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An Isothermal Dilution Calorimeter for Exothermic Heats of Mixing

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An isothermal dilution calorimeter is described which allows rapid and routine collection of accurate heat-of-mixing data for both exothermic and endothermic systems. Data are reported for the endothermic system benzene–carbon tetrachloride at 25° C. and for the exothermic systems acetone-dichloromethane at 0°, 15°, 30°, and 45° C.; methyl acetate–dichloromethane at 30° and 45° C.; and 1,4-dioxane–dichloromethane at 30° and 45° C.

THE isothermal dilution calorimeter for heats of mixing described by Savini *et al.* (6) has been modified so that it is now capable of measuring both exothermic and endothermic heats of mixing. This paper describes the modifications which have been made to Savini's endothermic calorimeter and presents some exothermic heat-of-mixing data which have been obtained with the new instrument. A detailed description of the present calorimeter and the associated instrumentation and operating procedures is given elsewhere (8).

EXPERIMENTAL

Use of an isothermal dilution calorimeter to determine exothermic heats of mixing requires removal of heat from the vessel in which the mixing occurs. In the present calorimeter, heat is removed from the mixing vessel at a constant rate by a thermoelectric cooling device. Before the mixing process is begun, heat is simultaneously added to the vessel at the same constant rate by means of an electric resistance heater. During the mixing process, the heater is turned off with the result that heat is removed from the mixing vessel at a net rate equal to the rate of energy addition by the heater before mixing. This type of cooling system can be made physically small; it has a very small thermal lag corresponding to the response time of the heater only; it can be made virtually independent of small (0.01° C.) variations in solution temperature during mixing; it does not require external calibration.

APPARATUS

Figure 1 shows the Teflon calorimeter plug in two views taken at right angles to each other. The drawing is somewhat schematic, and many of the components are shown in only one view. The figure shows the Teflon plug, *E*, supported by a 2-inch diameter stainless-steel tube, *A*, which is, in turn, attached to a support rack (not shown). View *b* of this figure shows the cooling system itself housed within the support tube *A*. The warm junctions of the 6-couple, 15-ampere cooling module *Z* (Frigistors Ltd., Montreal, Canada Type 1FB - 06 - 015 - G1) are in thermal contact with a copper heat sink *R* through which water from the thermostated bath in which the calorimeter is immersed is circulated. The cold junctions of the module are in thermal contact with a coin-silver bar, *Y*, which is, in turn, connected to a ⅛-inch diameter coin-silver rod, *U*, which passes through the Teflon plug into the mixing vessel. The lower end of the silver rod is surrounded by a small copper cup, *V*, the inside surface of which is amalgamated and which is filled with mercury. The mercury acts as a heat-transfer agent and as a bearing for the stirrer assembly. Two coin-silver paddles, shown at *L* in view *a*, are attached to the copper cup and act both as a heat transfer surface and as a stirrer for the solution in the Dewar flask, *S*. The entire cooling assembly is surrounded by a copper heat shield, *X*, which is an extension of the heat sink, *R*, to prevent inadvertent cooling of adjacent calorimeter parts. The free space within the support tube, *A*, is entirely filled with Santocell A insulating dust to reduce further the possibility of unwanted heat transfer. The cooling module is powered by a home-built current-regulated D.C. supply. This arrangement is capable of removing heat from the mixing vessel at a sufficiently constant rate to allow the collection of reliable exothermic heat-of-mixing data.

RESULTS AND DISCUSSION

The system benzene–carbon tetrachloride at 25° C. was studied to provide a basis for the comparison of this calorimeter with other calorimeters. When the calorimeter is used for endothermic systems such as this, the cooling rate is set to a low value which just compensates for the rate of energy addition by the stirrer thus avoiding the problem encountered by Savini and coworkers of having the temperature within the Dewar flask rise to a value slightly greater than that of the thermostated bath. The results of

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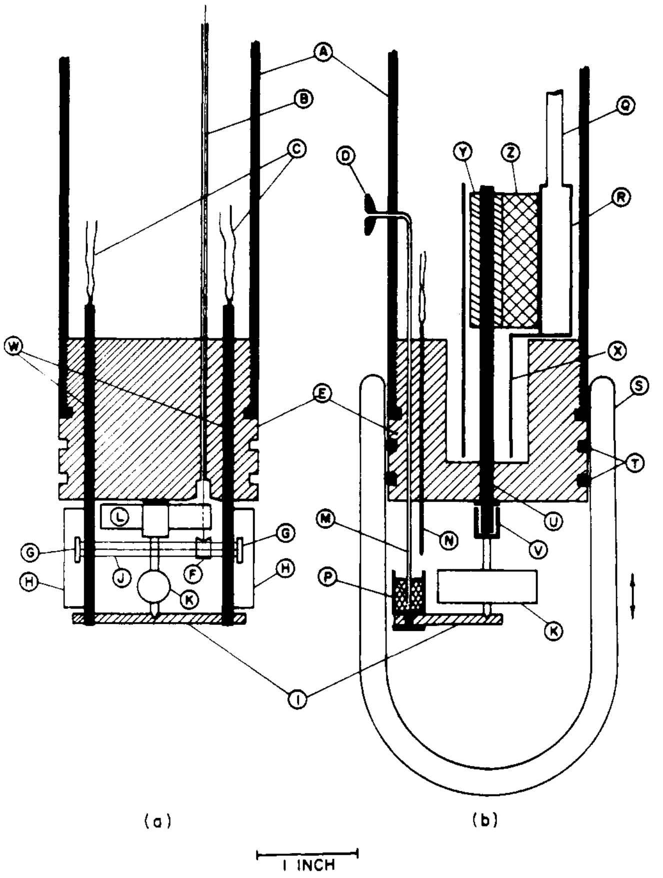

Figure 1. Calorimeter plug

A.	Stainless-steel support tube
B.	Vent tube
C.	Current and potential leads for heater
D.	Connector for feed tube
E.	Teflon plug
F.	Vent plug
G.	Heater-wire supports
H.	Baffles
I.	Teflon support
J.	Heater wires
K.	Stirrer magnet
L.	Stirrer paddle
M.	Feed tube
N.	Thermistor
P.	Teflon feed cup
Q.	Water inlet tube
R.	Copper heat sink
S.	150-ml. precision-bore Dewar flask
T.	O rings
U.	Coin-silver cooling rod
V.	Copper cup
W.	Coin-silver support rods
X.	Copper heat shield
Y.	Coil-silver bar
Z.	Cooling module

the benzene-carbon tetrachloride experiments were correlated by means of the least-squares cubic equation given in Table I. The results of several other investigators for this system are compared with this equation in Figure 2. The agreement between the results of this study and the data of Lundberg and those of Savini *et al.* is remarkably good, but the results of Bennett and Benson and those of Larkin and McGlashan deviate somewhat more. The reason for the discrepancies among the data of the various investigators is not immediately apparent, but the results of this work fall, along with the data of Lundberg and those of Savini and coworkers, about in the center of the spectrum of curves. No attempt was made to achieve the ultimate in reagent purity but all the reagents used in this study had a purity in excess of 99.5%. Table II summarizes the specifications of the reagents employed.

The exothermic systems studied consisted of mixtures of dichloromethane with acetone at 0°, 15°, 30°, and 45° C., with methyl acetate at 30° and 45° C., and with 1,4-dioxane at 30° and 45° C. The acetone-dichloromethane system was studied over a sufficiently wide range of temperatures to justify the construction of a plot of $\Delta H/x_1x_2$ *vs.* temperature for a set of given compositions as shown in Figure 3. The points were derived from cubic equations which gave the best fit to the raw data in the least squares sense at each of the four temperatures. The curves were drawn by eye to best correlate the points, and values of $\Delta H/x_1x_2$ at each of the four temperatures were then read from the temperature curves at intervals of 0.05 mole fraction. Cubic equations were again used to correlate these points thus giving a representation of the $\Delta H/x_1x_2$ data smoothed both with respect to temperature and composition. These last equations are given in Table I.

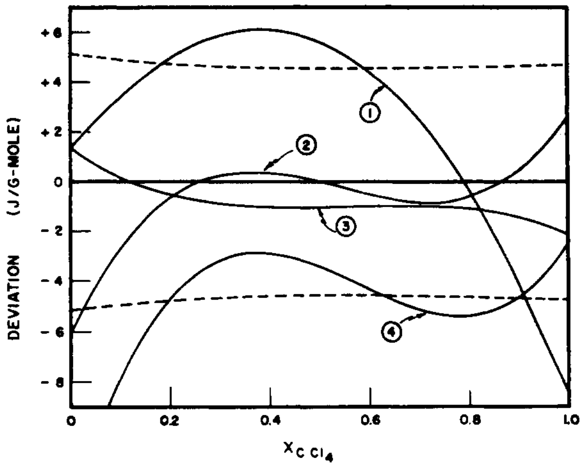

Figure 2. Deviation of literature values of $\Delta H/x_1x_2$ from those of this work for the benzene-carbon tetrachloride system at 25° C.

1 Data of Larkin and McGlashan (3)
2 Data of Savini *et al.* (6)
3 Data of Lundberg (4)
4 Data of Bennett and Benson (2)
---- ± 1% Deviation from this work

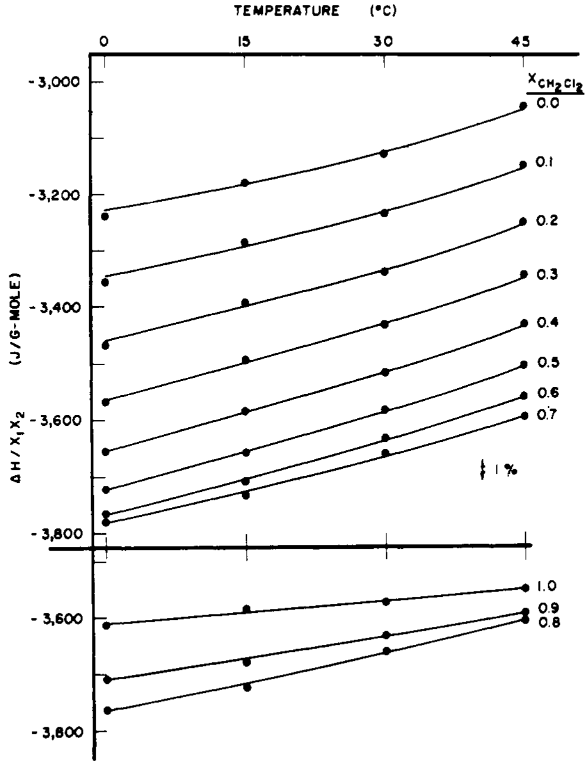

Figure 3. $\Delta H/x_1x_2$ vs. temperature for the system, acetone-dichloromethane

Table I. $\Delta H/x_1x_2$ Smoothing Functions[a]

$\Delta H/x_1x_2 = A + Bx_1 + Cx_1^2 + Dx_1^3$ (joules/gram mole)

Component 1	Component 2	Temp., ° C.	A	B	C	D	σ, %[b]
Carbon tetrachloride	Benzene	25	512.27	−216.53	249.06	−74.70	0.18
Dichloromethane	Acetone	0	−3,226.9	−1,201.2	35.9	780.9	0.23
		15	−3,180.8	−1,109.9	−51.0	750.4	0.21
		30	−3,123.8	−1,071.6	−19.2	643.5	0.20
		45	−3,048.8	−1,050.9	15.0	534.5	0.12
	1,4-Dioxane	30	−3,051.1	−2,629.2	16.4	636.1	0.27
		45	−3,088.9	−2,157.1	−528.0	851.5	0.20
	Methyl acetate	30	−2,722.9	−1,385.0	648.5	498.5	0.12
		45	−2,687.1	−1,088.6	176.7	637.8	0.14

[a] All raw data are given by Winterhalter (*8*). [b] σ is the root mean-square percentage deviation of the raw data points from the smoothing function.

Table II. Reagent Specifications

Reagent	Supplier and Grade	Purity[a], %	Refractive Index (25° C.) Experimental	Refractive Index (25° C.) Literature
Acetone	Matheson, Coleman & Bell Chromatoquality Reagent	99.9		
Benzene	Fisher Certified Reagent	99.9	1.49771	149792(*1*)
Carbon tetrachloride	Fisher Certified Reagent		1.45735	1.4570 (*5*)
Dichloromethane	Matheson, Coleman & Bell Chromatoquality Reagent	99.8	1.42105	1.4216 (*5*)
1,4-Dioxane	Matheson Coleman & Bell Chromatoquality Reagent	99.9	1.41995	1.4202 (*7*)
Methyl acetate	Fisher Certified Reagent Distilled under nitrogen blanket in a 150-theoretical-plate Podbielniak column	99.7		

[a] Via chromatographic analysis.

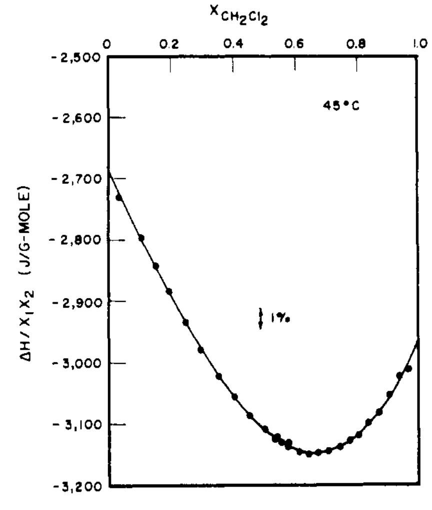

Figure 4. $\Delta H/x_1x_2$ vs. mole fraction dichloromethane for methyl acetate–dichloromethane at 45° C.

For the methyl acetate–dichloromethane system and the 1,4-dioxane–dichloromethane system, the equations reported in Table I represent the best least squares fit to the data points themselves. Figure 4 shows how well the raw data for the methyl acetate–dichloromethane system at 45° C. are correlated by the least squares fit of a cubic equation. This is typical of all the heat-of-mixing data reported here.

One finds it difficult to arrive at an objective estimate of the accuracy of an instrument as complex as the calorimeter described here. It was designed in the light of an error analysis, with the expectation that results would be accurate to well within 1%. As shown in Table I, the root mean-square percentage deviations of the raw data points from the smoothing functions lie between 0.12 and 0.27%. Clearly, the results are of high precision. They were also reproducible. Simulated runs made wherein acetone was mixed with acetone showed the absence of any stray thermal effects. Thus, it seems reasonable to conclude that all data reported are within ± 1% of the true values.

CONCLUSIONS

The calorimeter described allows the rapid and routine collection of accurate heat of mixing data for both endothermic and exothermic systems. It was possible to obtain a complete heat-of-mixing curve in a day. The calorimeter is, moreover, a most versatile instrument. It should be possible to use it with little or no modification to measure certain heats of reaction. Experiments performed with the system human blood-oxygen have demonstrated the feasibility of using it even for gas-liquid systems.

ACKNOWLEDGMENT

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Heat of Solution, Heat Capacity, and Density of Aqueous Urea Solutions at 25° C.

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Measurements were made of the heat of solution at 25° C. of urea in water over the concentration range 0 to 54.79% urea and of the densities and specific heats of the solutions. The partial molal heat contents were calculated from the results.

UREA, $(CONH_2)_2$, is used both as a solid and in solution in nitrogen fertilizers. As part of a continuing program of determination of thermochemical data on fertilizer compounds, measurements were made of the heat of solution of urea in water at 25° C. The measurement technique permitted the simultaneous determinations of the specific heats and densities of the solutions. The partial molal heat contents were calculated from the results.

MATERIALS AND APPARATUS

Reagent-grade urea was dissolved in water at 70° C. and the solution was filtered through fritted glass and allowed to cool slowly to room temperature. The crystals were filtered by suction on fritted glass, dried at 55° C. for 16 hours, and cooled and ground lightly to pass a 20-mesh screen. The product was stored in capped bottles until transferred to the thin-walled glass sample bulbs for use in the calorimeter. The filled bulbs were dried to constant weight at 55° C. before use.

The solution calorimeter has been described (*1*). Corrections for vaporization of water into the 160-cc. vapor space of the calorimeter were calculated to be less than 0.1% of the measured heats and were ignored. Temperature differences were determined to 0.0001° C. The unit of thermal energy was 1 defined calorie = 4.1840 absolute joules.

OBSERVATIONS

The concentration range 0 to 52.37% urea was covered in 40 measurements. A saturated solution at 25° C. was calculated to be 54.792% (20.181*m*) urea (*6*).

The observed integral heats of solution, all endothermic, are shown in Table I. The values of ΔH from Table I were fitted by a polynomial in molality. The equation giving the best fit was

$$\Delta H\text{, cal. per mole} = 3656.308 - 83.9082m + 5.54228m^2 - 0.24071m^3 + 0.00449022m^4 \qquad (1)$$

where m = concentration (molality) of urea. The mean probable error of Equation 1 was 0.624 cal. per mole urea, or ±0.02%. Integral heats of solution at even molalities to saturation are listed in Table II, together with partial molal quantities calculated by conventional methods (*2*).

Gucker and Pickard (*4*) measured heats of dilution directly in a differential calorimeter at low concentrations and at a few concentrations up to 12*m* urea. Their equation for the relative apparent molal heat content, ϕ_L, agrees with the present measurements with an average deviation of 6 cal. per mole urea, but they measured very small heat effects and their precision was of the order of 1%.

SPECIFIC HEATS

Electrical calibrations of the calorimeter system were made immediately before and after the dissolution of each portion of urea. The second electrical calibration for one dissolution and the first electrical calibration for the next dissolution referred to the same concentration of urea, and both values were used in the calculation of the specific heat of this solution. The weights of fixed volumes of solution, the observed temperature rise, and the electrical energy input permitted the calculation of the specific heat of each solution. The base for the specific heat calculations was the average of three determinations of the water equivalent of the calorimeter. The known specific heat of crystalline urea (*5*) at 25°C. permitted correction for variations in the weight and the sensible heat of the urea in the sample bulbs in the calorimeter before the bulbs were broken. The thin-walled glass bulbs were of uniform size and the variations in the amounts of glass were not significant.

The average temperature of the calibration period in each measurement was 25.1° to 25.7° C., but the values are listed in Table I as at 25° C. Since the specific heats at the observed concentrations fell on a smooth curve, errors introduced by the small variations in temperature from 25.0° C. were within the error of the observations. The observed values of specific heat from Table I were fitted to