# VAPOR PRESSURES AND THERMODYNAMIC PROPERTIES

OF BENZENE-CYCLOHEXANE SOLID MIXTURES

## VAPOR PRESSURES AND THERMODYNAMIC PROPERTIES

OF BENZENE-CYCLOHEXANE SOLID MIXTURES

BY

HAECHA CHUNG HA, B.Sc.

## A Thesis

Submitted to the School of Graduate Studies in Partial Fulfillment of the Requirements

for the Degree

Master of Science

McMaster University September, 1974 MASTER OF SCIENCE (1974) (Chemistry)

McMASTER UNIVERSITY Hamilton, Ontario

TITLE: Vapor Pressures and Thermodynamic Properties of Benzene-Cyclohexane Solid Mixtures

AUTHOR: Haecha Chung Ha, B.Sc. (Seoul National University) SUPERVISOR: Professor J. A. Morrison

NUMBER OF PAGES: (v), 54

SCOPE AND CONTENTS:

A modified dew point method for measuring vapor pressures of condensed phases is applied to solid mixtures of benzene and cyclohexane. From the measured vapor pressures, activity coefficients and excess Gibbs energies are derived. Much less accurate information about excess entropy and excess enthalpy is obtained. A comparison is made with the known properties of liquid mixtures of the same molecules.

Call of the part of the second

## TABLE OF CONTENTS

CHAPTER		Page
I	INTRODUCTION	1
II	THERMODYNAMICS OF A BINARY SOLUTION	5
III	EXPERIMENTAL	8
	Apparatus	8
	Materials	14
	Determination of the vapor pressures	14
	(a) Pure components	14
	(b) Mixtures	17
IV	RESULTS AND DISCUSSION	20
	Primary experimental data	20
	Derivation of the compositions of the solid phases	34
	Activity coefficients and excess Gibbs energies	35
	Comparison with liquid mixtures	47
V	SUMMARY	52
	REFERENCES	54

# LIST OF TABLES

TABLE		Page
1	List of Symbols	4
2	Measured Vapor Pressures	21
3	Vapor pressures at rounded values of the temperature	27
4	Activity coefficients and excess Gibbs energies at $T = 268$ K for some selected values of x and y	36
5	Activity coefficients and excess Gibbs energies at $T = 256$ K for some selected values of x and y	37
6	Activity coefficients and excess Gibbs energies at $T = 248$ K for some selected values of x and y	38

## LIST OF FIGURES

FIGURE		Page
1	Schematic drawing of the experimental arrangement	10
2	Condensation system	13
3	Plot of pressure against volume of the "compressor" for pure benzene at $T = 253.246$ K	16
4	Plot of pressure against volume of the "compressor" for a vapor mixture of 49.9% of benzene in cyclo- hexane at T = 248.240 K	19
5	A comparison of the measured vapor pressures of pure benzene with published values	24
6	A comparison of the measured vapor pressures of pure cyclohexane with published values	26
7	Vapor pressure as a function of $x_1$ or $y_1$ for $T = 268 \text{ K}$	29
8	Vapor pressure as a function of $x_1$ or $y_1$ for $T = 256$ K	31
9	Vapor pressure as a function of $x_1$ or $y_1$ for $T = 248$ K	33
10	Activity coefficients as functions of $x_1$ for $T = 268$ K	40
11	Activity coefficients as functions of $x_1$ for $T = 256$ K	42
12	Activity coefficients as functions of $x_1$ for $T = 248$ K	44
13	Excess Gibbs energy as a function of $\mathbf{x}_{l}$ at the three temperatures	46
14	Vapor pressures of liquid mixtures of benzene-cyclo- hexane at T = 313.15 K	49
15	Excess Gibbs energies of liquid mixtures of benzene- cyclohexane at T = $313.15$ K	51

v

#### CHAPTER I

## INTRODUCTION

Numerous studies of liquid mixtures have been made, with the main object of obtaining an understanding of molecular interactions in condensed systems. For binary mixtures, there is now a wealth of experimental data available for tests of models and theories (Rowlinson, 1969; Hildebrand and Scott, 1964). Much of the information is in the form of measured or derived thermodynamic quantities such as vapor pressures, heats of mixing, activity coefficients, excess thermodynamic functions, etc.

Considerably less is known about solid mixtures except possibly about metal alloys or solutions. The reason is that solid mixtures are subject to greater complexities. Whereas, in liquids, molecules of different shapes and sizes can usually be accommodated without much structural difficulty, crystalline solids need to conform to definite structures and thus can not sustain any appreciable amount of strain or distortion without undergoing phase separation. Thus, unless the mixture is composed of rather similar molecules, the range of homogeneous solid mixtures is expected to be small.

There is also an additional experimental difficulty. The attainment of equilibrium within a solid phase depends on diffusion which is a relatively slow process. Therefore, it can often be a serious impediment to experiment just ensuring that the solid phase has reached true equilibrium. For example, in a study of solid solutions

of N<sub>2</sub> and CO (Morrison, <u>et al</u>, 1968), it was found that equilibrium times were a few hours near the triple point and were estimated to be as long as a month at  $T = 0.8 \times T$  (triple point).

One way of overcoming the equilibrium problem is to design experiments in which only tiny amounts of solid are used. While this rules out calorimetric experiments, vapor pressure measurements are unaffected. A modified dew point method of measuring vapor pressures of small specimens of solid mixtures has been used successfully (Sommers, 1952; Morrison, <u>et al</u>, 1968) but the atoms and molecules were very simple: e.g.  ${}^{3}$ He,  ${}^{4}$ He, N<sub>2</sub> and CO.

The purpose of the work described in this thesis was to see if the dew point method could be applied to binary systems of larger and more complex molecules. The system of benzene-cyclohexane was chosen for several reasons, e.g., (i) the molecules are of similar size; (ii) the crystal structures of the pure solids are not vastly different (cubic versus orthorhombic) at higher temperatures; (iii) much information is available on the thermodynamics of liquid mixtures of the two components, some of it having been obtained by the dew point method (Brewster and McGlashan, 1973).

As will be seen in the experimental section, a suitable technique for measuring vapor pressures has been developed. Thus, in the temperature region 229 K<T<273 K, vapor pressures for the pure components and total vapor pressures for four mixtures were obtained. Subsequently, the primary experimental data are analysed formally to obtain activity coefficients and excess thermodynamic functions.

It was soon clear that the solid mixtures displayed far from ideal behavior. The dependence of total vapor pressure on vapor or solid composition was found to be very unusual, when compared with

the simple behavior of the liquid mixtures. Also, the mixtures behaved very differently in the extreme regions, of less than 20% and of more than 80% of benzene in the vapor. This might be due to structural effects and some speculation is indulged in.

T.i	st	of	ST	mbols	į.
	20	01	2	1110 LD	

Symbol	Definition
<sup>y</sup> 1' <sup>y</sup> 2	mole fractions of component l(benzene) and 2(cyclohexane) in the vapor
×1, ×2	mole fractions in the condensed phase
p	total vapor pressure
<sup>p</sup> <sub>1</sub> , <sup>p</sup> <sub>2</sub>	partial vapor pressures
$p_1^\circ, p_2^\circ$	vapor pressures of pure components
<sup>n</sup> 1, <sup>n</sup> 2	numbers of moles in the condensed phase
Υ <sub>1</sub> , Υ <sub>2</sub>	activity coefficients
μ <sub>1</sub> , μ <sub>2</sub>	chemical potentials
$\mu_1^E, \mu_2^E$	excess chemical potentials
-E G	molar excess Gibbs energy
-E S	molar excess entropy
H <sup>E</sup>	molar excess Helmholtz energy
R	molar gas constant
Т	temperature in Kelvins
Vg	molar volume of the vapor phase
Vc	molar volume of the condensed phase
$\overline{\mathrm{vc}}_{1}^{\circ}, \overline{\mathrm{vc}}_{2}^{\circ}$	molar volumes of the condensed phase for pure components
<sup>B</sup> 11′ <sup>B</sup> 22	molar second virial coefficients of pure components
<sup>B</sup> ]2	molar second virial coefficient for inter-

#### CHAPTER II

## THERMODYNAMICS OF A BINARY SOLUTION

In the dew point method, the point at which a relatively large amount of vapor of known composition  $(y_1, y_2)$  is in equilibrium with a small amount of solid is determined. Therefore, the measurable variables are p, T and  $y_1$  (or  $y_2$ ). Then, the Gibbs-Duhem relation allows one to derive  $x_1$  and  $x_2$  from them, as is shown in the following: At constant T, the Gibbs-Duhem relation becomes

$$\sum_{i=1}^{\infty} n_{i} d_{\mu} = V dp$$
(1)

For a solution, if the vapor in equilibrium with it can be assumed to be ideal,

$$d\mu_{i}^{\text{soln}} = \operatorname{RT} d\ln p_{i}$$
(2)

Substituting (2) into (1) gives

$$RT \sum_{i} n_{i} d \ln p_{i} = V dp$$
(3)

Dividing both sides of (3) by  $\sum_{i=1}^{n}$  gives

$$\sum_{i} x_{i} d \ln p_{i} = \frac{Vdp}{RT\Sigma n_{i}}$$
$$= \frac{\overline{Vc} dp}{RT} . \qquad (4)$$

Again, if the vapor can be assumed to be ideal, i.e., RT = pVg, (4) becomes

$$\sum_{i} x_{i} d \ln p_{i} = \frac{\overline{Vc}}{\overline{Vg}} d \ln p.$$
(5)

Since for a binary system,

$$p_1 = p y_1 \text{ and } p_2 = p y_2$$
, (6)

combination of (5) and (6) allows rewriting of (5), in terms of the total vapor pressure, as

$$x_1 d \ln p y_1 + x_2 d \ln p y_2 = \frac{\overline{v}c}{\overline{v}g} d \ln p.$$
 (7)

For most cases,  $\overline{Vc} \ll \overline{Vg}$  and thus (7) becomes, after rearrangement,

$$\left(\frac{\partial \ln p}{\partial y_1}\right)_{T} = \frac{y_1 - x_1}{y_1 y_2}, \qquad (8)$$

as a good approximation.

As long as the vapor can be regarded as ideal, it is rather simple to obtain the excess thermodynamic functions,  $\overline{G}^{E}$ ,  $\overline{S}^{E}$ ,  $\overline{H}^{E}$ , etc., which describe the departure from the ideal mixture. Under this situation, we can obtain

$$\mu_{1}^{E} = \operatorname{RT} \ln \gamma_{1} \text{ and } \mu_{2}^{E} = \operatorname{RT} \ln \gamma_{2}$$

$$\overline{G}^{E} = x_{1} \mu_{1}^{E} + x_{2} \mu_{2}^{E}$$

$$(9)$$

with the activity coefficients defined as

$$\gamma_1 = \frac{p \gamma_1}{p_1^{\circ} x_1}$$
 and  $\gamma_2 = \frac{p \gamma_2}{p_2^{\circ} x_2}$  (10)

The other excess functions are derived in the standard way, e.g.,

$$\overline{s}^{E} = -\left(\frac{\partial \overline{g}^{E}}{\partial T}\right)_{P,X}$$
(11)

When the vapor may not be treated as ideal, the  $\gamma_i$ 's (as well as the x's) must be obtained from expressions more complicated than (10) (than (8) for the x's) (see Brewster and McGlashan, 1973, for example):

$$\ln \gamma_{1} = \frac{\ln \left(\frac{py_{1}}{p_{1}^{\circ}x_{1}}\right) + \frac{(p-p_{1}^{\circ})(B_{11}-\overline{Vc}_{1}^{\circ})}{RT} + \frac{2y_{1}^{2}\delta_{12}p}{RT} }{\frac{p}{RT}}$$

$$\ln \gamma_{2} = \frac{\ln \left(\frac{py_{2}}{p_{2}^{\circ}x_{2}}\right) + \frac{(p-p_{2}^{\circ})(B_{22}-\overline{Vc}_{2})}{RT} + \frac{2y_{2}^{2}\delta_{12}p}{RT} }{RT} ,$$

$$(12)$$

where  $\delta_{12} = B_{12} - (B_{11} + B_{22})$ .

In the present work, the maximum pressure measured was 28 Torr. From estimates of B's (Dymond and Smith, 1969) for equimolar mixtures at the highest (268 K) and lowest (229 K) temperatures, the maximum contribution of the second terms on the right hand sides of (12) to the  $\gamma$ 's turned out to be 0.12%. Hence, corrections for gas imperfection were not needed.

#### CHAPTER III

#### EXPERIMENTAL

The essential physical measurement was the detection of the point at which a very small amount of solid was in equilibrium with vapor of known composition. This was accomplished by compressing the vapor into a cell and determining the desired point from the change of curvature of a plot of the observed pressure against the volume of the "compressor", which was a metal bellows driven by an attached micrometer screw.

#### Apparatus

The experimental arrangement is illustrated schematically in Figure 1. The material of construction was metal except for the Bourdon tube of the pressure gage, C. Since organic vapors obviously interact with the usual types of stopcock grease, it was necessary to use greaseless (metal) valves.

The vapor mixtures were prepared in a one-liter bulb, B, in the following way: One component (benzene) was admitted to B, with valves 1, 2 and 4 open and valve 3 closed. After the system was pumped out with valve 2 closed, the second component was added and the total pressure measured. The preparation of the vapor mixtures was done as quickly as possible (in less than 10 minutes). The accuracy of the compositions was mainly determined by the variation in room temperature,

Schematic drawing of the experimental arrangement

- A sample resevoirs for pure components
- B one-liter bulb for preparing mixtures
- C Bourdon pressure gage
- D metal bellows
- E micrometer screw
- F thermoelectric bath where condensation cell
   was mounted





since the bulb was not thermostatted. The mixtures were thoroughly mixed by freezing and evaporating them several times.

Pressures were measured to a precision of ±0.003 Torr with reference to vacuum, with a fused quartz Bourdon gage, C, (Texas Instruments Inc., model 140), which was calibrated in the range of 0 to 250 Torr by comparison with a Barocel electric manometer to an accuracy of 0.1%.

The volume of the system ( $\sim 5 \text{ cm}^3$ ), with values 1, 2 and 3 closed and value 4 open, was varied by expanding or compressing the metal bellows, D, by means of the attached micrometer screw, E. It proved to be convenient to make this volume comparable to the volume of the cell, G.

The temperature of the cell was controlled by balancing heat supplied by an electrical heater against cooling by a thermoelectric bath, F, (Cole Parmer Co., model 3851), which was capable of attaining -55°C. In order to have the cell as the coldest part of the system and also to reduce the temperature gradients in the cell, an arrangement of heaters, shown in Figure 2, was adopted. Condensation was made to take place in the cell in the copper block, H, which was mounted on a piece of Styrofoam to insulate it partially from the cooler. A copper-constant thermocouple (10 junctions) was attached to the top of the block and measured the temperature of the cell itself. Heaters were wound on the lower half of the block, on the German silver tube, I, and on the entire length of the copper tube, J. The temperature of the cooler was kept slightly lower than the desired one, an optimum amount of current was chosen for the heaters on the German silver and copper tubes and finally the heater on the block was controlled manually.

Condensation system

G	-	cell	(volume	∿5cm <sup>3</sup> )	

- H copper block
- I German silver tube (lmm 0.D., 0.1 mm wall thickness)
- J thick-walled copper tube
- K Styrofoam block
- F thermoelectric cooler



Figure 2

Thus, the temperature of the cell could be controlled to  $\pm 0.0002$  K for periods of hours. The values (in Kelvins) of the temperature of the cell were obtained from the e.m.f. of the thermocouple by means of a standard table appropriate for the constantan wire used.

#### Materials

Liquid benzene and cyclohexane that had been purified chromatographically (Benson, <u>et al</u>, 1970), were obtained from Mr. P. J. D'Arcy of the National Research Council in Ottawa. The liquids were kept in self-sealing ampoules and were used without further purification. They were thoroughly degassed before use by freezing, pumping and melting in the sample resevoirs (A in Figure 1).

## Determination of the vapor pressures

## (a) Pure components

Vapor at an appropriate pressure was drawn from one of the resevoirs into the system, and compressed by means of the bellows arrangement. Frequently, no marked change in curvature of p versus volume of the "compressor" could be seen, because the vapor supersaturated (see Thomas and Staveley, 1952, for a discussion of supersaturation magnitudes for a variety of substances). This effect was overcome by surging an excess of vapor into the system until condensation occurred and then removing it. Once solid had been formed in the cell, sufficient nuclei seemed to remain to prevent subsequent supersaturation.

A typical experimental result with one of the pure components is shown in Figure 3. As should be the case, the observed vapor pressure is independent of the volume of the "compressor" when the two phases are present. The data shown were also independent of the settings of the

Plot of pressure against volume of the "compressor" for pure benzene at T = 253.246 K

 $0, \square$  - compression  $\Delta$  - expansion



controls on the cooler and heaters on the German silver and copper tubes within moderate limits, thus indicating that temperature gradients in the condensation system (Figure 2) were being properly controlled.

## (b) Mixtures

A vapor mixture of known composition was drawn from the bulb B (Figure 1) into the cell step by step until the correct amount to suit the range of the "compressor" was found.

A typical experimental result with a mixture is shown in Figure 4. Because the system solid-vapor now has two degrees of freedom, the observed vapor pressure varies with the volume of the "compressor" and it becomes more difficult to determine the dew point accurately. This is reflected in the lower accuracy that is quoted in the following section.

Plot of pressure against volume of the "compressor" for a vapor mixture of 49.9% of benzene in cyclohexane at T = 248.240 K

0,□ - compression

 $\Delta$  - expansion





#### CHAPTER IV

#### RESULTS AND DISCUSSION

#### Primary experimental data

Vapor pressure data for the pure components and for four mixtures are given in Table 2. The estimated accuracy of the data for the pure components is  $\pm 0.006$  Torr. For the mixtures, it is estimated to be  $\pm 0.025$  Torr on the average and not lower than  $\pm 0.10$  Torr in the worst case. The data marked with an asterisk in the table are examples where difficulties with nucleation were most severe. They are therefore the least certain.

To compare the measured vapor pressures of pure benzene and pure cyclohexane with published values (Kiss, <u>et al</u>, 1972), difference plots are used. The difference between observed and calculated values is plotted as a function of temperature in Figures 5 and 6. As may be seen, the data in the present work are consistent with a smooth p-T relation within  $\pm 0.01$  Torr. The other data show considerably more scatter.

For the subsequent analysis of the experimental data, e.g. for the calculation of  $\gamma_i$ ,  $\overline{G}^E$ ,  $\overline{S}^E$  etc., vapor pressures at rounded values of the temperature were derived by reading the values of  $(p-p_{calc})$ from large size graphs of  $(p-p_{calc})$  against T. The results are given in Table 3, and those for the three temperatures 268, 256 and 248 K are plotted in Figures 7, 8 and 9. Clearly, the departure of the mixtures

# Measured Vapor Pressures

		Т (К)		p (Torr)
(a)	pure	benzene		
		228.692		0.481
		233.684		0.805
		238.604		1.299
		243.170		2.000
		248.240		3.210
		253.246		4.983
		255.726		6.176
		258.189		7.587
		260.635		9.278
		263.065		11.245
		265.747		13.918
		268.144		16.696
		270.527		19.937
		273.160		24.188
(h)	nuro	qualchours	a	
(D)	pure	Cycronexane		
		231.637		1.383
		237.453		2.245
		243.170		3.545
		248.240		5.196
		253.246		7.505
		257.370		10.014
		258.189		10.551
		263.065		14.602
		266.014		17.602
		268.144		20.064
		270.527		23.265
		273.160		27.284
$\langle z \rangle$		0.000		
(C)	y <sub>1</sub> =	0.236		
		228.988		1.16
		233.100		1.69
		238.317		2.60
		243.170		3.75
		248.800		5.72
		253.522		7.95
		258.462		11.06
		263.603		15.30
		268.939		21.12
		273.160		27.07

		T (K)	p(Torr)
(d)	$y_1 = 0.499$		x
		228.692 233.975 238.604 243.170 248.240 252.970 258.189 263.065 268.144	1.17 1.88 2.76 4.00 6.06 8.46 12.03 16.30 22.16
(e)	$y_1 = 0.684$	·	
		228.958 233.100 238.317 243.170 248.800 253.522 258.462 263.603 268.939 273.160	0.93* 1.48* 2.44* 3.67 5.66 7.94 11.06 15.44 21.66 28.10
(f)	$y_1 = 0.850$		
		228.692 233.684 238.604 243.170 248.240 253.246 258.189 263.065 268.144	0.72* 1.17* 1.84* 3.00* 4.89* 7.33 10.29 14.21 19.58

\* difficulties with nucleation (see text).

A comparison of the measured vapor pressures of pure benzene with published values

0	-	present results	
Δ	autor.	reference (Kiss <u>et al</u> , 1972)	
ln	P <sub>ca</sub>	alc (Torr) = 23.3922 - 5517.59/	Ί



Figure 5

A comparison of the measured vapor pressures of pure cyclohexane with published values

0 - present results
Δ - reference (Kiss, <u>et al</u>, 1972)
ln p<sub>calc</sub>(Torr) = 19.9526 - 4544.67/T



Та	b	1	е	3	

Vapor pressures at rounded values of the temperature

		I	p (Torr)			
У1	229 K	238 K	248 K	256 K	264 K	268 K
 0.000	1.10	2.35	5.11	9.11	15.50	19.92
0.236	1.17	2.52	5.40	9.40	15.68	19.96
0.499	1.21	2.64	5.94	10.40	17.27	22.00
0.684	0.94	2.37	5.34	9.41	15.84	20.42
0.850	0.77	1.73	4.79	8.87	15.09	19.40
1.000	0.50	1.24	3.15	6.32	12.14	16.52

Vapor pressure as a function of  $x_1$  or  $y_1$  for T = 268 K

\_\_\_\_\_\_ p versus y<sub>1</sub>
\_\_\_\_\_\_ p versus x<sub>1</sub>
\_\_\_\_\_\_ ideal solution



Figure 7

Vapor pressure as a function of  $x_1$  or  $y_1$  for T = 256 K\_\_\_\_\_\_\_\_\_ p versus  $y_1$ \_\_\_\_\_\_\_\_ p versus  $x_1$ 



Figure 8



-0-

ideal solution

Figure 9

Vapor pressure as a function of  $x_1$  or  $y_1$  for T = 248 K

p versus y<sub>l</sub>



Figure 9

from ideal behavior (dot-dashed curves) is considerable. It would appear that the dilute mixtures of benzene in cyclohexane (for  $y_1 < 0.2$ ) behave more simply than those of the reversed composition, i.e.  $y_1 > 0.8$ . The reason can only be speculated about. Cyclohexane is a plastic crystal and has a cubic structure in the temperature range investigated here. This probably means that the molecules can reorient fairly easily in the solid and therefore a few benzene molecules may not be troublesome. Solid benzene, on the other hand, has a more complicated structure that undoubtedly depends on strongly directional interactions. It is perhaps not surprising then that the addition of a second component produces a markedly non-ideal mixture.

## Derivation of the compositions of the solid phases

With liquid mixtures, it is usually possible to measure the three quantities p, x and y independently and equation (8) can then be used to test for thermodynamic consistency. But, in the present experiments, the solid compositions can not be measured directly. Therefore, they have to be calculated from equation (8). Values of  $\left(\frac{\partial \ln p}{\partial y_1}\right)_T$  at several values of  $y_1$  were obtained from a smooth curve drawn through plotted points of p against  $y_1$  within experimental error, as is shown in Figures 7, 8 and 9.

Insufficient experimental information was obtained to allow the shape of the curve of p against  $y_1$  to be determined in the region  $y_1>0.8$ . Thus, it was possible to obtain estimates of  $x_1$  only in the range  $x_1<0.75$ .

### Activity coefficients and excess Gibbs energies

At the three temperatures, activity coefficients and excess Gibbs energies were calculated from equations (9) and (10) for some selected values of x and y obtained from Figures 7, 8 and 9. The results are given in Tables 4, 5 and 6.

Graphs of  $\gamma_1$  and  $\gamma_2$  against  $x_1$  are shown in Figures 10, 11 and 12. Each pair of isothermal activity coefficient curves satisfy the following rules, which are based directly on the Gibbs-Duhem relation:

- (i) The curves for  $\gamma_1$  and  $\gamma_2$  as functions of  $x_1$  have opposite slopes at each composition.
- (ii) Where the curve for one component shows a maximum, that for the other component shows a minimum.
- '(iii) The gradient  $\partial \gamma_1 / \partial x_1$  remains finite as  $x_1$  tends to zero. This may be regarded as conformity to Henry's law.

(iv) 
$$\left(\frac{\partial \gamma_2}{\partial x_2}\right)_T \rightarrow 0 \text{ as } x_2 \rightarrow 1$$
. This is required by Raoult's law

As can be seen from Figure 13, in the solid composition range  $x_1 < 0.75$ , the excess Gibbs energies show positive deviations from ideal behavior at the three temperatures. That this would be the derived result is evident from the fact that the measured vapor pressures of the mixtures exceed those of hypothetical ideal mixtures (dot-dashed curves in Figures 7, 8 and 9).

The temperature dependence of the excess Gibbs energy at each fixed composition is related to the excess entropy by equation (11). However, only a crude estimate of  $\overline{s}^E$  can be made because of the size of the uncertainties in  $\overline{G}^E$ .  $\overline{s}^E$  is obviously positive throughout the range

Activity coefficients and excess Gibbs energies at  ${\tt T}$  = 268 K for some selected values of x and y

×l	Уl	Υl	*2	У2	Υ <sub>2</sub>	$\overline{G}^{\mathrm{E}}(J/mole)$
0.100	0.100	1.20±0.01	0.900	0.900	1.00	41.4±2.2
0.190±0.008	0.190	1.21±0.05	0.810±0.008	0.810	1.00±0.01	81.1±0.2
0.223±0.023	0.339	1.90±0.22	0.777±0.023	0.661	0.88±0.02	98 ±39
0.250±0.009	0.392	2.03±0.05	0.750±0.009	0.608	0.87±0.02	168 ± 33
0.387±0.017	0.457	1.57±0.07	0.613±0.017	0.543	0.98±0.03	358 ± 17
0.485	0.485	1.33	0.515	0.515	1.11	427 ± 2
0.628±0.002	0.532	1.12	0.372±0.002	0.468	1.38±0.01	421 ± 2 .
0.720	0.600	1.06	0.280	0.400	1.51	351 ± 6

Activity coefficients and excess Gibbs energies at T = 256 K for some selected values of x and y

Xl	yl	Υl	× 2	У <sub>2</sub>	Ϋ2	$\overline{G}^{E}$ (J/mole)
0.090±0.006	0.095	1.54±0.11	0.910±0.006	0.905	1.00	89.8±0.5
0.170±0.003	0.208	1.81±0.03	0.830±0.003	0.792	0.98	173±11
0.213±0.005	0.300	2.12±0.05	0.787±0.005	0.700	0.93±0.01	215±4
0.246±0.011	0.400	2.61±0.12	0.754±0.011	0.600	0.89±0.01	207±22
0.300±0.008	0.430	2.34±0.07	0.700±0.008	0.570	0.92±0.01	423±7
0.370±0.025	0.448	1.99±0.12	0.630±0.025	0.552	1.00±0.04	544±38
0.474	0.474	1.65	0.526	0.526	1.15	658±4
0.576±0.028	0.499	1.42±0.08	0.424±0.028	0.501	1.35±0.08	704±3
0.745±0.014	0.570	1.20±0.03	0.255±0.014	0.430	1.84±0.08	623±27

Activity coefficients and excess Gibbs energies at T = 248 K for some selected values of x and y

×l	yl	Υl	*2	У <sub>2</sub>	Υ <sub>2</sub>	$\overline{G}^{E}$ (J/mole)
0.100±0.001	0.125	2.08±0.03	0.900±0.001	0.875	0.99±0.01	136±7
0.200±0.009	0.273	2.38±0.13	0.800±0.009	0.727	0.97	311±9
0.300±0.002	0.406	2.49±0.01	0.700±0.002	0.594	0.96±0.01	503±19
0.350±0.007	0.451	2.42±0.08	0.650±0.007	0.549	0.97	600±6
0.380±0.009	0.472	2.35±0.05	0.620±0.009	0.528	0.99±0.01	651±23
0.495	0.495	1.90	0.505	0.505	1.16±0.01	810±7
0.600±0.015	0.519	1.63±0.03	0.400±0.015	0.481	1.39±0.06	876±11
0.700±0.023	0.542	1.44±0.04	0.300±0.023	0.458	1.74±0.15	872±5
0.760±0.005	0.594	1.40	0.240±0.005	0.406	1.86±0.05	838±4

Activity coefficients as functions of  $x_1$  for T = 268 K





Activity coefficients as functions of  $x_1$  for T = 256 K



Figure 11

Activity coefficients as functions of  $x_1$  for T = 248 K



Figure 12

Excess Gibbs energy as a function of  $\textbf{x}_{l}$  at the three temperatures

^	_	at	Ť	=	256	ĸ	
	_	at	T	=	248	K	



Figure 13

 $x_1 < 0.75$ . For the equimolar mixture,  $\overline{S}^E = 19$  J/mole deg. Hence, at T = 256 K, we get  $\overline{H}^E = \overline{G}^E + \overline{TS}^E = 5539$  J/mole. Again, because of accumulating uncertainties, it is not worthwhile to deduce anything else about the behavior of  $\overline{H}^E$ .

#### Comparison with liquid mixtures

The extensive available data for liquid mixtures are illustrated in Figure 14 (total vapor pressure versus  $x_1$  and  $y_1$ ) and Figure 15 (excess Gibbs energy versus  $x_1$ ). It is clear that the behavior of the liquid mixtures is rather simpler than that of the solid mixtures and therefore the derived thermodynamic quantities are more accurate. The magnitude of  $\overline{G}^E$  for the solid is obviously much greater than that for the liquid and this is perhaps to be expected.

Vapor pressures of liquid mixtures of benzene-cyclohexane at T = 313.15  $\mbox{K}$ 

0, ∇ - by Brewster and McGlashan (1973) Δ, □ - by Scatchard, et al (1939) \_\_\_\_\_\_ p versus y<sub>1</sub> \_\_\_\_\_ p versus x<sub>1</sub> \_\_\_\_\_ ideal solution



Figure 14

Excess Gibbs energies of liquid mixtures of benzenecyclohexane at T = 313.15 K

O - by Brewster and McGlashan (1973)

△ - by Scatchard, et al (1939)



Figure 15

#### CHAPTER V

#### SUMMARY

- A suitable technique for measuring total vapor pressures of solid mixtures was developed.
- Even though difficulties with nucleation were encountered, results of good accuracy were obtained.
- 3. The values obtained for the vapor pressures of pure solids are more precise and probably more accurate than existing values in the literature.
- 4. While it would have been desirable to obtain data for many more mixtures, much more time would have been required. The experiments on one mixture required several weeks.
- 5. Because the accuracy of the measured vapor pressures was good, it was possible to carry through the analysis of the data to obtain  $\gamma$ 's and  $\overline{G}^E$  for  $y_1 < 0.8$ .
- 6. The dependence of  $\gamma_1$  and  $\gamma_2$  on  $x_1$  was found to be reasonable.
- 7. The magnitude of  $\overline{G}^{E}$  for  $x_{1} < 0.75$  was established in the range 248<T<268 K.
- 8. Only rough estimates could be obtained for  $\overline{s}^{E}$  and  $\overline{H}^{E}$ .
- The behavior of the solid mixtures is evidently more complicated than that of liquid mixtures.

- 10. At this stage, it is premature to attempt any detailed comparison of the experimental results with predictions of theoretical models. Also, before that is attempted, one would want to obtain more experimental information.
- 11. It is concluded that the dew point method is capable of providing a reasonably adequate picture of the thermodynamics of solid mixtures - even of quite large molecules. It should be worth exploiting further.

#### REFERENCES

Benson, G. C., Murakami, S., Lam, V. T. and Singh, J., 1970, Can. J. Chem. 48, 211.

- Brewster, E. R. and McGlashan, M. L., 1973, J. Chem. Soc. Faraday Trans. I, 12,2046.
- Dymond, J. H. and Smith, E. B., 1969, The Virial Coefficients of Gases (Clarendon Press, Oxford).

Hildebrand, J.H. and Scott, R. L., 1964, The Solubility of Nonelectrolytes, 3rd edn. (Dover Publications, New York).

Kiss, I., Jakli, G. and Illy, H., 1972, Acta Chim. (Budapest) <u>71</u>, 59.
Morrison, J. A., Newsham, D.M.T. and Weir, R. D., 1968, Trans. Faraday
Soc. 64, 1461.

Rowlinson, J.S., 1969, Liquids and Liquid Mixtures, 2nd edn. (Butterworths, London).

Scatchard, G., Wood, S.E. and Mochel, J.M., 1939, J. Phys. Chem. <u>43</u>, 119. Sommers, H.S. Jr., 1952, Phys. Rev. <u>88</u>, 113.

Thomas, D. G. and Staveley, L. A. K., 1952, J. Chem. Soc., 4569.