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APPLICATION OF THE QUASI-LATTICE THEORY TO THE
HEATS OF MIXING OF SOME ALCOHOL-HYDROCARBON SYSTEMS

A Thesis

Submitted to the

Department of Chemistry

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In Partial Fulfillment

of Requirements for the Degree

Master of Science

by

Mar Lynn James

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This thesis by Mar Lynn James is accepted in its present form
by the Department of Chemistry as satisfying the thesis requirement for
the degree of Master of Science.

Signed:

Sept 1, 1960
Date

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INTRODUCTION

Extensive experimental work has been done on the solid and gaseous states of matter; and fairly adequate theoretical interpretations of these data have been made. In the liquid state, however, the progress has been much slower because of (1) difficulties in obtaining high quality experimental results,¹ and (2) inherent problems in formulating satisfactory theories of liquids.²

The thermodynamic quantities obtained upon mixing two liquids give a measure of the molecular interaction between the liquids; and, therefore, provide an excellent means of studying the liquid state. Several different approaches have been used in the determination of these properties.

One approach has been to determine the chemical potential by vapor-pressure equilibria measurements.³ The free energy of mixing can then be calculated and the excess entropy and heats of mixing can be obtained by differentiation of the free energy function. This approach, however, has the difficulty that any error in the free energy is magnified on differentiation to give errors in the excess entropy and heats of mixing of as much as ten times the error in the free energy.

An alternative procedure in determining the thermodynamic properties has been to determine the heats of mixing calorimetrically. Some of the early calorimeters which were developed were rather crude.⁴ One of the problems encountered with many of these calorimeters was

¹D. H. Everett, "Introduction to Experimental Work," Disc. Faraday Soc., 15, 126 (1953).

²R. L. Scott, "Theoretical Models and Real Solutions," Disc. Faraday Soc., 15, 44 (1953).

³G. Scatchard and C. L. Raymond, J. Am. Chem. Soc., 60, 1283-84 (1938).

⁴R. J. Sullivan, "Thermodynamic Properties of Some Non-electrolyte Solutions," Unpublished Master's Thesis, Department of Chemistry, Brigham Young University, 1, 1958.

the presence of the vapor phase. This lead to considerable error, which according to Van der Waals⁵ could result in an error of as much as one third of the total heat change.

A significant contribution to the calorimetric determination of thermodynamic properties was made by Scatchard et al.⁶ They designed a glass calorimeter which eliminated the vapor phase.

Cheeseman and Whitaker,⁷ and Moelwyn-Hughes and Missen⁸ went one step further in the development of their calorimeters by building a steel calorimeter consisting of two compartments separated by a thin metal foil. By puncturing the foil the liquids in the two compartments are caused to mix. The heats of mixing were then measured directly. These calorimeters gave very good results.

The calorimeter used in this study was patterned after that of Moelwyn-Hughes and Missen. Ott,⁹ Sullivan¹⁰ and the present investigator all obtained values for the heats of mixing with errors less than one per cent.

Two approaches to the theoretical interpretations of the liquid state have been: (1) Regard gases and liquids as being essentially alike; and, therefore, attempt to describe liquids by the same approach that has been used for gases; (2) consider the liquid as having a pseudo crystalline structure (the quasi-lattice theory).¹¹ The quasi-lattice

⁵J. H. Van der Waals and J. J. Hermans, Rec. Trav. Chim. Pays-Bas, 69, 949 (1940).

⁶G. Scatchard, L. B. Ticknor, J. R. Goates, and E. R. McCartney, J. Am. Chem. Soc., 74, 3721 (1952).

⁷C. H. Cheeseman and A. M. B. Whitaker, Proc. Roy Soc. (London), A212, 406-25 (1952).

⁸E. A. Moelwyn-Hughes and R. W. Missen, Trans. Faraday Soc., 53, 607 (1957).

⁹J. B. Ott, "Calorimetric Heats of Mixing of Some Non-electrolytic Binary and Ternary Solutions", Unpublished Master's Thesis, Department of Chemistry, Brigham Young University, 1956.

¹⁰Sullivan, op. cit.

¹¹J. H. Hildebrand, "Models and Molecules," Disc. Faraday Soc., 15, 10-11 (1953).

theory has been found to give a reasonably accurate description of simple systems.

In this investigation we have attempted to extend the experimental and theoretical knowledge of the liquid state by achieving the following objectives:

- (1) Determine the heats of mixing of the systems: $C_6H_6-CH_3OH$, $C_6H_6-C_2H_5OH$, $C_6H_{12}-C_2H_5OH$, over the entire range of composition.
- (2) Determine the applicability of the quasi-lattice theory to these rather complicated systems, in which association of molecules is possible.

EXPERIMENTAL APPARATUS AND PROCEDURE

Description of Calorimeter.--Two metal calorimeters were used in determining the heats of mixing (Figure 1). They consisted of two compartments (A and B) separated by a thin metal foil (C) held between two polyethylene gaskets (D). Varying sizes of metal weights (E) were placed in the lower compartment to allow an alteration of the volume of that compartment and thereby obtain varying concentrations of the solution. The weights also provided a means of breaking the foil to allow mixing of the liquids and stirring of the solution. The top compartment was screwed into the bottom compartment, thereby isolating the liquid in the bottom compartment. The top compartment was fitted with a screw-in plug (F) to allow isolation of the liquid in that compartment.

In preparing the calorimeter for an experimental run the bottom was filled with one of the liquids and sealed off by placing the gaskets, foil and upper compartment in place. Any liquid that was present in the top compartment was removed, and the entire calorimeter was placed in a vacuum chamber to remove any latent liquid on the exterior. The weight of the empty calorimeter had been determined previously and the weight of the liquid in the bottom compartment was obtained by difference. The top compartment was then filled with the other of the two liquids under examination, sealed off, dried and weighed.

The entire calorimeter was placed in a close fitting glass tube (G) which was covered with aluminum foil (H). A rubber stopper (I) was placed in the open end of the tube to seal it off, and melted paraffin (J) was poured in the joint to assure that an air tight seal was obtained. The entire assemblage was placed in a constant temperature water bath.

The calorimeter had a resistance wire (K) wrapped around the bottom compartment and insulated from the calorimeter by tissue paper impregnated with varnish. This wire was then wrapped with glass tape (L), and this was bound by a layer of cork (M). Leads (N) went from the

THE CALORIMETER

- A Bottom compartment
- B Top compartment
- C Metal foil diaphragm
- D Polyethylene gasket
- E Steel weight
- F Brass plug
- G Glass tube
- H Aluminum foil covering
- I Rubber stopper
- J Paraffin
- K Heating coil
- L Glass tape
- M Cork
- N Heating coil leads
- O Thermocouple

Figure 1

resistance wire out through an opening in the stopper. They were then threaded within tygon tubing to the point where they emerged from the bath and from there to a battery power source.

A single junction thermocouple (O) was placed in contact with the upper compartment to obtain temperature measurements. The leads from this went through another opening in the stopper into tygon tubing. From this point one of the leads went to a reference thermocouple junction contained in an oil filled dewar flask; the other lead went to a galvanometer.

Experimental Procedure.--The calorimeter was left in the water bath for approximately 4 to 5 hours to allow it to come to equilibrium with the temperature of the bath. After equilibrium was established the liquids were mixed by turning the calorimeter and contents over and shaking vigorously, causing the weight to break through the seal. The system was then placed in a mechanical rotator, which would rotate the system back and forth 6 times a minute. The heat change obtained on mixing would result in the lowering of the temperature (the systems studied were endothermic), and the change in temperature caused a potential to be produced in the thermocouple arrangement and thereby a deflection was produced in the galvanometer. The deflection was plotted against time (Figure 2) until a good extrapolation to the time of mixing was possible (A). After an extrapolation was obtained the calorimeter was heated by the use of the resistance coils and a battery source of electricity (B). The system was heated until it approached the zero point (C). The current was then turned off and the deflection curve passed through the zero point and came to a peak (D) and then started back to equilibrium (E). After this phase of the deflection the curve leveled off in a straight line (F). The electric current was again applied (G) for a period of time that would produce a deflection approximately the same as was obtained on mixing (H). The voltage, time of heating, and resistance of the coil were all measured. The deflection was plotted until it leveled off in a straight line, which made extrapolation to the time of heating possible. By comparison of the two deflections

Figure 2 Deflection Curve

the value of heat of mixing was obtained by calculation. A graph of the heats of mixing versus mole fraction was plotted for the value obtained. The experiment was repeated several times using varying concentrations until the heats of mixing for the complete range of concentration were obtained.

Dilution mixtures were run in the extremes of concentration where direct heats of mixing were not possible. The heats of mixing in this region were calculated indirectly. The heats of mixing were obtained from a combination of pure component with a mixture of the two in the same manner as used previously for pure components only. The heats of mixing due to the mixed part was determined by knowing the composition of the mixture and the total moles used. The heat due to this source was obtained directly from the previously determined heats of mixing curve. The value obtained experimentally and that read from the curve were added together giving the total heats of mixing for the dilution mixture.

Chemicals Used.--Chemicals used in this study were reagent grade benzene, cyclohexane, methanol, and ethanol. The purity of these liquids was determined by refractive index readings. Sodium metal was added to the benzene and cyclohexane to remove any latent water and they were then further purified by fractional crystallation by freezing methods. The methanol was further purified by refluxing with magnesium metal and then fractionally distilled. The reagent grade ethanol was found to be sufficiently pure that no further purification was carried out. The liquids were stored in closed glass containers covered by an atmosphere of dry nitrogen.

Experimental Uncertainties.--

1. Extrapolations obtained on mixing and heating curves were within ± 0.2 mm. On the deflection curves.
2. Time of heating was determined to ± 0.01 sec.
3. Resistance of the coil was obtained to ± 0.005 ohms.

4. Voltage was read to ± 0.001 volts.
5. Weighing of the calorimeter was within ± 2 . mg.
6. Temperature variation of the bath was constant to $\pm 0.005^{\circ}\text{C}$.
7. Sensitivity of the galvanometer was 0.2 uv/mm .

Percentage Error.--

1. Errors obtained from the extrapolation of the cooling curves were within 10%.
2. Errors in the calculation of the heats of mixing arising from the extrapolation error were less than 10% of the extrapolation error, therefore, giving an error of less than 1% due to inaccuracy of extrapolation.
3. Error in reading the time of heating was less than 0.1%.
4. Values of the resistance coil were within 0.01%.
5. Voltages of the batteries were read within 0.01%.
6. Weighing errors were less than 0.01%.
7. Error resulting from the vapor phase above the liquids was negligible.
8. Error due to temperature fluctuations of the bath and galvanometer variance were insignificant.
9. The error for direct heats of mixing determinations was within 1.0%.
10. The error for the dilution mixtures was within 2.0%.

The heats of mixing have, therefore, been determined within 1.0-2.0% error.

EXPERIMENTAL RESULTS

Table I lists the values for the heats of mixing for the system benzene-methanol determined experimentally and those calculated from equation 1. The percentage deviation of the experimental and calculated values for ΔH_X^M is also listed.

Table I

HEATS OF MIXING BENZENE (1) AND METHANOL (2) AT 25°C.

x_2 (Mole fraction)	ΔH_X^M (Experimental)	ΔH_X^M (Equation 1)	Percentage deviation
0.1276	152.8 cal/mole	152.3 cal/mole	+0.3%
.1531	159.4	161.6	-1.4
.2118	169.5	171.8	-1.3
.2356	172.4	173.5	-0.6
.2361	172.6	173.4	-0.5
.2388	171.7	173.6	-1.1
.2734	175.2	174.3	+0.5
.3429	175.4	172.9	+1.4
.3470	173.3	172.8	+0.3
.4022	170.5	169.5	+0.6
.5030	155.8	157.1	-0.8
.5199	152.9	153.2	-0.2
.5770	138.4	139.3	-0.6
.5978	130.7	132.6	-1.4
.6499	116.2	116.3	-0.1
.6755	107.3	107.4	-0.1
.7068	96.5	96.2	+0.3
.7453	84.3	82.6	+2.0
.7706	75.3	73.9	+1.8
.8078	63.3	62.0	+2.0
.8862	39.1	40.0	-2.3
.9025	32.1	35.7	-11.2
.9245	24.9	29.6	-18.9

Table II lists the experimental and calculated values for ΔH_X^M for the system benzene-ethanol along with the percentage deviation between the two values.

Table II

HEATS OF MIXING OF BENZENE (1) AND ETHANOL (2) AT 25°C

x_2 (Mole fraction)	ΔH_X^M (Experimental)	ΔH_X^M (Equation 2)	Percentage deviation
0.0983	165.6 cal/mole	154.4 cal/mole	+6.8%
.1723	204.0	200.8	+1.6
.2089	210.7	211.7	-0.5
.2572	213.9	217.6	-1.7
.3397	215.8	216.5	-0.3
.3618	215.1	214.2	+0.4
.4207	207.5	205.2	+1.1
.4677	196.4	195.3	+0.6
.5580	170.6	170.1	+0.3
.5668	165.6	167.2	-1.0
.5797	161.8	163.0	-0.7
.6515	136.4	137.0	-0.4
.6693	130.8	130.2	+0.4
.7227	107.6	109.1	-1.4
.7542	97.1	96.7	+0.4
.8751	50.3	50.6	-0.6
.9069	37.7	38.9	-3.2
.9687	11.4	14.6	-28.1

Table III gives the values for ΔH_x^M for the system cyclohexane-ethanol as determined both experimentally and by calculation. The percentage deviation between these two values is also listed.

Table III

HEATS OF MIXING OF CYCLOHEXANE (1) AND ETHANOL (2) AT 25°C.

x_2 (Mole fraction)	ΔH_x^M (Experimental)	ΔH_x^M (Equation 3)	Percentage deviation
0.0870	100.6 cal/mole	98.7 cal/mole	+1.9
.1056	109.3	110.2	-0.8
.1756	136.5	136.8	-0.2
.2536	149.3	149.3	0.0
.3061	152.2	153.4	-0.8
.3122	153.6	153.7	-0.1
.3758	156.5	156.2	+0.2
.4551	155.9	155.9	0.0
.5611	146.4	148.1	-1.2
.6812	129.8	128.1	+1.3
.7506	112.2	112.1	+0.1
.8029	99.5	98.3	+1.2
.8891	69.1	69.4	-0.4
.8916	64.9	68.3	-5.2
.9431	36.8	42.8	-16.3

The ΔH_x^M values for each of the three systems studied were plotted (Figures 3, 4, and 5). Asymmetric curves in the shape of distorted parabolas were obtained. The values obtained for the heats of mixing were relatively high as compared to the more ideal solutions. The data were fit mathematically by the use of a power series equation. Several forms of power series equations with both 4 and 5 constants were obtained by the use of an IBM computer. An analytical expression with four constants was sufficient for the $C_6H_6-CH_3OH$ system. Five constants were necessary in order to obtain an equation for the experimental data that was comparable with the experimental accuracy for the $C_6H_6-C_2H_5OH$ and $C_6H_{12}-C_2H_5OH$ systems. The expressions given below were found to give the best fit to the experimental values within the desired accuracy.

The benzene-alcohol systems reduced to essentially the same curve when plotted to scales that brought them to the same size.

Benzene-Methanol System.--The equation:

$$\Delta H_x^M = x_1 x_2 [628.4 + 365.7(x_1 - x_2) + 521.9(x_1 - x_2)^3 + 819.8(x_1 - x_2)^4] \quad (1)$$

where x_1 and x_2 are the mole fractions of benzene and methanol, respectively, was found to be the closest mathematical fit to the experimental data for this system. The experiment data for this system were plotted in Figure 3. It was found that a peak of 175 cal/mole was reached at a mole fraction for methanol of 0.3.

Benzene-Ethanol System.--The equation:

$$\Delta H_x^M = x_1 x_2 [748.8 + 534.1(x_1 - x_2) + 265.7(x_1 - x_2)^2 + 408.7(x_1 - x_2)^3 + 434.1(x_1 - x_2)^4] \quad (2)$$

with x_1 and x_2 being the mole fractions of benzene and ethanol, respectively, was obtained as the best correlation between the experimental values and the mathematical power series. Figure 4 shows the plot of the experimental ΔH_x^M and was found to reach a maximum value of 216 cal/mole.

Heats of Mixing of Benzene-Methanol

Figure 3

Figure 4 Heats of Mixing of Benzene-Ethanol at 25°C

at 0.3 mole fraction ethanol.

Cyclohexane-Ethanol System.--The equation:

$$\Delta H_x^M = x_1 x_2 [615.0 + 132.4(x_1 - x_2) + 195.9(x_1 - x_2)^2 + 251.5(x_1 - x_2)^3 + 521.7(x_1 - x_2)^4] \quad (3)$$

where x_1 and x_2 are the mole fractions of cyclohexane and ethanol, respectively, was determined to give the best duplication between experimental values and calculated values. Figure 5 gives a plot of the ΔH_x^M values obtained experimentally. The curve reached a maximum of 157 cal/mole at $x_2=0.4$.

Figure 5 Heats of Mixing of Cyclohexane-Ethanol at 25°C

QUASI-LATTICE INTERPRETATION OF ALCOHOL-HYDROCARBON SYSTEMS

Several approaches have been proposed for the theoretical interpretation of the liquid state by the quasi-lattice approximation. The approach formulated by J. A. Barker¹ for the explanation of associated systems seemed to be a logical method of interpreting the systems under examination in this study.

Barker's approach was similar to that of regular solution theory and the theory of polymer solutions, with each molecule occupying a certain number of sites on a well-defined lattice. In this approach a differentiation was made between the various types of sites on the molecule. The Bethe quasi-chemical approximation was used for the mathematical treatment, in order to derive a grand partition function for the system, from which the thermodynamic properties can be derived.

In order to use the quasi-lattice model certain parameters were fixed. Their values were obtained from assumptions based on the geometry and the chemistry of the molecules involved. The parameters needed were: z , the coordination number; r_A , the number of sites in the lattice occupied by the alcohol; r_S , the number of sites in the lattice occupied by the solvent. Four types of sites were possible: Q_S , solvent sites (C_6H_6 and C_6H_{12}); Q_I , sites on the hydrocarbon surface of the alcohol molecule; Q_O , sites on the oxygen surface of the alcohol molecule; Q_H , sites on the hydroxyl hydrogen in the alcohol molecule.

Table IV lists the values of the parameters used for the systems under investigation in this study.

¹J. A. Barker, J. Chem. Phys., 20, 1526 (1952).

Table IV
PARAMETERS FOR QUASI-LATTICE THEORY

	z	r _A	r _S	Q _S	Q _I	Q _O	Q _H
CH ₃ OH-C ₆ H ₆	4	2	6	12	3	2	1
C ₂ H ₅ OH-C ₆ H ₆	4	3	6	12	5	2	1
C ₂ H ₅ OH-C ₆ H ₁₂	4	3	6	12	5	2	1

The interaction energies for all binary combinations possible between the different sites are: U_{S-S} , U_{O-O} , U_{H-H} , U_{I-I} , U_{I-H} , U_{I-S} , U_{I-O} , U_{O-H} , U_{S-H} , U_{S-O} , with the subscripts representing the types of sites interacting. The U_{S-S} , U_{O-O} , U_{H-H} and U_{I-I} interaction energies are all taken as zero by definition. For the systems considered the U_{I-H} and U_{I-O} energies would be expected to be near to zero. The U_{S-H} and U_{S-O} would be expected to be small in value but significant enough that it must be taken into consideration. The U_{O-H} represents hydrogen bonding and would be expected to have the largest value of all the interactions. The U_{I-S} would be expected to be of significance because of the large number of such contacts.

According to the theory set forth by Barker,² the heats of mixing can be calculated by the use of equation (4);

$$\Delta H_x^M = -2RT \left[\sum_{\mu} \left(x_{\mu}^A x_{\mu}^A - \frac{1}{x_A} \frac{A_{\mu} A_{\mu}}{x_{\mu}^A x_{\mu}^A} \right) n_{\mu}^{AA} \ln n_{\mu}^{AA} + \sum_{\mu} \sum_{\nu} \frac{A_{\mu}^B A_{\nu}^B}{x_{\mu}^B x_{\nu}^B} n_{\mu\nu}^{AB} \right] \quad (4)$$

where x_A is the mole fraction of component A. x_{μ}^A values are determined by solving the equations $x_{\mu}^A \sum_{\mu} n_{\mu}^{AB} x_{\mu}^B = (Q_{\mu}^A/2) x_A$. x_{μ}^{A1} is the value for x_{μ}^A for $x_A = 1$. The n_{ij}^{MN} term has been used for $\exp. (-U_{ij}^{MN}/RT)$ with $ij=O-H$, $I-H$, $I-O$, $S-O$, $S-H$.

This approach has been used in attempting to correlate the experimental data with theoretically determined values. The special cases of Equation 4 which were used in this study are given in Appendix I.

²Ibid., 1528

COMPARISON OF EXPERIMENTAL AND THEORETICAL HEATS OF MIXING

The parameters given in Table IV were used in determining theoretical heats of mixing for the respective solutions by the quasi-lattice approach. Values for the interaction energies that most nearly reproduced experimental heats of mixing values were determined. These "best" values for the interaction energies were obtained in the following manner.

Various values for the different interaction energies for the $C_2H_5OH-C_6H_{12}$ system were tried in the calculation. These were altered until those values which most nearly fit the experimental heats of mixing were found. The I-S and O-H interactions were assumed to be the most significant interactions for this system. Through the use of these two parameters a close fit to the experimental values was obtained. The value for the O-H interaction energy thus obtained was utilized in the other two systems, since this interaction would be essentially the same in all three systems. The I-S interaction would be expected to be different for the benzene systems because of their aromatic nature. In determining the heats of mixing for the benzene systems the O-H interaction energy determined before was used, but a higher value for the I-S type interaction was required. The values for the I-S interaction energy for these systems was determined from the difference in heights of the two heats of mixing curves. The S-H and S-O interactions were also considered to be significant for the benzene systems. Arbitrary values for S-H and S-O were used until those values which gave the best fit of the experimental data were determined. The I-H and I-O interactions were assumed to be insignificant for all three systems.

Table V lists the values for the interaction energies determined in obtaining the best fits for the three systems studied.

Table V
INTERACTION ENERGIES

	U_{O-H}	U_{I-S}	U_{I-H}	U_{S-H}	U_{I-O}	U_{S-O}
$C_2H_5OH-C_6H_{12}$	-3200 cal	49 cal	-	-	-	-
$CH_3OH-C_6H_6$	-3200	87	-	-410 cal	-	-210 cal
$C_2H_5OH-C_6H_6$	-3200	87	-	-545	-	-300

Table VI lists the values for experimental and theoretical heats of mixing for the $C_2H_5OH-C_6H_{12}$ system. Percentage deviation between the two values is also given.

Table VI
HEATS OF MIXING OF CYCLOHEXANE (1) AND ETHANOL (2) AT 25° C

x_2	ΔH_x^M (Experimental)	ΔH_x^M (Theoretical)	Percentage Deviation
0.0870	100.6	105.5	+4.9%
.1056	109.3	112.7	+3.1
.1756	136.5	132.7	-2.8
.2536	149.3	146.9	-1.6
.3061	152.2	153.0	+0.5
.3122	153.6	153.7	+0.1
.3758	156.5	157.1	+0.4
.4551	155.9	156.1	+0.1
.5611	146.4	148.0	+1.1
.6812	129.8	128.8	-0.8
.7506	112.2	111.8	-0.4
.8029	99.5	94.8	-4.7
.8891	69.1	61.5	-11.0
.8916	64.9	60.5	-6.8
.9431	36.8	34.6	-6.0

Figure 6 Theoretical Heats of Mixing of Cyclohexane and Ethanol

Figure 6 gives the plot of the experimental and theoretical heats of mixing. Experimental values are shown as circles and the theoretical curve is represented by the broken line.

Table VII gives the values obtained for the system $\text{CH}_3\text{OH}-\text{C}_6\text{H}_6$. Percentage deviation is also listed.

Table VII

HEATS OF MIXING OF BENZENE (1) AND METHANOL (2) AT 25°C.

x_2	ΔH_x^M (Experimental)	ΔH_x^M (Theoretical)	Percentage Deviation
0.1276	152.8	141.8	-7.2%
.1531	159.4	153.3	-3.8
.2118	169.5	168.1	-0.8
.2356	172.4	171.6	-0.5
.2361	172.6	171.9	-0.4
.2388	171.7	172.9	+0.7
.2734	175.2	175.4	+0.1
.3429	175.4	176.3	+0.5
.3470	173.3	176.2	+1.7
.4022	170.5	171.9	+0.8
.5030	155.8	154.8	-0.6
.5199	152.9	151.0	-1.2
.5770	138.4	136.5	-1.4
.5978	130.7	130.9	+0.2
.6499	116.2	115.5	-0.6
.6755	107.3	107.1	-0.2
.7068	96.5	96.6	+0.1
.7453	84.3	82.8	-1.8
.7706	75.3	72.3	-4.0
.8078	63.3	59.5	-6.0
.8862	39.1	30.2	-22.8
.9025	32.1	24.4	-24.0
.9245	24.9	17.4	-30.1

The experimental values and theoretical curve for the heats of mixing are plotted in Figure 7.

Figure 7 Theoretical Heats of Mixing of Benzene and Methanol

Table VIII lists the theoretically and experimentally determined heats of mixing for the $C_2H_5OH-C_6H_6$ system along with percentage deviation between the two values.

Table VIII

HEATS OF MIXING OF BENZENE (1) AND ETHANOL (2) AT 25° C.

x_2	ΔH_x^M (Experimental)	ΔH_x^M (Theoretical)	Percentage Deviation
0.0983	165.6	125.5	-4.2%
.1723	204.0	186.6	-8.5
.2089	210.7	199.2	-5.5
.2572	213.9	209.2	-2.2
.3397	215.8	214.4	-0.6
.3618	215.1	213.4	-0.8
.4207	207.5	200.1	+0.3
.4677	196.4	200.6	+2.1
.5580	170.6	176.4	+3.4
.5668	165.6	173.7	+4.9
.5797	161.8	169.8	+4.9
.6515	136.4	143.0	+4.8
.6693	130.8	134.7	+3.0
.7227	107.6	111.8	+3.9
.7542	97.1	97.4	+0.3
.8751	50.3	41.7	-17.1
.9069	37.7	27.8	-26.3
.9687	11.4	7.6	-33.3

Figure 8 contains experimental values and the theoretical curve for the heats of mixing of the $C_2H_5OH-C_6H_6$ system.

Through the above approach it was possible to make an evaluation of Barker's quasi-lattice theory.¹ The values for the

¹Ibid., 1526

Figure 8 Theoretical Heats of Mixing of Benzene and Ethanol

different interaction energies required in the theoretical calculation would be expected to fall within a certain known range. The values used in fitting the experimental heats of mixing were within this expected range. Theoretical heats of mixing were obtained which correlated quite closely with experimental values. The degree of agreement between them can be seen in figures 6, 7 and 8. As a test of the consistency of the energy parameters in the two benzene systems the interaction energies in the $C_6H_6-CH_3OH$ system were used to calculate the heats of mixing of the $C_6H_6-C_2H_5OH$ system. This allowed no arbitrary choices for the energy parameters and yet the agreement between theory and experiment was still fairly good. The maximum value was the same, and it occurred at the same composition. The fit along the sides of the curve was not quite as good as in figure 8. It would not be expected that exactly the same energy parameters would apply to both systems because of the slight difference in the inductive effect of the ethyl and methyl radicals. Everything considered, the theory appears to do quite well and indicates that the quasi-lattice theory can be applied to associated as well as simple systems.

Some of the limitations of the theory are: (1) inadequacy of the geometrical models which are used, (2) insufficient detail in the types of interaction considered, (3) inadequacy of the quasichemical approximation, (4) neglect of vibrational or free-volume contributions, (5) neglect of long-range interactions, and (6) the possibility that molecular interactions other than those that were used are present in the systems studied.²

²Barker, J. A., I. Brown, and F. Smith, "Thermodynamic Properties of Alcohol Solutions," Disc. Faraday Soc., 15, 142 (1953).

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APPENDIX I

Equations used in calculating theoretical heats of mixing through the quasi-lattice theory.

Cyclohexane System:

Heats of mixing were determined from the equation $\Delta H_x^M = -2RT[(x_O x_H - x_A x_O' x_H') n_{O-H} \ln n_{O-H} + x_I x_S n_{I-S} \ln n_{I-S}]$ (2)

with the X parameters obtained as solutions of the equations

$$x_H [x_H + x_I + x_O n_{O-H} + x_S] = x_A/2$$

$$x_I [x_H + x_I + x_O + x_S n_{I-S}] = 5x_A/2$$

$$x_O [x_H n_{O-H} + x_I + x_O + x_S] = x_A/2$$

$$x_S [x_H + x_I n_{I-S} + x_O + x_S] = 6x_S$$

Benzene Systems:

The heats of mixing equation was $\Delta H_x^M = -2RT[(x_O x_H - x_A x_O' x_H') n_{O-H} \ln n_{O-H} + x_I x_S n_{I-S} \ln n_{I-S} + x_H x_S n_{H-S} \ln n_{H-S} + x_O x_S n_{O-S} \ln n_{O-S}]$ (4)

and the equations for determining the X parameters were

$$x_H [x_H + x_I + x_O n_{O-H} + x_S n_{H-S}] = Q_H x_A/2$$

$$x_I [x_H + x_I + x_O + x_S n_{I-S}] = Q_I x_A/2$$

$$x_O [x_H n_{O-H} + x_I + x_O + x_S n_{O-S}] = Q_O x_A/2$$

$$x_S [x_H n_{H-S} + x_I n_{I-S} + x_O n_{O-S} + x_S] = Q_S x_S/2$$

APPLICATION OF THE QUASI-LATTICE THEORY TO THE
HEATS OF MIXING OF SOME ALCOHOL-HYDROCARBON SYSTEMS

An Abstract
of a Thesis submitted to
the Department of Chemistry
Brigham Young University

In Partial fulfillment
of the Requirements for the Degree of
Master of Science

by
Mar Lynn James
August, 1960

ABSTRACT

Values for the heats of mixing were obtained calorimetrically for the systems $\text{C}_2\text{H}_5\text{OH}-\text{C}_6\text{H}_{12}$, $\text{CH}_3\text{OH}-\text{C}_6\text{H}_6$ and $\text{C}_2\text{H}_5\text{OH}-\text{C}_6\text{H}_6$ at 25° over the complete range of composition. Analytical equations which summarize these values are:

Benzene (1) - Methanol (2) System

$$\Delta H_x^M = x_1 x_2 [628.4 + 365.7(x_1 - x_2) + 521.9(x_1 - x_2)^3 + 819.8(x_1 - x_2)^4]]$$

Benzene (1) - Ethanol (2) System

$$\Delta H_x^M = x_1 x_2 [748.8 + 534.1(x_1 - x_2) + 265.7(x_1 - x_2)^2 + 408.7(x_1 - x_2)^3 + 434.1(x_1 - x_2)^4]]$$

Cyclohexane (1) - Ethanol (2) System

$$\Delta H_x^M = x_1 x_2 [615.0 + 132.4(x_1 - x_2) + 195.9(x_1 - x_2)^2 + 251.5(x_1 - x_2)^3 + 521.7(x_1 - x_2)^4]]$$

where x_1 is the mole fraction of component 1.

The experimental data were satisfactorily interpreted by a generalized quasi-lattice theory in which each molecule was assigned a definite number of sites in the lattice and three different types of contact points were assigned to the alcohol molecules.

The theory predicted interaction energies that were reasonable and consistent for all three systems, indicating that the quasi-lattice theory can be applied to systems in which association of molecules occurs.

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