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degree of

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BY

JOHN FRANCIS PEREIRA

Norman, Oklahoma

1963

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CHAPTER I

INTRODUCTION

Our present knowledge of the theory of solutions is not sufficient to enable us to calculate the thermodynamic properties of mixtures of polar liquids from the properties of the pure components. Attempts have been made by Barker (1), (2) and others (3) and (4) to treat polar liquids by means of a quasi-lattice model, where the lattice points are occupied by atoms or groups of atoms, and where intermolecular contact energies of various magnitudes are assumed to exist between the different atomic groups which are not connected by chemical bonds. This model makes necessary a complicated evaluation of the parameters (the energies of the different intermolecular contacts). It has been partially successful when applied to alcoholic systems, but unsuccessful when applied to mixtures of water with polar organic compounds (15). In mixtures where strong intermolecular attraction leads to the formation of stable aggregates of molecules, present theories are inadequate.

In the case of systems where strong hydrogen bonds are formed, it is necessary that reliable experimental measurements of thermodynamic constants be obtained before further improvements can be made on our current theories of solutions. Solutions of carboxylic acids are of particular interest because of the existence of strong hydrogen bonds and the tendency toward formation of dimers, as opposed to higher polymers, in dilute solutions. Self-association occuring via predominantly electrostatic type of interaction (5) of carboxylic acids and solutions of carboxylic acids in non-polar solvents has been widely investigated. Christian (6) has shown, from liquid-vapor equilibrium data, that the system propionic acid - acetic acid behaves ideally. Tendency to form hetero-dimers rather than the homo-dimers has been observed by Hansen and Christian (7) for the systems acetic acid - trifluoroacetic acid, propionic acid - pentafluoropropionic acid and n-butyric acid - hepta - fluoro-n-butyric acid, from liquid-vapor equilibrium studies. Added evidence for cross-dimer formation has been provided by an infra-red study of the system acetic acid - trichloroacetic acid in CCl_4 (8). As far as is known no calorimetric measurements have been reported for mixtures in which cross-association of the simple carboxylic acids would be expected to occur.

It is generally agreed (10),(11) and (12) that concentrated solutions of carboxylic acids and their halogen-substituted acids (and thus also the pure liquids) contain some polar aggregates larger than the dimer. There is no general agreement as to whether the individual hydrogen bonds of these aggregates are on the average weaker or stronger than those in the dimer (11),(12) and (13). Harris and Alder (14) advance the theory that there exists a zwitterion structure (in which the carboxylic acid homo-dimer forms an ion pair by transfer of a proton from one monomer unit to the other) in equilibrium with the non-polar dimer. This self-ionised model of the dimer has recently (10) been used in a dielectric study of the carboxylic acid dimers to account for larger dielectric constants of pure carboxylic acids than can be explained on the basis of a symmetric dimer and also to account for the significant increase in the dielectric constants with rising temperature. In any event, if the proposed zwitterion structure exists in the homo-dimer, then as suggested by Kohler (15) the zwitterion structure would be much more important in the hetero-dimer. In fact, the formation of a zwitterion structure may be one of the factors inducing the preferential formation of hetero-dimers.

The calorimetric investigations described here were undertaken to provide additional information on the associative behaviour of acetic acid and trifluoroacetic acid. Systems to be investigated were binary and ternary mixtures (in the CCl_4 - rich regions) containing trifluoroacetic acid, acetic acid and CCl_4. For the three binary systems to be investigated, the only calorimetric data which have been reported are heats of dilution of acetic acid in CCl_4 (9).

Since, in the present study sufficient quantities of all chemicals were available, it was not necessary to measure small heat effects with high precision in a simple calorimeter. Instead, it was proposed that a method be devised in which heat effects of the same order of magnitude would be measured in each experiment, so that errors due to heat exchange with the surroundings would be minimized. Further, it was essential that falsification of results by corrosion of the calorimeter material or by the presence of moisture be carefully avoided. In addition, it was required that errors due to volatilization of components and incomplete mixing be minimized.

CHAPTER II

OBJECTIVES

The primary object of this study was to determine heat of mixing values calorimetrically for binary and ternary mixtures involving the three compounds trifluoroacetic acid, acetic acid and CCl_4. Specifically, the following regions were to be investigated; a) all three binary systems over the entire concentration range; b) the ternary system obtained by adding pure acetic acid to 1:9 molar mixtures of trifluoroacetic acid-CCl_4; c) the ternary system obtained by adding pure trifluoroacetic acid to 1:9 molar mixtures of acetic acid - CCl_4; d) the ternary system obtained by adding increasing quantities of 1:9 molar mixtures of trifluoroacetic acid - CCl_4 to 1:9 molar mixtures of acetic acid - CCl_4.

The second major goal of the investigation was to interpret heat data in terms of interactions between functional groups present in the molecules. Of particular interest was the relation between formation of the hetero-dimer and the tendency toward exothermic mixing.

A third objective was to construct a suitable calorimeter and to develop an accurate method for investigating heat effects in the above systems, in which corrosive, hygroscopic and volatile mixtures would be involved.

CHAPTER III

EXPERIMENTAL

Materials

Except for the components of two test systems, distillation of all compounds was carried out in a 4 foot long vacuum-jacketed column, built here, packed with glass beads and employing a Whitmore-Lux type head. The middle fractions only of small samples of each component were collected in dry flasks and used as soon as possible after distillation. The distilled materials were stored away from light in small glass stoppered flasks over anhydrous calcium chloride in desiccators. Dioxan and chloroform were stored in flasks provided with a long capillary (to keep out moisture) and topped with standard glass stoppers.

Since the refractive indices of small batches of each material were measured at slightly differing temperatures, these were checked with the interpolated or extrapolated values, between two or more temperatures, of the best recently published data. The determined refractive indices (reduced to a single temperature for each component) and freezing points, together with the literature values are given in Table 1°.

Technical grade m-cresol and quinoline were each distilled once under reduced pressure. Dioxan (1:4 dioxan) and chloroform (both technical grades) were purified according to the method of Vogel (16). Analar

Table 1. Refractive Indices (see text) and Freezing Points

component	Refractive Index		F.P. (°C)	
	determined	literature	determined	literature
quinoline	-	-	-21.6 ±0.2	-19.5
m-cresol (18°C)	1.5425 ±0.0002	1.5425	-	
dioxan (23°C)	1.4222 "	1.4224	-	
$CHCl_3$ (23°C)	1.4442 "	1.4441	-	
CH_3COOH (20°C)	1.3715 "	1.3715	+16.6 ±0.2	+16.6
CCl_4 (20°C)	1.4604 "	1.4604	-	
CF_3COOH	-	-	-15.4 ±0.2	-15.25

Table 2. Comparision of experimental and interpolated literature (21) Q values for heats of solution of KCl at 25°C

H_2O (moles)	KCl (moles)	h H_2O(moles)/KCl(moles)	Q (calories) (experimental)	Q (calories) (literature)
5.6656	0	125.1515	+194.6	+189.4
5.8735	0	112.4751	+223.5	+218.0
5.7241	0.05653	50.6379	+232.2	+227.0

potassium chloride which had been dried for 48 hours at 150°C and had been stored over anhydrous calcium chloride in a desiccator and double distilled water were used in the heats of solution studies of KCl. Analar glacial acetic acid was dried by refluxing over P_2O_5 (17) and fractionally distilled once over P_2O_5. Trifluoroacetic acid, from Matheson Coleman and Bell Co., was first rapidly distilled to remove suspended impurities, and after drying over P_2O_5 (18) was fractionally distilled once over P_2O_5. Carbon tetrachloride (Analar) was purified by the method of Williams and Krchma (19) and then fractionally distilled once in a dry atmosphere.

Calorimeter

A cross section of the calorimeter , Figure 1, and a cross section of the mixing vessel, cover and its accessories, at right angles to Figure 1, is shown in Figure 2. The round bottom mixing vessel H, made of monel metal (0.05 cm thickness) has an effective volume of approximately 129 ml. Since the volume of the liquid in the mixing vessel has been slightly over 100 ml (see page 15) a vapor space of less than 30 ml existed in each set of experiments.

A carefully machined molded polyethylene stopper Q, permanently screwed to a wooden cover, fits both the mixing vessel and the commercial Dewar vessel M. To prevent accidental slipping of the mixing vessel, in the course of an experiment, small removable pins are inserted through holes drilled near its rim. Through the polyethylene stopper passes a monel metal shaft, fitted with two four-bladed coaxial monel metal stirrers. A constant speed electric motor, coupled to a long flexible drive shaft, rotates the stirrer at a moderate speed. The direction of rotat-

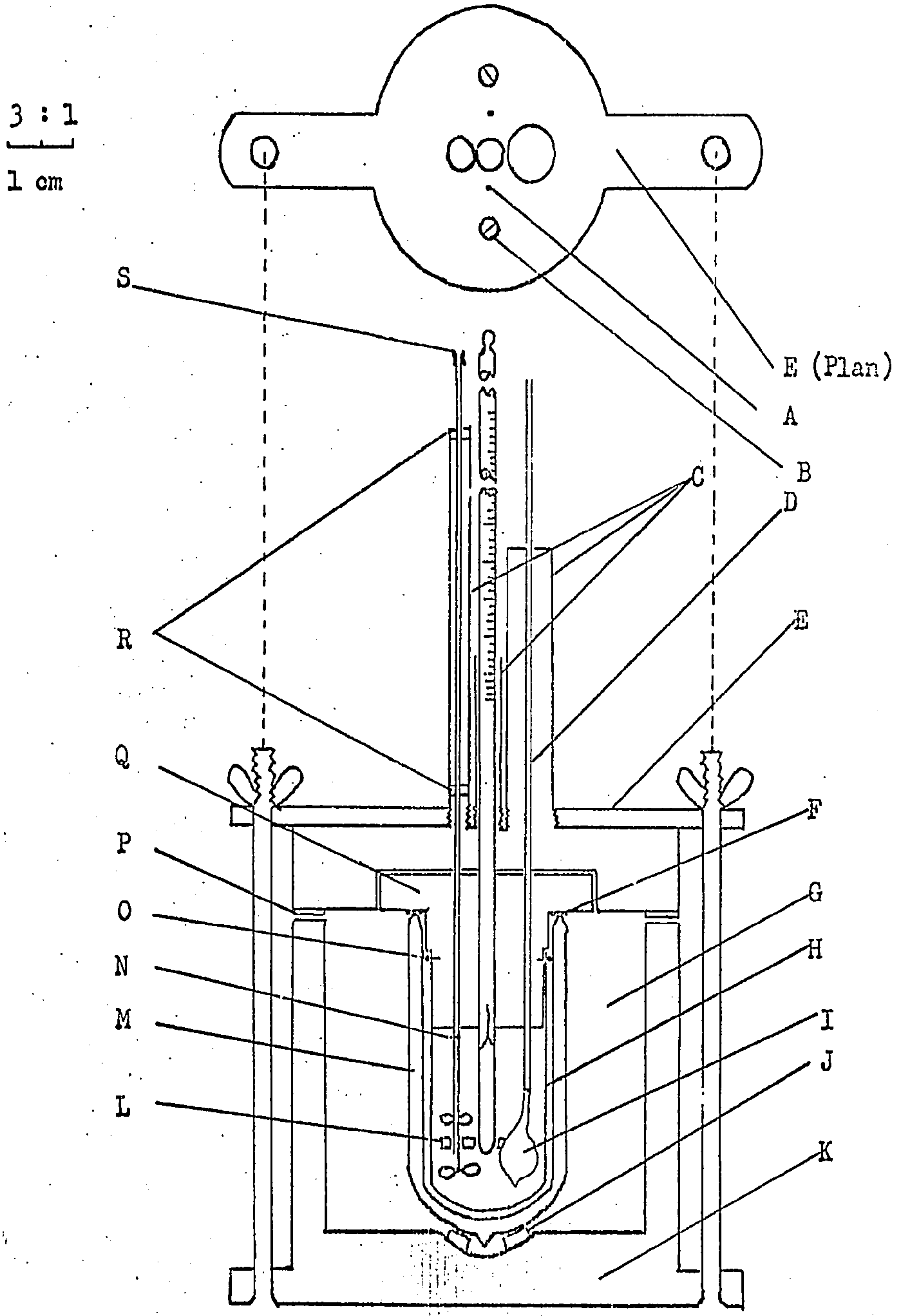


Fig. 1. Cross section of calorimeter: A, heater leads; B, screws; C, aluminum tubes; D, polyethylene tubing; E, aluminum plate; F, neoprene gasket; G, styrofoam packing; H, mixing vessel; I, glass ampoule; J, felt padding; K, wooden box; L, calorimeter heater; M, Dewar vessel; N, machined groove; O, steel pins; P, urethane foam; Q, polyethylene cover; R, teflon bearings; S, stirrer connection

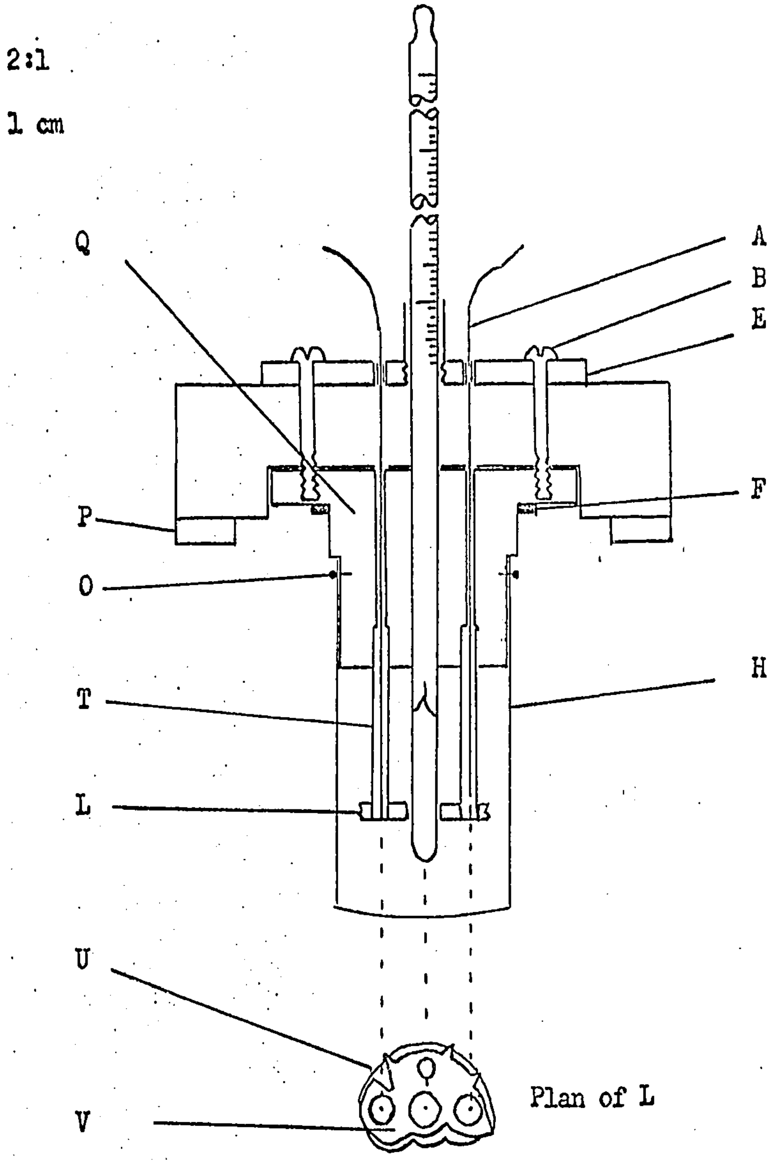


Fig. 2. Mixing vessel, cover and accessories: cross section at right angles to Fig. 1. A, heater leads; B, screws; E, aluminum plate; F, neoprene gasket; H, mixing vessel; L, calorimeter heater; T, teflon posts; O, steel pins; P, urethane foam; Q, polyethylene cover; U, constantan wire; V, teflon brace

ion is arranged to induce a downward flow of liquid. The stirrer shaft, which rides on two narrow teflon bearings R, has a machined constriction N to reduce heat flow along the stirrer shaft, either into or out of the mixing vessel.

On a serrated and grooved teflon brace V, Figure 2, held up by two teflon posts T, is wound non-inductively No. 24 B and S gage constantan wire having a resistance of approximately 0.5 ohms. This constitutes the calorimeter heater. Enamelled copper wires (No. 16 B and S) were silver soldered to the ends of the calorimeter heater and acted as current and voltage leads. The leads pass out of the calorimeter through the center of the teflon posts.

Sealed glass ampoules, I, containing 3 to 15 ml of accurately weighed liquid samples, were stored in darkness. While filling ampoules, using a hypodermic syringe and needle, the air space in the ampoule was kept to a minimum (15). All filling operations were conducted in the dry box. The loaded glass ampoules, in an experimental determination, are held in position in the calorimeter by the small amount of friction between the smooth polyethylene sleeve D (placed along the length of the aluminum tube C) and the glass rod fused to the ampoule. To mix the liquids the ampoule is crushed against the bottom of the mixing vessel by pushing down on the glass rod.

Auxillary Apparatus

In the electrical diagram, Figure 3, S_3 is a specially made spring loaded mercury-pool type switch. This switch, in addition to being rapid, also ensures good electrical contacts. The sodium silicate coated resistors, R_1, R_2 and R_3 (each of No. 24 B and S gage constantan)

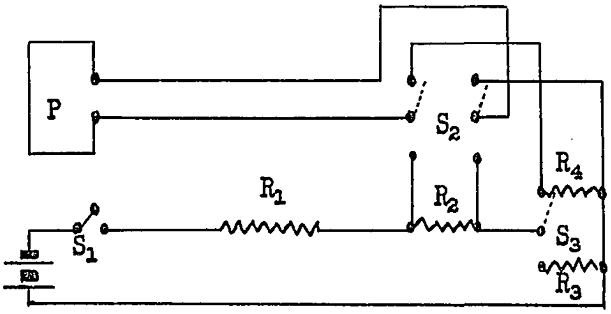


Fig. 3. The electrical circuit
P, Potentiometer; R_1, auxillary resistor; R_2, standard resistor; R_3, ballast resistor; R_4, calorimeter heater; S_1, switch; S_2, mercury pool switch; S_3, spring loaded mercury pool switch

are wound non-inductively on short length glass tubings and immersed in an oil-bath, whose temperature is maintained as close as possible to that existing in the mixing vessel. R_1 is the auxillary resistor (approximately 1 ohm), R_2 the standard resistor (approximately 0.5 ohm) and R_3 the ballast resistor (approximately 0.5 ohm). No. 16 B and S gage enamelled copper wires silver soldered to the ends of the resistors serves as current and voltage leads. Current is provided by two 6-volt accumulators connected in parallel and operating at about 70% efficiency. The accumulators are discharged for nearly an hour through the ballast resistor before switching on to the calorimeter heater . The voltage in the potentiometer circuit is provided by two 2-volt accumulators connected in parallel. Potential and resistance standards consist of a Weston cell and a Gray Institute and Co. 10 ohm resistor, respectively.

A Leeds and Northrup K_2 Type Potentiometer is used to measure the potential to ±0.0001 v, across the two approximately 0.5 ohm resistors, R_2 and R_4, during the heating period. The mean of periodically checked resistances of R_2 was, 0.4168 ±0.0008 ohm. With the calculated resistance (see equation 8) of R_4, the electrical energy passed during the heating period, for a specific length of time (determined by a calibrated stop-watch) is readily calculated. Correction for dissipation of electrical energy in the leads of R_2 and R_4 is negligible since the leads had approximately equal lengths. Temperatures are read to ±0.002°C with a 22-33°C calorimetric thermometer graduated to 0.01°C.

Procedures for Measurement and for Preparing Mixtures for the Various Systems

Since the volume of the ampoule was restricted, and since the heat effect should not exceed a certain limit, the content of the ampoule was added either to a pure component or to a mixture of suitable concentration. For binary systems, measurements were begun at one end of the mole fraction scale and were carried out to about 0.5 mole fraction. Between two and five replicate determinations were made when additions to a pure component were involved. Measurements were then made (i.e., when adding to mixtures) so that in a given determination the concentration before mixing was within, and then outside of, the final concentration range of the preceding determination. Similar measurements were repeated starting from the other end of the mole fraction scale. Several determinations were made around the mid-point of the mole fraction scale. For two ternary systems, where the mole ratio of two components was kept constant, measurements were made by adding a pure component initially to the standard binary mixture and subsequently to ternary mixtures consisting of the standard binary mixture and increasing amounts of the component contained in the ampoule. At least two measurements were made when two components only were present. Measurements were then made so that in a determination, the concentration before mixing was within, and then outside of, the final concentration range of the preceding measurement. The heats of mixing and derived heat values were plotted against the mole fraction of the component contained in the ampoule.

For one ternary system, system 8, (see Appendix I) where the mole fraction of one the components was kept constant, measurements were made starting from one end of the mole fraction scale of the deficient component (trifluoroacetic acid), by adding one standard binary mixture initially to the other standard binary mixture, and subsequently to mixtures of varying quantities of the two standard binary mixtures. Measurements were repeated starting from the other end of the same mole fraction scale.

Liquid mixtures were prepared by weight, to within ±0.0002 g, in 100 ml volumetric flasks whose standard ground glass stoppers and sockets were replaced by $ 15/35 ground glass stoppers and sockets. Each mixture was prepared with a minimum of vapor space in the volumetric flask, immediately prior to an actual measurement. The very small quantity of liquid remaining in the volumetric flask, after being emptied as quickly as possible into the calorimeter, was always weighed. Stock solutions of standard binary mixtures (for ternary systems) were prepared by weight. All mixture preparations and pouring operations were conducted in a dry box.

Actual Measurement

After loading the calorimeter, having ascertained that no liquid adhered in the capillary part of the ampoule, the mixing vessel and its contents were cooled below room temperature and assembled in the cooled and dried Dewar vessel (see Figure 1). The temperature of the contents in the mixing vessel was adjusted so that, in exothermic reactions after mixing and in endothermic reactions before mixing, the temperature would always be a few degrees (3-8°C) below room temperature yet in the vicinity of 25°C.

After a thermal equilibrium period lasting one to one and one-half hours, time temperature readings were made every half minute for 5 minutes, and during the mixing period every 15 seconds for 1 minute and then at 1/2 minute intervals for about 10 minutes. Stirring was continous, starting from the beginning of the thermal equilibrium period and ending with the last temperature of the after period. In the calibration experiment, which immediately followed, the entire procedure followed in the mixing period was repeated, except that the mixing period was replaced by the electrical heating period. The length of the heating period was adjusted so that the absolute magnitude of the temperature change and the temperature range closely approximated conditions in the mixing experiment. The time of the heating period and the potentials across R_2 and R_4 were measured.

Treatment of Temperature- Time Readings

In two of the test systems investigated, the temperature differences were obtained from time- temperature plots by extrapolation of the after period temperatures to the time of mixing; while for the remaining systems the temperature differences were calculated by the Roth (20) method. The theory of the method is given in Chapter IV and a sample calculation (for exothermic mixing) in Appendix III.

The difficulty of graphical extrapolation is that the exact time to which the extrapolation should be carried out depends on the "convergence temperature" in a complicated way. On the other hand, the Roth method avoids the necessity of selecting arbitrarily a time to which temperature-time curves must be extrapolated. Thus in the graphical extrapolation an unknown error is introduced; the relative importance of which varies with the magnitude of the correction for heat leakage.

The smaller the heat effect, the smaller the specific heat of the calorimeter and the poorer the insulation of the calorimeter the more significant this error becomes.

CHAPTER IV

CALCULATION PROCEDURES

Calculation of Temperature Changes by Roth (20) Method

The theory of the Roth method for calculating the magnitude of the temperature change in a calorimetric experiment is given below. (An example of the application of the method appears in Appendix III).

According to Newton, the rate of cooling (best for 1/2 minute temperature intervals) is given by

$$d\theta/dt = k(\theta - \theta_{\infty}) \tag{1}$$

where k is designated as "cooling constant" of the calorimeter and θ_{∞} the "convergence temperature" i.e., the temperature the calorimeter would attain at infinite time. If $\bar{\theta}_1$ and $\bar{\theta}_2$ represent mean temperatures and G_1 and G_2 the rates of cooling for the fore and after periods, respectively, then,

$$G_1 = k(\bar{\theta}_1 - \theta_{\infty})$$

$$G_2 = k(\bar{\theta}_2 - \theta_{\infty})$$

and upon eliminating θ_{∞} from the two equations, one obtains

$$G_1 - G_2 = k(\bar{\theta}_1 - \bar{\theta}_2)$$

or,

$$k = \frac{G_1 - G_2}{\bar{\theta}_1 - \bar{\theta}_2} \tag{2}$$

Substituting $\theta_{\infty} = \bar{\theta}_1 - G_1/k$ and for k, equation 1 becomes

$$d\theta/dt = \frac{G_1 - G_2}{\bar{\theta}_1 - \bar{\theta}_2}(\theta - \bar{\theta}_1) + G_1 \qquad (3)$$

For the sake of clarity, Kohler (15) has suggested the following two steps: according to the heat exchange with the surroundings, the temperature at the end of the reaction period appears to be

$\theta_{end} = \theta_{true} + \int_0^t \frac{d\theta}{dt}dt$, where θ_{true} is the (hypothetical) temperature if no heat exchange would occur and t is the interval of the reaction period. Therefore,

$$\theta_{true} = \theta_{end} - \int_0^t \frac{d\theta}{dt}dt$$

$$= \theta_{end} - \sum\left[k(\theta - \bar{\theta}_1) + G_1\right] \qquad (4)$$

where the summation extends over all time steps of the reaction period, and where θ is the mean temperature during each temperature interval.

G_1 and G_2 are taken as properly weighted averages of the temperature differences per time interval. If n (n being an even integer) temperature readings are made, then

$$d\theta/dt = G_1 = \frac{(n-1)(A_n-1) + (n-3)(A_{n-1} - A_2) + \ldots\left[n-(n-1)\right](A_{n/2+1} - A_{n/2})}{(n-1)^2 + (n-3)^2 + \ldots\ldots\ldots\left[n-(n-1)\right]^2}$$

$$= \frac{(n-1)(A_n-A_1)+(n-3)(A_{n-1}-A_2)+(n-5)(A_{n-2}-A_3)+\ldots}{n(n+1)(n-1)/1.2.3} \qquad (5)$$

where A_1 and A_n are the first and last temperature readings respectively.

Determination of Integral Molar Heats of Mixing

For binary systems, for the first points, the ΔH_{ij} (see Appendix II for symbols used) values were obtained by using the expression

$Q = \Delta H_{ij}$ (which is inserted in the plot at x_i, final)$x(n_i+n_j)$ (6)

where Q is given by

$$\frac{V_4\ t\ \Delta T_m}{r_4\ 4.1840\ \Delta T_c} \tag{7}$$

Here, V_4(volts) is the potential across R_4, t (seconds) is the electrical heating time and r_4 (ohms) is the resistance of R_4 and is calculated by

$$r_4 = V_4\ 0.4267/V_2 \tag{8}$$

For the next points

$Q + \Delta H_{ij}$ (read from a plot at x_i, initial) x $(n_i + n_j) = \Delta H_{ij}$ (which is inserted in the plot at x_i, final) x $(n_i+n_i'+n_j)$ (9)

Thus a plot of ΔH_{ij} versus $(x_i)_{ij}$, starting from $(x_i)_{ij} = 0$, is constructed. An identical procedure gives a plot of ΔH_{ij} versus $(x_i)_{ij}$, starting from $(x_i)_{ij} = 1$.

For ternary systems 6 and 7 (see Appendix I for abbreviations used) the expression

$Q + \Delta H_{ijk}$ (which is read off the plot at x_i, initial) x $(n_i+n_j+n_k)$
$= \Delta H_{ijk}$ (which is inserted in the plot at x_i,final) x $(n_i+n_i'+n_j+n_k)$ (10)

has been used to determine the ternary integral molar heats of mixing. An identical procedure as that followed for systems 6 and 7 has been applied to system 8 for determining $\Delta H_{12,23}(0,0)$ and $\Delta H_{12,23}$.

An independent calculation has been made which involves the experimental quantities in each measurement and the partial molar heats of the corresponding binary systems, for each system 6 and 7. For system 8, the integral molar heats of mixing were similarly obtained, due account being taken of the partial molar heats of the components in the ampoule (15). The results obtained by this method, for the three ternary systems, are in substantial agreement with the results obtained by the above graphical method.

CHAPTER V

RESULTS ON TEST SYSTEMS

Table 2 lists results of test determinations of the heat of solution of KCl in H_2O at 25°C. The observed experimental Q values (obtained using Roth (20) method to calculate temperature changes) are all within 3% of the interpolated literature values (21). The reaction and heating periods in each experiment were arranged to be the longest possible. Calculations indicated that corrections for enthalpy effects (22) in the vapor on mixing and for reducing the experimental Q values to a standard temperature (25°C) were negligible.

In Table 3 are represented the experimental heats of mixing values for the quinoline - m-cresol system, the first system investigated, and in Figure 4, the experimental and literature values of the heat of mixing have been plotted. The deviation from literature values is explained by the fact that in this test system each successive measurement, starting from either end of the mole fraction scale, was made by adding a pure component to the mixture of the preceding experiment. In all subsequent experiments the method was modified (see page 14) so that fresh mixtures were prepared for each measurement. In this way several independent determinations could be carried out for each concentration interval. The method of measuring potentials in the calibration experiments gave

Table 3. Experimental integral molar heats of mixing for system quinoline - m-cresol

quinoline (moles)	m-cresol (moles)	$x_{quinoline}$	Q (calories)	ΔH^E (cal/mole)
-	-	0	-	0
0	0.9356	0.0201	-108.34	-113.5
0.0192	"	0.0422	-118.87	-232.6
0.0412	"	0.0636	-118.55	-346.1
0.0634	"	0.0848	-118.29	-453.9
0.0867	"	0.1051	-117.01	-555.8
0.1100	"	0.1243	-108.96	-645.8
0.1328	"	0.1434	-112.11	-734.4
0.9092	0.1756	0.8187	- 88.52	-675.5
"	0.1507	0.8381	- 88.35	-610.0
"	0.1265	0.8579	- 85.36	-541.0
0.9748	0.1101	0.8824	- 69.67	-441.7
"	0.0867	0.8985	- 84.28	-385.6
"	0.0639	0.9183	- 83.48	-314.7
"	0.0400	0.9385	- 88.54	-241.2
"	0.0177	0.9606	- 81.46	-159.6
"	0	0.9822	- 80.55	- 81.1
-	-	1.0000	-	0

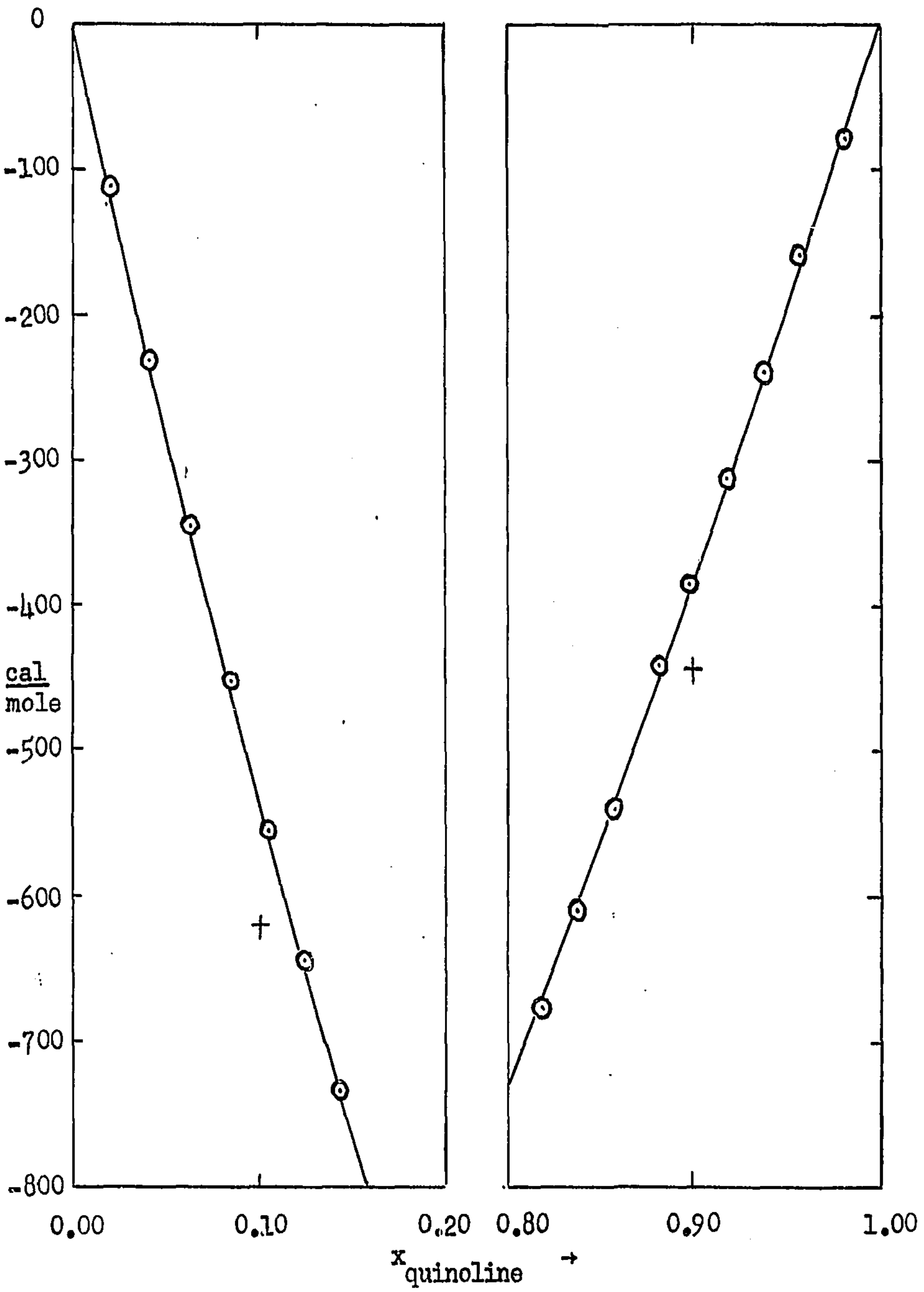


Fig. 4. Integral molar heats of mixing for system quinoline - m-cresol. Circles with dots, experimental; crosses, Tschamler and Krischai (23)

Table 4. Experimental integral molar heats of mixing for system dioxan-chloroform

dioxan (moles)	chloroform (moles)	x_{dioxan}	Q (calories)	ΔH^E (cal/mole)
-	-	0	-	0
0	1.53704	0.0271	-109.78	- 69.5
0	1.22724	0.0281	- 93.46	- 74.0
0	0.92209	0.0371	- 86.79	- 90.6
0.07995	1.14273	0.0941	- 72.81	-216.9
0.21280	0.99627	0.1986	- 56.09	-375.8
0.32318	0.88149	0.2918	- 41.03	-464.3
0.46288	0.73137	0.4037	- 18.39	-499.6
0.74368	0.43211	0.6048	- 47.77	-422.7
0.93650	0.23428	0.7717	- 47.38	-272.8
0.99697	0.12864	0.8532	- 49.94	-178.6
1.16263	0	0.9670	- 48.94	- 40.7
1.16209	0	0.9737	- 37.41	- 31.3
-	-	1.0000	-	0

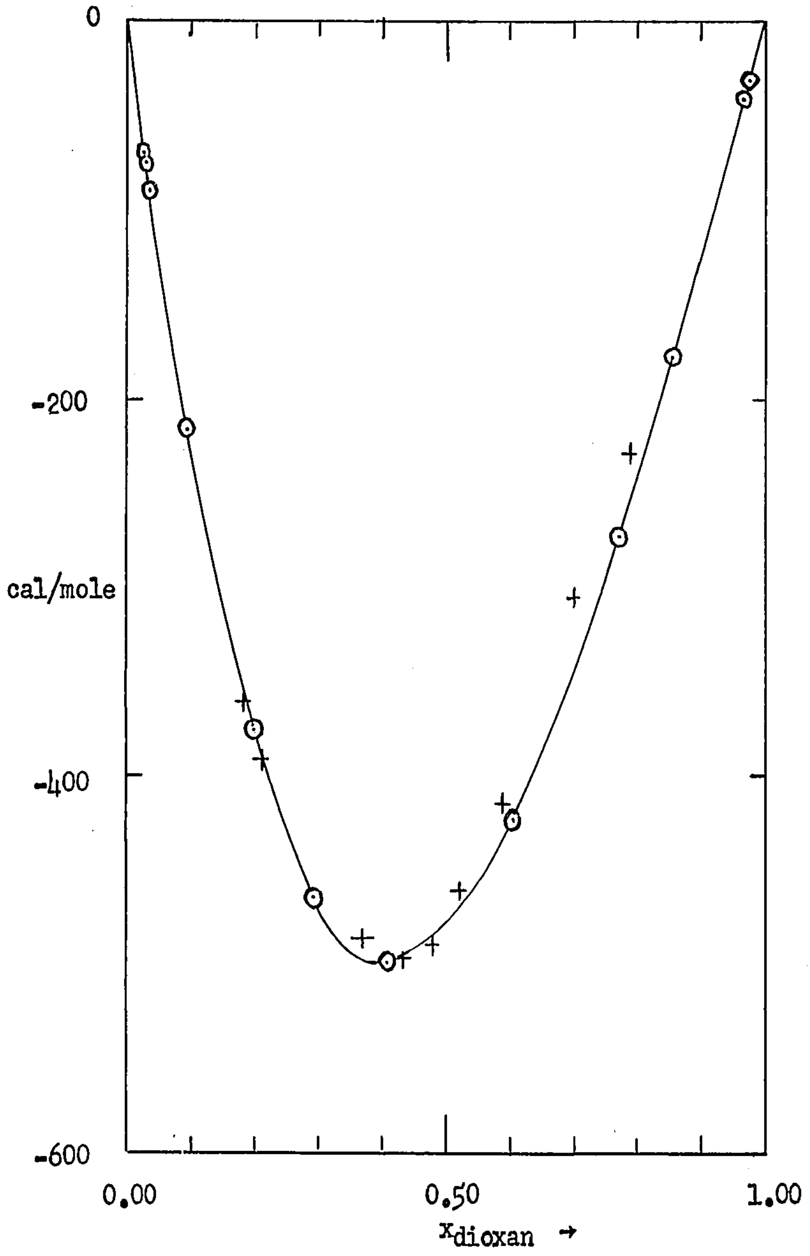


Fig. 5. Integral molar heats of mixing for system dioxan - chloroform. Circles with dots, experimental; crosses, Osipov, Panina and Yagubyan (24)

slightly low values for the electrical energy. This small source of error was remedied (see equation 8).

Use of equations 6 and 9 for determining graphically the heat of mixing - composition curves have been demonstrated for system dioxan - chloroform. As Figure 5 shows, the general agreement between experiment (Table 4) and literature (24) is satisfactory, except for some details in the concentration interval between $x_{dioxan} = 0.6$ and $x_{dioxan} = 0.8$.

CHAPTER VI

RESULTS

The results of the heat of mixing experiments for each of the binary systems trifluoroacetic acid - acetic acid, acetic acid - CCl_4 and trifluoroacetic acid - CCl_4 are given in the respective Tables 5-7 and are plotted in the corresponding Figures 6-8. All the determined ΔH_{ij} values, for each binary system, have been represented by the equation

$$\Delta H_{ij} = x_i(1-x_i)(A+Bx_i+Cx_i^2+Dx_i^3) \qquad (11)$$

The constants (values given in Table 8) in equation 11 for the binary systems, computed by a least square plot of $\Delta H_{ij}/x_i(1-x_i)$ versus x_i, were used to obtain the calculated ΔH_{ij} values.

The $(\Delta H_i)_{ij}$ values were calculated as follows: differentiating equation 11 with respect to x_i, the relation

$$d\Delta H_{ij}/dx_i = x_i(1-x_i)(B+2Cx_i+3Dx_i^2) + (A+Bx_i+Cx_i^2+Dx_i^3)(1-2x_i) \qquad (12)$$

is obtained. Substituting for ΔH_{ij} and $d\Delta H_{ij}/dx_i$ in the relation

$$(\Delta H_i)_{ij} = \Delta H_{ij} + (1-x_i)d\Delta H_{ij}/dx_i \qquad (13)$$

and arranging in powers of x_i finally yields

$$(\Delta H_i)_{ij} = A + 2(B-A)x_i + (A-4B+3C)x_i^2 + 2(B-3C+2D)x_i^3 + (3C-8D)x_i^4 + 4Dx_i^5 \qquad (14)$$

For the other component, j, substituting again for ΔH_{ij} and for $d\Delta H_{ij}/dx_i$ in the relation

$$(\Delta H_j)_{ij} = \Delta H_{ij} - x_i d\Delta H_{ij}/dx_i \qquad (15)$$

and arranging in powers of x_i one obtains

$$(\Delta H_j)_{ij} = (A-B)x_i^2 + 2(B-C)x_i^3 + 3(C-D)x_i^4 + 4Dx_i^5 \tag{16}$$

The calculated values, at integral mole fractions, of ΔH_{ij} (equation 11), $(\Delta H_i)_{ij}$ (equation 14), $(\Delta H_j)_{ij}$ (equation 15) and of the function $\Delta H_{ij}/x_i x_j$ (utilizing ΔH_{ij} calculated from equation 11) for each binary system are given in the respective Tables 9-11, and the plots of these quantities, for each binary system, in the corresponding Figures 6-8. It may be pointed out that from accurately known $(\Delta H_i)_{ij}$ and $(\Delta H_j)_{ij}$ values and by use of the relation

$$\Delta H_{ij} = x_i(\Delta H_i)_{ij} + x_j(\Delta H_j)_{ij} \tag{17}$$

ΔH_{ij} values may be readily calculated.

The results for the two ternary systems 6 and 7 are given in the respective Tables 9 and 10. The results for system 8 are given in Table 14 and plotted in Figure 11.

Table 5. Experimental ΔH_{31} and function $\Delta H_{31}/x_3x_1$ for system trifluoroacetic acid - acetic acid

n_3 (moles)	n_1 (moles)	x_3	Q (calories)	ΔH_{31} (cal/mole)	$\Delta H_{31}/x_3x_1$ (cal/mole)
-	-	0	-	0	-
0	1.72080	0.0183	- 78.32	- 44.7	-2492
0	1.76524	0.0284	- 99.18	- 54.6	-1978
0	1.73267	0.0316	-124.05	- 69.3	-2267
0	1.76106	0.0506	-154.32	- 83.2	-1731
0	1.75243	0.0525	-228.90	-123.8	-2488
0.11344	1.57109	0.0848	- 68.88	-182.0	-2344
0.07470	1.65568	0.0888	-187.69	-192.5	-2379
0.07648	1.64017	0.0901	-182.11	-191.3	-2333
0.22614	1.40590	0.1544	- 55.61	-326.4	-2500
0.20857	1.46460	0.1772	-173.44	-351.2	-2409
0.35659	1.24025	0.2379	- 43.12	-461.0	-2542
0.32827	1.27700	0.2498	-120.91	-462.6	-2469
0.47336	1.06865	0.3448	- 90.48	-566.2	-2506
0.57123	0.91936	0.4068	- 56.52	-594.0	-2462
0.60527	0.90237	0.4360	- 62.22	-597.3	-2429
0.68371	0.81764	0.4671	- 22.80	-601.6	-2417
0.67049	0.82443	0.4696	- 37.01	-600.0	-2409
0.73541	0.71440	0.4902	- 34.29	-594.9	-2381
0.74862	0.70133	0.4915	- 51.21	-594.5	-2379
0.69793	0.82031	0.4943	- 53.39	-593.7	-2375
0.81410	0.65806	0.5077	-102.48	-590.2	-2361
0.79541	0.63545	0.5398	- 34.62	-579.3	-2332
0.90334	0.53443	0.5772	-120.47	-560.2	-2296
1.10604	0.25538	0.7473	-104.83	-381.0	-2018
1.06989	0.27827	0.7658	- 67.78	-388.2	-2164
1.21094	0.12092	0.8301	-197.85	-292.7	-2075
1.21122	0.14725	0.8341	-162.73	-301.0	-2175
1.22354	0.08518	0.8716	-148.91	-224.1	-2002
1.28753	0	0.9269	-189.18	-136.2	-2011
1.28817	0	0.9378	-167.42	-121.6	-2088
1.27446	0	0.9710	- 73.54	- 56.0	-1991
1.27844	0	0.9717	- 58.38	- 44.4	-1614
-	-	1.0000	-	0	-

Table 6. Experimental ΔH_{12} and function $\Delta H_{12}/x_1x_2$ for system acetic acid - CCl_4

n_1 (moles)	n_2 (moles)	x_1	Q (calories)	ΔH_{12} (cal/mole)	$\Delta H_{12}/x_1x_2$ (cal/mole)
-	-	0	-	0	-
0	1.02116	0.0626	+20.46	+18.78	+320
0	1.01934	0.0668	+24.58	+22.50	+361
0	1.02074	0.0734	+27.68	+25.13	+370
0.05323	0.98958	0.1204	+17.37	+31.68	+299
0.12124	0.95039	0.1783	+20.21	+51.76	+353
0.25094	0.86881	0.2806	+10.54	+61.58	+305
0.80185	0.47174	0.6016	+ 4.77	+59.07	+246
1.16667	0.32681	0.7524	+ 8.81	+45.17	+242
1.44518	0.16715	0.8685	+ 9.29	+27.12	+237
1.52691	0.12298	0.8927	+12.16	+23.08	+241
1.59482	0.08196	0.9249	+10.19	+16.84	+242
1.66554	0.04154	0.9460	+11.86	+12.09	+237
1.71440	0	0.9719	+11.21	+ 6.36	+233
1.72664	0	0.9732	+11.75	+ 6.62	+254
1.72525	0	0.9750	+ 6.64	+ 3.75	+154
1.71841	0	0.9755	+ 9.71	+ 5.51	+231
-	-	1.0000	-	0	-

Table 7. Experimental ΔH_{23} and function $\Delta H_{23}/x_2x_3$ for system trifluoroacetic acid - CCl_4

n_2 (moles)	n_3 (moles)	x_3	Q (calories)	ΔH_{23} (cal/mole)	$\Delta H_{23}/x_2x_3$ (cal/mole)
-	-	0	-	0	-
1.05022	0	0.0557	+ 82.44	+ 74.1	+1410
1.02071	0	0.0828	+116.52	+104.7	+1379
0.96564	0	0.0922	+118.31	+111.2	+1329
0.92717	0.08636	0.1447	+ 63.59	+158.7	+1283
0.85297	0.15994	0.2178	+ 55.71	+207.2	+1216
0.85259	0.22718	0.2590	+ 44.82	+229.1	+1194
0.79973	0.27545	0.3220	+ 41.41	+243.8	+1117
0.72773	0.36973	0.3821	+ 44.24	+280.1	+1186
0.66827	0.43379	0.4455	+ 39.34	+286.1	+1158
0.62435	0.50857	0.5046	+ 41.61	+290.3	+1161
0.58665	0.54132	0.5237	+ 30.48	+289.2	+1159
0.50428	0.64484	0.5263	+ 21.77	+289.7	+1162
0.40800	0.78238	0.6174	+ 29.70	+284.8	+1206
0.35915	0.84311	0.6687	+ 26.62	+272.5	+1230
0.29226	0.90966	0.7135	+ 40.35	+263.3	+1288
0.22800	0.98538	0.7505	+ 61.38	+248.2	+1325
0.14932	1.11276	0.8109	+ 92.40	+200.4	+1307
0.07807	1.21765	0.8845	+ 98.22	+141.9	+1389
0	1.29649	0.9198	+141.25	+100.2	+1358
-	-	1.0000	-	0	-

Table 8. Constants for equations 11, 14 and 16

system	A	B	C	D
CF_3COOH - CH_3COOH	-2165	-2271	+4848	-2321
CH_3COOH - CCl_4	+363	-251	+168	-58
CF_3COOH - CCl_4	+1516	-2246	+4025	-1910

Table 9. Calculated integral and partial molar heats of mixing and the function $\Delta H_{31}(\text{calcd})/x_3x_1$ for system trifluoroacetic acid - acetic acid

x_3	ΔH_{31} (cal/mole)	$(\Delta H_3)_{31}$ (cal/mole)	$(\Delta H_1)_{31}$ (cal/mole)	$\Delta H_{31}(\text{calcd})/x_3x_1$ (cal/mole)
0	0	-2165	0	-
0.10	-211.1	-2011	-11	-2346
0.20	-391.0	-1641	-79	-2444
0.30	-519.3	-1211	-224	-2473
0.40	-587.0	- 809	-438	-2446
0.50	-594.8	- 490	-700	-2379
0.60	-548.2	- 265	-972	-2284
0.70	-456.8	- 125	-1228	-2175
0.80	-330.7	- 48	-1455	-2067
0.90	-177.7	-110	-1665	-1974
1.00	0	0	-1909	-

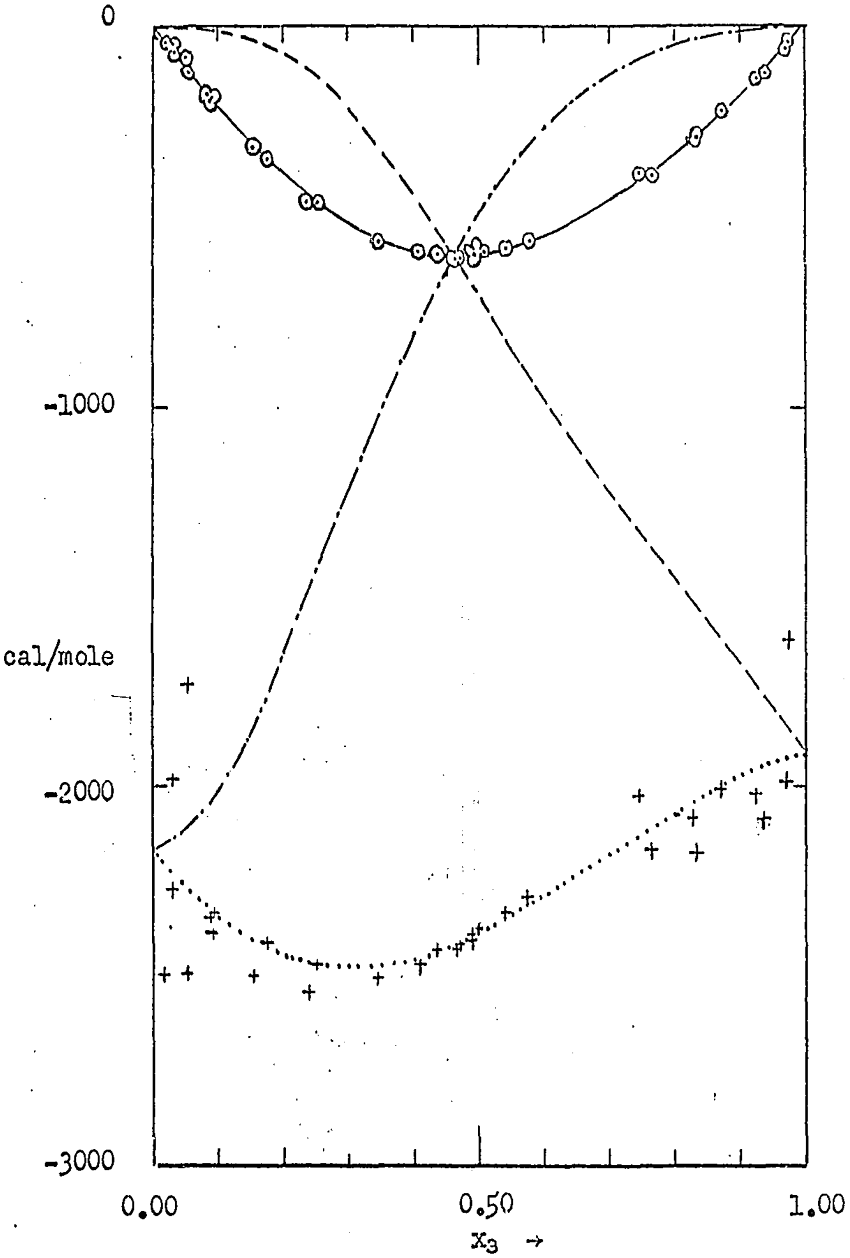


Fig. 6. Experimental ΔH_{31} (circles with dots); calculated ΔH_{31} (solid line); calculated $(\Delta H_3)_{31}$ (dot dashed line) and $(\Delta H_1)_{31}$ (dashed line); functions $\Delta H_{31}/x_3x_1$ (crosses) and $\Delta H_{31}(\text{calcd})/x_3x_1$ (dotted line) for system trifluoroacetic acid - acetic acid.

Table 10. Calculated integral and partial molar heats of mixing and function ΔH_{12}(calcd)/x_1x_2 for system acetic acid - CCl_4

x_1	ΔH_{12} (cal/mole)	$(\Delta H_1)_{12}$ (cal/mole)	$(\Delta H_2)_{12}$ (cal/mole)	ΔH_{12}(calcd)/x_1x_2 (cal/mole)
0	0	+363	0	-
0.10	+30.5	+257	+5	+339
0.20	+51.0	+180	+19	+319
0.30	+63.2	+123	+38	+301
0.40	+68.5	+82	+60	+285
0.50	+68.0	+52	+84	+272
0.60	+62.5	+31	+110	+260
0.70	+52.5	+16	+138	+250
0.80	+38.4	+7	+166	+240
0.90	+20.8	+2	+194	+231
1.00	0	0	+222	-

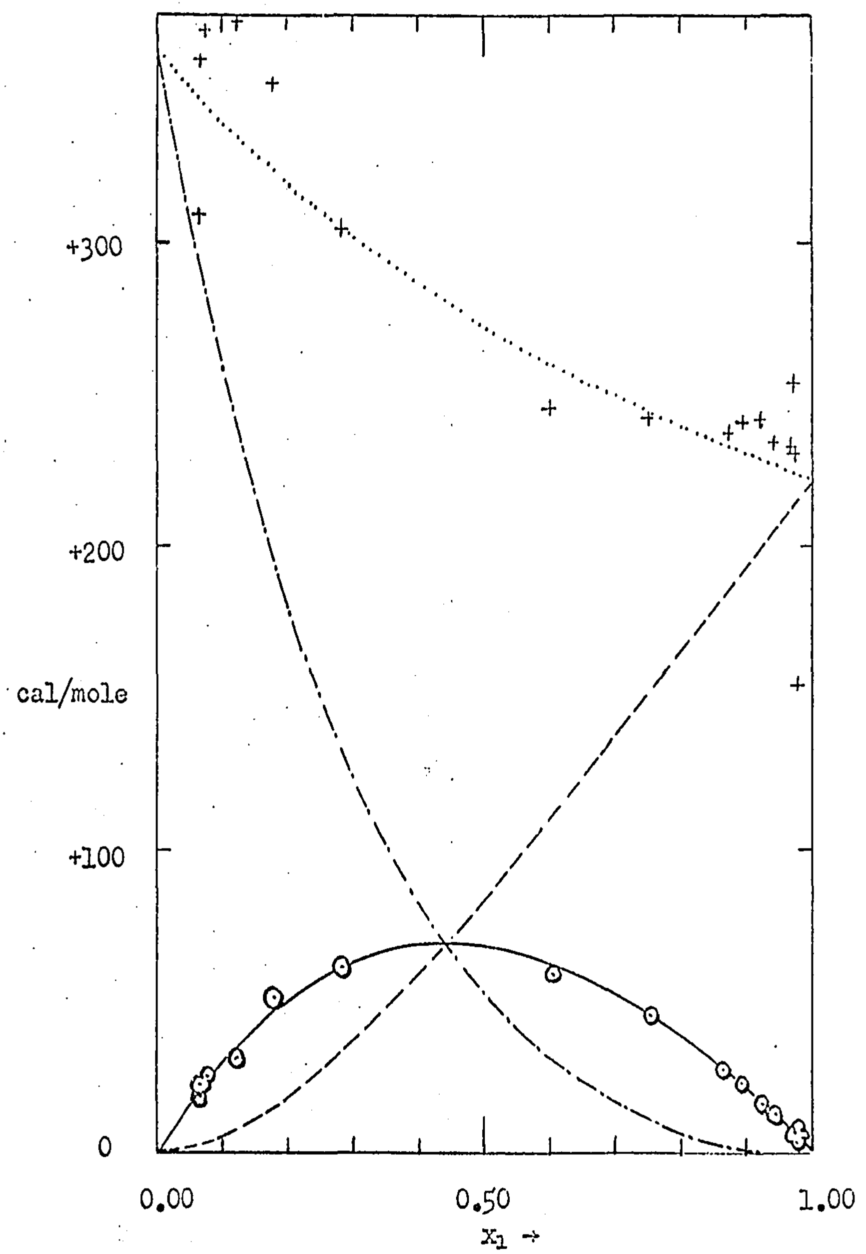


Fig. 7. Experimental ΔH_{12} (circles with dots); calculated ΔH_{12} (solid line); calculated $(\Delta H_1)_{12}$ (dot dashed line) and $(\Delta H_2)_{12}$ (dashed line); functions $\Delta H_{12}/x_1x_2$ (crosses) and $\Delta H_{12}(\text{calcd})/x_1x_2$ (dotted line) for system acetic acid - CCl_4.

Table 11. Calculated integral and partial molar heats of mixing and the function ΔH_{23}(calcd)/x_2x_3 for system trifluoroacetic acid - CCl_4

x_3	ΔH_{23} (cal/mole)	$(\Delta H_2)_{23}$ (cal/mole)	$(\Delta H_3)_{23}$ (cal/mole)	ΔH(calcd)/x_2x_3 (cal/mole)
0	0	0	+1516	-
0.10	+119.6	+27	+956	+1329
0.20	+193.9	+77	+666	+1212
0.30	+241.7	+125	+512	+1151
0.40	+273.1	+178	+417	+1138
0.50	+289.5	+247	+333	+1158
0.60	+288.4	+359	+242	+1202
0.70	+264.2	+531	+151	+1258
0.80	+210.2	+773	+ 69	+1314
0.90	+122.3	+1072	+ 18	+1359
1.00	0	+1381	0	-

Table 12. $\Delta H_{123}(0,0)$ and ΔH_{123} along n_2/n_3 = 0.10321 for system acetic acid - CCl_4 - trifluoroacetic acid (system 6)

n_1 (moles)	n_1' (moles)	x_1	Q (calories)	$\Delta H_{123}(0,0)$ (cal/mole)	ΔH_{123} (cal/mole)
-	-	0	-	0	+116.5
0	0.05091	0.0468	-51.42	-47.2	+ 63.8
0.03563	0.05029	0.0775	-40.43	-68.2	+ 37.7
0	0.09819	0.0852	-80.91	-70.2	+ 36.4
0	0.10109	0.0869	-84.01	-72.2	+ 34.2
0.07389	0.06039	0.1186	-23.43	-80.5	+ 21.8
0.07562	0.10707	0.1547	-26.62	-80.8	+ 17.4
0.11089	0.10085	0.1780	-14.03	-86.0	+ 14.5
0.15645	0.10826	0.2184	- 7.51	-82.7	+ 11.5
0.22377	0.12064	0.2739	- 4.85	-81.4	+ 7.2
0.34782	0.11081	0.3472	- 1.67	-74.6	+ 5.1

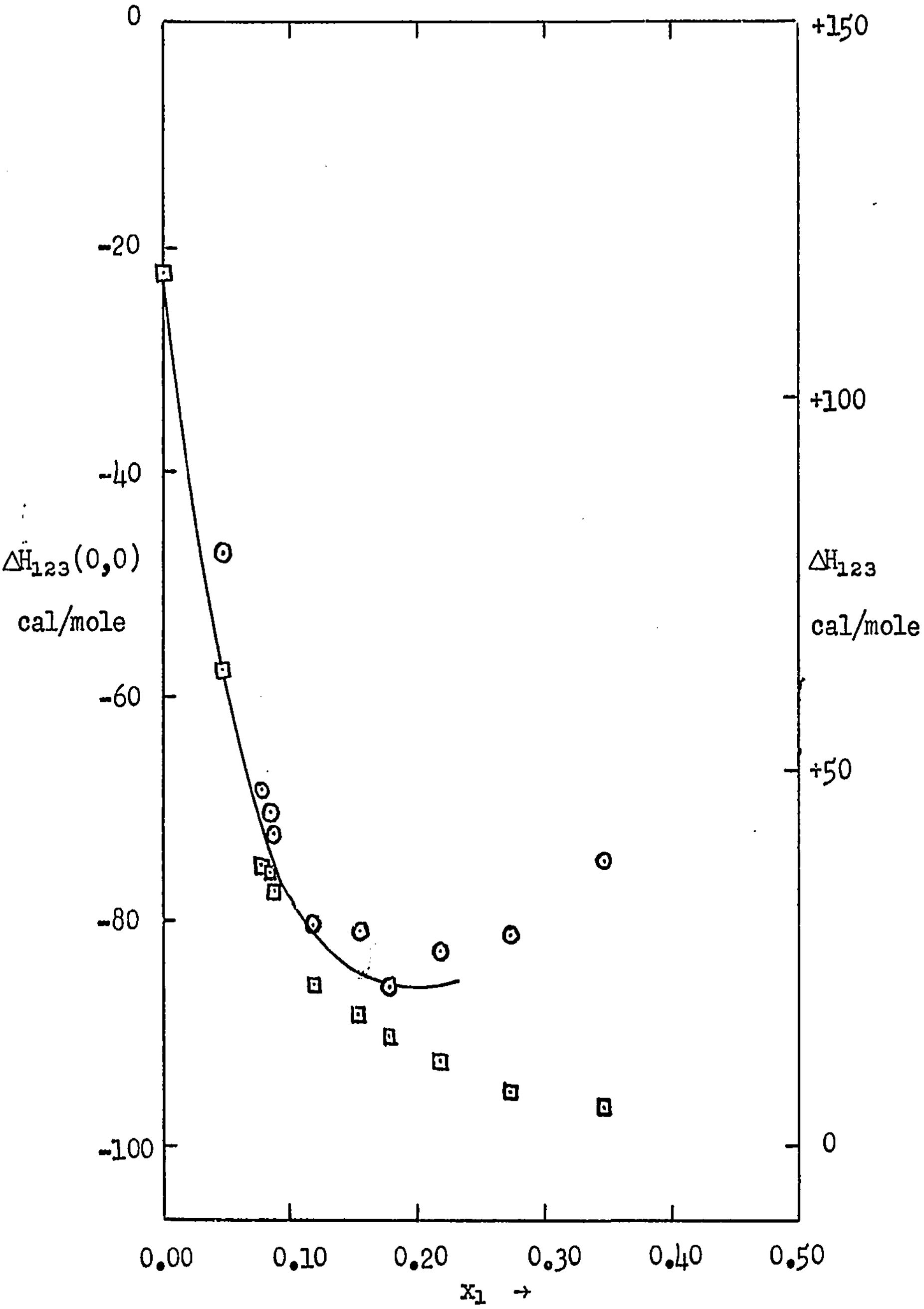


Fig. 9. Experimental $\Delta H_{123}(0,0)$ (circles with dots), experimental ΔH_{123} (squares with dots) and calculated ΔH_{123} (solid line) for system acetic acid - CCl_4 - trifluoroacetic acid, along $n_3/n_2 = 0.10321$.

Table 13. Experimental $\Delta H_{312}(0,0)$ and ΔH_{312} along $n_1/n_2 = 0.11317$ for system trifluoroacetic acid - acetic acid - CCl_4 (system 7)

n_3 (moles)	n_3' (moles)	x_3	Q (calories)	$\Delta H_{312}(0,0)$ (cal/mole)	ΔH_{312} (cal/mole)
-	-	0	-	0	+ 33.1
0	0.04029	0.0359	-10.00	-8.9	+ 23.0
0	0.05698	0.0507	-11.29	-10.0	+ 21.4
0	0.10335	0.0874	- 2.13	-1.8	+ 28.4
0.04078	0.07711	0.1021	+17.17	+6.5	+ 35.9
0.09938	0.09742	0.1664	+57.86	+49.0	+ 76.9
0.26050	0.05978	0.2701	+28.95	+106.5	+131.6
0.39480	0.08873	0.3940	+31.88	+158.2	+175.1
0.51264	0.07840	0.4909	+22.39	+185.0	+194.8
0.83008	0.10344	0.7150	+11.90	+175.0	+189.0

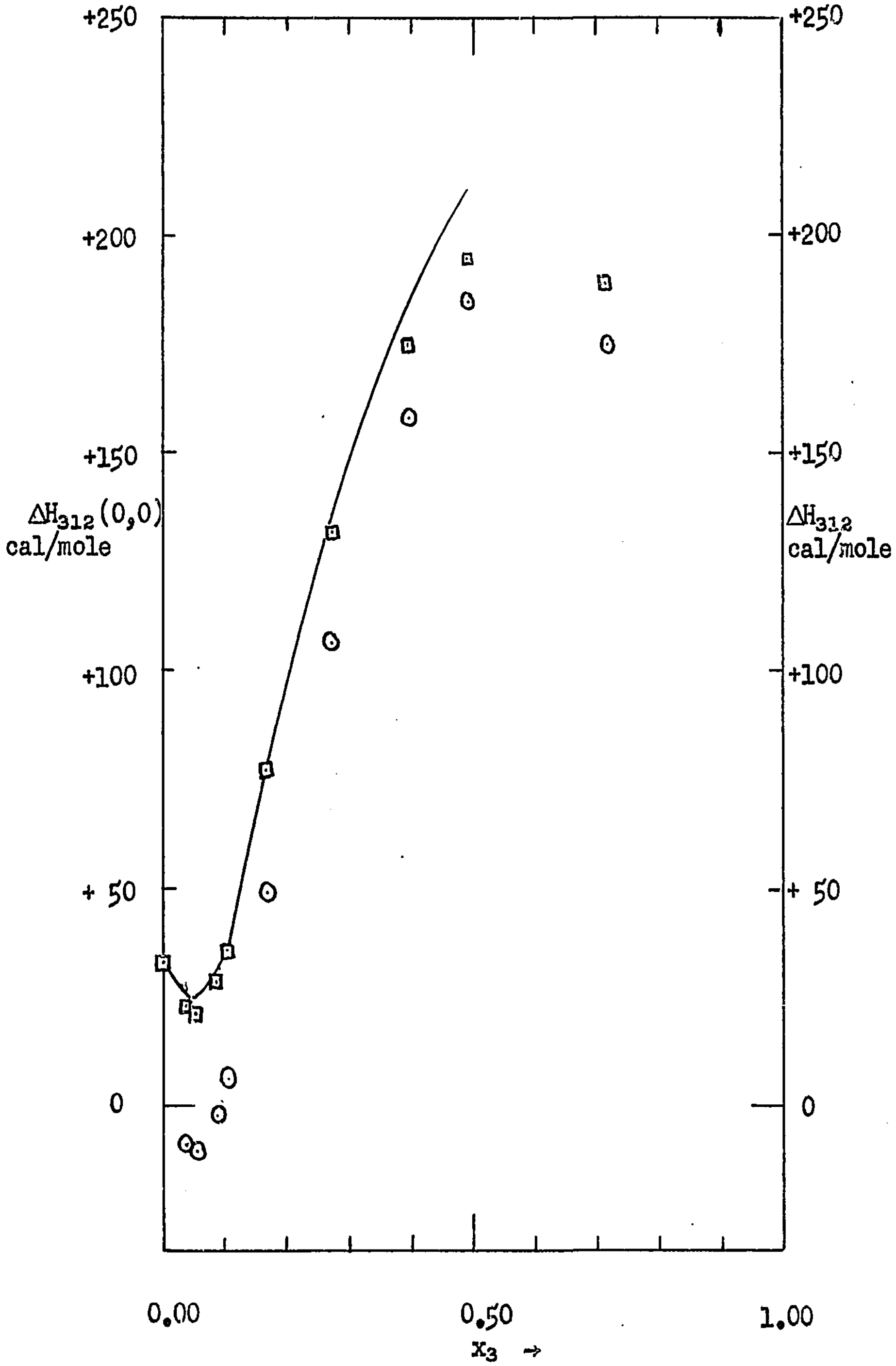


Fig. 10. Experimental $\Delta H_{312}(0,0)$ (circles with dots), experimental ΔH_{312} (squares with dots) and calculated ΔH_{312} (solid line) for system trifluoroacetic acid - acetic acid - CCl_4 along $n_1/n_2 = 0.11317$ (system 7)

Table 14. Experimental $\Delta H_{12,23}(0,0)$ and $\Delta H_{12,23}$ along $n_1/n_2 = 0.107551$ and along $n_3/n_2 = 0.10111$ for system acetic acid - CCl_4 - trifluoroacetic acid (system 8)

n_3 (moles)	n_1 (moles)	x_3	Q (calories)	$\Delta H_{12,23}(0,0)$ (cal/mole)	$\Delta H_{12,23}$ (cal/mole)
-	-	0	-	0	+ 32.8
0	0.10582	0.0036	-6.19	-5.5	+ 30.5
0	0.10324	0.0047	-7.75	-6.9	+ 30.1
0.00534	0.09825	0.0100	-7.98	-14.1	+ 27.6
0.01804	0.08416	0.0218	-6.85	-27.4	+ 25.5
0.06351	0.03414	0.0565	-7.44	-35.3	+ 49.0
0.07613	0.02124	0.0674	-6.69	-24.5	+ 68.4
0.08732	0.00942	0.0782	-7.24	-15.4	+ 87.3
0.08246	0	0.0854	-7.27	- 7.5	+101.7
0.09487	0	0.0862	-7.05	- 6.4	+103.5
-	-	0.0918	-	0	+115.0

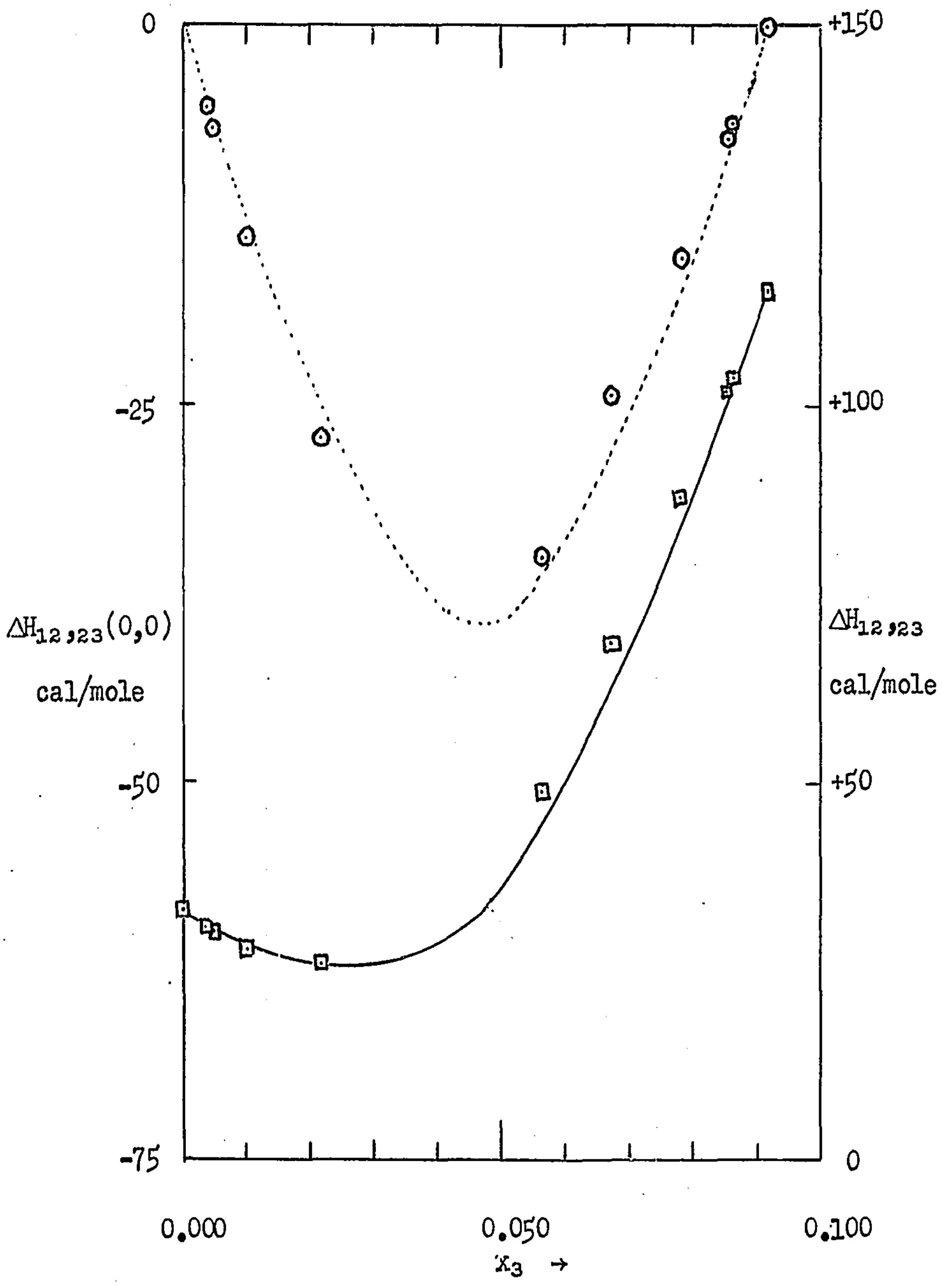


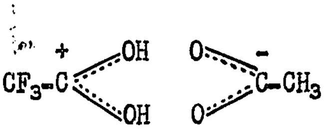
Fig. 11. Experimental $\Delta H_{12,23}(0,0)$ (circles with dots) and calculated $\Delta H_{12,23}(0,0)$ (dotted line); experimental $\Delta H_{12,23}$ (squares with dots) and calculated $\Delta H_{12,23}$ (solid line) for system acetic acid - CCl_4 - trifluoroacetic acid, along $n_1/n_2 = 0.10755$ and along $n_3/n_2 = 0.10111$. (system 8).

CHAPTER VII

DISCUSSION

The positive and slightly asymmetric heat of mixing - composition curves for systems acetic acid - CCl_4 and trifluoroacetic acid - CCl_4 are ascribed in part to the breaking of hydrogen bonds between the self-associated acetic acid and trifluoroacetic acid molecules. The more positive heat of mixing values for system trifluoroacetic acid - CCl_4, as compared to the system acetic acid - CCl_4 (at identical mole fractions of CCl_4) is in accord with the fact that perfluoroalkane - alkane liquid mixtures show large deviations from ideality. It may be pointed out that the thermodynamic quantities of perfluoroalkanes - alkanes can be obtained with remarkable accuracy if the interaction energy between unlike molecules is calculated (not by the geometric mean law, but) by a suitable approximation to the London theory of dispersion energy (25) and (26).

For the system trifluoroacetic acid - acetic acid, the rather large negative heat effects and the nearly symmetrical heat of mixing - composition curve suggest the formation of a 1:1 hydrogen bonded complex and indicate that the interaction energy between trifluoroacetic acid - acetic acid is the dominating factor. The phenomenon of preferential hetero-dimerization (6), (7) and (8) may be due in part to the formation of a zwitterion structure (15)



(see pages 2 and 3).

That the exothermic interaction energy between trifluoroacetic acid and acetic acid predominates even in dilute solutions of either acid in CCl_4 may be noted from the initial portions of the heat of mixing - composition curves (Figures 9 and 10) for the respective systems 6 and 7. Some support for the 1:1 hydrogen bonded complex is given by the marked change of slope of these curves in the regions where the concentrations of the two acids (in each of the two systems 6 and 7) are approximately equal.

The exothermic intercation between trifluoroacetic acid and acetic acid is more pronounced even in very dilute solutions of the two acids in CCl_4 (system 8) as has been shown from calculations of the partial molar heats in the ternary systems from the known partial molar heats of the corresponding binary systems (27). The calculations are based on Kohler s assumption that the 1-2 interactions do not depend on the number of 3-molecules in the surrounding of the contact. These calculations reveal that the presence of the third component makes the contacts more exothermic; more precisely, the ΔH_{ijk} values are more exothermic (or less endothermic than the experimentally determined ones. Two possible reasons have been offered for this behaviour. First - due to cross-dimerization. For if one adds a very small quantity of trifluoroacetic acid to the 1:9 molar standard binary mixture acetic acid - CCl_4, most of the CF_3COOH would go into the energetically favoured cross-dimers and one would not have to furnish the heat of dissociation for the homo-dimers as one would have to furnish when trifluoroacetic acid is mixed with pure CCl_4. The second possibility is the formation of some zwitterions which could polarize the F-atoms very effectively and provide by this inductive energy and exothermic contribution to the overall interaction energy (15).

An alternate method of treating heat of mixing data in the CCl_4-rich regions is to interpret heat effects in terms of the hetero- and homo-dimerization reactions of the acids. Although polymers higher than the dimer may form, it is assumed that the data in the ternary system 8 can be explained in terms of the reaction

$$(CF_3COOH)_2 + (CH_3COOH)_2 \rightleftharpoons 2(CF_3COOH.CH_3COOH)$$

in CCl_4. Changes in solvation of the individual dimers resulting from variations in the relative amounts of trifluoroacetic acid and acetic acid are neglected.

For system 8, let x = total mole fraction of acetic acid, a-x = total mole fraction of trifluoroacetic acid and 1-a = mole fraction of CCl_4, where a = 0.09 and y = mole fraction of cross-dimers formed. Then, substituting in the expression for the equilibrium constant, K, for the above reaction one obtains

$$\frac{y^2}{\left(\frac{x-y}{2}\right)\left(\frac{a-x-y}{2}\right)} = K \qquad (18)$$

Also, $\Delta H_{12,23}(0,0) = y\left(\frac{\Delta H_D}{2}\right)$ (19)

where ΔH_D is the enthalpy change for the above reaction. Eliminating y in equations 18 and 19 and substituting $z = \Delta H_{12,23}(0,0)/\left(\frac{\Delta H_D}{2}\right)$ yields

$$\frac{4(z)^2}{(x-z)(a-x-z)} = K \qquad (20)$$

Rearranging and substituting for z, finally yields

$$\frac{x(a-x)}{\Delta H_{12,23}(0,0)} - \frac{a}{\Delta H_{12,23}(0,0)} = (4/K-1)(1/\frac{\Delta H_D}{2})\ \Delta H_{12,23}(0,0) \qquad (21)$$

The intercept of a plot of $x(a-x)/\Delta H_{12,23}(0,0)$ versus $\Delta H_{12,23}(0,0)$ gives ΔH_D and from the slope and the known value of $\frac{\Delta H_D}{2}$, K may be calculated.

Equation 21 has been applied to the data in Figure 11, yielding $\Delta H_D = 2.5$ kcal/mole and K = 16. It is observed (Figure 11) that the calculated $\Delta H_{12,23}(0,0)$ curve, from these values of ΔH_D and K, and experimental values are in good agreement.

In Figures 9-11 are calculated values of ΔH_{123}, ΔH_{312} and $\Delta H_{12,23}$ for each of the respective systems 6,7 and 8, in which the mole fraction of CCl_4 is greater than 0.5. There is excellent agreement between the predicted and experimental integral molar heats of mixing in the regions where x_2 is greater than 0.9. At values of x_2 less than 0.9, systematic deviations between theory and experiment occur. It is interesting to note that in system 6 a value of ΔH_D 25% greater than the value chosen would bring the calculated and observed curves into close agreement at the higher values of x_1. On the other hand, a greater value of the parameter ΔH_D would lead to poorer agreement between the calculated and experimental curves for system 7.

If it is assumed that the reaction

$$(CF_3COOH)_2 + (CH_3COOH)_2 \rightleftharpoons 2(CF_3COOH.CH_3COOH)$$

adequately accounts for the heat effects in the two limiting regions of the binary system $CF_3COOH - CH_3COOH$, values of ΔH_D may be calculated from the limiting values of the partial molar enthalpies of the respective species present as the minor component. In the trifluoroacetic acid - rich region the value ΔH_D = 3800 cal/mole has been obtained and in the acetic acid - rich region the values calculated has been ΔH_D = 4350 cal/mole. Thus the interaction between CF_3COOH and CH_3COOH appears to be more exothermic when the pure acids are mixed than when the mixing occurs in the CCl_4 - rich region.

Errors in reported values of integral molar heats of mixing are believed not to exceed 3% except in mixtures where the integral heats are very small. In systems where heat effects were small it is believed that the absolute error in the integral heat of mixing did not exceed 4 cal/mole. These estimates are based on a) a comparision of literature and present results b) and examination of the discrepancies between experimental integral molar heats of mixing and values calculated from the computed least square polynomials representing heat data and c) an error analysis introduced in the calculation of temperature differences from temperature - time data. An internal check on the consistency of the present results is provided by the values of integral heat of mixing obtained independently from data for the ternary systems 6 and 7 at the point where the two acids are present in equal concentration. From the data for system 6 the calculated integral heat of mixing for mixture at x_1 = 0.09, x_2 = 0.82 and x_3 = 0.09 is 31 cal/mole; from the data for system 7, the experimental integral molar heat of mixing at identical concentrations as in system 6, is 31.7 cal/mole.

Results of the present investigation, in addition to providing quantative heat data for the binary and ternary systems, indicate the importance of hetero-dimerization in determining the conditions under which exothermic mixing occurs. In the binary system, trifluoroacetic acid - acetic acid, the tendency toward formation of hetero-aggregates is great enough to overcome the expected endothermic interaction between CF_3- and CH_3- groups. For ternary solutions in which CCl_4 is the major component, the preferential formation of complexes between trifluoroacetic acid and acetic acid partially obscures the tendency toward endothermic mixing expected for contacts between CCl_4 and the individual acids. It is hoped that in the near future further studies will be made of the heat effects and equilibrium properties relating to hetero-association reactions of carboxylic acids.

CHAPTER VIII

SUMMARY

The heats of mixing at approximately 25°C have been determined for binary systems and for some concentration lines in the CCl_4 - rich regions of the ternary systems, formed by mixtures of trifluoroacetic acid, acetic acid and CCl_4. Small heat effects, of nearly the same order of magnitude, have been measured for each system so as to minimize errors due to heat exchange with the surroundings. Furthermore, errors arising from corrosion of the calorimeter material and from the presence of moisture have been very carefully avoided. Roth's (20) method has been employed to calculate the magnitudes of the temperature changes.

The integral molar heats of mixing values have been obtained graphically and the partial molar heats (for the three binary systems) have been calculated by an expression derived from an analytical equation representing the integral molar heats of mixing. The ternary integral molar heats of mixing have also been calculated utilizing the known partial molar heats of the corresponding binary systems (15). The results are in substantial agreement with those determined graphically.

The maximum value of the heat of mixing - composition curve for system trifluoroacetic acid - CCl_4 has been found to be more endothermic than that for the system acetic acid - CCl_4. The heat effects for system trifluoroacetic acid - acetic acid have been found to be strongly exothermic. Calculations of the ternary integral molar heats of mixing (based on Kohler's assumption that the strength of the interaction along a 1-2 contact is independent of the number of 3-molecules (27) have been made. From a comparison of the calculated with the experimentally determined ternary heats it follows that the exothermic interaction energy between trifluoroacetic acid and acetic acid predominates even in CCl_4 - rich solutions and that the exothermic interaction energy between the two acids is even more exothermic in the presence of lagre excesses of CCl_4 than if part of the CCl_4 were absent (15).

Predicted values of the ternary integral molar heats of mixing have been obtained by assuming that the reaction

$$(CF_3COOH)_2 + (CH_3COOH)_2 \rightleftarrows 2(CF_3COOH.CH_3COOH)$$

predominates, insofar as the acid species are concerned, in the CCl_4 - rich regions of the ternary systems. The ternary integral heats of mixing calculated by this approach are in good agreement with the experimentally determined values.

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APPENDIX I

ABBREVIATIONS FOR SYSTEMS

System	Abbreviation
quinoline - m-cresol	1
dioxan - chloroform	2
trifluoroacetic acid - acetic acid	3
acetic acid - CCl_4	4
trifluoroacetic acid - CCl_4	5
acetic acid - CCl_4 - trifluoroacetic acid along $n_3/n_2 = 0.10321$	6
trifluoroacetic acid - acetic acid - CCl_4 along $n_1/n_2 = 0.11317$	7
acetic acid - CCl_4 - trifluoroacetic acid along $n_1/n_2 = 0.10755$ and along $n_3/n_2 = 0.10111$	8
heat of solution of KCl	9

APPENDIX II

LIST OF SYMBOLS

n_1,	moles of acetic acid
n_2,	moles of CCl_4
n_3,	moles of trifluoroacetic acid
(n_i+n_j),	standard binary mixture i.e., n_i/n_j = constant (for ternary systems)
n_i,	moles of component i in the mixing vessel
n_i,	moles of component i in the ampoule
$(x_i)_{ij}$,	mole fraction of component i in the binary system i-j
$\Delta T_m{}^{o}C$,	temperature change in the mixing experiment
$\Delta T_c{}^{o}C$,	temperature change in the calibration experiment
Q,	measured heat change
$(\Delta H_i)_{ij}$,	partial molar heat of mixing of component i in the binary system i-j. ($\Delta H_i = H_i - H_{i0}$, where H_{i0} = enthalpy content of pure component i)
ΔH_{ij},	integral molar heat of mixing, defined as cal/mole of mixture, when pure components are mixed
$\Delta H_{123}(0,0)$,	ΔH_{123} less ΔH_{23} at $(x_3)_{23} = 0.0936$
ΔH_{123},	integral molar heat of mixing along $n_3/n_2 = 0.10321$
$\Delta H_{312}(0,0)$,	ΔH_{312} less ΔH_{12} at $(x_1)_{12} = 0.1017$
ΔH_{312},	integral molar heat of mixing along $n_1/n_2 = 0.11317$

$\Delta H_{12,23}(0,0)$,	$\Delta H_{12,23}$ less the additive value of the binary integral molar heats of mixing in the corresponding binary systems at $(x_1)_{12} = 0.0971$ and $(x_3)_{23} = 0.0918$
$\Delta H_{12,23}$,	integral molar heat of mixing along $n_1/n_2 = 0.10755$ and along $n_3/n_2 = 0.10111$
ΔH_D	heat of hetero-dimerization

(+) signs represent endothermic and (-) signs exothermic quantities

APPENDIX III

An Example of the Application of the Roth (20) Method

The following is a sample calculation of temperature change (for exothermic mixing) by the Roth method. (For the theory of the method see Chapter IV).

Fore period temperatures (°C)		
24.349		
24.365	$24.456 - 24.349 = +\ 0.107$	$0.107 \times 7 = 0.749$
24.380	$24.440 - 24.365 = +\ 0.075$	$0.075 \times 5 = 0.375$
24.394	$24.426 - 24.380 = +\ 0.046$	$0.046 \times 3 = 0.138$
24.410	$24.410 - 24.394 = +\ 0.016$	$0.016 \times 1 = \underline{0.016}$
24.426		Sum $= \underline{\underline{1.278}}$
24.440		
24.456		

Since $n = 8$, $n(n+1)(n-1)/1.2.3 = 84$

Hence from equation 5, $G_1 = 1.278/84 = +0.0152$

Multiplying G_1 by 7 and adding to 24.349°; G_1 by 6 and adding to 24.365° and so forth, one gets

24.349	24.365	24.380	24.394	24.410	24.426	24.440	24.456
+0.1064	+0.0912	+0.076	+0.0608	+0.0456	+0.0304	+0.0152	+0.000
24.455	24.456	24.456	24.455	24.456	24.456	24.455	24.456

The corrected last temperature and the mean temperature of the fore period are $\theta_1 = 24.456$°C and $\theta_1 = 24.403$°C, respectively.

After period temperatures (°C)		
24.693		
24.710	$24.787 - 24.693 = +0.094$	$0.094 \times 7 = 0.658$
24.720	$24.773 - 24.710 = +0.063$	$0.063 \times 5 = 0.315$
24.732	$24.760 - 24.720 = +0.040$	$0.040 \times 3 = 0.120$
24.746	$24.746 - 24.732 = +0.014$	$0.014 \times 1 = 0.014$
24.760		Sum = 1.107
24.773		
24.787		

Since n= 8, from equation 5, $G_2 = 1.107/84 = +0.0132$

Multiplying G_2 by 0 and subtracting from 24.693°C; G_2 by 1 and subtracting from 24.710°C and so forth, one gets

24.693	24.710	24.720	24.732	24.746	24.760	24.773	24.787
-0.000	-0.0132	-0.0264	-0.0396	-0.0528	-0.0660	-0.0792	-0.0924
24.693	24.697	24.694	24.692	24.693	24.674	24.694	24.695

The corrected first temperature and the mean temperature of the after period are $\theta_2 = 24.694$°C and $\theta_2 = 24.740$°C, respectively.

From equation 2, $k = -0.0059$

Reaction period temperatures (°C)	θ	$(\theta - \theta_1)$	$k(\theta - \theta_1)$	$k(\theta - \theta_1) + G_1$
24.456				
24.570	24.513	+0.110	-0.0007	+0.0145
24.596	24.583	+0.180	-0.0011	+0.0141
24.612	24.604	+0.201	-0.0012	+0.0140
24.630	24.621	+0.218	-0.0013	+0.0139
24.640	24.635	+0.232	-0.0014	+0.0138
24.656	24.648	+0.245	-0.0015	+0.0137
24.670	24.663	+0.260	-0.0015	+0.0137
24.680	24.675	+0.272	-0.0016	+0.0136
24.693	24.687	+0.284	-0.0017	+0.0135
			Sum =	+0.125

or, $\sum\left[k(\theta - \bar{\theta}_1) + G_1\right] = 0.125^\circ$

Substituting for $\theta_{end} = \theta_2 - \theta_1 = +0.238^\circ$ and for $\sum\left[k(\theta - \bar{\theta}_1) + G_1\right] = +0.125$ in equation 4, the value of θ_{true} or $\Delta T_m = 0.113$ is obtained.