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Calorimetric heats of mixing of some nonelectrolytic binary and ternary solutions

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CALORIMETRIC HEATS OF MIXING
OF SOME NONELECTROLYTIC BINARY AND
TERNARY SOLUTIONS

Graduate School
copy

A THESIS
SUBMITTED TO THE
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In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
James Bevan Ott
May, 1956

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

May 16, 1956

Date

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TABLE OF CONTENTS

I: LIST OF TABLES

II: LIST OF ILLUSTRATIONS

III: INTRODUCTION

The heat of mixing of two nonelectrolytic liquids is a direct measure of the molecular interraction between the liquids. The experimental determination of this heat change therefore provides a good method for testing any theories concerned with the mixing of liquids. However, a lot of data needs to be obtained before any significant correlation can be made from theoretical considerations. In view of this, it is surprising to find that very few data seem to be available in the literature and it is evident that few measurements have been made.

The lack of data available is probably due to the difficulty encountered in measuring these heat changes with any accuracy. The heat changes are usually positive and very small, being of the order of 25-50 calories per mole. Furthermore, the liquids which are mixed are usually quite volatile. Consequently, a vapor phase is present above the liquids and a correction should be made to the results in order to eliminate thermal effects due to the change in the composition of this phase on mixing. In the work done by previous workers, notably Hirobe[1] in 1925, Carroll and Mathews[2] in 1934, Vold[3] in 1937, Boissonnas and Cruchard[4] in

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[1] H. Hirobe, *J. Faculty Sci. Imp. Univ. Tokyo*, *1*, 155 (1925). [*C.A.*, 20, 3122 (1926).]

[2] B. H. Carroll and J. H. Mathews, *J. Am. Chem. Soc.*, *46*. 30 (1934).

[3] R. D. Vold, *J. Am. Chem. Soc.*, *59*. 1515 (1937).

[4] C. G. Boissonnas and M. Cruchard, *Helv. Chim. Acta*, *27*. 994 (1944).

1944, and van der Waals and Hermans[5] in 1950, the vapor phase was present. Most of these workers ignored this vapor phase correction. Vold[3] states, however, that calculations have shown it to be negligible in his work due to the small volume of the vapor phase. Van der Waals,[5] on the other hand, found while working with mixtures of hexane and hexadecane that the correction which had to be made due to this vapor phase change was sometimes as much as one third of the total heat change. Since there is considerable inaccuracy in determining this correction, probably at least 10%, the accuracy of the measurements is seriously limited. A calorimeter was designed by Scatchard, *et. al.*[6] in 1950 which eliminated the vapor phase. The serious drawback with their calorimeter was that the mixing vessel was made of glass. This posed serious problems as to heat conduction and introduced errors in their measurements. Another calorimeter in which the vapor phase was eliminated was designed by Cheesman and Whitaker[7] in 1950. Their calorimeter consists essentially of a metal mixing vessel with two compartments separated by a tin foil diaphragm. The two compartments are filled with two different liquids. When these liquids are to be mixed, a sharp pointed metal weight is drawn with a magnet through the tin foil diaphragm. The design of the calorimeter also includes a thermocouple for measuring the heat change and a heating coil for calibrating the apparatus. This appears to be the best type of calorimeter to be found in the literature. It is upon this basic

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

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

[7] G. H. Cheesman and A. M. Beryl Whitaker, *Proc. Roy. Soc. (London) A 212*, 406-25 (1952).

design with considerable modifications that Dr. J. Rex Goates and I made our calorimeter.

The mixing vessels which have been used by various workers usually have been surrounded by an insulating jacket such as a dewar flask. We have found that suspending the mixing vessel directly into an evacuated tube gives good insulation. Electrical heating has usually been used to calibrate the apparatus. We have found that this is probably the best method of calibration.

In most of the methods previously used, mixing was carried out by either breaking a glass bulb (which contained one of the components) into the other component, or else by inverting a small closed vessel in which the liquids were originally in separate compartments. It is the latter procedure that we liked the best and used in our measurements.

Considerable work has been done by Scatchard _et. al._[8,8,9,10] on indirect measurements of the heats of mixing. From vapor-liquid equilibria at various temperatures, he measured the free energies of mixing and expressed them as a function of temperature. From these, he calculated the entropies and heats of mixing. There seems to have been quite a bit of inaccuracy in his method, however, since the results of recent calorimetric measurements differ widely from his values.

In summary the experience of previous workers have led us to formulate the following desirable characteristics for our calorimeter:

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[8] G. Scatchard, S. E. Wood, and J. M. Mochel, _J. Phys. Chem._, _43_, 119 (1939).

[9] G. Scatchard, S. E. Wood, and J. M. Mochel, _J. Am. Chem. Soc._, _61_, 3206 (1939).

[10] G. Scatchard, S. E. Wood, and J. M. Mochel, _J. Am. Chem. Soc._, _62_, 712 (1940).

(1) The over-all error in the measurements shall not exceed 1%.

(2) The quantity of each component shall be kept small (of the order of a few milliliters) to eliminate temperature gradients which might arise in the liquids due to poor thermal conductivity.

(3) The calorimeter shall be constructed so that the heat changes in it can be extrapolated to zero time.

(4) Changes in the vapor phase shall be eliminated.

It is felt that all of these requirements have been met, and that the data obtained are quite reliable.

IV: DISCRIPTION OF THE APPARATUS

The Mixing Vessel

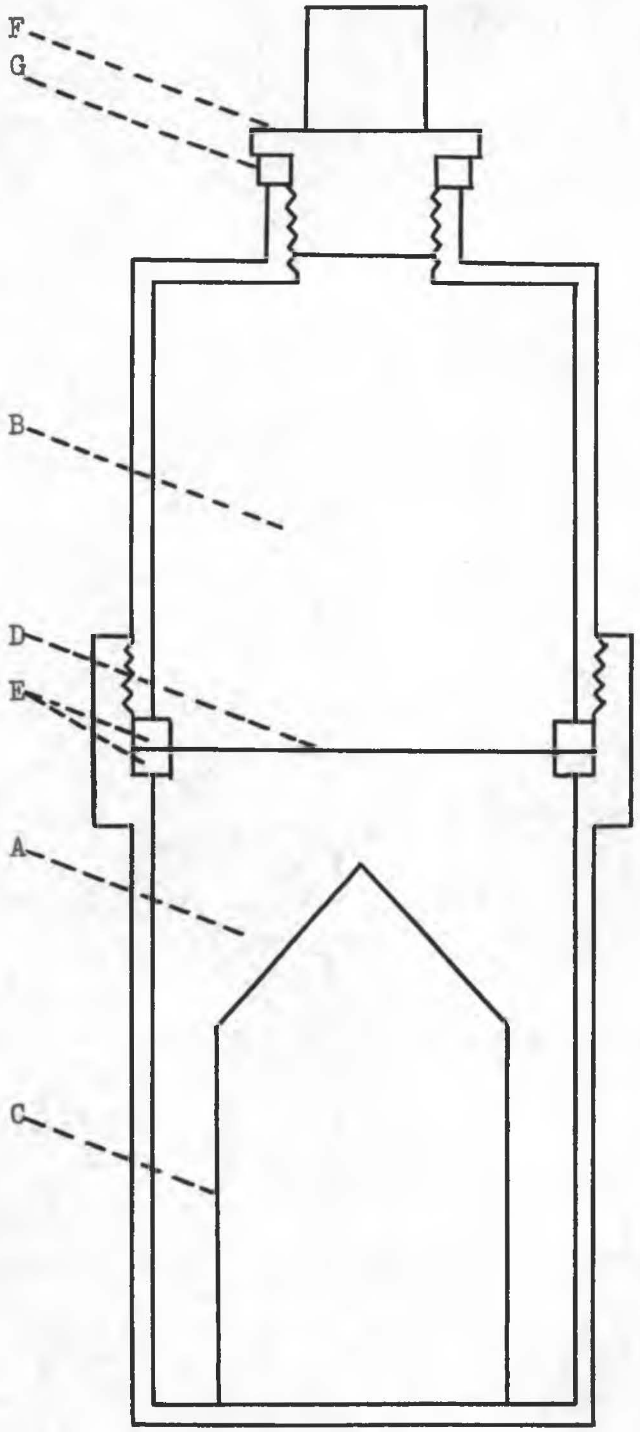
Figure 1 is a diagram of the mixing vessel. The lower section (A) is made of stainless steel and is internally threaded so that the top compartment (B), also made of stainless steel, can be screwed into it. Four different sizes of stainless steel weights (C) are put in the bottom compartment to vary its volume and to stir the liquids. The volume of the top compartment is 12.3 ml, and the volume of the bottom compartment is 13.2, 14.9, 16.0, 19.1, and 19.9 ml. depending upon the weight used.

Separating the two compartments is an aluminum foil diaphragm (D). This diaphragm is placed between two polyethylene gaskets (E) to seal the compartments from each other and also to make the joint vacuum tight. The top of B is open in order that the compartment can be filled with liquid. This hole is sealed by screwing a small brass plug (F) into it. Again a thin polyethylene gasket (G) is placed between the plug and the compartment to insure a vacuum seal. Care is used in filling the top compartment to eliminate any air that may be left under the brass plug. By this arrangement, the vapor phase is virtually eliminated.

Mixing and Stirring

The mixing of the two liquids is accomplished by tipping the calorimeter upside down. This causes the sharp pointed weight in the bottom compartment to fall, piercing the aluminum foil diaphragm and

Figure 1



Key

A - Lower Compartment
B - Upper Compartment
C - Weight
D - Aluminum Foil Diaphram
E - Polyethylene Gaskets
F - Brass Plug
G - Polyethylene Gasket

Diagram of the Mixing Vessel
(Scale 2:1)

mixing the liquids. Continuous stirring is accomplished by tipping the calorimeter over causing the weight to again fall and further mix the liquids.

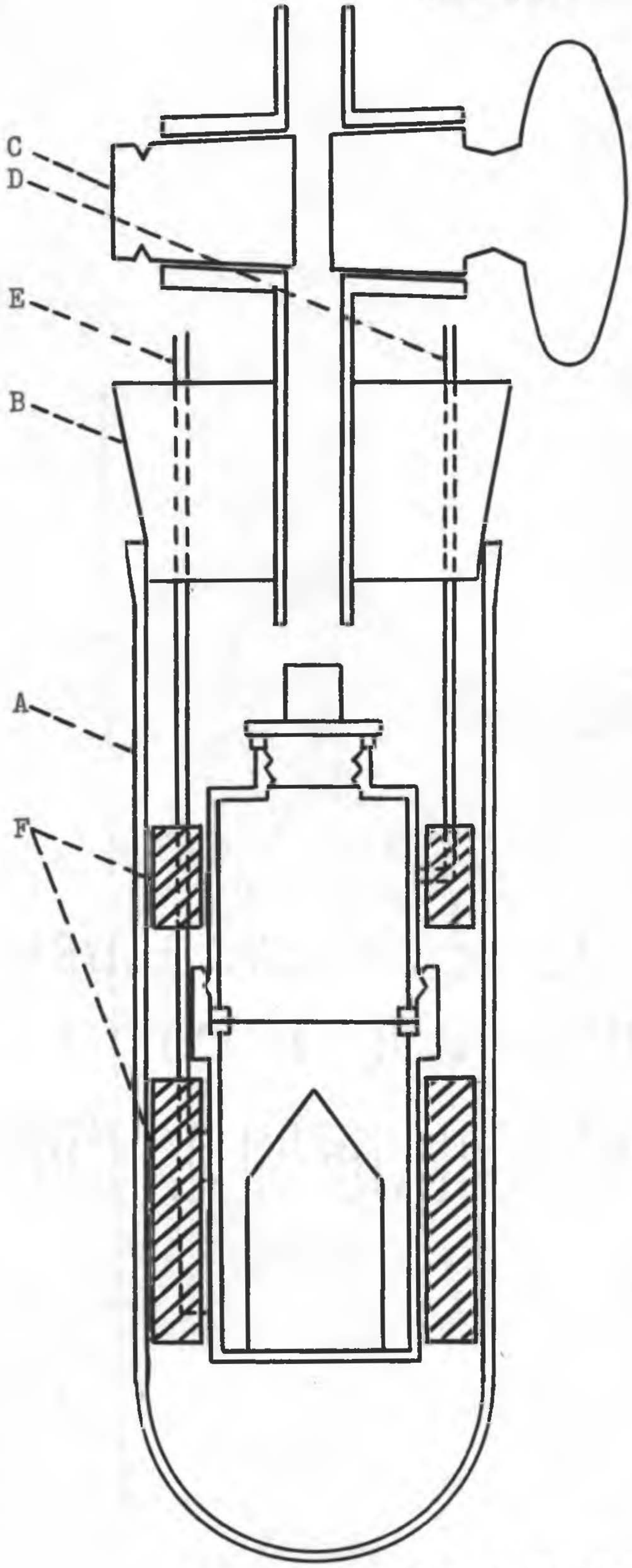
Insulation

Since the heat changes which are to be measured are very small, an essential requirement for accurate measurements is that the heat exchange between the mixing vessel and its surroundings should be as slow as possible and that it should proceed at a uniform rate. This is necessary in order that any graph of change of temperature with time can be accurately extrapolated to the time at which the change began.

The insulation is accomplished by putting the mixing vessel inside an adiabatic jacket, the design of which is shown in figure 2. The tube (A) has a diameter of 4.5 cm and a length of approximately 15 cm. One end of the tube is sealed to form a round bottom. The other end is sealed with a large neoprene rubber stopper (B). There are three holes in the stopper. A vacuum stopcock assembly (C) is put in one of the holes and the leads from the thermocouple (D) and the heating coil (E) are drawn from the other two holes. When a run is to be made the joints are sealed with paraffin wax and the system is evacuated using an oil diffusion pump backed by a Cenco-Pressovac vacuum pump. Finally, the entire tube is wrapped in aluminum foil to cut down on radiation losses and gains.

It was necessary to support the calorimeter inside the tube in some way. Furthermore, the thermal conductivity of the material used for support had to be very low since this material would provide a means for the conduction of the heat from the calorimeter to the glass jacket

Figure 2



Key

A - Glass Tube
B - Neoprene Stopper
C - Vacuum Stopcock
D - Thermocouple Leads
E - Heating Coil Leads
F - Cork Supports

The Calorimeter
(Scale 1:1)

and from there to the surroundings. It was found that cork would provide a very excellent non-conductor. Hence, the mixing vessel was built up in two places as shown in the diagram with layers of sheet cork (F) until it fit snugly in the tube.

The cold junction of the thermocouple was insulated also. It was placed in a silvered dewar flask filled with oil. This junction of the thermocouple was threaded through a neoprene rubber stopper, which fits into the top of the dewar flask. All joints on the cold junction end were also sealed with wax insuring a water-tight seal. This was done because it was found that the entire cold junction, mixing vessel, thermocouple, and at least a foot of the heating coil leads had to be immersed in the constant temperature bath. This was necessary because heat conduction through both the thermocouple and the heating coil leads, due to the temperature gradient between the bath and the surroundings, introduced serious errors in the measurements.

When the thermocouple and heating coil leads were immersed in the bath, some method had to be devised for protecting these wires from the thermostat bath water. The heating coil leads were chosen with a plastic waterproof insulation. The thermostat wires were protected by completely enclosing them in rubber latex tubing. The two ends of the tubing were sealed water tight to the neoprene rubber stoppers by successive applications of rubber latex paint. The entire tube was then painted with rubber latex paint to keep it from rotting.

It was found that with this type of insulation, good heating and cooling curves were obtained which could be very nicely extrapolated.

Thermostatic Control of the Bath

Because of the size of the apparatus, it was necessary to use a large tank for the constant temperature bath in order to insure adequate circulation of the water and a uniform temperature. The volume of the tank used was approximately 12.5 cubic feet. A temperature regulator was used which shows no periodic variation and which maintains the temperature of the bath constant to 0.01°C. Since both ends of the thermocouple were insulated, it was found that this slight variation of the temperature produced no measurable variation in the galvanometer readings.

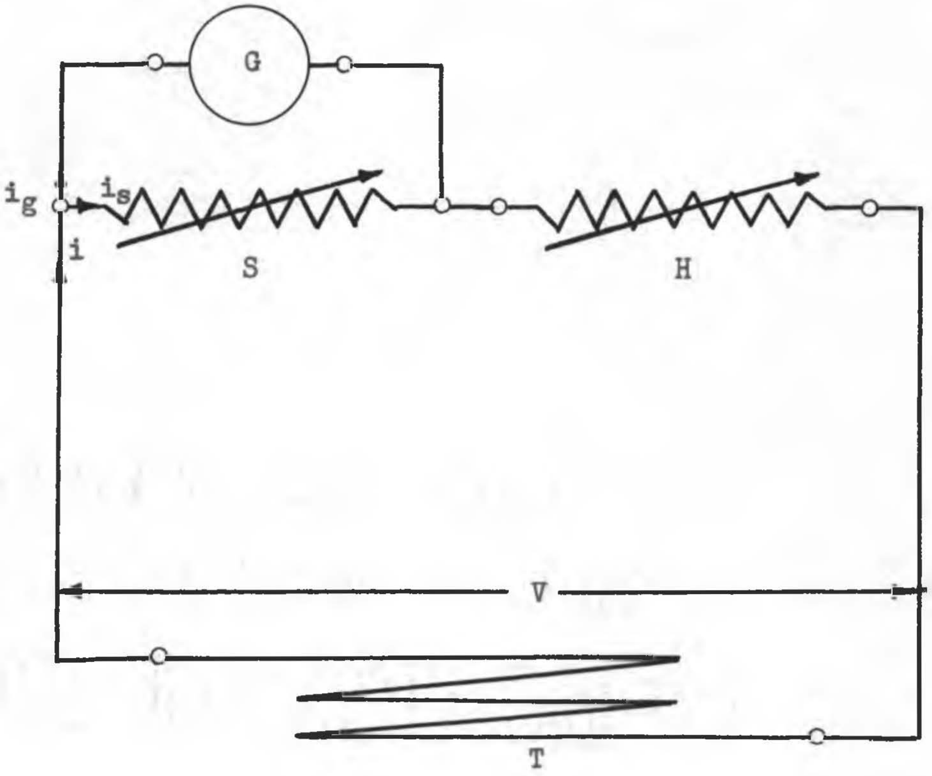
Electrical Circuits

The description of the electrical circuits may be conveniently divided into two parts. Figure 3 shows the thermocouple circuit. S and H are two variable resistors with a range from 0-999 ohms. T is a double junction thermocouple made of 28 gauge copper and 28 gauge constantan wire. The upper part of the mixing vessel has wound on it a thin strip of tissue paper impregnated with shellac. The one end of the thermocouple was placed on this paper and held in position by the cork strips which have been previously described. The output from the thermocouple was fed to the galvanometer G.

This galvanometer is a Leeds and Northrup type 2285 B, the sensitivity of which is 0.2 micro volts per mm. deflection if the scale is placed one meter from the mirror of the galvanometer. The external critical damping resistance is 45 ohms, the period is 5.2 sec., and the resistance of the galvanometer is 17.7 ohms.

The resistances S and H are included in the circuit to cut down

Figure 3



The Thermocouple Electrical Circuit

Key

G - Galvanometer
H - Variable Resistor
S - Variable Resistor
T - Thermocouple
V - Potential Drop Across the Thermocouple
i - Current From the Thermocouple
i_g- Current Through the Galvanometer
i_s- Current Through S

the sensitivity of the galvanometer. The systems measured varied so widely in the size of the temperature change upon mixing that it was not possible to keep the galvanometer mirror on the scale for all the measurements if the same sensitivity was used.

The resistances needed to decrease the current a given amount were calculated as follows: If V is the potential drop across the thermocouple, i is the current from the thermocouple, and i_g and i_s are the currents through the galvanometer G and the shunt S respectively, then by Kirkhoff's Laws of electrical circuits

(1) $i = i_g + i_s$

(2) $Gi_g = Si_s$

(3) $V = iH + Si_s$

(4) $V = iH + Gi_g$

Combining (1) and (3), we get

(5) $V = iH + S(i - i_g) = i(H + S) - Si_g$

Or, solving for i

(6) $i = \frac{V + Si_g}{H + S}$

Next, substituting for "V" in (6) from (4)

(7) $i = \frac{iH + Gi_g + Si_g}{H + S}$

Or,

(8) $iH + iS = iH + Gi_g + Si_g$

Rearranging

(9) $i_g = i\frac{S}{G + S}$

However, as a good approximation, the current through the galvanometer is proportional to the deflection of the galvanometer.[11] If we let d_o be the deflection of the galvanometer when S is taken from the circuit, i.e., when the total current i goes through the galvanometer, and let d_g be the deflection when S is in the circuit, then

$$(10) \quad i_g = kd_g$$

$$(11) \quad i = kd_o$$

Hence, substituting into (9), we get

$$(12) \quad d_g = d_o \frac{S}{S + G}$$

Or,

$$(13) \quad \frac{d_g}{d_o} = \frac{S}{G + S}$$

Therefore, by knowing G, values of S can be calculated to give any desired fraction of the original sensitivity.

Figure 4 shows the heating coil circuit. S and H are again two variable resistors. The range of H (which includes the resistance of the leads ae and bod) is from 0-2000 ohms and the range of S is from 0-999 ohms. These resistances were used as a voltage divider because the potentiometer used in the potential measurements would measure only up to 1.6 volts, and approximately four volts needed to be measured.

The potential drop V_c across the heating coil is calculated from the potentiometer reading V as follows: If i_c is the current through the coil, i_p is the current through the rest of the circuit, R_L is the resistance of the leads from a to b, and R_c is the resistance of the heating coil, then from Kirkhoff's Laws of electrical circuits

$$(14) \quad V_c = i_c R_c$$

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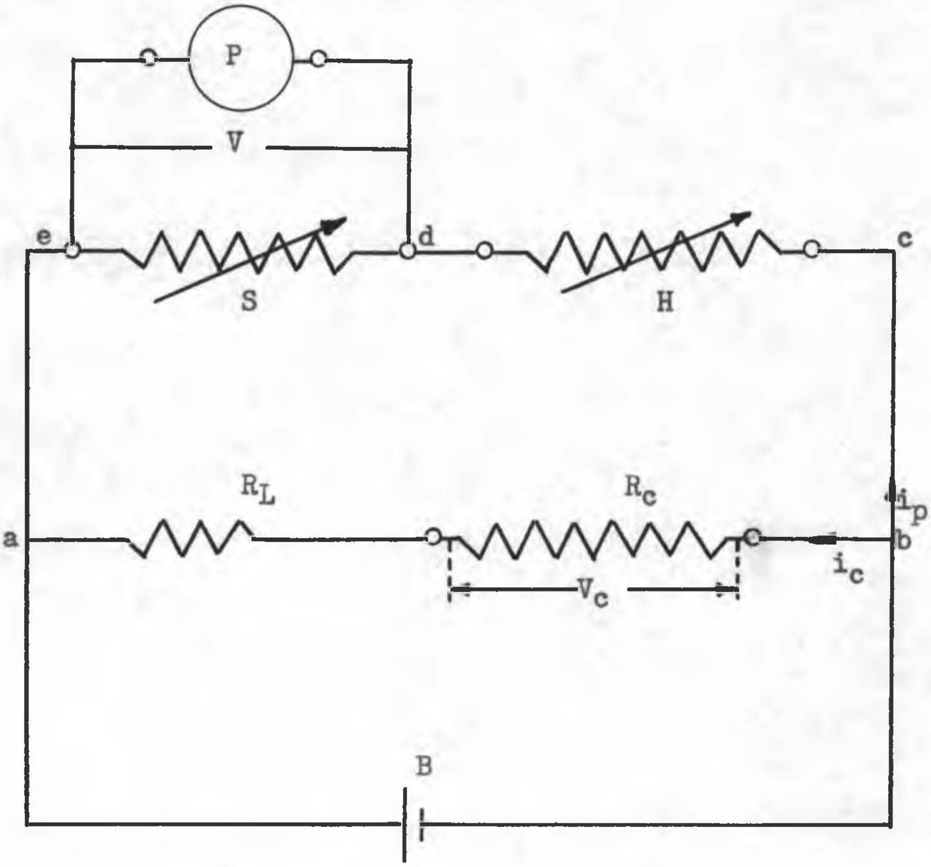
[11] The deflection characteristics of the galvanometer are discussed in more detail under "Experimental Accuracy" on page 45.

Figure 4



The Heating Coil Electrical Circuit

Key

B - Battery
S - Variable Resistor
H - Variable Resistor
R_L- Resistance of the Leads
R_c- Resistance of the Heating Coil
P - Potentiometer
V - Potential Drop Across the Potentiometer
V_c- Potential Drop Across the Heating Coil
i_c- Current Through the Heating Coil
i_p- Current Through the Potentiometer

$$(15) \quad V = Si_p$$

$$(16) \quad V_c = (H + S)i_p - R_L i_c$$

Now, substituting for i_p in (16) from (14) we get

$$(17) \quad V_c = \frac{(H + S)V}{S} - R_L i_c$$

Substituting for V_c in (17) from (13) and rearranging

$$(18) \quad i_c = \frac{V(H + S)}{S(R_c + R_L)}$$

Now, substituting (18) into (17) we get

$$(19) \quad V_c = \left(\frac{V(H + S)}{S}\right)\left(\frac{R_c}{R_c + R_L}\right)$$

But, for our purpose, we want V_c to be about four times as large as V so we let $H = 3S$ then

$$(20) \quad V_c = 4V\left(\frac{R_c}{R_c + R_L}\right)$$

In practice, H is set at 1500 ohms and S at 500 ohms.

The potentiometer used was a Leeds and Northrup type K-2 with a General Electric catalog no. 32C galvanometer as a detection device. The source of electrical energy for the heating coil was from lead storage cells (B).

In the actual construction of the heating coil, two different methods were tried. The first time the heating coil was attached to the mixing vessel, the lower part of the mixing vessel was wound with a strip of tissue paper impregnated with shellac. The heating coil, consisting of approximately 3 feet of 28 gauge constantan wire with a resistance of about 7 ohms, was wound onto this insulation. Leads of 18 gauge plastic coated copper wire were soldered to the ends of the heating coil. The coil was then covered with cork to hold it in place. It was found, however, that insulated constantan wire could be wound directly onto the calorimeter without the tissue paper insulation. This was done using approximately 4 feet of 28 gauge insulated constantan wire which had a resistance of about 12 ohms. The heating coil leads and the rest of the wiring as previously described were not changed.

Timing Measurements

In all cases, the time during which the heating current was passed through the heating coil, was measured with a stop watch. The reading of the stop watch used can be estimated to 0.01 seconds. The measurement was made by simultaneously starting the stop watch and throwing the switch to complete the heating circuit. When the proper amount of heat had been introduced into the system, the switch was then opened at the same time that the stop watch was stopped. It is thought that with this type of measurement, the time interval can be measured to within 0.05 seconds.

Weighing

Because the mass (being about 175 gms.) and the volume of the calorimeter used were large, and the difference in weight upon filling being only from 10-20 gms, the empty calorimeter was balanced against a counterpoise of approximately the same size as the calorimeter to cut down on the errors which might arise due to bouyancy. The counterpoise consisted of a bottle of approximately the same size as the calorimeter. Sand was put in the bottle and the amount adjusted until a balance was obtained against the calorimeter.

The analytical balance used has a sensitivity with 175 gms. on each pan of 3.4 divisions per 10 milligrams, hence, it is possible to weigh to better than at least two milligrams.

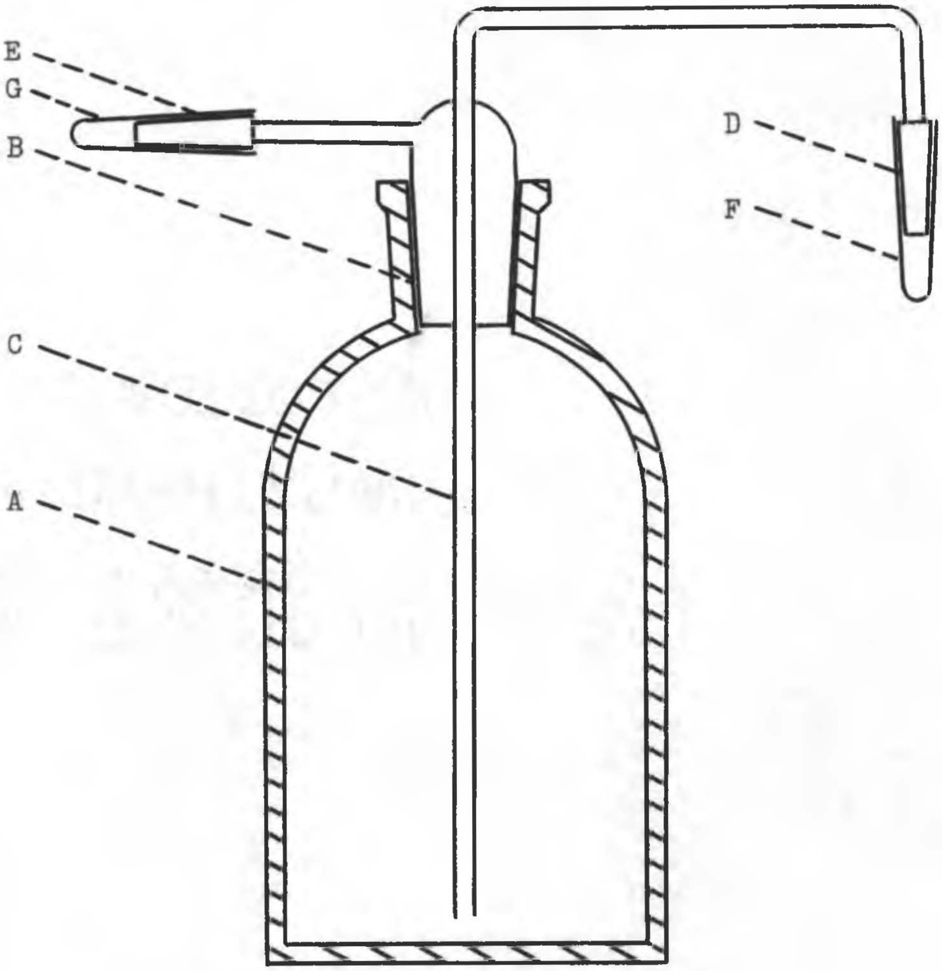
Stirring Apparatus

Since the liquids had to be stirred frequently during the run, a method had to be devised which would facilitate rapid and easy stirring. To do this, a large wheel was attached to the side of the constant temperature bath. This wheel was connected by a shaft to a small pulley. A belt was run from this pulley to a similar pulley down in the water. The latter pulley was connected to a shaft which was supported by a grease sealed bearing. On the other end of this shaft is a clamp which holds the calorimeter. By turning the large wheel the pulley turns. This in turn tips the calorimeter over so the weight can fall and mix the liquids. Enough slack is left in the heating coil and the thermocouple leads so they won't get tangled up when the calorimeter is tipped over.

Storage of the Liquids

Some type of container had to be constructed for the storing of the liquids which would keep moisture out of them, and at the same time, provide an easy means of dispensing the liquids. Figure 5 shows the type of container used. (A) is a liter reagent bottle with a standard taper ground glass joint (B). (C) is a long glass tube which starts at the bottom of the reagent bottle and ends up attached to the ground glass joint (D). (E) is also a ground glass joint while (F) and (G) are ground glass caps which fit over the joints (D) and (E) respectively. These caps are sealed on the joints with a stopcock grease which is insoluble in organic liquids. The joint at (B) is sealed with wax. When some liquid is to be dispensed, the caps (F) and (G) are removed and a ground glass sleeve is connected to (E). This sleeve is also connected to a source of

Figure 5



Storage Container for the Liquids

Key

A - Liter Reagent Bottle
B - Ground Glass Joint
C - Glass Tube
D - Ground Glass Joint
E - Ground Glass Joint
F - Ground Glass Cap
G - Ground Glass Cap

compressed nitrogen. By running compressed nitrogen into the bottle at (E), the liquid is forced out at (D) where it can be caught in the calorimeter and used.

Before the nitrogen is used, it is dried by running it through a large calcium sulphate drying tube. It is also filtered before it is used. This is done by running it through a cotton and glass wool plug.

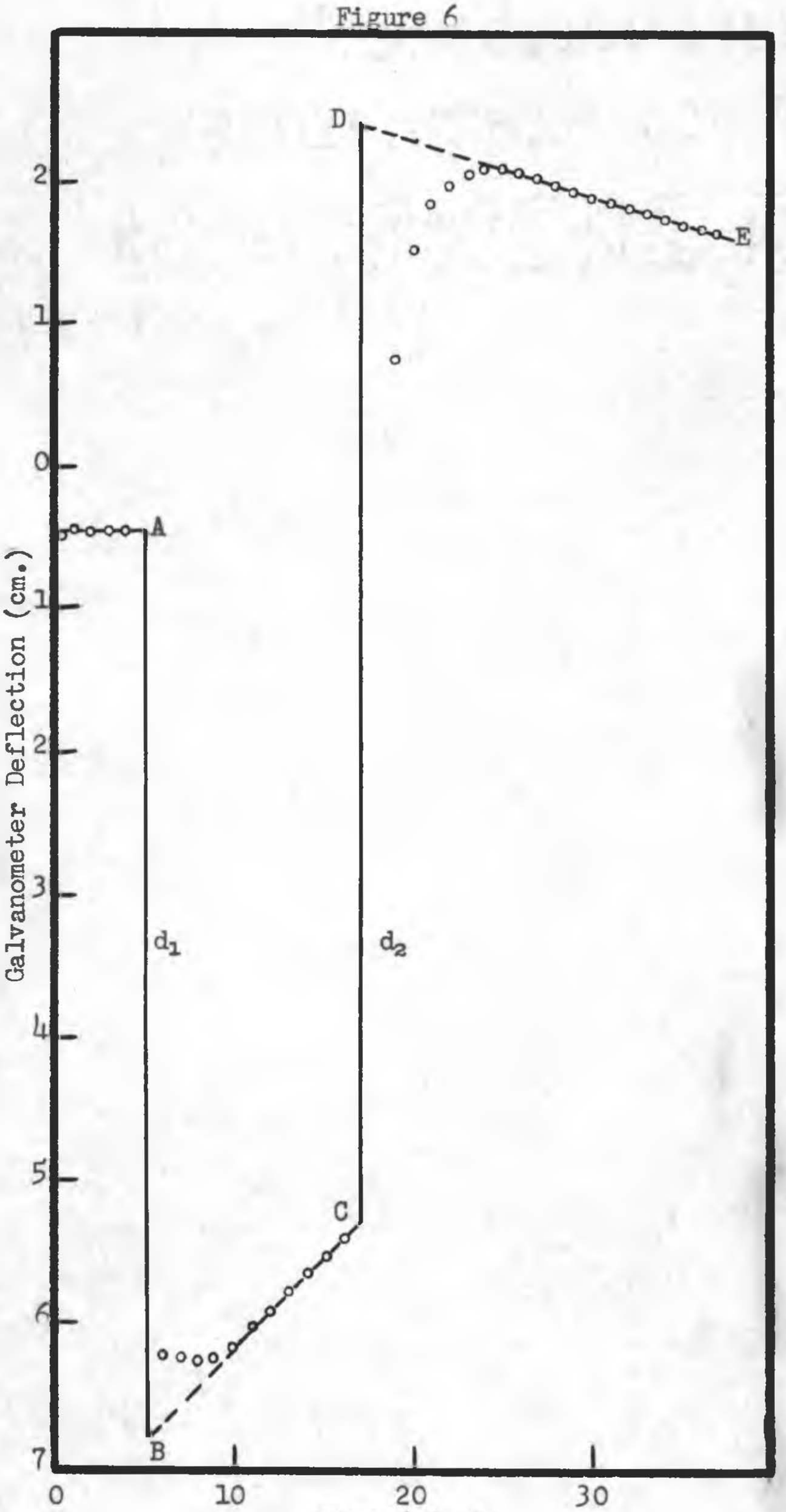
V: EXPERIMENTAL PROCEDURE

The mixing vessel, consisting of the two sections which hold the liquids along with the metal weight, gaskets, brass plug, aluminum foil diaphragm, and the heating coil with about 4" of leads, was first balanced against the counterpoise. The bottom one of the two polyethylene gaskets which hold the aluminum foil diaphragm in place was left in position in the mixing vessel. The bottom section was then filled to the top of the gasket with one of the liquids to be mixed. The aluminum foil diaphragm was then put into place. Care was taken that no air was left under the diaphragm in the bottom compartment. Next, the other polyethylene gasket was put in place and the top section with the brass plug removed was screwed down tightly on the gasket. Any liquid which might have gotten into the top section was blown out using compressed nitrogen. The brass plug was screwed tightly in place. The whole apparatus was then placed in a bell jar and the air was pumped from the bell jar to removo the liquid from the threads of the mixing vessel. The calorimeter was then removed from the bell jar and weighed to determine the weight of the liquid now in the mixing vessel. In the next step the brass plug in the top was removed and the top compartment was filled with the second liquid leaving only enough space in the compartment so the brass plug could be screwed in place. The mixing vessel was then blown off with compressed nitrogen to remove any liquid that remained on it and again weighed. The difference between this weighing and the first weighing gave the weight of the second liquid.

Next, a piece of tissue paper was wrapped around the top compartment of the mixing vessel and painted with shellac. After sufficient time had been allowed for drying of the shellac, the thermocouple junctions were put in place. Care was taken to keep the two junctions separated from each other in order that they did not short out. A piece of cork sheet was then placed over the thermocouple junctions and clamped on firmly to hold them in place. Next, since the heating coil leads had been cut in order to remove the calorimeter for weighing, they were soldered back together and painted with tygon paint to serve as an insulation in case the wires came in contact. The assembled calorimeter was then placed in the glass tube. The rubber stopper was put in place; the joints were sealed with wax; and the air was pumped from the tube with the vacuum pump. The aluminum foil was then wrapped around the tube and the whole apparatus was immersed in the bath and left overnight so the temperature of the calorimeter could come to equilibrium with the bath temperature.

The next day after equilibrium had been established, the two liquids were mixed. The course of a typical mixing experiment is shown in figure 6. Before mixing, the galvanometer deflection was observed for about five minutes to insure that equilibrium had been reached. The liquids were then mixed by tipping the calorimeter upside down. Point A shows the time at which the liquids were mixed. The liquids were then stirred at a constant rate for the remainder of the run. The stirring was usually done at the rate of once every ten seconds. Readings of the galvanometer were taken every 30 seconds until a steady slope on the graph was obtained. This corresponds to the line BC. At point C, the heating current was switched on for the time interval that was necessary to compensate for the heat absorbed in the mixing. During this time, the

Figure 6



Plot of Galvanometer Deflection Against Time for a Typical Mixing Experiment potential drop V as previously described in section IV was carefully measured. The heating current was then switched off and galvanometer readings corresponding to the readings for line DE were noted until a steady slope was again obtained.

The galvanometer deflection d_1 corresponding to the heat change due to the heat of mixing (H_1^M) was obtained by extrapolating the line CB back to the time where mixing occurred. This is shown in figure 6. Similarly, the galvanometer deflection d_2, corresponding to the rise in temperature due to the electrical heat supplied (H_1^E), was obtained by extrapolating the line DE back to the time at which the heating current was switched on. From the values of d_1 and d_2, which can be measured on the graph, as illustrated by figure 6, and the other data which had been measured, the heat of mixing can be calculated. This is done as follows: First, we must assume that the deflection of the galvanometer is proportional to the heat change in the calorimeter.[11] Experiments with the calorimeter show that this is a valid assumption. Now, if this is true, then

$$(21) \quad d_1 = kH_1^M$$

$$(22) \quad d_2 = kH_1^E$$

Dividing (21) by (22)

$$(23) \quad \frac{d_1}{d_2} = \frac{H_1^M}{H_1^E}$$

Hence

$$(24) \quad H_1^M = \frac{d_1 H_1^E}{d_2}$$

However, the heat change (H_1^E) is given by

$$(25) \quad H_1^E = i_c V_c t$$

where i_c is the current through the heating coil, V_c is the potential drop across the heating coil, and t is the time of heating. If i_c is measured in amperes, V_c in volts, and t in seconds, then H_1^E will be given in joules. But, from Ohm's Law

$$(26) \quad i_c = \frac{V_c}{R_c}$$

Substituting (26) into (25)

$$(27) \quad H_1^E = \frac{V_c^2 t}{R_c}$$

Moreover, from equation (20), page 15, the potential drop across the coil (V_c) is given by

$$(28) \quad V_c = 4V \frac{R_c}{R_c + R_L}$$

Where R_c is the resistance of the heating coil, R_L is the resistance of the leads, and V is the potentiometer reading from figure 4.

Substituting (28) into (27)

$$(29) \quad H_1^E = \frac{(\quad 4V \quad)^2 R_c t}{(R_c + R_L)^2}$$

Hence, substituting (29) into (24), we get

$$(30) \quad H_1^M = \frac{d_1(\quad 4V \quad)^2 R_c t}{d_2(R_c + R_L)^2}$$

However, this gives the heat of mixing for the number of moles of solution we have in the calorimeter, and we want the heat of mixing per mole, hence, we divide by the total number of moles n_t and get

$$(31) \quad H_1^M/\text{mole} = \frac{1}{n_t} \frac{d_1(\quad 4V \quad)^2 R_c t}{d_2(R_c + R_L)^2}$$

But, if we mix liquids a and b, then

$$(32) \quad \text{Moles of a} = \frac{\text{Wt. of a}}{\text{Mol. Wt. of a}} = n_a$$

$$(33) \quad \text{Moles of b} = \frac{\text{Wt. of b}}{\text{Mol. Wt. of b}} = n_b$$

Therefore, the total moles of solution is given by

$$(34)\quad n_t = n_a + n_b$$

Hence, substituting (34) into (31), we get

$$(35)\quad H_1^M/\text{mole} = \frac{1}{n_a + n_b}\,\frac{d_1}{d_2}\,\frac{(4V)^2 R_c t}{(R_c + R_L)^2}$$

Heats of Mixing From Heats of Dilution Measurements

The procedure previously described for the measurement of the heats of mixing works well over a wide range of mole fractions. However, the amount of the two liquids which could be put in the calorimeter was limited to the extent that some of the extreme mole fractions could not be obtained by these direct measurements. These extreme mole fractions had to be obtained from heats of dilution measurements. These measurements were made in the same way as the direct heats of mixing measurements as previously described, with the exception that a mixture of liquids, whose heat of mixing is known, was weighed into one of the compartments. The weight of each liquid in this mixture was obtained by multiplying the total weight of the solution by the weight fraction of each component as determined in the measurement of the heat of mixing of this solution. One of the pure liquids was put into the other compartment and the heat change was measured in exactly the same way as previously described on page 21. This heat change measured was a heat of dilution. From this, and by knowing the heat of mixing of the already mixed solution in the one compartment, call it solution No. 1, we can calculate the heat of mixing at a new mole fraction. This is done as follows: If solution No. 1 is composed of liquids a and b, with the mole fraction of liquid a being x_1 and the mole fraction of liquid b being x_2, then if the heat of mixing per mole of solution No. 1 is H_1^M,

$$(36) \quad x_1 a + x_2 b \longrightarrow \text{Solution No. 1}, \quad \Delta H = H_1^M$$

Now, if n_3 moles of solution No. 1 and n_4 moles of a are mixed and the heat change is found to be H_1^D, then,

$$(37) \quad n_3 \text{ Solution No. 1} + n_4 a \longrightarrow (n_3 + n_4)\text{Solution No. 2}, \quad \Delta H = H_1^D$$

And if we divide (37) by n_3,

$$(38) \quad \text{Solution No. 1} + \frac{n_4}{n_3} a \longrightarrow \frac{n_3 + n_4}{n_3} \text{ Solution No. 2}, \quad \Delta H = \frac{H_1^D}{n_3}$$

Next, we add (36) and (38) and get

$$(39) \quad \left(x_1 + \frac{n_4}{n_3}\right) a + x_2 b \longrightarrow \frac{n_3 + n_4}{n_3} \text{ Solution No. 2}, \quad \Delta H = H_1^M + \frac{H_1^D}{n_3}$$

Now we divide by $\dfrac{n_3 + n_4}{n_3}$

$$(40) \quad \frac{x_1 n_3 + n_4}{n_3 + n_4} a + \frac{x_2 n_3}{n_3 + n_4} b \longrightarrow \text{Solution No. 2}, \quad \Delta H = \frac{n_3}{n_3 + n_4} H_1^M + \frac{H_1^D}{n_3 + n_4}$$

But, $(x_1 n_3 + n_4)/(n_3 + n_4)$ is just the mole fraction (x_3) of liquid a present at the new concentration and $x_2 n_3/(n_3 + n_4)$ is the mole fraction (x_4) of b present at the new concentration, hence;

$$(41) \quad x_3 a + x_4 b \longrightarrow \text{Solution No. 2}, \quad \Delta H = \frac{n_3}{n_3 + n_4} H_1^M + \frac{H_1^D}{n_3 + n_4}$$

Heats of Mixing of Ternary Solution

The heats of mixing of the ternary solutions are measured in the same way as the heats of dilution. A mixture of liquids a and b (solution No. 3) for which the number of moles of a is n_1, the number of moles of b is n_2, and the heat of mixing is H_2^M, so that

$$(42) \quad n_1 a + n_2 b \longrightarrow (n_1 + n_2)\text{Solution No. 3}, \quad \Delta H = H_2^M$$

is put in one of the compartments. n_3 moles of liquid c are put in the other compartment and the heat of mixing (H_3^M) is measured. This is expressed by

$$(43) \quad (n_1 + n_2)\text{Solution No. 3} + n_3 c \longrightarrow (n_1 + n_2 + n_3)\text{Solution No. 4}, \quad \Delta H = H_3^M$$

Adding (42) and (43), we get

$$(44) \quad n_1 a + n_2 b + n_3 c \longrightarrow (n_1 + n_2 + n_3)\text{Solution No. 4}, \quad \Delta H = H_2^M + H_3^M$$

To find the ternary heat of mixing per mole of solution, we divide (44) by $n_1 + n_2 + n_3$ and get

$$(45) \quad x_1 a + x_2 b + x_3 c \longrightarrow \text{Solution No. 4}, \quad \Delta H = \frac{H_2^M + H_3^M}{n_1 + n_2 + n_3},$$

where $x_1 = n_1/(n_1 + n_2 + n_3)$ is the mole fraction of a, $x_2 = n_2/(n_1 + n_2 + n_3)$ is the mole fraction of b, and $x_3 = n_3/(n_1 + n_2 + n_3)$ is the mole fraction of c.

These ternary heats of mixing are then correlated in terms of the binary heats of mixing.

VI: EXPERIMENTAL RESULTS

The systems chosen for study were the three liquid pairs formed between benzene, carbon tetrachloride, and cyclohexane, and the ternary mixture of the three. These three were chosen because they are representative of the non-polar type of molecule.

A graph and a table of results are given for the systems studied. The heat of mixing in calories per mole is plotted as ordinate against the mole fraction of one of the components as abcissa. The curves obtained are smooth and follow closely the equation for the parabola. Because of this it was thought desirable to summarize the results in terms of an equation. Several semi-empirical equations have been developed in the literature. Notable among these are those by Scatchard *et. al.*[8,10] in which he expresses his thermodynamic function as a power series expansion of mole fractions, and by Hildebrand[12] who expresses his thermodynamic functions in terms of what he calls "solubility parameters" and volume fractions. It was thought, however, that probably the best equation to use is that developed by Redlich and Kister.[13] Their equation expresses the thermodynamic function as a power series expansion of mole fractions expressed in such a way that the higher order terms are corrections for the terms of lower order. This is done to avoid the inconvenience of having the result appear as a small difference of large numbers.

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[12] J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," 3rd Ed., Reinhold Publishing Corporation, New York, N.Y., 1950, p. 129.

[13] O. Redlich and A. T. Kister, *Ind. Eng. Chem.*, *40*, 345 (1948).

The equation is semi-empirical, and the development depends largely upon intuitive reasoning. Since the curve follows closely the equation of a parabola, it is convenient to express the equation in the form of a parabola with some higher order terms introduced to serve as corrections for the slight inconsistencies which develop.

Since $Q = 0$ for $x = 0$ and $x = 1$, where Q is a thermodynamic function and x is the mole fraction, each term must contain the factor $x(1 - x)$. It is also desirable to develop the series in terms of a variable which is somehow symmetrical with respect to the two components. The simplest variable of this kind is $(2x - 1)$, which merely changes sign upon exchange of the components. Thus, the most useful development appears to be

$$(46)\quad Q = x(1 - x)\left[B + C(2x - 1) + D(2x - 1)^2 + \text{---}\right]$$

where B, C, D, etc. are empirical constants which can be evaluated for the particular system in question.

The further development of Q into a power series for multi-component systems follows without difficulty. If we remember that $x_1 = 1 - x_2$, we can rewrite the preceding equation in the more symmetric form

$$(47)\quad Q_{12} = x_1x_2\left[B_{12} + C_{12}(x_1 - x_2) + D_{12}(x_1 - x_1)^2 + \text{---}\right]$$

Intuitively then, the series for a ternary system can be represented by the sum of the three binaries plus a cross product term which is introduced for symmetry. If this is done, then

$$(48)\quad Q_{123} = Q_{23} + Q_{31} + Q_{12} + x_1x_2x_3\left[C_{123} + D_1(x_2 - x_3) + D_2(x_3 - x_1) + \text{---}\right]$$

Scatchard[10] has discussed the evaluation of the cross product constants, C_{123}, D_1, D_2, etc. He has come to the conclusion that if the systems studied deviate only slightly from the symmetrical expression, the cross product terms can be neglected. This effect will be discussed further in the general discussion.

Scatchard[6] has found, however, in his treatment of the carbon tetrachloride-methanol system that mixtures containing a polar component have large higher order terms and require a more complete analysis.

The evaluation of the empirical constants in equation 47 would be done by the method of least squares if we were trying to do the best job possible. Scatchard[14] has suggested a method which although not nearly as exact, is much less tedious. His method is as follows: To evaluate B_{12} from equation 47, we let $x_1 = x_2 = .5$ then

$$(49)\quad H^M_{x_1=0.50} = (.5)(.5)B_{12} = .25\ B_{12}$$

So,

$$(50)\quad B_{12} = 4H^M_{x_1=0.50}$$

Also at $x_1 = 1/4$, $x_2 = 3/4$

$$(51)\quad H^M_{x_1=0.25} = 3/16\left[B_{12} - 1/2\ C_{12} + 1/4\ D_{12}\right]$$

And at $x_1 = 3/4$, $x_2 = 1/4$

$$(52)\quad H^M_{x_1=0.75} = 3/16\left[B_{12} + 1/2\ C_{12} + 1/4\ D_{12}\right]$$

Subtracting (51) from (52), we get

$$(53)\quad H^M_{x_1=0.75} - H^M_{x_1=0.25} = 3/16\left[B_{12} + 1/2\ C_{12} + 1/4\ D_{12} - B_{12} + 1/2\ C_{12} - 1/4\ D_{12}\right]$$

Or,

$$(54)\quad C_{12} = 16/3\left[H^M_{x_1=0.75} - H^M_{x_1=0.25}\right]$$

D_{12} is obtained by adding equations (51) and (52). When this is done, we get

$$(55)\quad D_{12} = 32/3\left[H^M_{x_1=0.75} + H^M_{x_1=0.25}\right] - 4B_{12}$$

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[14] G. Scatchard, Chem. Rev., 44, 7 (1949).

These constants are all that is usually needed to specify the systems. Further terms can be obtained, however, by taking mole fractions of 1/8 and 7/8 and repeating the above procedure.

The Benzene-Carbon Tetrachloride System

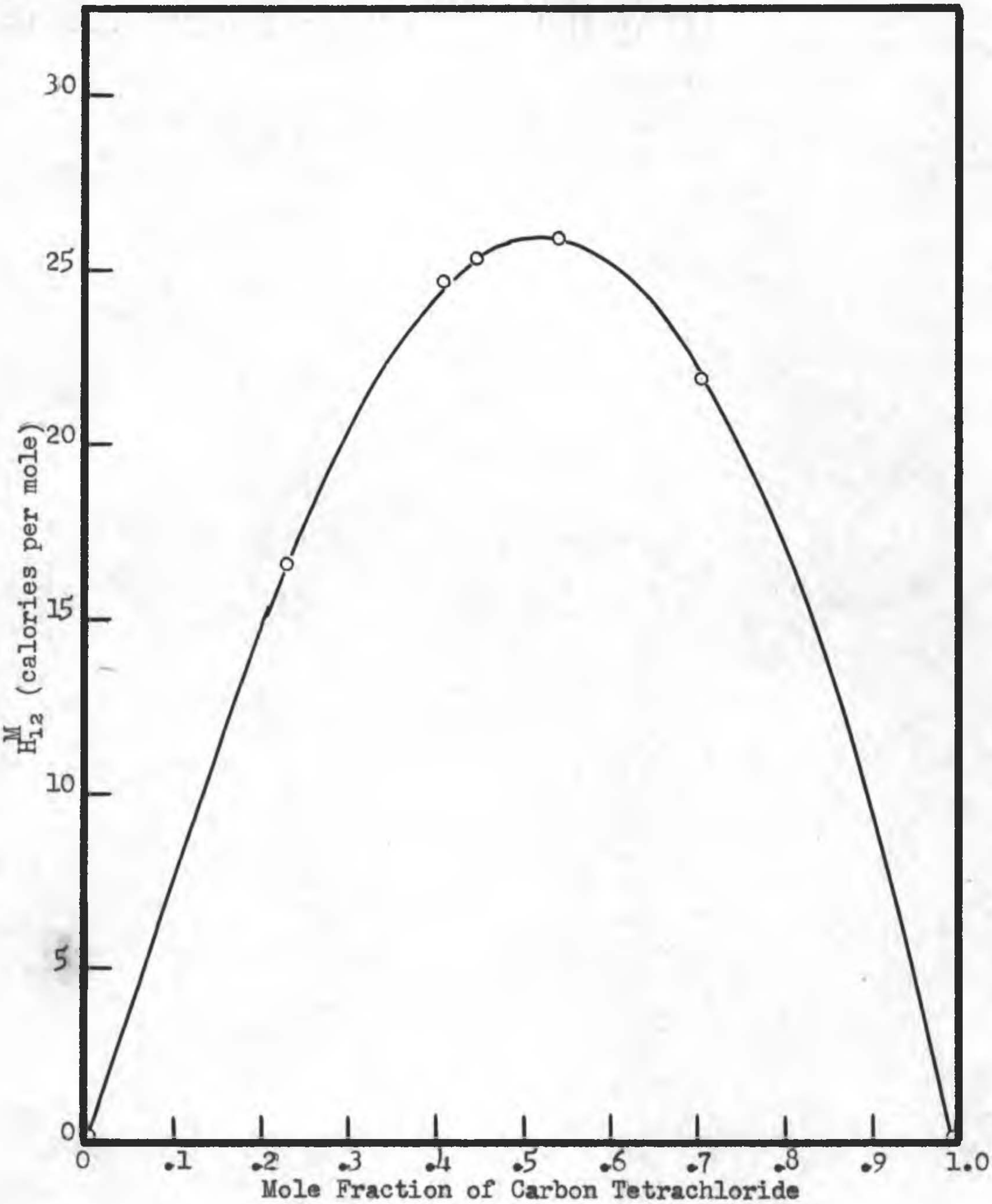
The first system studied was the benzene-carbon tetrachloride system. This was done because many consistent results had been obtained for this system with which we could compare our data. Table 1 gives the results we obtained for this system. Table 2 shows a comparison of our values for an equal molar mixture of benzene and carbon tetrachloride with those found in the literature. It is seen that our result of 25.6 cal./mole agrees well with most of the literature values. Figure 7 shows that the heat of mixing is quite symmetrical with respect to mole fraction.

Table 1

Carbon Tetrachloride (1) + Benzene (2) at 25.00°C

x_1	H^M_{12} (cal/mole)
.2313	16.6
.4113	24.7
.4460	25.3
.5456	25.9
.7056	21.9

Figure 7



Plot of Heat of Mixing Against Mole Fraction For the Carbon Tetrachloride(1)-Benzene(2) System

Table 2

Heats of Mixing in Calories Per Mole For Equal Molar Mixtures of Carbon Tetrachloride (1) and Benzene (2)

Date	Method	T °C	H^M_{12}	Reference
1925	Calor.	25	25.6	Hirobe[1]
1937	Calor.	25	21.0	Vold[8]
1940	V-L	40-70	30.0	Scatchard *et. al.*[10]
1944	Calor.	20	24.3	Boissanas and
		30	27.8	Cruchard[4]
1950	Calor.	20	31.0	Scatchard *et. al.*[9]
1952	Calor.	24.7	25.8	Cheesman and Whitaker[7]
1956	Calor.	25	25.6	This Work

The measurements were all made at 25.00°C.

The equation which best fits the data is given by

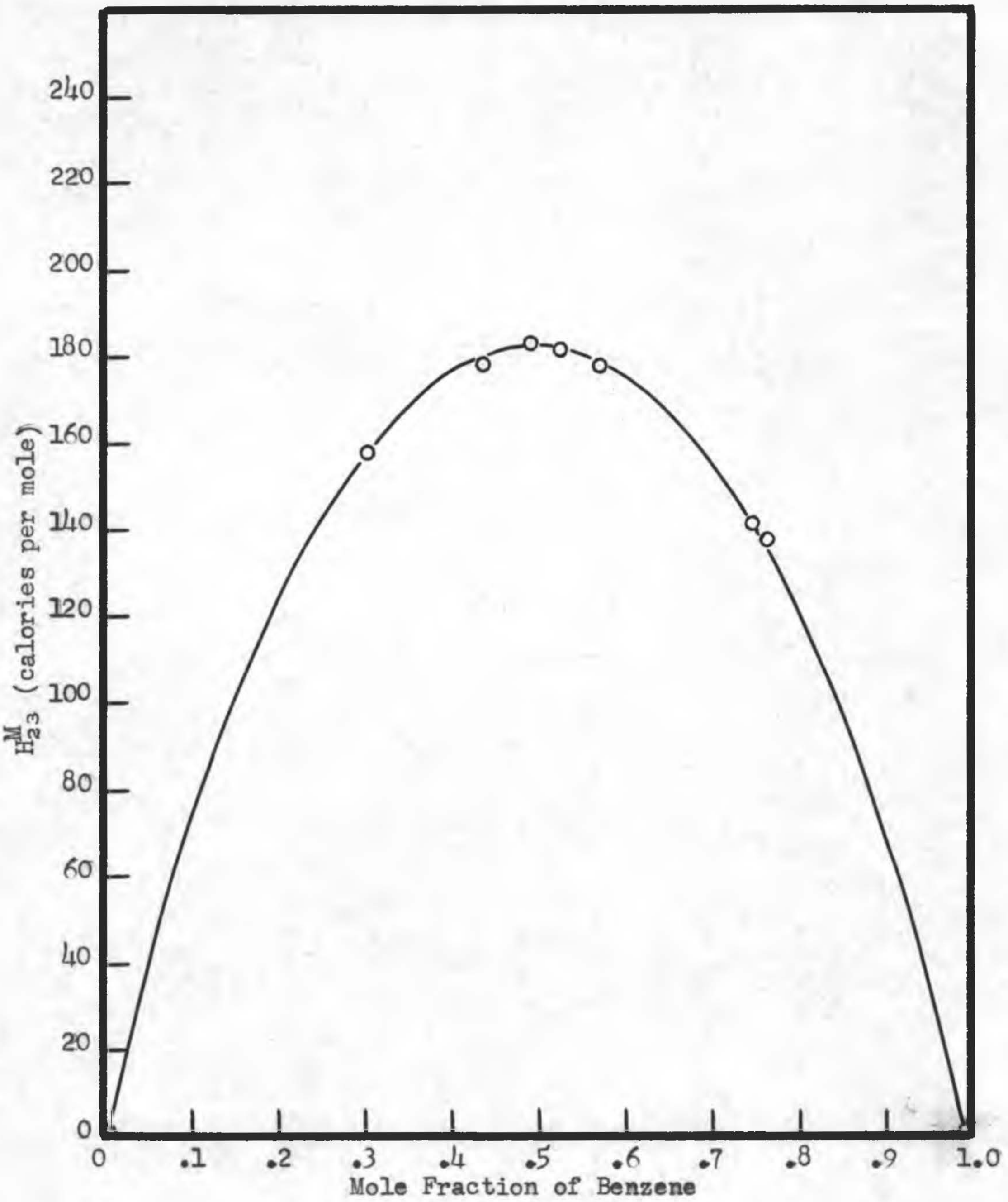
$$(56)\quad H^M_{12} = x_1x_2\left[103.2 + 13.1(x_1 - x_2) - 13.3(x_1 - x_2)^2\right]$$

where (1) is carbon tetrachloride and (2) is benzene. The value of H^M_{12} as calculated from the equation has the dimensions of cal./mole.

The Benzene-Cyclohexane System

Table 3 and figure 8 show the results for this system at 25.00°C. The maximum value of the heat of mixing is 182.4 calories per mole. The graph shows that the heat of mixing is approximately symmetrical with respect to mole fraction.

Figure 8



Plot of Heat of Mixing Against Mole Fraction For the Benzene(2)-Cyclohexane(3) System

Table 3

Benzene (2) + Cyclohexane (3) at 25.00°C

x_2	H^M_{23} (cal./mole)
.3059	157.7
.4384	178.9
.4914	182.3
.5279	181.0
.5747	177.9
.7489	141.2
.7641	137.7

The equation which best fits the data is

$$(57)\quad H^M_{23} = x_2 x_3 \left[729.6 + 102.4(x_2 - x_3)^2\right]$$

where benzene is (2) and cyclohexane is (3). The value for H^M_{23} as calculated from the equation has the dimensions of cal./mole.

The Carbon Tetrachloride-Cyclohexane System

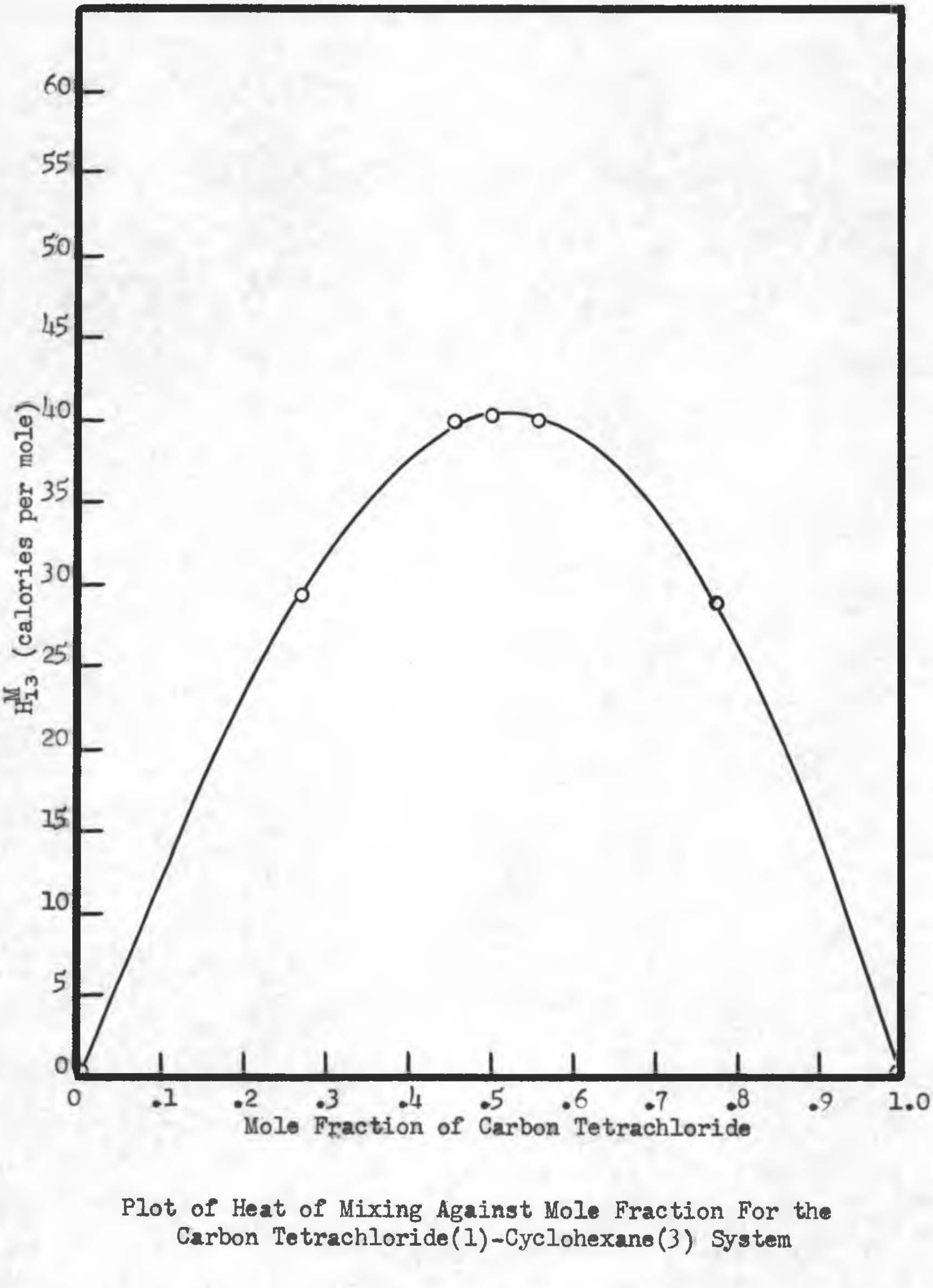
Results obtained for this system are shown in table 4 and figure 9. The measurements were made at 25.00°C. The maximum value of the heat of mixing is 40.2 cal./mole. The results again appear to be approximately symmetrical with mole fraction.

Table 4

Carbon Tetrachloride (1) + Cyclohexane (3) at 25.00°C

x_1	H^M_{13} (cal./mole)
.2714	29.2
.4542	39.8
.5019	40.1
.5599	39.9
.7746	28.9

Figure 9



Plot of Heat of Mixing Against Mole Fraction For the Carbon Tetrachloride(1)-Cyclohexane(3) System

The equation which best fits the points obtained for this system is given by

$$(58)\quad H^M_{13} = x_1x_3\left[160.8 + 18.9(x_1 - x_3) - 20.2(x_1 - x_3)^2\right]$$

where (1) is carbon tetrachloride and (3) is cyclohexane. H^M_{13} calculates out in calories per mole.

The Carbon Tetrachloride-Benzene-Cyclohexane System

Table 5 and figure 10 show the results obtained for this system at 25.02°C. In the measurements made, equimolar amounts of benzene and carbon tetrachloride were used in all cases, hence, the mole fractions of benzene and of carbon-tetrachloride are equal.

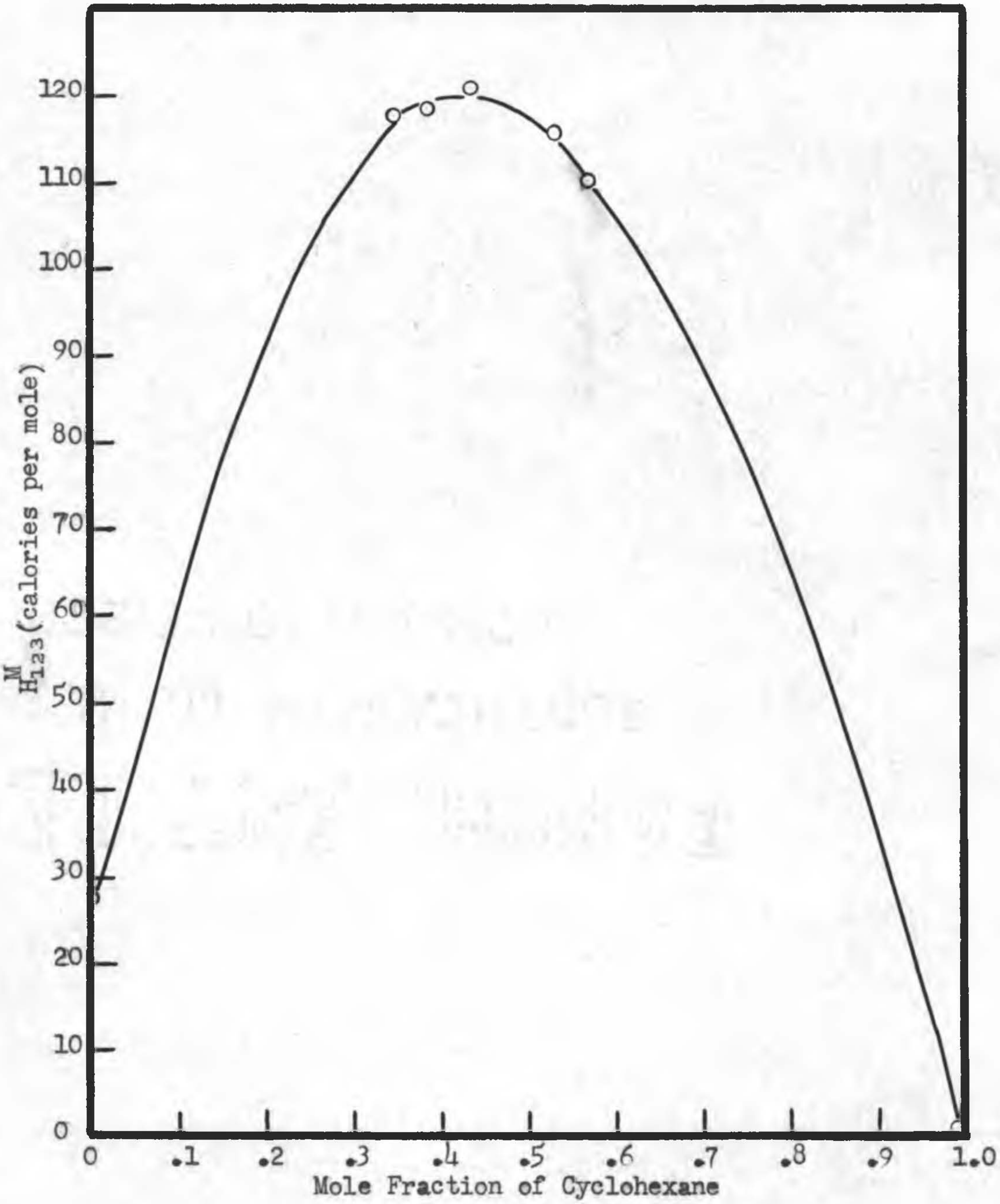
Table 5

Carbon Tetrachloride (1) + Benzene (2) + Cyclohexane (3)
at 25.02°C

x_1	x_2	x_3	H^M_{123} (cal./mole)
.500	.500	.000	25.8
.325	.325	.350	117.2
.306	.306	.388	118.2
.280	.280	.440	120.5
.233	.233	.534	115.3
.213	.213	.574	109.7

The maximum value for the heat of mixing for this system is 120.5 calories per mole. This value is displaced from the mid-point of the graph, occurring at a mole fraction of cyclohexane of 0.44. The heat of mixing does not go to zero when the mole fraction of cyclohexane is zero because there is still a heat of mixing between carbon tetrachloride and benzene even when cyclohexane is absent. The equation of the curve in figure 10 is given by

Figure 10



Plot of Heat of Mixing Against Mole Fraction For the Carbon Tetrachloride(1)-Benzene(2)-Cyclohexane(3) System

$$(59)\quad H^{M}_{123} = x_1x_2\left[103.2 + 13.1(x_1 - x_2) - 13.3(x_1 - x_2)^2\right]$$
$$+ x_1x_3\left[160.8 + 18.9(x_1 - x_3) - 20.2(x_1 - x_3)^2\right]$$
$$+ x_2x_3\left[729.6 + 102.4(x_2 - x_3)^2\right]$$
$$+ x_1x_2x_3\left[128 + 161(x_1 - x_3) - 1636(x_1 - x_3)^2\right]$$

where carbon tetrachloride is (1), benzene is (2), and cyclohexane is (3). The value for the heat of mixing calculates out in cal./mole.

VII: GENERAL DISCUSSION

Discussion of Data

The plots of the heat of mixing against mole fraction for the three binary solutions follow closely the equation for a parabola.[15] The maximum value for the heat of mixing appears at a mole fraction of 0.500 for all three binaries. The Benzene-Cyclohexane system is symmetrical with respect to the x = 0.500 line. The carbon tetrachloride-benzene and the carbon tetrachloride-cyclohexane systems, however, are slightly distorted.

The plot of heat of mixing against mole fraction of cyclohexane for the ternary solution of carbon tetrachloride-benzene-cyclohexane deviates to some extent from the parabola equation.

The maximum value for the heat of mixing for this ternary system is displaced from the 0.500 mole fraction line. It appears at a mole fraction of cyclohexane of 0.44. The curve, however, is symmetrical with respect to the line x_3 = 0.44. Figure 11 shows a plot of mole fraction of cyclohexane against heat of mixing for this system. The solid line shows the curve which best fits the data, and the broken line shows the curve which would be predicted by the addition of the equations for the binaries. It is evident that there is a slight discrepancy between the two curves, but this discrepancy does not exceed 5%. The experimental curve is slightly displaced and slightly higher than the theoretical curve.

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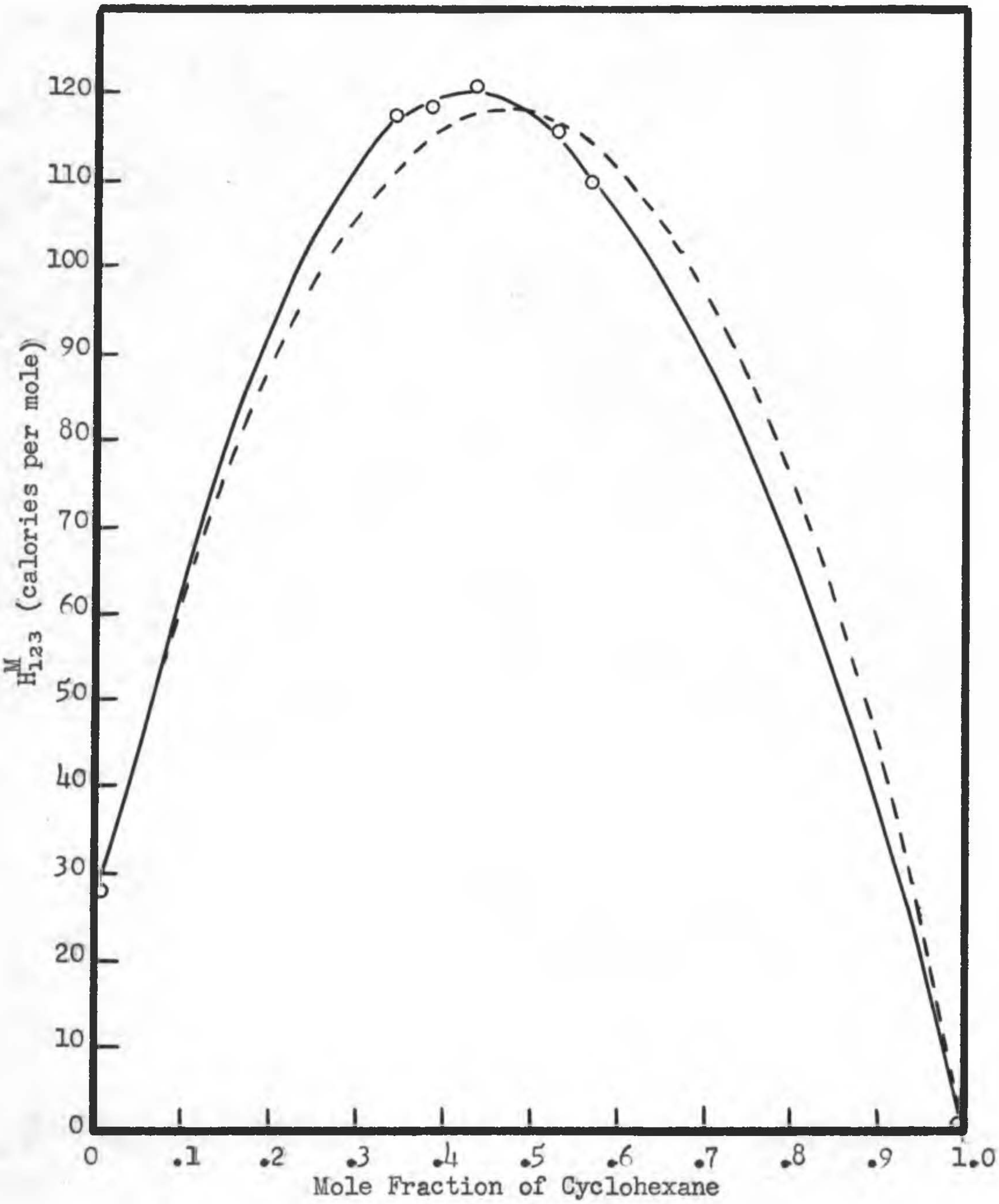
[15] For these graphs, refer back to figures 7, 8, and 9 on pages 32, 34, and 36 respectively.

Figure 11



Plot Comparing Predicted Curve With Experimental Curve For the Carbon Tetrachloride(1)-Benzene(2)-Cyclohexane(3) System

The heats of mixing measured were very small heat changes. As a comparison, the heats of vaporization[16] of carbon tetrachloride at 0°C, benzene at 25°C, and cyclohexane at 25°C are respectively 8015, 8092, and 7894 cal./mole. The maximum heat of mixing measured was 182.4 calories per mole. This is about 2% of the value for the heat of vaporization. The average heat change measured was about 25 cal./mole. This would represent only about 0.3% of the heat of vaporization.

Since these heat changes are so small, it appears that the behavior of the solutions approach very closely to the behavior of the ideal solution. The ideal solution according to Glasstone[17] is one which obey's an idealized form of Raoult's Law, namely, that the partial vapor pressure of any component of a liquid solution is equal to the product of its mole fraction and its vapor pressure in the pure state over the whole range of composition and at all temperatures and pressures. From this definition, it can be shown that the heat of mixing for an ideal solution is zero.[18] It is for this reason that we say that our solutions deviate only slightly from the ideal solution.

Experimental Accuracy

Calculations showed that the maximum error in the weighing of the liquids did not exceed 0.05%. The maximum error in the measurement of the amount of electrical energy disipated in the heating coil was found not to exceed 0.10%.

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[16] Lange, ed., "Handbook of Chemistry," 7th Ed., Handbook Publishers Inc., Sandusky, Ohio, 1949, pp. 1555-1557.

[17] S. Glasstone, "Thermodynamics for Chemists," D. Van Nostrand Company, Inc., New York, N. Y., 1953, p. 317.

[18] For proof of this cf. Ibid., p. 318.

The stirring of the liquids was a source of error since the falling of the weight in the calorimeter produced heat. This effect was compensated for by stirring at a constant rate. When this was done, the slope of the cooling curve was changed but it extrapolated back to the same point as it would have if there had been no stirring. Therefore, the heat caused by the stirring cancels out, and there was no appreciable error in neglecting the stirring effect.

Probably one of the most important sources of error in the measurements was the uncertainty in extrapolating the heating and cooling curves back to zero time. The cooling curves obtained were linear and so the uncertainty was probably small. Nevertheless, there was a certain amount of uncertainty in the extrapolations due to slight fluctuations in the galvanometer. In order to estimate this uncertainty, the following procedure was used: For each of several different experiments covering a range of deflection, the maximum and minimum values for the deflections d_1/d_2 were calculated and the % difference between these values obtained. Table 6 shows the results of these calculations.

Table 6

Percentage Difference Between the Ratio (d_1/d_2) max. and (d_1/d_2) min. for Different Values of d_1

d_1 (avg.)	% Difference
2.04	4.0
2.34	3.6
6.40	1.2
7.55	.9
14.78	1.0

As would be expected, the percentage difference was greater when the heat change was smaller and hence, any instability in the system leading to an uncertainty in the extrapolations was more serious here. It must be realized, however, that these values represented the extreme extrapolations and did not correspond to the best possible straight lines which could be drawn through the points. It is estimated that the probable error in obtaining the best possible lines in the extrapolations does not exceed half of that given in table 6. The error in correcting for extrapolation would probably not exceed 1% for deflection of the galvanometer greater than about 4 cm. and would not exceed 2% for deflections between 2 and 4 cm.

Any impurities present in the liquids might lead to erroneous results. For this reason, care was taken in the selection and purification of these liquids, in order that practically no error would be introduced due to any impurities which might be present. In the case of the benzene and carbon tetrachloride, reagent grade materials were chosen. These liquids were then fractionally distilled in a Todd still with a 2.5 x 100 cm. "Heli-pack" filled column at a reflux ratio of about 10:1. When this was done the refractive index of the liquids agreed with the best published values[19] to 2 parts in 4000. To get this agreement with the benzene, it was necessary to fractionally crystalize the benzene out of its own solution. When this was done, the refractive index of the benzene agreed with the best published values to 1 part in 5000. In the case of the cyclohexane, spectro grade material was used. No further purification was thought necessary since the refractive index of the

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[19] Timmermans, J., "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., New York, N. Y., 1950.

cyclohexane agreed to within 3 parts in 4000 with the literature values.[19]

It is thought that after this procedure, the purity of the liquids would be such that any impurities present would introduce no measurable errors in the determinations. These impurities would be so like the liquid whose heat of mixing is to be measured, that their contribution to the heat change in the calorimeter would be about the same as if it were the same liquid as that whose heats of mixing is being measured.

It had been assumed in the measurements of these heats of mixing that the deflection of the galvanometer is proportional to the electrical current through it and also to the heat change in the calorimeter. It was therefore necessary to test the galvanometer to find if this was a valid assumption before any significance could be given to the results. It was shown that the deflection of the galvanometer is proportional to the current through it as follows: The electrical circuit was set up as shown in figure 12. Here R, H, and S, are variable resistors; G is a galvanometer; B is a battery whose terminal potential difference is V; and i, i_s, and i_g are currents through the various circuit elements as shown in the diagram. From the values of R, H, S, G, and V, the current through the galvanometer can be calculated. This is done as follows: From Kirchhoff's laws of electrical circuits

$$(60)\quad (G + H)i_g = S(i - i_g)$$

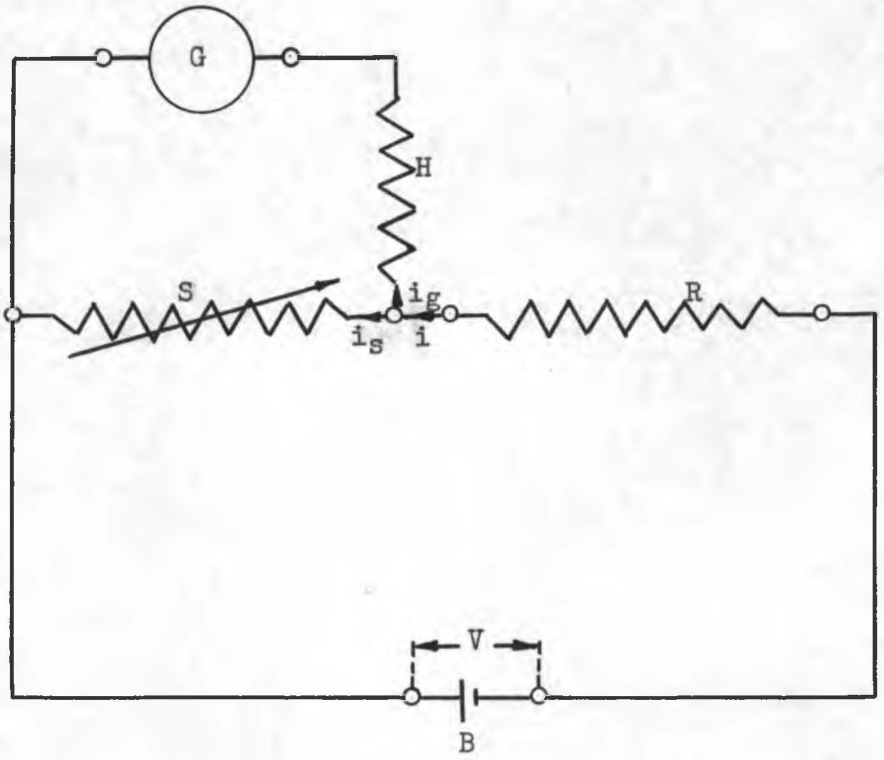
$$(61)\quad V = iR + S(i - i_g)$$

From these, we eliminate i and get

$$(62)\quad i_g = \frac{SV}{(G + H + S)(R + S) - S^2}$$

In our experiments, we set H at 10,000 ohms, R at 5,000 ohms, and measured G to be 17.7 ohms and V to be 2.874 volts. S was then

Figure 12



Electrical Circuit Used for Testing the Linearity of the Galvanometer

Key

B - Battery
G - Galvanometer
H - Resistor
R - Resistor
S - Shunt
V - Potential Drop Across the Battery
i - Current from the Battery
i_g- Current through the Galvanometer
i_s- Current Across the Shunt

varied to get different deflections. Table 7 and figure 13 show the results of these measurements. A double pole-double throw switch was put into the circuit thus making it possible to take deflections on both sides of the scale.

Table 7

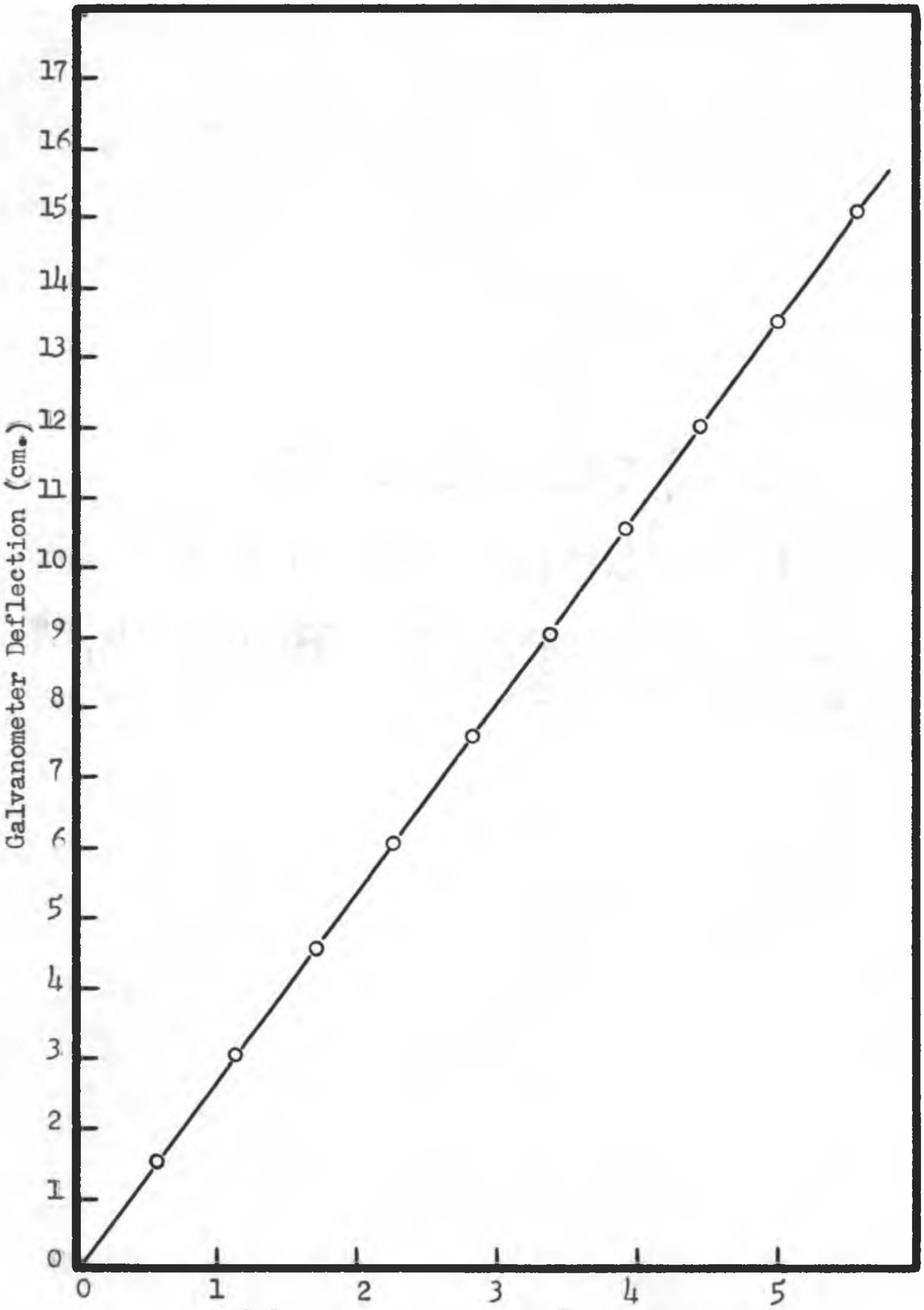
The Deflection of the Galvanometer on Both Sides of the Scale for a Given Current Through the Galvanometer

$i_g \times 10^6$ (amperes)	d (red)	d (black)
.572	1.53	1.52
1.141	3.06	3.05
1.706	4.58	4.58
2.268	6.08	6.08
2.826	7.57	7.56
3.382	9.06	9.06
3.933	10.55	10.57
4.482	12.02	12.02
5.027	13.48	13.52
5.570	14.92	15.07

It is evident from figure 13 that the data from table 7 plot a straight line and that there is very little difference between the deflection on the different sides. The assumption then that the deflection of the galvanometer is proportional to the current through it is a valid one.

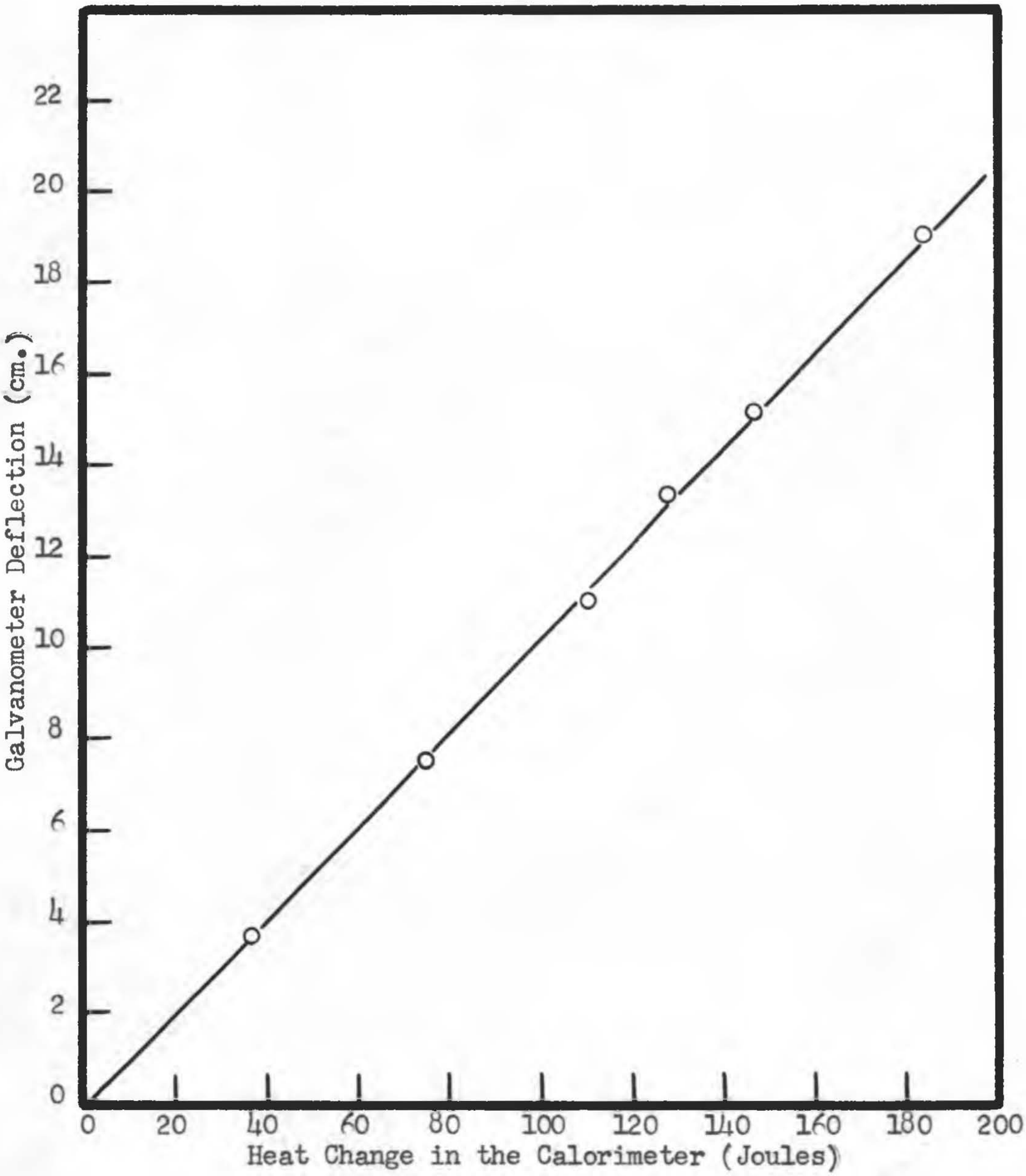
To show that the deflection of the galvanometer is proportional to the heat change in the calorimeter, different amounts of electrical heat were put into the calorimeter and the deflection of the galvanometer noted. Figure 14 and table 8 show the results of these experiments.

Figure 13



Plot of Deflection of the Galvanometer Against the Current Through the Galvanometer Which Causes This Deflection

Figure 14



Plot of Deflection of the Galvanometer Against the Heat Change in the Calorimeter Which Causes the Deflection

Table 8

Deflection of the Galvanometer for a Given Heat Change in the Calorimeter

Deflection (cm)	H (joules)
3.66	37.2
7.42	74.2
11.01	110.5
13.30	127.7
15.18	147.8
18.52	184.0

It is evident from figure 14 that the assumption that the deflection of the galvanometer is proportional to the heat change in the calorimeter is a valid one. There appears to be a slight curve in the line toward the upper end. However, very few measurements were made in which the deflection went this high. Also, in the calculations of the heats of mixing, only ratios of deflections were taken. These deflections were roughly the same and so any nonlinearity would partly cancel out.

In summary, it is thought that for the most part the accuracy of the measurements is within 1%.

Future Work

There is still much work to be done with heats of mixing. Before any significant theoretical considerations can be made for nonelectrolytic solutions, more thermodynamic data such as volume, entropy, free energy, and energy changes must be obtained. This paper presents data dealing with solutions in which there are only nonpolar molecules present. There is still much work to be done with these types of systems, but

There is even more work to be done with systems which contain polar molecules. Scatchard[8] has done some work with the methanol-carbon tetrachloride system. His results indicate that there are regions in his plot of mole fraction against heat of mixing in which the heats of mixing are positive and other regions where the heats of mixing are negative. Furthermore, although there are not enough data available to draw any definite conclusions, there appear to be points of discontinuity on his curve where the slope changes abruptly. M. L. Huggins[20] has recently published what appears to be a successful approach to the interpretation of this type of data. He described partial molar volume versus composition curves for the systems methanol-water, dioxane-water, ethanol-water, and methanol-(butyl-sebacate) and observed the same type of behavior as Scatchard[8] did for his methanol-carbon tetrachloride system. He postulated that the breaks in the curves when any extensive thermodynamic property is plotted against a composition function are due to the formation of loosely co-ordinated stoichiometric compounds. These compounds he calls "structons." He has also done some work with two-component silicate glasses. By the choice of reasonable sets of structon types, he has been able to account quantitatively for the abrupt breaks in the volume-composition curves for the glasses. Much work still needs to be done, however, to investigate further his proposals.

Summary

A calorimeter was constructed for accurately measuring the heats of mixing of various nonelectrolytic solutions. The heats of mixing were

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[20] M. L. Huggins, J. Phys. Chem., 58, 1141 (1954).

then measured at 25.0°C for the binary systems carbon tetrachloride-benzene, benzene-cyclohexane, and carbon tetrachloride-cyclohexane, and for the ternary system carbon tetrachloride-benzene-cyclohexane. The heats of mixing were measured at various mole fractions and the results expressed empirically as a function of mole fraction by use of the equations developed by Redlich and Kister.[13]

The behavior of the systems were then discussed and correlated with the use of the Redlich and Kister[13] equation.

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CALORIMETRIC HEATS OF MIXING OF SOME NONELECTROLITIC BINARY AND TERNARY SOLUTIONS

AN ABSTRACT
OF A THESIS SUBMITTED TO
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In Partial Fulfillment
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Master of Science

by
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ABSTRACT

The heat of mixing of nonelectrolytic liquids is important in predicting the type of molecular interactions which exist in solutions of nonelectrolytes. The problem was to construct a calorimeter in which these heats of mixing could be measured accurately. Once constructed, the calorimeter was used to measure the heats of mixing of some binary and a ternary solution.

The systems chosen for study were the three liquid pairs formed between benzene, carbon tetrachloride, and cyclohexane, and the ternary mixture of the three. The results of the experimentation are summarized by the following equations.

$$(1)\quad H_{12}^{M} = x_1x_2\left[103.2 + 13.1(x_1 - x_2) - 13.3(x_1 - x_2)^2\right]$$

$$(2)\quad H_{23}^{M} = x_2x_3\left[729.6 + 102.4(x_2 - x_3)^2\right]$$

$$(3)\quad H_{13}^{M} = x_1x_3\left[160.8 + 18.9(x_1 - x_3) - 20.2(x_1 - x_3)^2\right]$$

$$(4)\quad H_{123}^{M} = H_{12}^{M} + H_{23}^{M} + H_{13}^{M} + x_1x_2x_3\left[128 + 161(x_1 - x_3) - 1636(x_1 - x_3)^2\right]$$

where H^M stands for heat of mixing and x for mole fraction. Here, (1) is carbon tetrachloride, (2) is benzene, and (3) is cyclohexane. The value of the heat of mixing as calculated from the equation has the dimensions of calories per mole. The measurements were all made at 25.0°C.

The plots of heat of mixing against mole fraction for the three binaries are approximately symmetrical with respect to the line x = 0.500. The plot for the ternary mixture is symmetrical with respect

to the line $x_3 = 0.44$. Furthermore, the heats of mixing of the ternary can be predicted from the binaries to within 5%.