

# Thermodynamics of Solutions

## New Equipment for Measuring Heats of Solution Data for Five Systems

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THE THERMODYNAMIC properties of solutions, free energy, entropy, and enthalpy, can be calculated from vapor-liquid equilibrium measurements; however, in many instances, this procedure results in substantial uncertainties in the entropy and enthalpy functions. A combination of phase equilibrium and enthalpy of mixing measurements leads to greater confidence in over-all results. Development of equipment to measure enthalpies of solutions to supplement our work on vapor-liquid equilibria (5) was begun.

Calorimetric experiments involving solutions can be divided into two types, isothermal and adiabatic, depending on whether the bath temperature surrounding the calorimeter is held constant or follows the temperature inside the calorimeter. In the study of nonelectrolyte systems, where the temperature drops on mixing, the bath temperature can be held constant, and electrical energy added to the calorimeter to maintain the temperature constant as mixing occurs.

Gucker and Schminks (3) described the construction of an adiabatic calorimeter which utilized a differential thermopile of 24 thermocouples connected to a galvanometer circuit which actuated the adiabatic control heater. A reciprocating stirrer constructed of Formica (to reduce heat conduction) was used to agitate the solution. Daniels (2) used the same approach to control a weak electrolytic solution as the bath fluid. The energy input to the bath was accomplished by impressing a direct current voltage between two electrodes immersed in the bath fluid, the bath being constructed so that the inner wall would serve as one electrode and the convection shield (around the calorimeter) as the other electrode.

Tsao and Smith (9) described a calorimeter constructed from a modified Dewar flask. A Beckman thermometer was used to measure temperature; Manganin wire was used for

the electric heater; and the second fluid was added from an external buret. The usual voltage and current measurements were made, and the energy input by the electric heater was obtained. Elaborate precautions were taken to reduce heat transfer into the calorimeter. A manual stirrer provided a means for mixing the liquids.

An improved design to eliminate the vapor space was proposed by Scatchard and Ticknor (6). The calorimeter was constructed from a glass tube bent into a crescent with the two ends open to permit filling. A volume of mercury at the bottom of the crescent separated the fluids. The calorimeter was mounted on an apparatus which rotated the tube alternately in opposite directions through about 270° at a constant rate causing the two fluids to mix. Two wells were provided, one for the heater and one for the thermocouple.

Adcock and McGlashan (1) also describe a calorimeter designed to eliminate the vapor space completely; 1 to 2 ml. of each component are confined in separate parts of the calorimeter and mixed by puncturing a glass membrane. A similar design has been used recently by Williamson and Scott (11).

The calorimeter described herein combines the ideas of numerous investigators, and in many respects is similar to that of Tsao and Smith (9)

### EXPERIMENTAL APPARATUS

**Calorimeter.** The vessel was a Dewar type container with a capacity of 230 ml. The leads for two thermistors, a heater, a stirrer, and the inlet for the fluid to be added during the mixing process were contained in a silvered evacuated stopper. The propeller type stirrer was driven by a synchronous electric motor.

The fluid to be added to the calorimeter was placed in a 100 ml. water-jacketed buret. A water bath was used to maintain the surroundings of the calorimeter and buret at a desired temperature level. The water completely covered the calorimeter vessel. A Bronwill circulator, consisting of a pump and heating unit, a temperature sensing device (mercury expansion type), and an electronic controller, was used to circulate and control the temperature of the water at a desired level ( $\pm 0.01^\circ$  to  $0.05^\circ$  C.). A cooling coil was submerged in the water bath to remove energy at temperatures below  $35^\circ$  C.

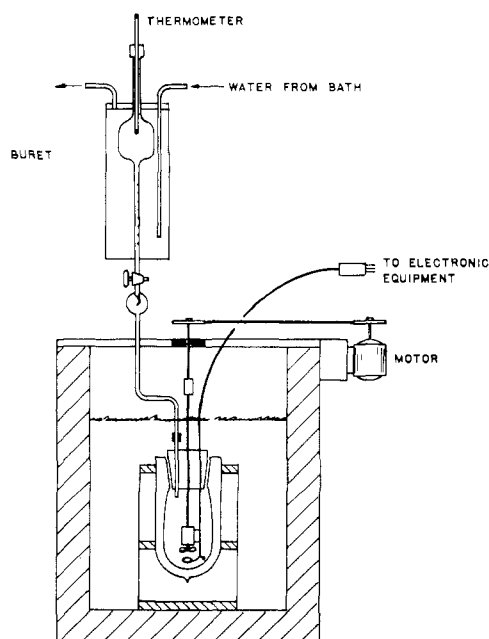


Figure 1. Calorimeter and auxiliaries

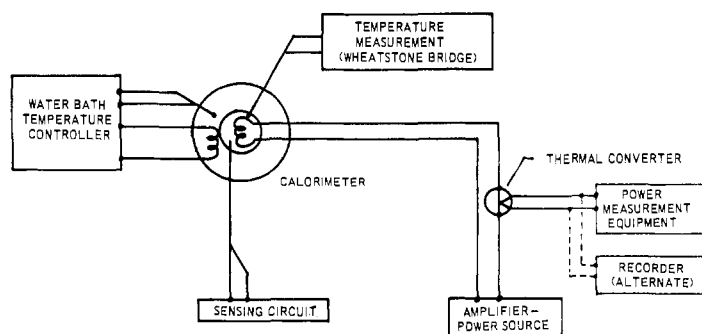


Figure 2. Control and measurement equipment

Figure 1 shows the arrangement of the calorimeter and auxiliaries.

**Control and Measurement.** The circuitry was designed to sense the temperature drop due to solution effect, add electrical energy to restore the temperature, and measure the amount of the energy input simultaneously. Three principle components of equipment were required; a sensing element and circuit, a power source, and a power measuring circuit. The first two did not present any difficulty, but a power measuring device which would follow the power input was not immediately apparent.

Initially, a thyatron relaxation oscillator, using the voltage drop across the calorimeter heater, was used, but subsequent experiments indicated instability and lack of reproducibility, so it was abandoned. The final circuit evolved uses a thermal converter, which generates a stable direct current voltage proportional to the current squared, direct current amplifier, a transistor oscillator, and a digital counting device.

Figure 2 is a block diagram of the control and measurement equipment showing the various components. Details of the circuits follow.

Two thermistors are used to sense the temperature of the solution: one as a resistance thermometer (1694 ohms at 28° C. with a coefficient of -67 ohms per ° C.) calibrated against a certified platinum resistance thermometer, and a second (1200 ohms, coefficient -65 ohms per ° C.) to detect the temperature change of the solution.

**Sensing.** This circuit (Figure 3) responds to a decrease in temperature due to solution effect causing an unbalance

in the Wheatstone bridge. The magnitude of the unbalance is directly proportional to the temperature change and approximately equal to 35 millivolts per ° C., (3.0 volts across the bridge). The direct current signal passes into the filter (the diode serves as a safety device to prevent complete runaway due to the negative coefficient of the thermistor), the purpose of which is to filter out any alternating current that might be picked up by the leads. The filtered signal passes into the direct current-alternating current converter (Leeds and Northrup Part No. 354156) where it is converted into a 60-cycle square wave, and then stepped up  $\frac{1}{10}$  by the transformer for feed into the power amplifier.

**Amplifier.** The power source (Figure 4) consists of an amplification stage, a phase inversion stage, and a 25-watt push-pull power amplifier. A variable cathode resistor in the push-pull section permits variation of the amplification level. A signal from the sensing circuit, proportional to a temperature decrease in the calorimeter, is amplified and produces output power for feed back to the calorimeter heater. Typically a 30-ohm resistance change in the calorimeter thermistor (equivalent to approximately 0.5° C.) will produce a 10-watt power output from the amplifier. The load circuit (secondary of the output transformer) of the amplifier contains the calorimeter heater (No. 36 gage, Karma wire, total resistance  $241.25 \pm 0.05$  ohms) and a thermal converter (Model T, Sensitive Research Corp.) in series. The thermal converter has a millivolt output (approximately 0 to 12 mv.) which is directly proportional to the square of the current flowing, and consequently to the power dissipated by the heater.

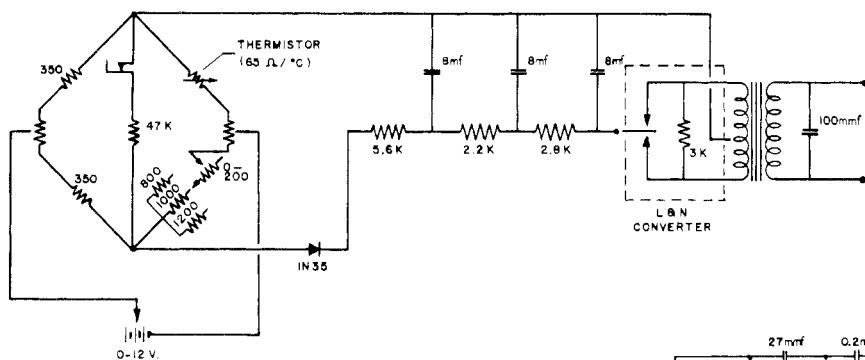


Figure 3. Sensing circuit

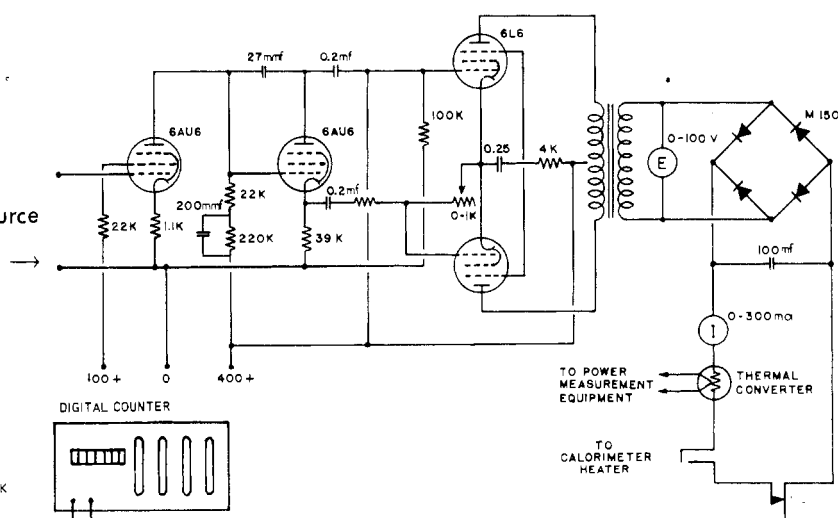


Figure 4. Amplifier, power source

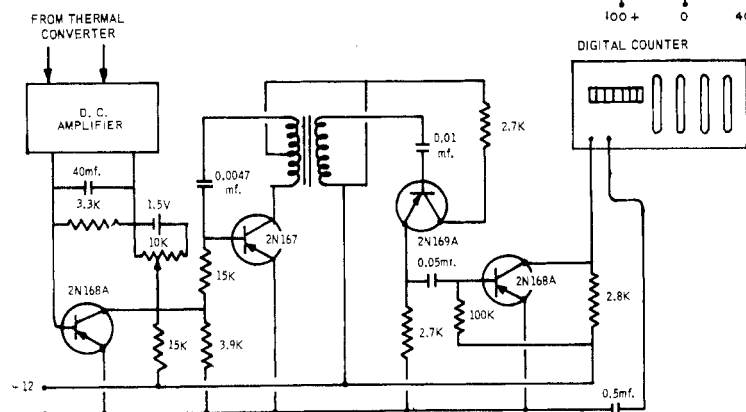


Figure 5. Power measurement equipment

**Power Measurement.** This section consists of three parts: a direct current amplifier, a pulse generator, and a digital counter; (see Figure 5). The direct current amplifier which converts low level direct current (0–12 mv.) to high level (0 to 5 volts), is a Weston Inductronic Amplifier (Model 1411), and was chosen because it exhibits infinite impedance to the thermal converter, has an excellent output ratio, and is linear ( $\pm 0.10\%$ ). The amplifier is coupled to the pulse generator by a transistor (2N168A) cathode follower circuit.

The signal is fed to the transistor oscillator and produces a positive going square wave output of frequency range 4000 to 9000 cycles per second; after amplification, the alternating current wave drives a digital counter.

The counter is of conventional design and utilizes an amplitude discriminator, four Berkley decimal counting units (No. DCU 705A), and a mechanical register (Veeder Root, No. 1205); maximum count rate is  $5 \times 10^5$  per second, total count of  $10^9$ , and a resolution of one pulse. The total integral of the current squared-time function can be calculated from the total pulses and the length of the experiment.

An alternate method used for determining the power dissipated is to record the thermal converter output as a function of time with a millivolt recorder—e.g. (Sargeant Model No. S 72150) and integrate graphically.

Direct current voltages for the various electronic circuits are supplied from conventional selenium rectifier, filtered, and regulated power supplies.

#### CALIBRATION OF APPARATUS

The basic equation for enthalpy of mixing when components are mixed at constant pressure and temperature is

$$\Delta H^M = \frac{Q_h}{m} + \frac{\theta}{m} (q_s + q_a + q_t) \quad (1)$$

The individual heat effects, on the right hand side of the equation, are as follows.

Heat dissipated by the heater,  $Q_h$ , is of the form

$$Q_h = \int_0^{\theta} \frac{i^2 R}{j} d\theta \quad (2)$$

As previously discussed, the measurement circuitry is such that the current squared is a linear function of the counting frequency; actually, linearity is relative, and for several thermal converter elements used the deviation from linearity was approximately 1–2%. Consequently, the best procedure was to write

$$i^2 = a_0(\nu - \nu_0) + a_1(\nu - \nu_0)^2 \quad (3)$$

and

$$Q_h = \frac{R}{j} \int_0^{\theta} [a_0(\nu - \nu_0) + a_1(\nu - \nu_0)^2] d\theta \quad (4)$$

Now  $\nu_0\theta = C_0$ , the number of counts at the base frequency when  $i = 0$  and  $\int_0^{\theta} \nu d\theta$  is the total counts at the end of the experiment; then

$$Q_h = \frac{R}{j} [a_0(C - C_0) + a_1(\overline{\nu - \nu_0})^2\theta] \quad (5)$$

Since the second term on the right is small compared to the first, the average of the frequency difference squared is approximated by

$$\overline{(\nu - \nu_0)^2} = \left(\frac{C - C_0}{\theta}\right)^2 \quad (6)$$

and finally

$$Q_h = \frac{R}{j} \left[ a_0(C - C_0) + \frac{a_1(C - C_0)^2}{\theta} \right] \quad (7)$$

Heat transferred from the surroundings,  $q_s$ , follows the Fourier equation,

$$\frac{dq_s}{d\theta} = q_s = -k\Delta T \quad (8)$$

where,  $k$ , was determined by actual experiment to be  $4.9 \times 10^{-3}$  cal. per degree per second for our calorimeter.

Heat added by stirring,  $q_a$ , was determined by experiment to be  $1.44 \times 10^{-3}$  cal. per second at a stirring rate of 336 r.p.m.

Heat dissipated by the thermistor,  $q_t$  is of the same form as Equation 2, but since the total effect is small, an average rate was determined to be approximately  $0.80 \times 10^{-3}$  cal. per second. Uncertainties in the determination of  $\Delta H^M$  and the composition have been assessed and minimized insofar as possible by design and proper operation of the equipment. Temperature mismatch at the beginning and end of the experiment, calibration of the power measuring device, and heat transfer from the surroundings are contributing errors. The sum of all errors in  $\Delta H^M$  is estimated to be 1.5 to 2.5% maximum for 400 cal. per mole systems and 2 to 3.5% for 200 cal. per mole systems. The maximum error in composition at half mole fraction is estimated to be 0.3%.

A typical run involving recent measurements proceeded as follows: 120 ml. of benzene was placed in the calorimeter, 100 ml. of iso-octane in the buret, and the temperature of each adjusted to 28° C. The counter and timer were started at zero, and iso-octane was allowed to flow into the calorimeter at about 0.5 ml. per sec. After about 220 seconds, the automatic feed back of energy from the amplifier to the calorimeter heater reached a peak of 168 milliamperes. The current began to fall at 0.38 to 0.41 milliamperes per second to a final level of about 85 milliamperes as the initial temperature was again approached.

After an elapsed time of 465.6 seconds the solution reached 28° C. Registered counts totaled 2,977,433 which corresponded to 415.8 calories. Since the temperature in the calorimeter had dropped as much as 1.7° C. below the water bath during the run, and energy had also been added by stirring,  $q_s$  and  $q_a$  corrections were made. A total correction of 2.7 calories was added, giving a final value for  $\Delta H^M$  of 213.5 cal. per mole of solution.

Heat capacity measurements also can be made with the equipment by adding a known amount of energy and observing the temperature rise.

In the case where the heat of solution leads to a temperature rise, the heat effect can be determined by adding and measuring sufficient energy to give the same temperature rise of the mixed components.

#### EXPERIMENTAL RESULTS

Methanol-benzene heat of solution effects have been measured by numerous investigators (4, 7, 8, 9, 11) from 20° to 45° C. Data of this kind, at constant temperature, can be represented by the empirical series,

$$\Delta H^M = X_1 X_2 \sum_i b_i (X_1 - X_2)^i \quad (9)$$

Scatchard and others (7) determined the constants in the polynomial at 20° C. and Williamson and Scott (11) determined the constants at 25° C. and 45° C.

	$b_0$	$b_1$	$b_2$	$b_3$	$b_4$
20° C.	600	-250	0	-550	800
25° C.	580	-407	351	-247	0
45° C.	799	-448	466	-434	0

Table I. Heat of Solution Values

Mole Fraction, First Component	$\Delta H^M$ , (Cal./Mole)	Mole Fraction, First Component	$\Delta H^M$ , (Cal./Mole)
Methanol-Benzene, 25° C.			
0.0986	140.0		
0.3280	171.6		
0.3920	162.3		
0.6370	129.1		
2,4-Dimethylpentane-Cyclohexane, 28° C.			
0.1758	25.9		
0.3767	38.0		
0.4653	41.1		
0.6130	31.0		
0.7115	24.4		
Benzene-2,2,4-Trimethylpentane, 28° C.			
0.1566	102.0		
0.2922	164.2		
0.4644	220.7		
0.6076	243.2		
0.6903	213.5		
0.8631	139.5		
2,2,4-Trimethylpentane-Toluene, 28° C.			
0.1465	96.4		
0.2311	115.0		
0.3491	137.3		
0.4426	153.5		
0.5800	148.1		
0.6864	115.2		
0.8652	54.6		
Cyclohexane-1,4-Dioxane, 28° C.			
0.1999	218.5		
0.3698	322.1		
0.4862	369.7		
0.6280	345.5		
0.7428	282.7		
0.8948	153.6		

To check the equipment, measurements were made at 25° C. and are given in Table I and plotted in Figure 6. The curve in Figure 6 for 45° C. was calculated using the Williamson and Scott constants, and the one at 20° C. using the Scatchard constants. The curve at 25° C. represents the average of all data by investigators previously listed.

Benzene-2,2,4-trimethylpentane, 2,2,4-trimethylpentane-cyclohexane, and cyclohexane-1,4-dioxane measurements determined at 28° C. are presented in Table I and Figure 7.

A least squares fit of the benzene-2,2,4-trimethylpentane data gave

$$\Delta H^M = X_1 X_2 [909.7 + 287.1 (X_1 - X_2) + 120 (X_1 - X_2)^2] \quad (10)$$

The average deviation at the points from the curve is 3.8 cal.

Recently, Weissman and Wood (10) reported  $\Delta H^M$  values calculated from *V-L* equilibrium measurements; at half mole fraction, 265 and 196 cal. per mole at 40° and 70° C. respectively. The difference between their value and ours is not readily apparent.

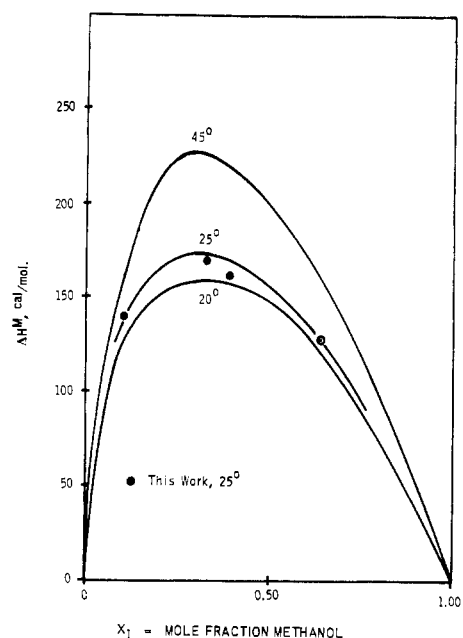


Figure 6. Methanol-benzene,  $\Delta H^M$

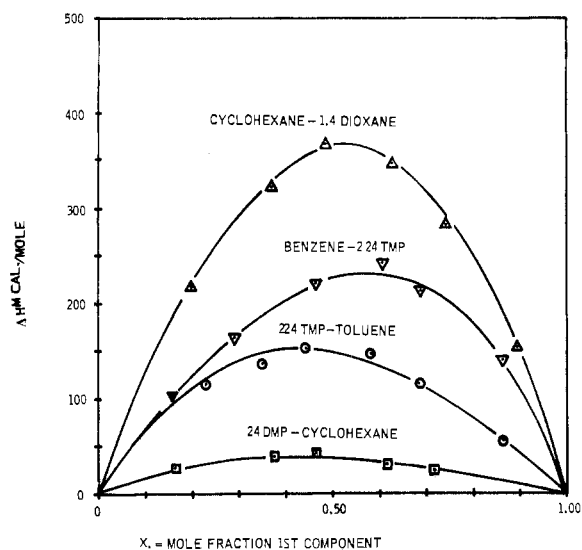


Figure 7.  $\Delta H^M$  at 20° C.

Table II. Energy Change on Mixing at 25° C.

	Benzene	$X_1 = X_2 = 0.5$	2,2,4-TMP	$X_1 = X_2 = 0.5$	Toluene	2,4-DMP	$X_1 = X_2 = 0.5$	Cyclohexane
$\Delta H^V$ , cal./mole	8102		8402		9083	7872		7908
$\Delta(PV)$	590.3		589.4		591.1	587.5		588.6
$\Delta E^V$	7512		7813		8492	7285		7319
$\rho$ , g./ml.	0.87370		0.68777		0.86230	0.66832		0.77389
$M$	78.108	96.166	114.224	103.179	92.134	100.198	92.177	84.156
$V$ , ml./mole	89.399		166.07		106.85	149.92		108.74
$V_1/V_2$		0.5383		1.554			1.379	
$(\Delta E^V/V)^{1/2}$	9.1670		6.8590		8.9065	6.9709		8.2041
$\alpha \times 10^3$ , deg. <sup>-1</sup>	1.197		1.204		1.021	...	...	...
$\beta \times 10^{-4}$ , atm. <sup>-1</sup>	0.98		1.15		0.95	...	...	...
$\Delta V^M$ , ml./mole		0.52		0.09			$\cong 0$	
$\Delta H^M$ , cal./mole		235		160			40	
$\Delta E^M$ (calcd.)		155		136			48	
$\Delta E^M$ (exptl.)		192		153			40	

<sup>a</sup> Not required for calculation, since  $\Delta V^M \cong 0$ .

A least squares fit for 2,2,4-trimethylpentane-toluene gave

$$\Delta H^M = X_1 X_2 [597.1 - 171.8 (X_1 - X_2)] \quad (11)$$

The average deviation is 5.1 cal.

A least squares fit for 2,4-dimethylpentane-cyclohexane gave

$$\Delta H^M = X_1 X_2 [147 - 58 (X_1 - X_2)] \quad (12)$$

Average deviation is 1.2 cal.

A least squares fit for cyclohexane-1,4 dioxane gave

$$\Delta H^M = X_1 X_2 [1462 + 172 (X_1 - X_2)] \quad (13)$$

Average deviation is 6.2 cal.

The methanol (Bakers reagent grade) was refluxed in a Soxhlet extractor over CaO. The benzene and toluene were Mallinckrodt reagent grade and dried over P<sub>2</sub>O<sub>5</sub>. The 2,4-dimethylpentane (Phillips pure grade) and the isooctane and cyclohexane (Eastman spectrograde) all were dried over P<sub>2</sub>O<sub>5</sub>. The dioxane (Eastman histological grade) was distilled from metallic sodium.

## DISCUSSION

The theoretical aspects of the thermodynamic mixing properties are being investigated in this laboratory, and although that is not the purpose of this particular article, certain interesting comparisons are possible for the three hydrocarbon systems.

Values for  $\Delta E^M$  were calculated by the Scatchard-Hildebrand equation,

$$\Delta E^M = \left( \frac{X_1 X_2 V_1 V_2}{X_1 V_1 + X_2 V_2} \right) \left[ \left( \frac{\Delta E_1^V}{V_1} \right)^{1/2} - \left( \frac{\Delta E_2^V}{V_2} \right)^{1/2} \right]^2 \quad (14)$$

and compared to the values derived from the experimental heat of mixing results by

$$\Delta E^M = \Delta H^M - T(\alpha/\beta) \Delta V^M - \dots \quad (15)$$

The values at 25° C. along with other pertinent quantities are presented in Table VI, and indicate only fair agreement.

For the 2,4-dimethylpentane-cyclohexane system, where the molecules do not deviate substantially from spherical symmetry and  $\Delta V^M$  is essentially zero, the comparison is satisfactory.

The greatest difference is for the benzene-2,2,4-trimethylpentane system where the molecules are approximately prolate and oblate ellipsoids respectively, and  $\Delta V^M$  is substantial.

## NOMENCLATURE

$a_0, a_1$  = constants, Equation 3.  
 $b_0, b_1$  = constants, Equation 9.  
 $C$  = total counts

$C_0$  = base frequency, counts  
 $\Delta E^M$  = energy change on mixing at constant volume  
 $\Delta E^V$  = energy of vaporization  
 $\Delta H^M$  = enthalpy change on mixing  
 $i$  = current  
 $k$  = constant in Equation 8  
 $M$  = molecular weight  
 $m$  = mass of solution  
 $P$  = pressure  
 $Q_h$  = heat dissipated by calorimeter heater  
 $q_s$  = heat transferred from surroundings  
 $q_{st}$  = heat added by stirring  
 $q_t$  = heat dissipated by the thermistor  
 $R$  = resistance of calorimeter heater  
 $\Delta T$  = temperature difference  
 $V$  = volume  
 $\Delta V^M$  = volume change on mixing  
 $X$  = mole fraction  
 $\alpha$  = coefficient of thermal expansion  
 $\beta$  = isothermal coefficient of compressibility  
 $\theta$  = time  
 $\nu$  = frequency, counts/sec.  
 $\nu_0$  = base frequency  
 $\rho$  = density

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