \quad (4.5.1)$$

where X_1 and X_2 are obtained by the solution of the pair of equations,

$$X_1(X_1 + \eta_{12}X_2) = x_1Q_1/2 \quad \dots \quad (4.5.2)$$

$$X_2(\eta_{12}X_1 + X_2) = x_2Q_2/2 \quad \dots \quad (4.5.3)$$

where Q_1 and Q_2 represents the number of contact sites on species 1 and 2 respectively and η_{12} is given by,

$$\eta_{12} = \exp(-u_{12}/RT) \quad \dots (4.5.4)$$

and u_{12} is the energy of interaction between type 1 and type 2 sites.

The excess Helmholtz free energy and excess entropy are given by,

$$\begin{aligned} A^E/RT = & x_1 [Q_1 \ln(X_1/x_1 X_1^0) + r_1(Z/2 - 1) \ln(\frac{r_1 x_1 + r_2 x_2}{r_1})] \\ & + x_2 [Q_2 \ln(X_2/x_2 X_2^0) + r_2(Z/2 - 1) \ln(\frac{r_1 x_1 + r_2 x_2}{r_2})] \end{aligned} \quad \dots (4.5.5)$$

$$S_v^E = \frac{U^E - A^E}{T} \quad \dots (4.5.6)$$

where r_1 and r_2 are the number of sites occupied by the molecular species 1 and 2 while X_1^0 and X_2^0 are the values of X_1 and X_2 at mole fractions of $x_1 = 1$ and $x_2 = 1$ respectively. In applying this theory, benzene was assumed to have 12 aromatic hydrogen type contact sites,¹³³ carbon tetrachloride 12 chloride type contact sites¹³⁰ and OMCTS 24 aliphatic hydrogen type contact sites.

Substitution of equations (4.5.2) and (4.5.3) into (4.5.1) gave the excess energy in the form

$$U^E = -2RT(Q_1 x_1/2 - X_1^2) \ln \left| \frac{Q_1 x_1/2 - X_1^2}{X_1 (X_1^2 + Q_2 x_2/2 - Q_1 x_1/2)^{1/2}} \right| \quad \dots (4.5.7)$$

This equation was solved for X_1 at $x_1 = .4$ using the appropriate experimental excess energy. It should be noted that the excess energy, rather than the excess enthalpy, is calculated from this model as the model refers to a mixing process at constant volume, a restriction

imposed in using the lattice model. The argument of the \ln term in the above equation is n_{12} . From the value of n_{12} excess energies over the total concentration range were calculated along with values of X_1 and X_2 and the latter values were substituted into equation (4.5.5) to give the excess Helmholtz free energy. If the number of lattice sites occupied is assumed to be proportional to the volumes of the molecular species, the calculated excess entropies do not agree with experiment.

The number of lattice sites occupied by OMCTS (r_1) was chosen to give a fit to the experimental entropy at $x_1 = .4$. Values of u_{12} , r_1 , r_2 and the excess entropies and energies for the system OMCTS - C_6H_6 are listed in Table 4.5.1. Benzene was assumed to occupy four lattice sites¹³².

For the system OMCTS - CCl_4 the value of r_1 obtained from the previous calculation was employed, and r_2 (the number of lattice sites occupied by CCl_4) was chosen to give a fit to the entropy. Results for this system are given in Table 4.5.2. The ratio $r_{CCl_4}/r_{C_6H_6}$ was found to equal the ratio of the molar volumes.

The most important feature of this theory is its ability to calculate contact energies between different types of contact areas. The contact energy calculated for interaction between an aromatic hydrogen on benzene and an aliphatic hydrogen on OMCTS was found to be $47.8 \text{ cal mole}^{-1}$, in excellent agreement with the value given by McLure et al.,¹³³ $48.4 \text{ cal mole}^{-1}$, obtained from a study of the enthalpy of

mixing data for mixtures of benzene and a number of alicyclic compounds.

The search for a constant contact energy between an aliphatic hydrogen and a chlorine atom proved fruitless, as can be seen from the contact energies listed in Table 4.5.3. The other contact energies were calculated from the excess enthalpy and excess volume data for the systems $C_6H_{12} - CCl_4$ ^{134,135} and $C(CH_3)_4 - CCl_4$ ^{136,137}.

In the above discussion it has been assumed that the oxygen atoms on the OMCTS molecule are buried under the layer of 24 hydrogen atoms and that they do not contribute to the interaction energy².

Summary

The quasi-lattice model requires too many adjustable parameters to make it a suitable working theory. It is interesting that the aliphatic - aromatic hydrogen contact energy should agree with those calculated from similar systems but this agreement may be fortuitous in light of the difficulty in finding a consistent contact energy for a chlorine - aliphatic hydrogen interaction.

TABLE 4.5.1

Quasi-Lattice CalculationsOMCTS (1) - C₆H₆ (2) - 25°C

	$Q_1 = 24$	$r_1 = 10.63$		
	$Q_2 = 12$	$r_2 = 4.0$		
	$Z = 4$	$u_{12} = 47.8 \text{ cal mole}^{-1}$		
x_1	S_V^E/R (calc.)	S_V^E/R (exp.)	U^E (calc.)	U^E (exp.)
.1	.119	.140	92	103
.2	.197	.222	148	160
.3	.244	.258	178	186
.4	.265	.268	189	190
.5	.264	.256	184	178
.6	.243	.227	167	155
.7	.204	.181	138	122
.8	.150	.127	100	87
.9	.082	.069	54	47
	$U^E \text{ units} - \text{cal mole}^{-1}$			

TABLE 4.5.2Quasi-Lattice CalculationsOMCTS (1) - CCl₄ (2) - 25°C

$Q_1 = 24$	$r_1 = 10.63$			
$Q_2 = 12$	$r_2 = 4.33$			
$Z = 4$	$u_{12} = 13.7 \text{ cal mole}^{-1}$			
x_1	S_V^E/R (calc.)	S_V^E/R (exp.)	U^E (calc.)	U^E (exp.)
.1	.078	.094	27	36
.2	.130	.147	44	53
.3	.162	.167	53	57
.4	.175	.175	56	56
.5	.174	.169	54	52
.6	.159	.146	49	47
.7	.133	.119	40	36
.8	.098	.082	29	25
.9	.053	.043	16	12
U^E units - cal mole ⁻¹				

TABLE 4.5.3Contact Energy Between Aliphatic Hydrogen and Chlorine

<u>System</u>	u_{12} (cal mole ⁻¹)
OMCTS - CCl ₄ (25°C)	13.7
C ₆ H ₁₂ - CCl ₄ (25°C)	7.6
C(CH ₃) ₄ - CCl ₄ (25°C)	36.2

4.6 SCALED PARTICLE THEORY

The theories considered so far have shown moderate success in predicting the size and concentration dependence of the total excess entropy, but have failed to give an accurate account of the partial molar excess entropy. The fitting of a partial molar excess function is a more crucial test of any theory. It will be shown in this section that the equation calculated from the scaled particle theory predicts the correct form of the partial molar excess entropy with astonishing accuracy.

In the scaled particle theory one considers a fluid composed of spherically symmetrical molecules which possess a hard core of diameter a , the rigid sphere diameter, but occupy a volume related to the molar volumes of the molecules. Reiss, Frisch and Lebowitz¹³⁸ have determined an equation of state for this system of rigid spheres which takes the form,

$$p = \rho kT(1 + y + y^2)/(1 - y)^3 \quad \dots (4.6.1)$$

where $y = \pi a^3 \rho / 6$ and is equal to the ratio of the hard core volume to the volume occupied by the molecule. ρ is the number density given by,

$$\rho = N/V \quad \dots (4.6.2)$$

where N is the number of molecules occupying a volume V .

The above equation of state can also be derived from the exact solution¹³⁹ of the Percus - Yevick equation¹⁴⁰. It should also be noted

that this equation of state gives good agreement with machine calculations on hard sphere systems¹⁴¹. Recently Lebowitz¹⁷ has considered the case of mixtures of hard spheres and derived a general equation of state for a multicomponent system. For a two component system the equation of state becomes

$$p/kT = \{(\rho_1 + \rho_2)(1 + \epsilon + \epsilon^2) - [(18/\pi)\gamma_1\gamma_2(a_2 - a_1)^2]x \\ [a_1 + a_2 + a_1a_2(\gamma_1a_1^2 + \gamma_2a_2^2)]\}(1 - \epsilon)^{-3} \quad \dots \quad (4.6.3)$$

where

$$\gamma_i = \pi N_i/6V$$

$$\epsilon = \pi(N_1a_1^3 + N_2a_2^3)/6V$$

Yosim¹⁸ has calculated the excess entropy for the mixing of two liquids by considering a thermodynamic cycle involving the following five steps:

- (i) The two pure liquids were converted into systems of rigid spheres of diameter a , but occupying the same volume. This process may be achieved by "discharging" the intermolecular potential i.e. the intermolecular attractive potential was removed and the intermolecular repulsive potential was changed to one which was zero when the spheres were separated by a distance greater than the diameter of the spheres and was infinite when the separation between the spheres was less than or equal to the diameters. Yosim termed this a discharging entropy and it is given by,

$$\Delta S_1 = n_1 \Delta S_{\text{dchg}(1)} + n_2 \Delta S_{\text{dchg}(2)} \quad \dots (4.6.4)$$

where n_1 and n_2 are the number of moles of component 1 and 2 respectively.

- (ii) The rigid spheres were then expanded to a pressure sufficiently low that the behaviour of the hard sphere gas could be regarded as ideal. Yosim and Owens¹⁴² have shown that, for a pure liquid, the entropy change in this process is given by $\int (dq_{\text{rev.}}/T)$ and, since for a hard sphere gas the change in internal energy on compression is zero, the entropy for this step is

$$\Delta S = \int_{v^l}^{v^g} (p/T) dv \quad \dots (4.6.5)$$

and for the mixture

$$\Delta S_2 = n_1 \int_{v_1^l}^{v_1^g} (p/T) dv + n_2 \int_{v_2^l}^{v_2^g} (p/T) dv \quad \dots (4.6.6)$$

The entropy change for this step may be calculated by substituting the equation of state (4.6.1) for each component.

- (iii) The expanded gases were then mixed at constant pressure. For an ideal gas the entropy of mixing is ideal

$$\Delta S_3 = -n_1 R \ln x_1 - n_2 R \ln x_2$$

where x_1 and x_2 are the mole fractions of each component.

- (iv) The gas mixture was then compressed to the volume of the

solution v_s^l . The entropy change in this step is given by

$$\Delta S_4 = \int_{v_s^g}^{v_s^l} (p/T) dV \quad \dots (4.6.7)$$

where p is obtained from the equation of state for the hard sphere mixture, (4.6.3).

(v) The intermolecular attractive potential was then restored and the repulsive potential was changed from the hard core model repulsive potential to the repulsive potential of the system. In other words the mixture was "recharged".

$$\Delta S_5 = (n_1 + n_2) S_{\text{chg.}(1,2)} \quad \dots (4.6.8)$$

The entropy of mixing to form the solution is given by the sum of the entropy changes involved in the five steps.

$$\Delta S^m = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 + \Delta S_5 \quad \dots (4.6.9)$$

and the excess entropy ,

$$S^E = \Delta S^m + n_1 R \ln x_1 + n_2 R \ln x_2 \quad \dots (4.6.10)$$

$$\therefore S^E = \Delta S_1 + \Delta S_2 + \Delta S_4 + \Delta S_5 \quad \dots (4.6.11)$$

Yosim assumed that the "charging" entropies were small and that the difference between the charging entropy of the solution and the pure components could be neglected. Therefore $\Delta S_1 = -\Delta S_5$, and $S^E = \Delta S_2 + \Delta S_4$ and, after assuming $v_1^g = v_2^g = v_s^g$, and reverting to the symbolism v_i^o instead of v_i^l for the pure components, he derived the following equation, in terms of the hard sphere diameters, for

the excess entropy for one mole of liquid mixture,

$$\begin{aligned}
 S^E/R &= x_1 \ln \left| \frac{V_s - c(x_1 a_1^3 + x_2 a_2^3)}{(V_1^o - ca_1^3)} \right| + x_2 \ln \left| \frac{V_s - c(x_1 a_1^3 + x_2 a_2^3)}{(V_2^o - ca_2^3)} \right| \\
 &+ \frac{3c}{2} \left| x_1 a_1^3 \frac{(2V_1^o - ca_1^3)}{(V_1^o - ca_1^3)^2} + x_2 a_2^3 \frac{(2V_2^o - ca_2^3)}{(V_2^o - ca_2^3)^2} \right| \\
 &+ 3/2 \left| V_s - c(x_1 a_1^3 + x_2 a_2^3) \right|^{-2} \{ c^2 [x_1^3 a_1^6 + x_1^2 x_2 (2a_1^5 a_2 - a_1^4 a_2^2 + 2a_1^3 a_2^3) \\
 &+ x_1 x_2^2 (2a_1^3 a_2^3 - a_1^2 a_2^4 + 2a_1 a_2^5) + x_2^3 a_2^6] \\
 &- 2V_s c [x_1^2 a_1^3 + x_1 x_2 (a_1 a_2^2 + a_1^2 a_2) + x_2^2 a_2^3] \} \quad \dots (4.6.12)
 \end{aligned}$$

$$\text{where } V_s = x_1 V_1^o + x_2 V_2^o + V^E \quad \dots (4.6.13)$$

$$c = \pi N/6$$

$$N = \text{Avagadro's Number.}$$

If we define the following reduced variables,

$$a_2 = a_1(1 + \epsilon), \quad \epsilon = (a_2 - a_1)/a_1 \quad \dots (4.6.14)$$

$$V_2^o = V_1^o(1 + \phi), \quad \phi = (V_2^o - V_1^o)/V_1^o \quad \dots (4.6.15)$$

$$\alpha = V^E/V_1^o \quad \dots (4.6.16)$$

$$y = ca_1^3/V_1^o \quad \dots (4.6.17)$$

then the excess entropy is given by,

$$\begin{aligned}
S^E/R &= x_1 \ln \left\{ \frac{1 + x_2 \phi + \alpha - y[x_1 + x_2(1 + \epsilon)^3]}{(1 - y)} \right\} \\
&+ x_2 \ln \left\{ \frac{1 + x_2 \phi + \alpha - y[x_1 + x_2(1 + \epsilon)^3]}{[1 - y(1 + \epsilon)^3 + \phi]} \right\} \\
&+ \frac{3}{2} y \left\{ \frac{x_1(2 - y)}{(1 - y)^2} + x_2(1 + \epsilon)^3 \frac{[2 + 2\phi - y(1 + \epsilon)^3]}{[1 - y(1 + \epsilon)^3 + \phi]^2} \right\} \\
&+ \frac{3}{2} (y^2 \{x_1^3 + x_1^2 x_2 [2(1 + \epsilon) - (1 + \epsilon)^2 + 2(1 + \epsilon)^3] \\
&+ x_1 x_2^2 [2(1 + \epsilon)^3 - (1 + \epsilon)^4 + 2(1 + \epsilon)^5] + x_2^3 (1 + \epsilon)^6\} \\
&- 2y(1 + x_2 \phi + \alpha) \{x_1^2 + x_1 x_2 [(1 + \epsilon)^2 + (1 + \epsilon)] + x_2^2 (1 + \epsilon)^3\}) \\
&\times (1 + x_2 \phi + \alpha - y[x_1 + x_2(1 + \epsilon)^3])^{-2} \quad \dots (4.6.18)
\end{aligned}$$

To calculate the excess entropy it is necessary to know the molar volumes of the two components V_1^0 and V_2^0 , the excess volume V^E and the hard core diameters, a_1 and a_2 .

Determination of "a"

The hard core diameter, a , can be considered as the diameter at which the intermolecular potential becomes repulsive¹⁴³. To determine "a" it is necessary to know the virial coefficients and the form of the intermolecular potential.

Alternatively Reiss, Frisch, Helfand and Lebowitz¹⁴⁴ have shown that the heat of vaporization can be expressed in terms of the scaled particle parameter y by,

$$\Delta H_v = RT + \alpha RT^2 (1 + 2y)^2 / (1 - y)^3 \quad \dots (4.6.19)$$

where α is the coefficient of thermal expansion. These authors now consider this equation to be superseded by the Yosim and Owens equation,¹⁴²

$$\Delta H_v = RT \{ \ln[v^g/v^l(1 - y)] + 3y(2 - y)/2(1 - y)^2 \} \dots (4.6.20)$$

where v^g and v^l are the volumes occupied by the gas and liquid respectively. The heat of vaporization can be determined from vapour pressure measurements provided the virial coefficients are available. If the vapour pressure is expressed in the form

$$\log p = A + B/(C + t)$$

the heat of vaporization is

$$\Delta H_v = - \frac{2.3026RT^2 B [1 + (B_{11} - v^l)/v^g]}{(C + t)^2} \quad \dots (4.6.21)$$

where

$$v^g = RT/p + B_{11} \quad \dots (4.6.22)$$

B_{11} is the second virial coefficient and p is the pressure¹⁴⁵. When the virial coefficient is not known it may be calculated from the Dieterici equation,¹⁴⁶

$$B_{11} = \frac{1}{2}V_c - 2T_c V_c / T \quad \dots (4.6.23)$$

where T_c and V_c are the critical temperature and volume respectively.

The hard sphere parameter y can also be calculated from the coefficient of thermal expansion and the compressibility¹⁴⁷. The equations relating the parameter to the experimentally measured quantities are given below.

$$\alpha = (1 - y^3)/T(1 + 2y)^2 \quad \dots (4.6.24)$$

$$\beta = \pi a^3(1 - y)^4/6kTy(1 + 2y)^2 \quad \dots (4.6.25)$$

In Tables 4.6.1 and 4.6.2 the values of a and y calculated from equations (4.6.19), (4.6.20), (4.6.24) and (4.6.25) are listed. The values of the parameter are not consistent.

Equation (4.6.20) appears to be preferred,¹⁴⁷ particularly as it expresses most closely the temperature dependence of " a " expected for "real" systems. For OMCTS the measured vapour pressures at the working temperatures are quite small and, consequently, the heat of vaporization determined from the above methods must be rather inaccurate. For this reason, the hard sphere diameter of OMCTS was adjusted so that the calculated and experimental excess entropy agreed at $x_1 = .4$ for the system OMCTS - benzene. The value found to give fit at $x_1 = .4$ 8.418 Å, was reasonably close to the calculated value, 8.588 Å. The hard sphere diameter of benzene, 5.309 Å, at 25°C, was calculated from equation (4.6.20). Excess volumes were calculated from equations previously discussed.

The partial molar excess entropy of component two was calculated

from the formula¹⁴⁸

$$\bar{S}_2^E = S_{(3)}^E - 8.33333x_1[S_{(1)}^E - S_{(5)}^E - 8(S_{(2)}^E - S_{(4)}^E)]$$

where $S_{(1)}^E$, $S_{(2)}^E$, $S_{(3)}^E$, $S_{(4)}^E$ and $S_{(5)}^E$ were the values of S^E calculated for mole fractions of $x_1 = .02$, $x_1 = .01$, x_1 , $x_1 + .01$ and $x_1 + 0.02$ respectively. The calculated values of S^E and \bar{S}_2^E for the system OMCTS - benzene are listed in Table 4.6.3. Results are compared with the constant pressure entropy data. The agreement between the calculated total and partial molar excess entropy and the experimental results is astonishingly good.

Using the hard core diameter of OMCTS obtained by the adjustment method and the hard sphere diameter calculated for carbon tetrachloride, the theoretical excess entropy for the system OMCTS - CCl_4 was calculated. The values are listed in Table 4.6.4. The predicted values for this system are slightly high, but are about as good as could be expected in view of the uncertainties in the experimental results. In fact the agreement is most encouraging for two reasons:

- (a) The most disturbing feature of this theory is the very strong dependence of the excess entropy on the hard sphere diameter values. In changing the hard sphere diameter of one of the components by 0.023\AA , a change in the excess entropy (expressed as S/R) of 0.020 is noted. To prove that this dependence is correct will require much more experimental data. The fact that there is such good agreement for the system

OMCTS - CCl_4 indicates that this dependence does exist and it explains the unexpected differences in the excess entropy for the two systems.

- (b) Part of the excess entropy for the system OMCTS - CCl_4 can be attributed to expansion effects. This theory appears to allow successfully for this.

As an alternative the hard sphere diameter of CCl_4 was adjusted so that the experimental and calculated values for S^E agreed at $x_1 = .4$. The value of "a" for OMCTS used was the value calculated from the system OMCTS - C_6H_6 . The value required to give fit, 5.394\AA , differed slightly from the value of 5.417\AA used previously, calculated from equation (4.6.20). This exercise was carried out so that the variation of the calculated excess entropy with concentration could be compared with the experimental results. The results are listed in Table 4.6.5. Again there is very good agreement over the entire concentration range.

A further interesting conclusion follows when the hard core diameters are put equal to zero. If the excess volume is also zero, equation (4.6.12) becomes

$$S^E = x_1 \ln V_s/V_1^0 + x_2 \ln V_s/V_2^0$$

which is simply the volume fraction statistics equation. Furthermore, this equation can be derived if the equation of state is given by the ideal gas law $pV = RT$ and the five steps of the thermodynamic cycle

TABLE 4.6.1Comparison of Hard Sphere Diameter "a" from Various Equations

		<u>(4.6.19)</u>	<u>(4.6.20)</u>	<u>(4.6.24)</u>	<u>(4.6.25)</u>
C_6H_6	25°C	5.250 Å	5.309 Å	4.477 Å	5.007 Å
C_6H_6	60°C	5.158	5.292	4.196	4.915
CCl_4	25°C	5.377	5.417	4.603	5.143
CCl_4	60°C	5.271	5.397	4.286	5.045
OMCTS	25°C	8.274	8.588	6.825	7.717
OMCTS	60°C	8.195	8.625	6.460	7.836

TABLE 4.6.2Comparison of Hard Sphere Parameter γ from Various Equations

		<u>(4.6.19)</u>	<u>(4.6.20)</u>	<u>(4.6.24)</u>	<u>(4.6.25)</u>
C_6H_6	25°C	.5106	.5277	.3165	.4429
C_6H_6	60°C	.4631	.5000	.2493	.4006
CCl_4	25°C	.5046	.5126	.3167	.4419
CCl_4	60°C	.4549	.4883	.2445	.3988
OMCTS	25°C	.5724	.6399	.3213	.4643
OMCTS	60°C	.5326	.6208	.2609	.4655

TABLE 4.6.3Excess Entropy from Scaled Particle TheoryOMCTS (1) - C₆H₆ (2)

$$V_1^0/V_2^0 = 3.489$$

$$y_2 = 0.5277$$

$$\text{Core diam 1/Core diam 2} = 1.5865$$

$$a_1 = \text{Core diam 1} = 8.418 \text{ \AA}$$

x_1	S^E/R (calc.)	S^E/R (exp.)	\bar{S}_2^E/R (calc.)	\bar{S}_2^E/R (exp.)
.1	.135	.136	.032	.040
.2	.214	.215	.100	.102
.3	.254	.252	.182	.181
.4	.264	.264	.267	.263
.5	.254	.255	.353	.352
.6	.226	.227	.437	.441
.7	.185	.182	.517	.524
.8	.132	.128	.594	.598
.9	.070	.070	.666	.660

TABLE 4.6.4Excess Entropy from Scaled Particle TheoryOMCTS (1) - CCl₄ (2)Value of a₁ from OMCTS - C₆H₆ data

$$V_1^0/V_2^0 = 3.2145$$

$$y_2 = 0.5162$$

$$\text{Core diam 1/Core diam 2} = 1.5544$$

$$\text{Core diam 1} = 8.418 \text{ \AA}$$

x_1	S^E/R (calc.)	S^E/R (exp.)	\bar{S}_2^E/R (calc.)	\bar{S}_2^E/R (exp.)
.1	.064	.060	.013	.016
.2	.105	.095	.042	.044
.3	.128	.111	.080	.076
.4	.137	.118	.124	.118
.5	.136	.116	.171	.156
.6	.124	.104	.221	.196
.7	.104	.086	.274	.235
.8	.076	.061	.329	.274
.9	.041	.033	.385	.314

TABLE 4.6.5Excess Entropy from Scaled Particle TheoryOMCTS (1) - CCl₄ (2)

Using fixed value of a_1 and varying a_2 to give fit
 to S^E at $x_1 = .4$

$$V_1^0/V_2^0 = 3.214$$

$$y_2 = 0.5106$$

$$\text{Core diam 1/Core diam 2} = 1.5606$$

$$\text{Core diam 2} = 5.394 \text{ \AA}$$

x_1	S^E/R (calc.)	S^E/R (exp.)	\bar{S}_2^E/R (calc.)	\bar{S}_2^E/R (exp.)
.1	.054	.060	.010	.016
.2	.089	.095	.034	.044
.3	.109	.111	.066	.076
.4	.118	.118	.103	.118
.5	.117	.116	.144	.156
.6	.108	.104	.188	.196
.7	.091	.086	.236	.235
.8	.066	.061	.285	.274
.9	.036	.033	.336	.314

are repeated.

(i) Since there is no hard core and the liquid is composed of an "ideal gas" $\Delta S_1 = 0$.

(ii) The "ideal gas" liquid is expanded,

$$\begin{aligned}\Delta S_2 &= n_1 \int_{v_1^l}^{v_1^g} (p/T) dV + n_2 \int_{v_2^l}^{v_2^g} (p/T) dV \\ &= -n_1 R \ln v_1^l - n_2 R \ln v_2^l + n_1 R \ln v_1^g + n_2 R \ln v_2^g\end{aligned}$$

(iii) The expanded gases are mixed at constant pressure

$$\Delta S_3 = -n_1 R \ln x_1 - n_2 R \ln x_2$$

(iv) The mixture is compressed to the volume of the solution.

$$\begin{aligned}v_s^l &= n_1 v_1^l + n_2 v_2^l \\ \Delta S_4 &= \int_{v_s^g}^{v_s^l} (p/T) dV \\ &= R \ln v_s^l - R \ln v_s^g\end{aligned}$$

(v) The charging entropy is zero.

The excess entropy per mole of mixture is given by,

$$\begin{aligned}S^E/R &= (x_1 + x_2) \ln v_s^l - x_1 \ln v_1^l - x_2 \ln v_2^l \\ &\quad - (x_1 + x_2) \ln v_s^g + x_1 \ln v_1^g + x_2 \ln v_2^g\end{aligned}$$

and since the expanded gas is ideal, $v_s^g = v_1^g = v_2^g$. Removing the superscript l , and reverting to the previous symbols, the excess entropy becomes

$$S^E/R = x_1 \ln v_s/v_1^0 + x_2 \ln v_s/v_2^0$$

Thus the entropy of mixing of an "ideal gas" compressed to the volume of the solution is not ideal and is given by volume fraction statistics. The introduction of the hard spheres can be considered as a perturbation on the volume fraction statistics which can either give an increase or a decrease from the value depending on the diameters of the hard spheres. It could be argued that the model presented in this section is rather artificial, but if the excess entropy and excess energy are not related, which should be so if the excess energy is small compared with RT , then the entropy of mixing equations presented should give a reasonably valid representation of the processes occurring in the mixture. This is so if the equations of state used are valid for hard sphere fluids at the densities under consideration.

The scaled particle theory equation of state gives good agreement with machine calculations on mixtures of hard spheres over the whole fluid range. It does not however predict a discontinuity at a reduced density $y = .74$, which corresponds to close packing of rigid spheres. The ability of the equation of state to describe approximately the behaviour of real fluids at high reduced densities remains in doubt.

4.7 EQUILIBRIUM PROPERTIES - SUMMARY AND CONCLUSIONS

Using adjusted solubility parameters the Scatchard - Hildebrand equation gives a good representation of the total and partial excess energy. By carrying out an analysis similar to that used to calculate U^E for the system OMCTS - CCl_4 , the excess energy for the system cyclohexane - OMCTS can be predicted. This system will be studied in the near future.

Barker's quasi-lattice theory, although it predicts the correct interaction energy between an aliphatic and an aromatic hydrogen, requires too many adjustable parameters. According to this theory, the excess energy for the system cyclohexane - OMCTS should be zero.

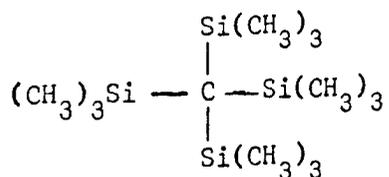
Flory's theory predicts the approximate form of the excess energy (or enthalpy?) and gives a very good account of the total excess entropy for the system OMCTS - C_6H_6 if the calculated excess volumes are used. For the system OMCTS - CCl_4 better agreement between theory and experiment results if the excess energy and entropy for the constant volume process are considered.

The scaled particle theory gives the best representation of both the total and partial excess entropy for both systems. Further developments to this theory are to be expected. Hauge and others^{147,149} have suggested methods for including in the equation of state an attractive intermolecular potential associated with the soft core, the θ function, so as to bring the model more in line with the concept of a

"real" liquid. Mathematical difficulties inevitably arise when an extension of a theory is contemplated.

None of the theories considered makes any sense of the excess volume. Prigogine's corresponding states average potential theory⁷ can predict negative excess volumes when G^E is positive but this theory is strictly limited to the case where molar volumes of the liquids are approximately equal. Likewise, Guggenheim's lattice theory⁶ has been developed to deal with hydrocarbons consisting essentially of monomer, dimer, trimer etc. mixtures. For this reason his theory has not been considered. Eyring's significant structure theory,¹⁵⁴ applied to liquid mixtures, is still in the developmental stage.

The argument that octamethylcyclotetrasiloxane is not a truly spherical molecule and that the oxygens present may not be completely isolated from interactions must hold some weight. A number of other "large" molecules have been recently synthesized. One of particular interest is tetrakis (trimethyl silyl) methane⁴⁶ which has the following structure

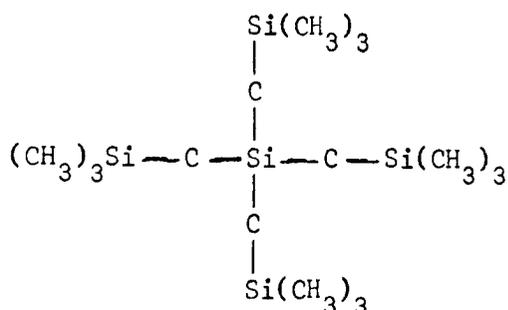


Molar volume is approximately 330 ml mole⁻¹.

This molecule is, in many ways, an ideal spherical molecule. Unfortunately this compound is a solid subliming at > 200°C. Systems

involving this compound will, however, provide valuable information on the properties of mixtures involving large and small molecules.

Another spherical molecule of interest, tetrakis (trimethylsilylmethyl) silane has been synthesised,¹⁵⁰ having the structure shown below.



This compound is a liquid above 28.5°C and its molar volume is considerably greater than those previously considered (400 ml mole⁻¹). Further studies involving these compounds along the lines described in this thesis are anticipated. To clear up doubts regarding the determination of the excess enthalpy and excess entropy from the temperature dependence of the activity coefficients, direct determinations of the excess enthalpy will be made.

More accurate excess volumes are required. The pyknometer method described, requires a number of "hidden" corrections. The dilatometer method described by Stokes¹⁵¹ and Dunn¹⁵² will be adapted to non-aqueous mixtures.

Briefly considering more complex mixtures, Stokes¹⁵³ has shown that the thermodynamics of mixtures of alcohols and non polar liquids can be

well represented by splitting the excess enthalpy into two terms, one term representing the energy of mixing to be expected if the alcohol was non-polar (Hildebrand - Scatchard type equation) and the other term representing the energy involved in hydrogen bonding. A constant energy for hydrogen bonding results only if the mixing process is assumed to be governed by volume fraction statistics.

4.8 DIFFUSION AND VISCOSITY

The diffusion and viscosity coefficients at rounded concentrations were determined by interpolation from large scale plots of diffusion coefficients versus mole fraction and $\Delta\eta$ versus mole fraction respectively. Viscosities were calculated from

$$\eta_{12} = x_1(\eta_1 - \eta_2) + \eta_2 - \Delta\eta$$

The thermodynamic correction factor $(1 + x_2 \partial \ln f_2 / \partial x_2)$ was calculated from the slopes of $\ln f_2$ determined from large scale plots of $\ln f_2$ against x_2 . Values of this correction factor are listed in Tables 4.8.1 and 4.8.2 along with the diffusion coefficients and viscosities. The 18°C thermodynamic term was obtained by extrapolation of the higher temperature data.

Mutual diffusion coefficients for the systems studied will be considered from the following aspects:

- (i) The prediction of limiting mutual diffusion coefficients from molecular properties.

- (ii) The variation of the mutual diffusion coefficient, at a particular concentration, with temperature.
- (iii) The variation of the mutual diffusion coefficient with concentration.

(1) Theories applicable to limiting mutual diffusion coefficients

For this case, the viscosity is that of the pure solvent and the thermodynamic correction factor is unity.

(a) Hydrodynamic theories

Stokes, Sutherland and Einstein,^{155,156} by considering the forces acting on a spherical particle of radius r , moving in a continuous medium of viscosity η , derived the formula

$$D = \frac{kT (1 + 3\eta/\beta r)}{6\pi\eta r(1 + 2\eta/\beta r)} \quad \dots (4.8.1)$$

for the diffusion coefficient. Since β , the coefficient of sliding friction, can have values between zero and infinity, the two limiting cases are:

$$\beta = 0, D = \frac{kT}{4\pi\eta r} \quad \dots (4.8.2)$$

$$\beta = \infty, D = \frac{kT}{6\pi\eta r} \quad \dots (4.8.3)$$

Equation (4.8.3) applies when there is no slip at the boundary of the solute particle and Sutherland¹⁵⁶ has suggested that this equation is applicable when the solute molecule is much larger than the solvent molecule. Equation (4.8.2) holds when the solvent and

TABLE 4.8.1

 D_{12} , η_{12} and $\frac{\partial \ln a_2}{\partial \ln x_2}$ at Rounded Concentrations

CMCTS (1) - C₆H₆ (2)

x_1	D_{12}	η_{12}	$\frac{\partial \ln a_2}{\partial \ln x_2}$	x_1	D_{12}	η_{12}	$\frac{\partial \ln a_2}{\partial \ln x_2}$
<u>18°C</u>				<u>35°C</u>			
0	1.011	.6703	1.000	0	1.352	.5235	1.000
.05	.933	.709	.849	.05	1.273	.5506	.871
.1	.903	.748	.800	.1	1.246	.5858	.848
.2	.921	.852	.790	.2	1.272	.667	.846
.3	.958	.983	.831	.3	1.328	.764	.877
.4	.993	1.135	.904	.4	1.381	.873	.944
.5	1.021	1.304	.946	.5	1.417	.993	.971
.6	1.030	1.493	.972	.6	1.437	1.125	.990
.7	1.025	1.710	.990	.7	1.437	1.271	1.007
.8	1.005	1.949	1.012	.8	1.416	1.433	1.014
.9	.976	2.222	1.010	.9	1.379	1.614	1.011
.95	.961	2.368	1.006	.95	1.360	1.708	1.006
1.0	.942	2.520	1.000	1.0	1.341	1.806	1.000
<u>25°C</u>				<u>45°C</u>			
0	1.152	.6024	1.000	0	1.579	.4603	1.000
.05	1.069	.6348	.858	.05	1.508	.4850	.882
.1	1.034	.6763	.814	.1	1.479	.5137	.864
.2	1.057	.771	.810	.2	1.516	.5840	.873
.3	1.107	.884	.852	.3	1.585	.6664	.904
.4	1.153	1.015	.920	.4	1.646	.759	.968
.5	1.177	1.161	.957	.5	1.692	.858	.988
.6	1.182	1.324	.979	.6	1.713	.966	.998
.7	1.180	1.508	.996	.7	1.714	1.087	1.014
.8	1.165	1.710	1.013	.8	1.699	1.219	1.016
.9	1.130	1.940	1.010	.9	1.666	1.364	1.010
.95	1.106	2.064	1.006	.95	1.648	1.438	1.005
1.0	1.085	2.191	1.000	1.0	1.632	1.514	1.000

D_{12} units - $\text{cm}^2 \text{sec}^{-1} \times 10^{-5}$, η_{12} units - centipoise

TABLE 4.8.2

D_{12} , n_{12} and $\frac{\partial \ln a_2}{\partial \ln x_2}$ at Rounded Concentrations

OMCTS (1) - CCl_4 (2)

x_1	D_{12}	n_{12}	$\frac{\partial \ln a_2}{\partial \ln x_2}$	x_1	D_{12}	n_{12}	$\frac{\partial \ln a_2}{\partial \ln x_2}$
<u>18°C</u>				<u>35°C</u>			
0	.641	1.001	1.000	0	.865	.7817	1.000
.05	.652	1.079	1.010	.05	.887	.836	1.018
.1	.665	1.154	1.023	.1	.909	.889	1.030
.2	.697	1.284	1.080	.2	.957	.988	1.085
.3	.726	1.417	1.105	.3	.999	1.080	1.107
.4	.743	1.554	1.115	.4	1.028	1.173	1.115
.5	.750	1.695	1.125	.5	1.041	1.267	1.125
.6	.751	1.841	1.100	.6	1.051	1.362	1.100
.7	.746	1.994	1.075	.7	1.049	1.464	1.075
.8	.733	2.161	1.050	.8	1.040	1.572	1.050
.9	.714	2.338	1.025	.9	1.024	1.688	1.025
.95	.704	2.429	1.013	.95	1.014	1.747	1.013
1.0	.693	2.520	1.000	1.0	1.003	1.806	1.000
<u>25°C</u>				<u>45°C</u>			
0	.722	.901 ₁	1.000	0	1.015	.686 ₆	1.000
.05	.738	.967	1.013	.05	1.042	.731	1.019
.1	.756	1.034	1.027	.1	1.072	.775	1.036
.2	.795	1.146	1.082	.2	1.130	.861	1.090
.3	.831	1.260	1.106	.3	1.183	.938	1.109
.4	.852	1.375	1.115	.4	1.225	1.013	1.115
.5	.861	1.498	1.125	.5	1.251	1.087	1.125
.6	.862	1.622	1.100	.6	1.262	1.162	1.100
.7	.855	1.755	1.075	.7	1.262	1.243	1.075
.8	.844	1.894	1.050	.8	1.256	1.330	1.050
.9	.829	2.039	1.025	.9	1.245	1.420	1.025
.95	.820	2.114	1.013	.95	1.238	1.468	1.013
1.0	.810	2.188	1.000	1.0	1.230	1.514	1.000

D_{12} units - $\text{cm}^2 \text{sec}^{-1} \times 10^{-5}$, n_{12} units - centipoise

solute molecules are of equal size. The values calculated from equations (4.8.2) and (4.8.3) are listed in Table 4.8.3.

(b) Eyring's theory

Application of Eyring's theory of kinetics²⁰ to the process of diffusion leads to equation (4.8.4). This equation drastically overestimated the diffusion coefficient.

$$D = \frac{kT}{2\eta r} \quad \dots (4.8.4)$$

Li and Chang,¹⁵⁷ by modifying Eyring's theory to account for obvious errors in the viscosity term, derived the equation,

$$D = \frac{kT}{12\eta r} \quad \dots (4.8.5)$$

Diffusion coefficients calculated from this equation are listed in Table 4.8.3. Reference to this table shows that the equation suitable for mixtures of molecules of unequal size is far from adequate. Li and Chang's equation and the Stokes-Einstein equation with slip ($\beta = 0$) give a valid representation of the limiting value of the mutual diffusion coefficient at $x_1 = 0$, D_{12}^0 , in both the benzene and the carbon tetrachloride systems.

All three equations fail to account for the mutual diffusion coefficients at $x_1 = 1$, D_{12}^1 , representing either the diffusion of trace amounts of carbon tetrachloride or benzene into OMCTS.

In the above equations it is the radius and not the volume which determines the diffusion coefficient. For the systems studied the

radius ratio is about 1.5. Longworth¹⁵⁸ has found that equation (4.8.3) holds for molecules with sizes similar to that of OMCTS, when they are diffusing into water. However, the radius ratio with water as the solvent would be much greater than above; viz, 2.65. The radius ratio between glycine and water is approximately equal to the ratio between OMCTS and carbon tetrachloride. Similar discrepancies from equation (4.8.3) have been noted for the glycine - water system¹⁵⁸.

One must conclude that for systems where the radius ratio is less than 1.5 the Stokes-Einstein equation with $\beta = 0$ is the more valid equation. Radius ratios must be greater than 2.5 before the $\beta = \infty$ equation becomes applicable.

Furthermore, the hydrodynamic theory, and, under certain conditions, the Eyring equation, predict that $D_{12}^{\circ} n_2$ should be constant for a given solute in a series of solvents. This conclusion is approximately correct for the diffusion of trace amounts of OMCTS into either benzene or carbon tetrachloride - Table 4.8.4.

TABLE 4.8.4

Temperature °C	$D_{12}^{\circ} n_2$ (OMCTS - C_6H_6) (dyne $\times 10^7$)	$D_{12}^{\circ} n_2$ (OMCTS - CCl_4) (dyne $\times 10^7$)
18	0.677	0.642
25	0.694	0.651
35	0.708	0.676
45	0.727	0.697

Stokes¹⁵⁹ has investigated the diffusion coefficients of trace

TABLE 4.8.3

Limiting Mutual Diffusion Coefficients from Various Theories

Temp.	OMCTS (1) - C_6H_6 (2)		D_{12}^0 - limiting value of D_{12} as $x_1 \rightarrow 0$	
	D_{12}^0 (4.8.2)	D_{12}^0 (4.8.3)	D_{12}^0 (4.8.5)	D_{12}^0 (expt.)
18	0.960	0.640	1.005	1.011
25	1.091	0.727	1.142	1.152
35	1.292	0.862	1.354	1.352
45	1.512	1.008	1.583	1.579
	D_{12}^1	D_{12}^1	D_{12}^1	D_{12}^1
18	0.387	0.258	0.406	0.942
25	0.455	0.303	0.476	1.085
35	0.568	0.379	0.595	1.341
45	0.697	0.464	0.730	1.632
	OMCTS (1) - CCl_4 (2)			
	D_{12}^0 (4.8.2)	D_{12}^0 (4.8.3)	D_{12}^0 (4.8.5)	D_{12}^0 (expt.)
18	0.642	0.428	0.673	0.641
25	0.729	0.486	0.764	0.722
35	0.865	0.577	0.906	0.865
45	1.013	0.675	1.061	1.015
	D_{12}^1	D_{12}^1	D_{12}^1	D_{12}^1
18	0.377	0.251	0.395	0.693
25	0.443	0.295	0.464	0.810
35	0.553	0.368	0.579	1.003
45	0.678	0.452	0.710	1.230
Temp Units - °C	D_{12} Units - $cm^2 \text{ sec}^{-1} \times 10^{-5}$			

amounts of carbon tetrachloride in various solvents and obtained a correlation between the molar volume of the solvent and the product $D_{12}^1 n_1$. The product obtained for a trace amount of CCl_4 in OMCTS falls on the line corresponding to the non-polar elongated paraffins (hexane, n-heptane, iso-octane), as shown in Fig. 4.8.1. It does not fall on the line corresponding to the roughly spherical non-polar molecules as would be expected from the molecular structure of OMCTS.

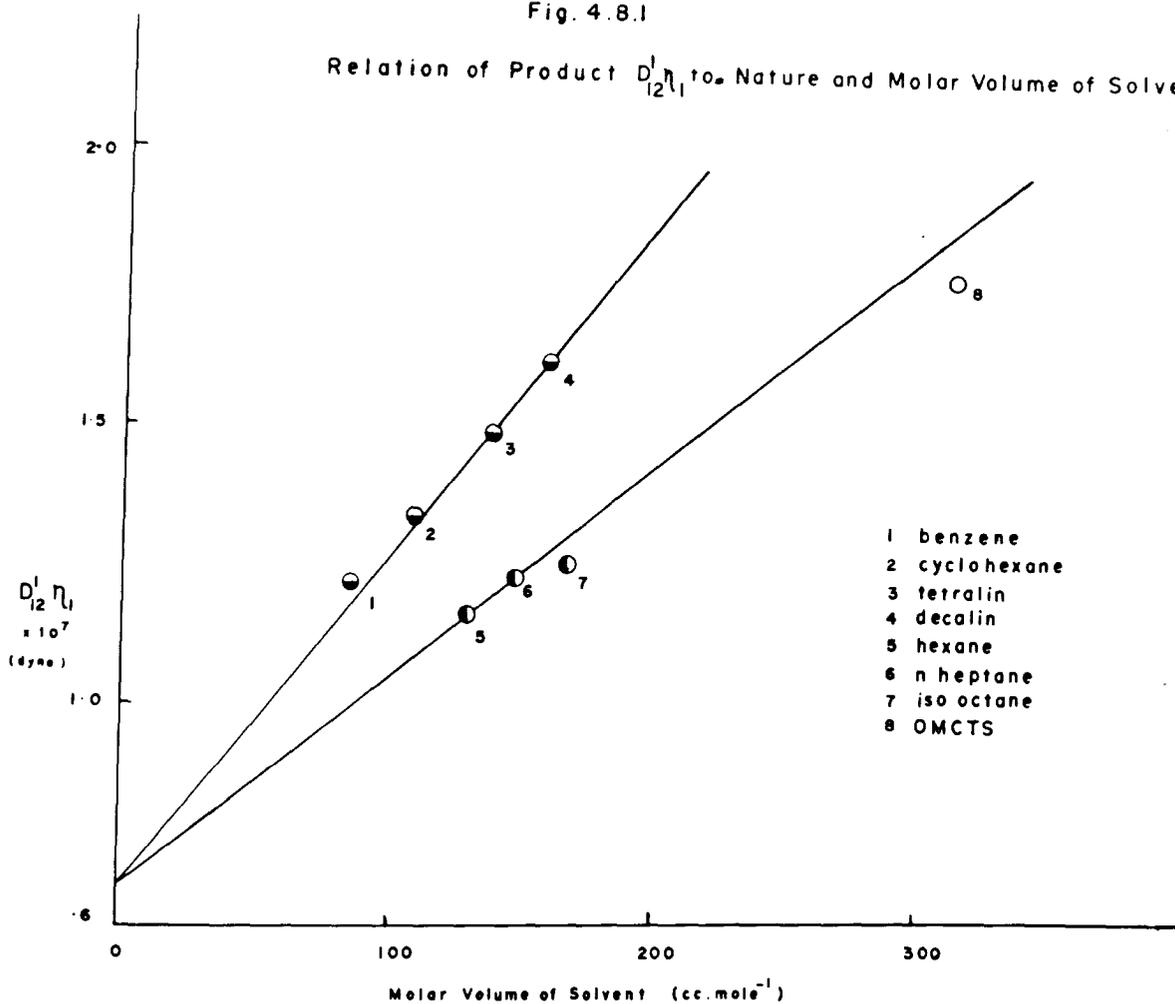
(2) Variation of mutual diffusion coefficients with temperature

The hydrodynamic theories and the simplified Eyring theory predict that $D_{12} n_{12}/T$ should be a constant, while the more exact formulation of the Eyring rate constant theory predicts a logarithmic relationship between the diffusion coefficient and the absolute temperature²⁰. It would undoubtedly be more valid to consider the term $D_{12} n_{12}/[T(\frac{\partial \ln a_2}{\partial \ln x_2})]$ when dealing with the variation of diffusion coefficients with temperature over the total concentration range²³. In the following tables the variations with temperature of the three terms, $D_{12} n_{12}/T$, $T \ln D_{12}$ and $D_{12} n_{12}/[T(\frac{\partial \ln a_2}{\partial \ln x_2})]$ are listed.

In the system OMCTS - C_6H_6 , the product $D_{12} n_{12}/T$ is virtually constant with temperature at low x_1 . At high OMCTS concentrations deviation becomes more marked. Surprisingly, the inclusion of the thermodynamic correction term, which incidentally varies considerably with temperature, leads to a product which is less constant with temperature. The term $T \ln D_{12}$ is not as constant with temperature as the previous product and inclusion of the thermodynamic correction term

Fig. 4.8.1

Relation of Product $D_{12}^1 \eta_1$ to Nature and Molar Volume of Solvent



makes little difference.

The product $D_{12}\eta_{12}/T$ for the system OMCTS - CCl_4 shows a similar behaviour; however, in this case, the inclusion of the thermodynamic correction term has little effect since, for this system, the correction term does not vary excessively with temperature. Eyring's product is again less constant than those previously discussed.

Attention is again drawn to the deviation from "model" behaviour at high OMCTS concentration. One infers that a system where small molecules are diffusing amongst much larger molecules does not correspond to any of the models on which the abovementioned theories have been based.

(3) Variation of mutual diffusion coefficients with concentration

A number of equations have been used to describe the variation of mutual diffusion coefficients with concentration. These are discussed below.

(a) Gordon Equation

$$D_{12}\eta_{12} = D_{12}^{\circ}\eta_2 \left(\frac{\partial \ln a_1}{\partial \ln c_1} \right) \quad \dots (4.8.6)$$

where D_{12}° is the limiting mutual diffusion coefficient as $c_1 \rightarrow 0$, η_2 is the viscosity of pure 2, η_{12} is the solution viscosity and $(\partial \ln a_1 / \partial \ln c_1)$ is the concentration-based thermodynamic correction term²¹. This is an empirical equation suggested by Gordon to correlate mutual diffusion coefficients of dilute aqueous solutions of 1:1 electrolytes. It has since been widely used to interpret experimental

TABLE 4.8.5Variation of $D_{12}\eta_{12}/T$ with Temperature

x_1	18°C	25°C	35°C	45°C
<u>OMCTS (1) - C₆H₆ (2)</u>				
0	.233	.233	.230	.228
.2	.270	.273	.275	.278
.4	.387	.392	.391	.392
.6	.528	.525	.525	.521
.8	.673	.668	.658	.651
1.0	.815	.797	.786	.777
<u>OMCTS (1) - CCl₄ (2)</u>				
0	.220	.218	.219	.219
.2	.307	.306	.307	.306
.4	.397	.393	.391	.390
.6	.475	.469	.465	.461
.8	.544	.537	.531	.525
1.0	.599	.595	.588	.585

Units - dyne deg⁻¹ x 10⁻⁷

TABLE 4.8.6

Variation of $D_{12}^n/T(\partial \ln a_2/\partial \ln x_2)$ with Temperature

x_1	18°C	25°C	35°C	45°C
<u>OMCTS (1) - C₆H₆ (2)</u>				
0	.233	.233	.230	.228
.2	.341	.337	.325	.319
.4	.428	.426	.414	.406
.6	.543	.536	.530	.521
.8	.665	.660	.649	.641
1.0	.815	.797	.786	.777
<u>OMCTS (1) - CCl₄ (2)</u>				
0	.220	.218	.219	.219
.2	.285	.283	.283	.280
.4	.356	.353	.351	.350
.6	.432	.427	.423	.419
.8	.518	.511	.505	.500
1.0	.599	.595	.588	.585

Units - dyne deg⁻¹ x 10⁻⁷

TABLE 4.8.7Variation of $T_{ln} D_{12}$ with Temperature

x_1	18°C	25°C	35°C	45°C
<u>OMCTS (1) - C₆H₆ (2)</u>				
0	-3.35	-3.39	-3.45	-3.52
.2	-3.38	-3.42	-3.47	-3.53
.4	-3.35	-3.39	-3.45	-3.50
.6	-3.34	-3.38	-3.44	-3.49
.8	-3.35	-3.39	-3.44	-3.49
1.0	-3.37	-3.41	-3.46	-3.51
<u>OMCTS (1) - CCl₄ (2)</u>				
0	-3.48	-3.53	-3.59	-3.66
.2	-3.46	-3.50	-3.56	-3.62
.4	-3.44	-3.48	-3.54	-3.60
.6	-3.44	-3.48	-3.53	-3.59
.8	-3.44	-3.48	-3.54	-3.59
1.0	-3.46	-3.50	-3.55	-3.60

Units - deg x 10³

data in solutions of electrolytes and nonelectrolytes. Tyrrell⁴⁸ has suggested that the equation is not applicable to concentrated solutions because no allowance has been made for solvent counterflow. This conclusion is at variance with Bearman's formulations, derived from a statistical mechanical approach.

(b) Hartley-Crank equation

Hartley and Crank derived the equation¹⁹

$$D_{12}^{id} = \frac{RT}{N\eta} \left(\frac{x_1}{\alpha_1} + \frac{x_2}{\alpha_2} \right) \quad \dots (4.8.7)$$

where α_1 and α_2 are parameters having the dimension of length and $D_{12}^{id} = D_{12} / \left(\frac{\partial \ln a_2}{\partial \ln x_2} \right)$. Carman and Stein¹⁶⁰ considered the case where α_1 and α_2 were independent of composition and η was the viscosity of the solution, and derived the equation

$$D_{12}^{id} \eta_{12} = x_1 \eta_1 D_{12}^1 + x_2 \eta_2 D_{12}^0 \quad \dots (4.8.8)$$

Bearman²² and Mills⁵¹ have questioned the validity of the derivation of the Hartley-Crank equation and both conclude that the correct form is

$$D_{12}^{id} = x_1 D_2^* + x_2 D_1^* \quad \dots (4.8.9)$$

where D_1^* and D_2^* are the tracer diffusion coefficients of 1 and 2 at the composition in question. Extension of this equation to (4.8.8) requires the assumptions

$$D_{12}^1 \eta_1 = D_2^* \eta_{12} \quad \dots (4.8.10)$$

$$D_{12}^0 n_2 = D_1^* n_{12} \quad \dots (4.8.11)$$

i.e.

$$\frac{D_2^*}{D_1^*} = \frac{D_{12}^1 n_1}{D_{12}^0 n_2} \quad \dots (4.8.12)$$

(c) Eyring equation

$$D_{12} = D_1^* \frac{\partial \ln a_1}{\partial \ln x_1}$$

Bearman finds that if the activity correction in the form $\partial \ln a_2 / \partial \ln c_2$ and not $\partial \ln a_2 / \partial \ln x_2$ is used, then the Eyring equation becomes identical with the Gordon equation provided equation (4.8.11) is valid.

(d) Bearman equation

From a statistical mechanical approach to the diffusion process, Bearman²² has concluded that, if the radial distribution function is independent of composition and the volumes are additive, (i.e. zero excess volume), the following equations are valid,

$$D_1^* / D_2^* = V_2^0 / V_1^0 \quad \dots (4.8.13)$$

and

$$D_{12} = D_1^* (\partial \ln a_1 / \partial \ln c_1) \quad \dots (4.8.14)$$

$$\text{since } (\partial \ln a_1 / \partial \ln c_1) = (\partial \ln a_1 / \partial \ln x_1) \frac{(x_1 V_1^0 + x_2 V_2^0)}{V_2^0} \quad \dots (4.8.15)$$

$$D_{12}^{id} = \frac{x_1 D_1^* V_1^0}{V_2^0} + x_2 D_1^* \quad \dots (4.8.16)$$

Substitution of equation (4.8.13) into (4.8.16) gives

$$D_{12}^{id} = D_1^* x_2 + D_2^* x_1 \quad \dots \quad (4.8.17)$$

which is the modified form of the Hartley-Crank equation.

Bearman then made similar assumptions to Carman and Stein and derived equation (4.8.8), the generally accepted form of the Hartley-Crank equation. Bearman has also shown that the Hartley-Crank equation and the Gordon equation are identical provided equations (4.8.12) and (4.8.13) are valid.

From the foregoing discussion, it becomes clear that the Gordon, Hartley-Crank and Eyring equations are equivalent providing $D_1^*/D_2^* = D_{12}^0 \eta_2 / D_{12}^1 \eta_1 = V_2^0 / V_1^0$ and $D_1^* \eta_{12} = D_{12}^0 \eta_2$. These equations are expected to hold for that class of solutions for which the radial distribution function is independent of composition and molar volumes are approximately equal²². Clearly, the systems under consideration do not fit into this class and lack of data on the tracer diffusion coefficients further restricts any direct tests of the more fundamental equations.

The Gordon and the Hartley and Crank equations are tested in Table 4.8.9. Owing to the complete lack of correlation between experimental and calculated results over most of the composition range, only 25°C data is presented in this form. A similar behaviour is observed at the other temperatures. The 25°C results are shown graphically in Figs. 4.8.2 and 4.8.3. In Table 4.8.10 the ratio $D_{12}^0 \eta_2 / D_{12}^1 \eta_1$ is compared with the ratio of the molar volumes, V_2^0 / V_1^0 .

Fig. 4.8.2

Diffusion - OMCTS(l) - C₆H₆(2)

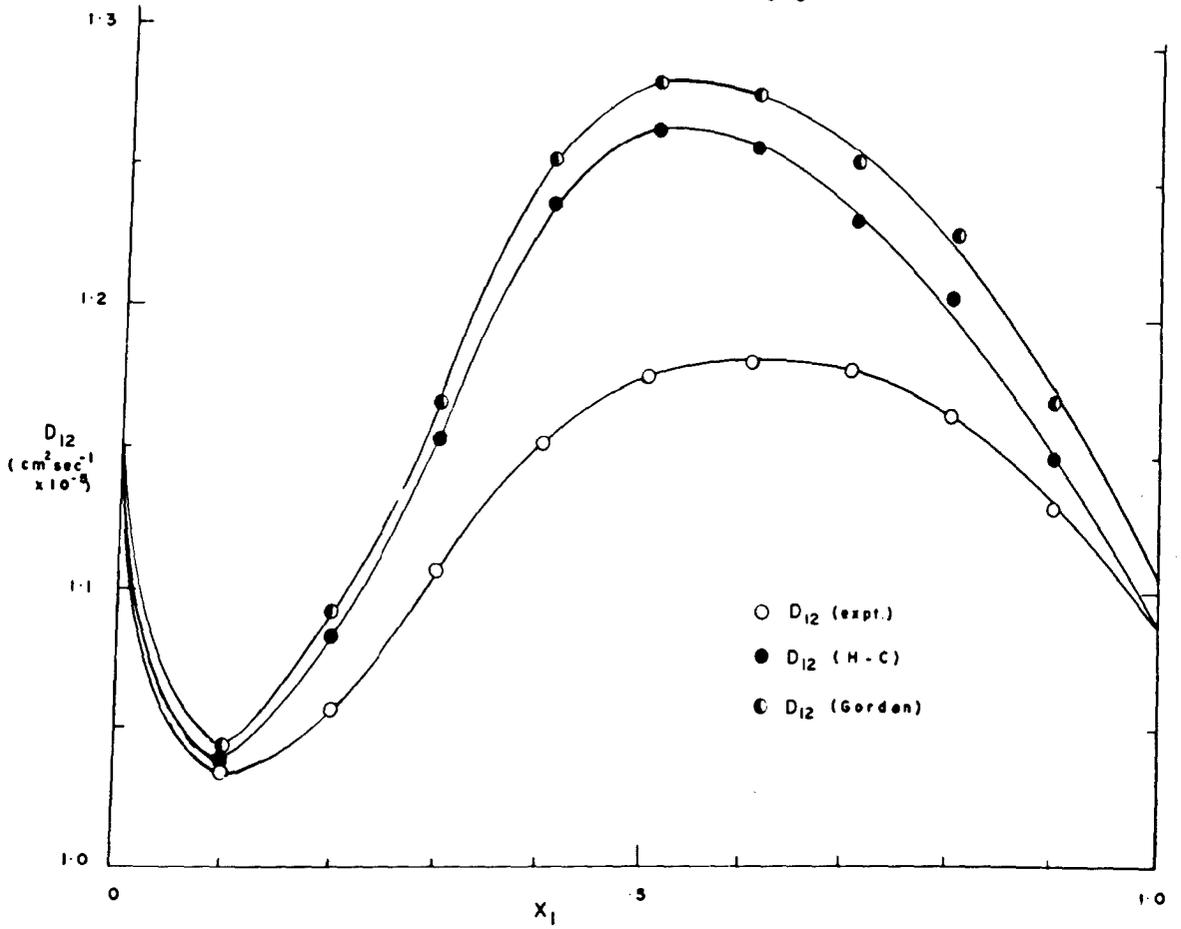


Fig. 4.8.3
Diffusion - OMCTS - CCl₄

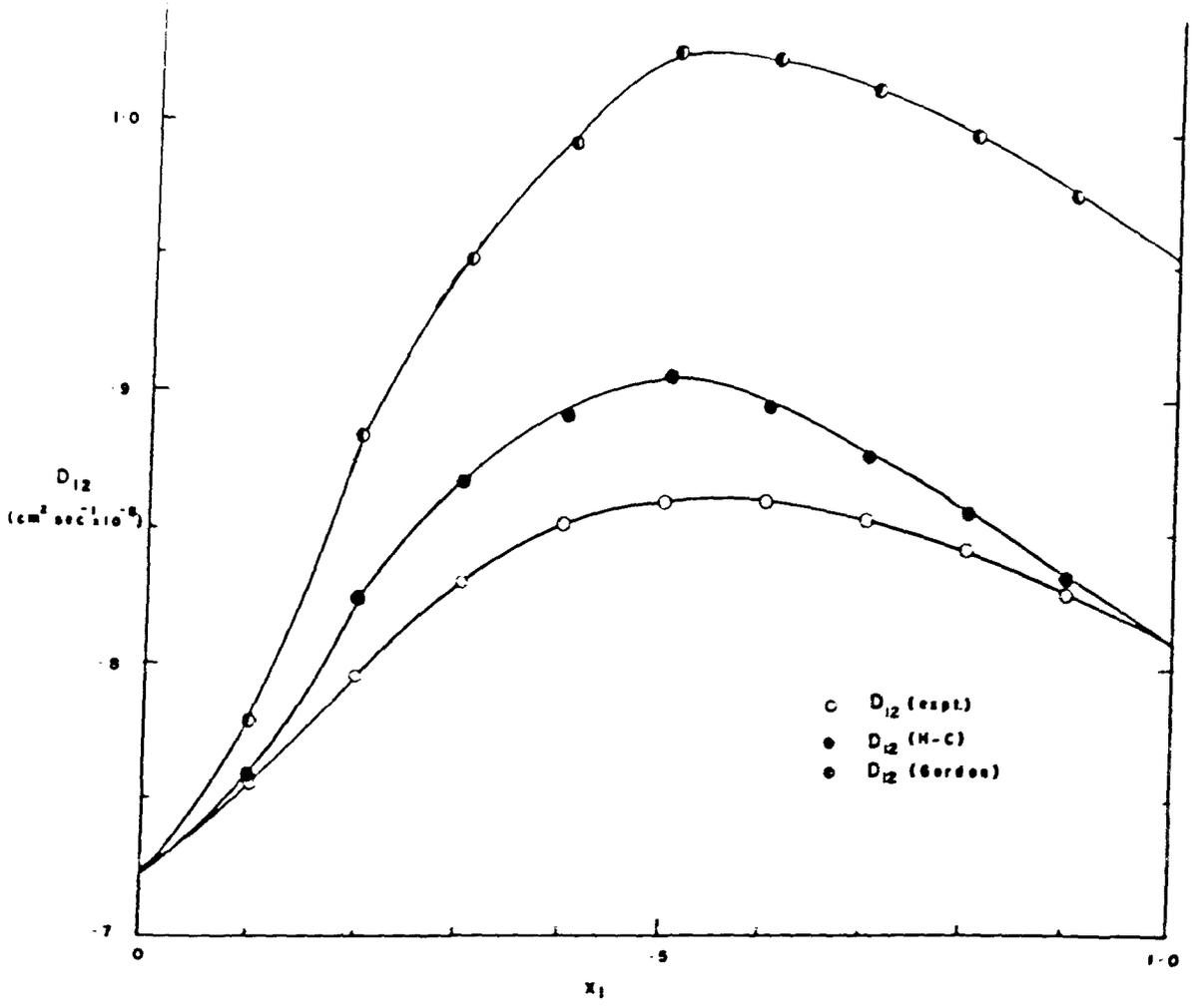


TABLE 4.8.8

Test of Gordon and Hartley-Crank Equations - 25°C

x_1	D_{12} (Gordon)	D_{12} (HC)	D_{12} (expt.)
<u>OMCTS (1) - C₆H₆ (2)</u>			
0	1.152	1.152	1.152
.1	1.043	1.038	1.034
.2	1.092	1.083	1.057
.3	1.167	1.155	1.107
.4	1.255	1.239	1.153
.5	1.284	1.266	1.177
.6	1.280	1.260	1.182
.7	1.256	1.235	1.180
.8	1.230	1.208	1.165
.9	1.170	1.149	1.130
1.0	1.105	1.085	1.085
<u>OMCTS (1) - CCl₄ (2)</u>			
0	.722	.722	.722
.1	.789	.758	.756
.2	.885	.825	.795
.3	.950	.867	.831
.4	.994	.891	.852
.5	1.028	.910	.861
.6	1.026	.897	.862
.7	1.015	.879	.855
.8	.999	.858	.844
.9	.977	.834	.829
1.0	.955	.810	.810
D_{12} Units - cm ² sec ⁻¹ x 10 ⁻⁵			

A surprising agreement occurs for the OMCTS - benzene system but disagreement in the other system suggests that this result may be fortuitous.

TABLE 4.8.9

Test of Bearman's Ratios

Temp.	$D_{12}^1 \eta_1 / D_{12}^0 \eta_2$	V_1^0 / V_2^0
<u>OMCTS (1) - C₆H₆ (2)</u>		
18°	3.503	3.492
25°	3.425	3.490
35°	3.422	3.490
45°	3.399	3.489
<u>OMCTS (1) - CCl₄ (2)</u>		
18°	2.721	3.218
25°	2.727	3.215
35°	2.679	3.214
45°	2.672	3.213

It is possible to relate deviations from the Hartley-Crank equation to the fact that either (a) the bulk viscosity term does not represent the viscosity of the mixture at the molecular level, or (b) the terms α_1 and α_2 in the Hartley-Crank equation are not independent of composition.

Harned,¹⁶¹ following Lyons suggestion,²³ considered these deviations to be a function of the relative viscosity and obtained an equation to cover the whole concentration range.

$$D_{12}^{id} \eta_{12} = x_1 \eta_1 \left[D_{12}^1 + k_1 \frac{(\eta_1 - \eta_{12})}{\eta_1} \right] + x_2 \eta_2 \left[D_{12}^0 + k_2 \frac{(\eta_2 - \eta_{12})}{\eta_2} \right]$$

By adjusting k_1 and k_2 this equation was found to represent the diffusion data for both systems to better than 1%. Values of k_1 and k_2 and the experimental and calculated mutual diffusion coefficients at 25°C are listed in Table 4.8.10, while for the other temperatures the coefficients and the average deviation is given in Table 4.8.11.

Summary and Conclusions

The Gordon and Hartley-Crank equations do not predict the experimental results to better than approximately 10%. This is to be expected when one considers the conditions necessary for these equations to be valid. It is noted that the experimental diffusion coefficients do not change by more than $\pm 10\%$ over the entire concentration range, so a better theoretical prediction that this is needed.

For further understanding of the diffusion processes occurring in the systems studied it will be necessary to determine the tracer diffusion coefficients. Dr. R. Mills of the Australian National University has kindly offered to undertake this task.

TABLE 4.8.10

Harned's Semi-empirical Equation

x_1	$D_{12}(\text{calc.})$	$D_{12}(\text{expt.})$
<u>OMCTS (1) - C₆H₆ (2)-25°C</u>		
	$k_1 = 0.7$	
	$k_2 = 1.64$	
0	1.152	1.152
.1	1.034	1.033
.2	1.057	1.058
.3	1.107	1.107
.4	1.153	1.168
.5	1.177	1.184
.6	1.182	1.179
.7	1.180	1.161
.8	1.165	1.152
.9	1.130	1.117
1.0	1.085	1.085
<u>OMCTS (1) - CCl₄ (2)-25°C</u>		
	$k_1 = -0.2$	
	$k_2 = -0.059$	
0	.722	.722
.1	.756	.742
.2	.795	.797
.3	.831	.831
.4	.852	.852
.5	.861	.870
.6	.862	.862
.7	.855	.851
.8	.844	.839
.9	.829	.824
1.0	.810	.810
D_{12} Units - $\text{cm}^2 \text{sec}^{-1} \times 10^{-5}$		
k Units - $\text{cm}^2 \text{sec}^{-1} \times 10^{-5}$		

TABLE 4.8.11Constants k_1 and k_2 for Harned's Equation

Temp	k_1	k_2	Av. Dev. (%)
<u>OMCTS (1) - C₆H₆ (2)</u>			
18°	.50	1.30	.6
25°	.70	1.64	.7
35°	.70	1.68	.9
45°	.70	1.80	.9
<u>OMCTS (1) - CCl₄ (2)</u>			
18°	-.20	- .089	.7
25°	-.20	- .059	.6
35°	-.40	- .221	.6
45°	-.40	- .133	.4
k Units - cm ² sec ⁻¹ x 10 ⁻⁵			

Further advances in the theories of diffusion processes in solutions are now desperately needed. It appears that Bearman's statistical mechanical treatment,¹⁶² without the restrictions now imposed, offers the most promising approach.

Note:

The relatively light treatment of diffusion and viscosity processes in liquid mixtures is felt to be justified because of the lack of adequate theories to cover the type of mixtures investigated. When tracer diffusion coefficients become available a much more detailed analysis can be made.

NOTES ON APPENDIX

Nearly all the calculations presented in this thesis were obtained with the aid of computer programmes. These were run on an I.B.M. 1620 II computer. As most of the programmes were straight forward, they have not been included in this thesis. Programmes were written in either FORTRAN IID or FOR-TO-GO.

Appendix I

This programme calculates activity coefficients of a volatile component in a two component mixture. It is necessary for the second component to be relatively involatile.

Input data includes,

A1 - molecular weight of component 1

A2 - molecular weight of component 2

V - volume of vapour pressure cell to the reference mark

At statement 1, temperature, vapour pressures and densities of the pure components and the virial coefficient of the volatile component are accepted. At statement 6 the masses of each component and the height of the reference mark are read. Finally the meniscus height, total vapour pressure and the activity coefficient of the involatile component (as $\ln f_1$) are accepted. It is possible to run the programme initially with $\ln f_1$ equal to zero. The programme repeats the calculations three times and outputs values from the last two cycles. It should be noted that

the negative sign for the activity coefficient of OMCTS in OMCTS - CCl_4 mixtures is absent. This data was run with the necessary alteration to the programme.

Appendix II

This programme calculates the parameters of the Antoine equation' from the vapour pressure data at the various temperatures. The parameters of the specified equation are adjusted to give the minimum standard deviation. The adjusting of the parameters is carried out in the subroutine MAXQ12. The experimental vapour pressures of the three compounds are listed. The subroutine MAXQ12 was devised by Dr.E.J. Burr.

Appendix III

This programme calculates the excess entropy, excess enthalpy and excess volume from the various equations listed by Flory. A number of subroutines are used.

- (a) WHATIS - used to print a title.
- (b) ATWILL - a subroutine to input data in free format.
- (c) FITTER - this subroutine adjusts an unknown parameter (in this case the X_{21} term) until agreement occurs between a calculated and an experimental result (in this case the excess energy, or enthalpy, at $x_1 = .4$).

Calculations are carried out to give the excess functions for both the calculated and experimental excess volume. The data output format in this

programme is not very good.

Appendix IV

This programme calculates the excess entropy from Yosim's equation. Input data includes,

RV - ratio of molar volumes (V_1^0/V_2^0)

V2 - molar volume of component 2

VV1 - volume occupied by one mole of hard spheres
(given by $y_1 V_1^0$) - optional

A, B, C and DD - constants for equation for the excess volume

TX1 - mole fractions at which the calculations are
to be performed

Y - value of y_2

RD - ratio of hard sphere diameters (a_1/a_2).

Output gives the volume fraction, excess entropy and partial molar excess entropy of component 2 at specified mole fractions.

The operator has the option (by sense switch 3) of reading in values of y_2 instead of a_1/a_2 , if the value of VV1 is included. In effect one can work with y_1 fixed and y_2 varying or vice versa.

The programmes have a number of sense switch controls. These were convenient control devices since the author operated the computer during the execution of the programmes.

APPENDIX I

```

##JOB 3
##XEQSFORG
C C ACTIVITY COEFFICIENTS
  READ,A1,A2,V1
  PRINT20
20 FORMAT(7X,15HSECOND ESTIMATE,15X,14HTHIRD ESTIMATE)
  PRINT5
  5 FORMAT(//10HMOLE FRACT,2X,6HLN ACT,3X,7HLOG ACT)
  DIMENSION P(6,5)
  DO1 J=1,5
  1 READ2,(P(I,J),I=1,6)
  2 FORMAT(F4.1,1X,F4.3,1X,F6.3,1X,F6.5,1X,F7.5,1X,F7.1)
  6 READ,W1,W2,Y
  PRINT30
30 FORMAT(//)
  IF(W1)8,8,7
  7 R1=W1/A1
  R2=W2/A2
  X1=R1/(R1+R2)
  R=6236.2
  DO 4 J=1,5
  I=1
  TT=P(I,J)
  I=2
  P10=P(I,J)
  I=3
  P20=P(I,J)
  I=4
  D1=P(I,J)
  I=5
  D2=P(I,J)
  I=6
  B=P(I,J)
  READ,YY,PP,G
  T = 273.16+TT
  P1 = X1*P10*EXP (G)
  P2 = PP-P1
  V = V1-W1/D1-W2/D2+(Y-YY)*.7854
  RR1=R1-P1*V/(R*T)
  RR2 = R2-P2*V/(R*T+B*P2)
  X1 = RR1/(RR1+RR2)
  PP1 = X1*P10*EXP (G)
  PP2 = PP-PP1
  RRR1 = R1-PP1*V/(R*T)

```

APPENDIX I (CONT)

```

RRR2 = R2-PP2*V/(R*T+B*PP2)
X2 = RRR2/(RRR1+RRR2)
Z1 = LOG(PP2/(P20*X2))
Z2 = -B*(P20-PP2)/(R*T)
Z3 = A2*(P20-PP2)/(D2*R*T)
AC = Z1+Z2+Z3
GAC = AC/2.3026
X1 = 1.-X2
PPP1 = X1*P10*EXP (G)
PPP2 = PP-PPP1
RRR3 = R1-PPP1*V/(R*T)
RRR4 = R2-PPP2*V/(R*T+B*PPP2)
XX2 = RRR4/(RRR3+RRR4)
ZZ1 = LOG(PPP2/(P20*XX2))
ZZ2 = -B*(P20-PPP2)/(R*T)
ZZ3 = A2*(P20-PPP2)/(D2*R*T)
ACC = ZZ1+ZZ2+ZZ3
GACC = ACC/2.3026
PRINT3,X1,AC,GAC,XX2,ACC,GACC
3 FORMAT(6F10.6)
4 CONTINUE
GO TO 6
8 STOP
END

```

EXPERIMENTAL DATA OMCTS BENZENE

```

296.64 78.114 118.40
25.0 .100 09.520 .95042 0.87370 -1455.0
35.0 .202 14.837 .93898 0.86310 -1330.0
45.0 .389 22.364 .92749 0.85210 -1232.0
55.0 .714 32.722 .91594 0.84110 -1145.0
60.0 .952 39.170 .91016 0.83570 -1105.0
5.12011 8.04039 23.11
14.47 8.357 .187
14.18 12.997 .157
9.35 19.517 .118
16.33 28.468 .081
14.76 34.025 .072
7.14737 7.05589 23.13
18.34 7.826 .113
15.57 12.121 .095
19.18 18.183 .065
13.03 26.473 .042
13.14 31.607 .032

```

APPENDIX I (CONT)

5.12011 2.39139 23.11
 14.68 6.529 .028
 13.63 10.060 .017
 10.20 14.995 .007
 9.50 21.643 -.002
 14.68 25.772 -.007
 7.14737 2.31535 23.13
 14.34 5.704 .010
 13.49 8.754 .005
 17.39 13.022 -.003
 13.75 18.778 -.008
 14.20 22.317 -.011
 7.14737 1.26554 23.14
 19.34 4.210 -.001
 18.39 6.443 -.003
 16.64 9.516 -.005
 13.90 13.656 -.008
 14.51 16.198 -.009
 20.65985 3.27730 23.13
 15.60 3.972 -.002
 14.64 6.104 -.003
 13.87 9.040 -.005

7.67220 .75836 23.11
 16.26 2.888 -.004
 15.85 4.403 -.004
 14.88 6.508 -.004
 13.26 9.322 -.004
 10.60 11.052 -.004
 9.53123 .75836 23.11
 16.31 2.466 -.003
 16.08 3.768 -.003
 15.37 5.581 -.003
 14.07 8.039 -.003
 13.16 9.550 -.003
 13.66465 .75836 23.11
 18.73 1.875 -.002
 18.84 2.880 -.002
 18.57 4.288 -.002
 17.82 6.218 -.002
 17.22 7.416 -.002
 20.65985 .75836 23.13
 19.25 1.346 -.001
 21.70 2.081 -.001
 19.65 3.146 -.001
 19.34 4.594 -.001
 19.00 5.515 -.001

APPENDIX I (CONT)

EXPERIMENTAL DATA OMCTS CCL4

296.64	153.839	118.40			
25.0	.100	11.423	.95042	1.58446	-1675.0
35.0	.202	17.480	.93898	1.56504	-1531.0
45.0	.389	25.917	.92749	1.54547	-1401.0
55.0	.714	37.358	.91594	1.52597	-1282.0
60.0	.952	44.421	.91016	1.51622	-1227.0
.50899	2.91099	22.75			
13.11	10.430	.181			
9.73	15.928	.185			
13.77	23.552	.192			
13.54	33.825	.198			
13.43	40.137	.203			
1.59597	2.91099	22.75			
15.91	8.737	.132			
14.38	13.310	.134			
16.88	19.617	.136			
16.32	28.052	.138			
15.50	33.199	.139			
16.78032	14.15129	22.73			
9.69	6.827	.078			
10.39	10.432	.079			
13.05	15.434	.079			
14.42	22.185	.081			
16.75	26.340	.082			
16.78032	9.31475	22.73			
13.42	5.601	.052			
14.40	8.542	.053			
15.28	12.627	.054			
18.16	18.147	.055			
18.37	21.539	.055			
4.04006	1.43989	22.73			
16.25	4.240	.027			
15.93	6.432	.027			
14.21	9.437	.028			
14.06	13.415	.028			
16.29	15.825	.029			

APPENDIX I (CONT)

11.17232	2.91099	22.75
16.39	3.474	.017
16.41	5.306	.017
15.76	7.841	.017
14.71	11.254	.017
13.58	13.355	.017
3.97058	78210	22.74
14.27	2.777	.009
14.63	4.211	.009
14.48	6.194	.009
14.35	8.786	.009
14.55	10.353	.009
10.95440	1.43989	22.73
15.69	2.058	.004
16.37	3.160	.004
16.92	4.697	.004
19.62	6.801	.004
19.95	8.101	.004
16.78032	1.43989	22.73
12.97	1.457	.002
13.10	2.258	.002
15.41	3.389	.002
17.15	4.954	.002
19.56	5.938	.002
0.0	0.0	0.0

APPENDIX II

CALCULATION OF ANTOINE EQUATION

*FANDK1204

```

DIMENSION B(20)
COMMON MODE,N,FX,B,ACCX,DELTA
PRINT50
50 FORMAT(26HSW3 ON TO TYPE OUT RESULTS)
PRINT51
51 FORMAT(29HSW4 ON TO TAKE NEW ACCX DELTA)
ACCEPT TAPE1,NTOT
1 FORMAT(I3)
ACCEPT TAPE 10,(B(J),J=1,3)
10 FORMAT(3F10.8)
ACCEPT TAPE11,ACCX,DELTA
11 FORMAT(2F7.6)
DIMENSION T(40),P(40),PCALC(40),DEL(40)
ACCEPT TAPE 2,(T(I),P(I),I=1,NTOT)
2 FORMAT(F6.3,1X,F6.2)
N = 3
MODE = 1
FN = NTOT
3 CALL MAXQ12
IF(SENSE SWITCH 4)15,14
15 PAUSE
ACCEPT TAPE11,ACCX,DELTA
PRINT60,ACCX,DELTA
60 FORMAT(2F8.6)
14 IF (MODE - 2)34,5,5
5 S = 0.0
34 DO 7 I=1,NTOT
PCALC(I) = EXP(2.30258*(B(1)-B(2)*1000.0/(B(3)*100.0+T(I))))
7 S = S+((PCALC(I)-P(I))/P(I))**2
IF(MODE+1)4,40,9
9 FX = -((S/(FN-1.0))**.5)
IF(SENSESWITCH3)40,3
40 DO 30 I=1,NTOT
DEL(I) = P(I) - PCALC(I)
30 PRINT8,T(I),P(I),PCALC(I),DEL(I)
8 FORMAT(F8.3,3F8.2)
TT = 25.0
42 PCAL = EXP(2.30258*(B(1)-B(2)*1000.0/(B(3)*100.0+TT)))
PRINT20,TT,PCAL
20 FORMAT(F8.3,F8.2)
TT = TT+5.0
IF(TT-60.0)22,22,24
22 CONTINUE
GO TO 42
24 CONTINUE
IF(MODE+1)4,4,3
4 CALL EXIT
END

```

APPENDIX II (CONT)

VAPOUR PRESSURE DATA BENZENE

24.889	94.75	
24.998	95.19	
30.188	120.34	
39.891	182.11	FIRST AMPOULE
49.979	271.28	
49.989	271.39	
59.977	391.35	
59.973	391.33	
24.999	95.21)
60.005	391.79)

25.021	95.29	
25.125	95.75	
24.961	95.05	
30.003	119.36	
30.064	119.69	
30.106	119.92	
34.956	148.12	
34.993	148.36	
39.957	182.61	
40.057	183.34	
44.948	223.19	
45.006	223.72	LAST AMPOULE
50.005	271.51	
50.053	272.00	
50.146	272.95	
54.944	326.55	
54.990	327.11	
54.993	327.14	
54.995	327.17	
59.956	391.06	
60.003	391.75	
60.017	391.92	
59.988	391.50	
59.988	391.50	
24.999	95.21)
59.979	391.45)
59.985	391.50	REPEAT

APPENDIX II (CONT)

VAPOUR PRESSURE DATA CARBON TETRACHLORIDE

24.999	114.24
24.984	114.15
25.042	114.44
30.002	141.94
30.201	143.12
34.919	174.27
34.962	174.57
35.002	174.81
35.009	174.89
39.996	213.60
39.998	213.63
39.996	213.62
40.021	213.82
40.008	213.70
44.972	258.93
44.997	259.15
45.007	259.27
49.950	311.64
49.983	311.99
50.015	312.35
49.994	312.10
54.942	372.78
54.974	373.22
55.013	373.73
55.004	373.62
54.984	373.36
59.949	443.46
59.996	444.17
60.007	444.32
59.999	444.23

FIRST AMPOULE

25.033	114.38
60.004	444.30

PORTION PUMPED OFF

24.981	114.16
59.978	443.87
59.981	443.93

LAST AMPOULE

APPENDIX II (CONT)

VAPOUR PRESSURE DATA OMCTS

24.998	1.00
30.232	1.45
39.964	2.79
49.981	5.33
55.939	7.55
59.995	9.54

FIRST AMPOULE

24.990	1.00
59.948	9.52
34.929	2.00
45.038	3.90

LAST AMPOULE

APPENDIX III

```

##JOB 3
##FORX32
3 DIMENSIONE(101),VB(2),HM(2),UU(9),V(9),VVB(2),VVEC(9)
H(9,2),HH(9,2),Z(2)
CALL WHATIS
CALL ATWILL(E,1)
A1 = E(1)
A2 = E(2)
G1 = E(3)
G2 = E(4)
V1 = E(5)
V2 = E(6)
T = E(7)
T = 273.16+T
VB1 = (A1*T/(3.*(1.+A1*T))+1.)**3
VB2 = (A2*T/(3.*(1.+A2*T))+1.)**3
TB1 = (VB1**(1./3.)-1.)/(VB1**(4./3.))
TB2 = (VB2**(1./3.)-1.)/(VB2**(4./3.))
VS1 = V1/VB1
VS2 = V2/VB2
TS1 = T/TB1
TS2 = T/TB2
PS1 = G1*T*(VB1**2)
PS2 = G2*T*(VB2**2)
F1 = .4*VS1/(.4*VS1+.6*VS2)
F2 = 1.-F1
PRINT60,T,VB1,VB2,TB1,TB2,VS1,VS2,TS1,TS2,PS1,PS2,F1,F2
60 FORMAT(5F15.8/4F15.8/4F15.8)
CALL ATWILL(E,I)
U = E(1)
VE = E(2)
VBO = F1*VB1+F2*VB2
TBO = (VBO**(1./3.)-1.)/(VBO**(4./3.))
DO106 J=1,2
X12 = 10.
N = -1
DEL = .1*X12
ACCA = .0001*X12
T2 = F2/(F1*((VS1/VS2)**(-1./3.))+F2)
102 S = 0.
TB = (F1*PS1*TB1+F2*PS2*TB2)/((F1*PS1+F2*PS2)
*(1.-F1*T2*X12/(F1*PS1+F2*PS2)))
IF(J-1)105,105,1
105 VBE = VBO**(7./3.)*(TB-TBO)/(4./3.-VBO**(1./3.))

```

APPENDIX III (CONT)

```

VB(J) = VBE+VBO
VEC = VBE*(.4*VS1+.6*VS2)
GO TO 107
1  VBEEEX = VE/(.4*VS1+.6*VS2)
  VB(J) = VBEEEX + VBO
107 CONTINUE
  HM1 = .4*PS1*VS1*(1./VB1-1./VB(J))
  HM2 = .6*PS2*VS2*(1./VB2-1./VB(J))
  HM3 = .4*VS1*T2*X12/VB(J)
  HM(J) = HM1+HM2+HM3
  S = S+ABS(U-HM(J))
  IF(N)100,101,100
100 CALL FITTER(N,X12,DEL,ACCA,S)
  GO TO 102
101 CONTINUE
  PRINT61,VBO,TBO,T2,TB,VBE,VB(1),VB(2),VEC,VBEEEX
  61 FORMAT(/4F15.8/5F15.8)
106 Z(J) = X12
  PRINT108
108 FORMAT(/5X,7HVE(EXP),5X,7HVE(CAL),2X,10HUM(VE CAL),7X,
  1HU,5X,10HX12(VE AL))
109 FORMAT(/5X,7HVE(EXP),2X,10HUM(VE EXP),7X,1HU,5X,
  11HX12(VE EXP))
  PRINT110,VE,VEC,HM(1),U,Z(1)
110 FORMAT(2F12.3,2F12.1,F12.3)
  PRINT 109
  PRINT111,VE,HM(2),U,Z(2)
111 FORMAT(F12.3,2F12.1,F12.3)
  PRINT8
  8 FORMAT(/35HVALUE OF X12 FITS ENERGY AT X1 = .4)
  CALL ATWILL(E,I)
  DO9 J=1,I
  9 UU(J) = E(J)
  CALL ATWILL(E,I)
  DO10 J=1,I
  10 V(J) = E(J)
  DO 14 J=1,9
  XXXX = J
  X1 = XXXX/10.
  X2 = 1.-X1
  FF1 = X1*VS1/(X1*VS1+X2*VS2)
  FF2 = 1.-FF1
  TT2 = FF2/(FF1*((VS1/VS2)**(-1./3.))+FF2)
  TT1 = 1.-TT2
  VVBO = FF1*VB1+FF2*VB2
  TTBO = (VVBO**(1./3.)-1.)/(VVBO**(4./3.))

```

APPENDIX III (CONT)

```

PRINT62,X1,X2,FF1,FF2,TT2,TT1,VVBO,TTBO
62 FORMAT(/4F12.4/2F12.4,2F12.7)
DO14K=1,2
TTB = (FF1*PS1*TB1+FF2*PS2*TB2)/((FF1*PS1+FF2*PS2)
      *(1.-FF1*TT2*Z(K)/(FF1*PS1+FF2*PS2)))
IF(K-1)11,11,12
11 VVBE = VVBO**(7./3.)*(TTB-TTBO)/(4./3.-VVBO**(1./3.))
VVB(K) = VVBE + VVBO
VVEC(J) = VVBE*(X1*VS1+X2*VS2)
PRINT63,VVBE,VVB(K),VVEC(J)
63 FORMAT(3F12.6)
GO TO 13
12 VVBEX = V(J)/(X1*VS1+X2*VS2)
VVB(K) = VVBEX+VVBO
PRINT64,VVBEX,VVB(K)
64 FORMAT(2F12.6)
13 CONTINUE
Y = VVB(K)**(1./3.)-1.
YA = VB1**(1./3.)-1.
YB = VB2**(1./3.)-1.
PRINT65,Y,YA,YB
65 FORMAT(3F12.6)
H1 = X1*PS1*VS1*(1./VB1-1./VVB(K))
H2 = X2*PS2*VS2*(1./VB2-1./VVB(K))
H3 = X1*VS1*Z(K)*TT2/VVB(K)
H(J,K) = H1+H2+H3
PRINT32,H(J,K)
32 FORMAT(F12.2)
AA = 3.*Y/(T*(1.-3.*Y))
PRINT66,AA
66 FORMAT(3F12.6)
HH(J,K) = PS2*VS2*((1./VB2-1./VVB(K))+AA*T*(TB2-TTB)/
      (VVB(K)*TTB))+VS2*Z(K)*TT1**2*(1.+AA*T)/VVB(K)
PRINT32,HH(J,K)
SR1 = -3.*X1*PS1*VS1*TB1*LOG(YA/Y)/T
SR2 = -3.*X2*PS2*VS2*TB2*LOG(YB/Y)/T
SR = SR1+SR2
SI = -1.987*(X1*LOG(X1)+X2*LOG(X2))
SC = -1.987*(X1*LOG(FF1)+X2*LOG(FF2))
SE = (SR-SI+SC)/1.987
PRINT36,SE
36 FORMAT(F12.4)
S2I = -1.987*LOG(X2)
S2C = -1.987*(LOG(FF2)+FF1*(1.-VS2/VS1))
S2R1 = -PS2*VS2*(3.*TB2*LOG(YB/Y)/T-AA*(TB2-TTB)/
      (TTB*VVB(K)))

```

APPENDIX III (CONT)

```

S2R2 = AA*VS2*Z(K)*TT1*TT1/VVB(K)
S2R = S2R1+S2R2
S2 = (S2C-S2I+S2R)/1.987
PRINT36,S2
S1I = -1.987*LOG(X1)
S1C = -1.987*(LOG(FF1)+FF2*(1.-VS1/VS2))
S1R1 = -PS1*VS1*(3.*TB1*LOG(YA/Y)/T-AA*(TB1-TTB)/(TTB*
VVB(K)))
S1R2 = AA*VS1*Z(K)*TT2*TT2/VVB(K)
S1R = S1R1+S1R2
S1 = (S1C-S1I+S1R)/1.987
14 PRINT36,S1
IF(SENSESWITCH4)3,200
200 CALLEXIT
END

```

CALCULATION OF EXCESS PROPERTIES FLORY EQUATIONS

```

SYSTEM OMCTS(1) - C6H6(2) 25 DEG
.001202,.001218,.1907,.2961,312.1,89.41,25.00,*
189,-.017,*
102,158,184,189,178,155,122,87,47,*
-.017,-.028,-.027,-.017,-.007,.001,.006,.006,.004,*

```

```

SYSTEM OMCTS(1) - BENZENE(2) 60 DEG
.001334,.001316,.14187,.2341,325.92,93.464,60,*
189,-.027,*
102,158,184,189,178,155,122,87,47,*
-.025,-.040,-.037,-.027,-.017,-.010,-.005,-.002,-.001,*

```

```

SYSTEM OMCTS(1) - CCL4(2) 25 DEG
.0012019,.001217,.19065,.2716,312.1,97.09,25.00,*
56,-.269,*
36,53.4,56.7,55.9,51.8,46.5,35.7,25.2,12.1,*
-.138,-.226,-.257,-.269,-.258,-.210,-.165,-.108,-.054,*

```

```

SYSTEM OMCTS(1) - CCL4(2) 60 DEG
.0012733,.001334,.14187,.2152,325.92,101.52,60,*
56,-.292,*
36,53.4,56.7,55.9,51.8,46.5,35.7,25.2,12.1,*
-.148,-.236,-.272,-.292,-.272,-.220,-.175,-.118,-.060,*

```

APPENDIX IV

```

##JOB 3                                EXCESS ENTROPY YOSIM K.N.MARSH
##FORX32
  6 DIMENSIONE(101),TX1(101),SE(5)
    CALL WHATIS
    CALL ATWILL(E,NN)
    RV=E(1)
    V2=E(2)
    VV1 = E(3)
    CALL ATWILL(E,I)
    A=E(1)
    B=E(2)
    C=E(3)
    DD=E(4)
    CALL ATWILL(TX1,NP)
    CALLATWILL(E,NN)
    Y = E(1)
    CALLATWILL(E,NN)
    RD=E(1)
52  R2 = RD*RD
    R3 = R2*RD
    R4 = R3*RD
    R5 = R4*RD
    R6 = R5*RD
20  P = RV-1.
    E1=2.*RD-R2+2.*R3
    E2 = 2.*R3-R4+2.*R5
    E3 = R2+RD
    D = 1.+P-Y*R3
    PRINT5,RV,Y,R3,RD
  5  FORMAT(///30X6HV1/V2=,F8.5/22X14HCORE VOL.2/V2=,F8.5
    /14X22HCORE VOL 1/CORE VOL.2=,F8.5/12X24HCORE DIAM.1
    /CORE DIAM.2=,F8.5//22X2HX1,6X3HPH2,6X2HSE,7X2HS2/)
25  DO30 I=1,NP
    X1 = TX1(I)-.03
    DO28 J=1,5
    X1 = X1+.01
    X2 = 1.-X1
    VE = X1*X2*(A+B*(1.-2.*X2)+C*(1.-2.*X2)**2)/
    ((1.-DD*(1.-2.*X2))*V2)
    F = 1.+X1*P+VE-Y*(X2+X1*R3)
    T1 = X2*LOG(F/(1.-Y))
    T2 = X1*LOG(F/D)
    T3A = X2*(2.-Y)/((1.-Y)*(1.-Y))
    T3B = X1*R3*(1.+P+D)/(D*D)

```

APPENDIX IV (CONT)

```

T3 = 1.5*Y*(T3A+T3B)
F4 = 1.5/(F*F)
27 T4A = Y*Y*(X2*X2*X2+X2*X2*X1*E1+X2*X1*X1*E2+X1*X1*X1*R6)
T4B = -2.*Y*(1.+X1*P+VE)*(X2*X2+X1*X2*E3+X1*X1*R3)
T4 = F4*(T4A+T4B)
28 SE(J) = T1+T2+T3+T4
G = 8.333333*(SE(1)-SE(5)-8.*(SE(2)-SE(4)))
S2 = SE(3)-TX(I)*G
PH2 = TX1(I)*RV/(1.-TX1(I)+TX1(I)*RV)
30 PRINT9, TX1(1), PH2, SE(3), S2
29 FORMAT(20XF5.3, F9.5, 2F9.4)
IF(E(2)-10.)53, 32, 53
53 IF(SENSESWITCH3)50, 51
50 CALLATWILL(E, NN)
Y = E(1)
RD = (VV1/(V2*Y))**(1./3.)
GOTO52
51 CALLATWILL(E, NN)
RD = E(1)
GOTO52
32 IF(SENSESWITCH4)6, 33
33 CALLEXIT
END

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