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An Isothermal Displacement Calorimeter for Measuring Enthalpies of Mixing

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An isothermal displacement calorimeter of the Van Ness type has been constructed. The calorimeter was tested on three systems, benzene+cyclohexane, cyclohexane+*n*-hexane, and benzene+dichloromethane, at 25°C, and the performance of the calorimeter was discussed in connection with the literature values. The precision of the new calorimeter was within 0.5%; this was equal to, or better than, that of calorimeters of a similar type which have been constructed by several investigators.

After the pioneering work of Van Ness and his coworkers[1-3] in isothermal dilution calorimetry, several calorimeters based upon a similar principle have been constructed and relatively precise enthalpies of mixing have been measured for various kinds of binary systems.

We have great interest in the measurements of enthalpies of mixing for non-ideal solutions at a high dilution, and this type of calorimeter seems to be most suitable for our purpose. The calorimeter was designed with the following features. (a) It is capable of measuring both exothermic and endothermic heats of mixing without any external calibration.[3] (b) The wall inside the mixing vessel is kept free from any dampness from the bath water by employing a vessel of fixed dimensions, the type of calorimeter designed by Stockes and his coworkers.[4,5] (c) By adopting a flange-type lid for sealing the vessel, the calorimeter is simple and can easily be washed after a run. Furthermore, the use of a flange-type lid makes a precision bore tube unnecessary.

The principle and the operation of this type of calorimeter have been fully described by Van Ness and his co-workers, so only a brief outline describing some improvements in our instrument will be given in the next section.

Apparatus and Procedure

A schematic drowing of the apparatus is shown in

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[1] R. V. Mrazek and H. C. Van Ness, *Amer. Inst. Chem. Engrs. J.*, **7**, 190 (1961).

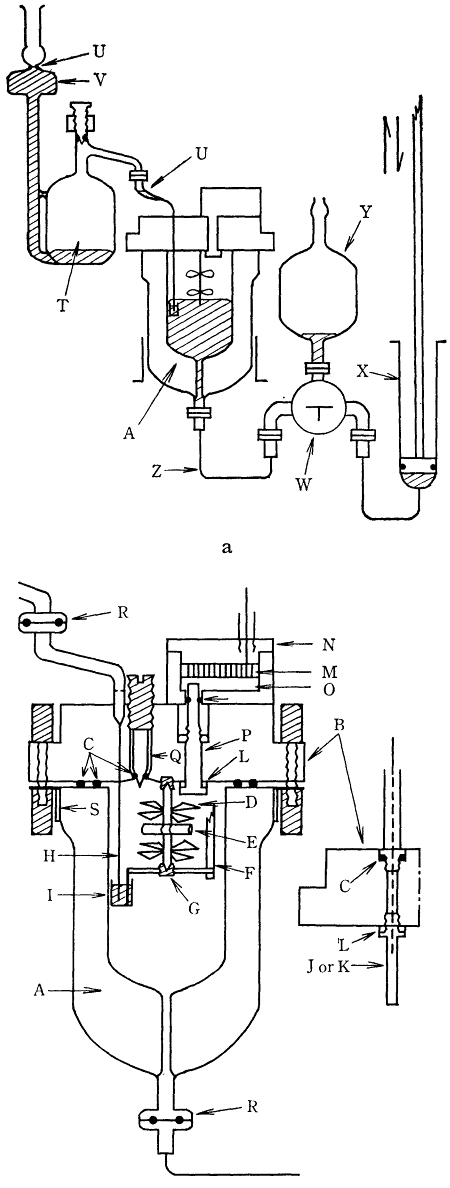
[2] C. G. Savini, D. R. Winterhalter, L. H. Kovach, and H. C. Van Ness, *J. Chem. Eng. Data*, **11**, 40 (1966).

[3] D. R. Winterhalter and H. C. Van Ness, *ibid.*, **11**, 189 (1966).

[4] R. H. Stokes, K. N. Marsh, and R. P. Tomlins, *J. Chem. Thermodynamics*, **1**, 211 (1969).

[5] M. B. Ewing, K. N. Marsh, R. H. Stokes, and C. W. Tuxford, *ibid.*, **2**, 751 (1970).

Fig. 1, accompanied by enlarged sections of the mixing vessel. The vessel, A, is a 130 m*l* Dewar flask which is silvered and which has a strip window. The upper face of the vessel is polished flat, and on it lid, B, is fitted with two O-rings, C, held by six bolts, to provide a tight seal. The lid contains six main parts: the stirrer, the feed tube to introduce the second component, the air vent to introduce the first component, the thermistor, the heater, and the cooling assembly.



a

b

Fig. 1. Diagram of isothermal displacement calorimeter. A, silvered Dewar flask with strip window, capacity 130 ml; B, lid of Teflon impregnated with molybdenum disulphide and carbon; C, Viton O-ring; D, 4-blade propllar (stainless steel), 19 mm diameter; E, magnet coated with Teflon attached to stirrer axle; F, stainless steel frame for stirrer; G, stainless teel screw to support stirrer; H, feed tube (needle of hypodermic syringe); I, mercury cup of stainless steel, capacity 1 m*l*; J, 37 KΩ thermistor in blass tube; K, 50 Ω manganin wire heater in brass tube; L, Teflon washer; M, cooling module; N, stainless steel heat sink; O, copper cooling plate; P, copper cooling rod, 6 mm diameter; Q, air vent, sealed with bakelite screw and Teflon needle; R, glass or Teflon connector; S, brass collar, cemented to Dewar. T, feed bulb for second component, capacity 70 m*l*; U, meniscuss; V, mercury reservior, capacity 15 m*l*; W, three way tap, Teflon-glass; X, precision piston burette; Y, mercuty reservior; Z, stainless steel tube, 0.8 mm internal diameter.

The stirrer, D, is supported between the bottom of the lid and the stainless steel frame, F. It is rotated at 430 min^{-1}, activated by an external magnet by means of a constant-speed motor. The feed tube, H, is inserted through the lid into the cup, I, located on the stirrer frame. The cup is filled with mercury in order to separate the second component from the first.

The thermistor, J, about 37KΩ at 25°C, is used as the temperature-sensing element in the calorimeter vessel; it is mounted in a thin-walled brass tube containing a drop of oil in order to improve the thermal contact. The thermistor is balanced against a D.C. bridge, and its output signal is amplified and taken to a recorder. The thermistor is calibrated against the bath temperature each time before a run begins.

The wire heater, K, with a resistance of about 50Ω, consists of manganin wire wound on a small glass capillary and mounted in a thin-walled brass tube. The brass tube contains grease to make a good thermal contact and is sealed on the top with a small Teflon plug to prevent heat leakage from the top of the tube. The heater is connected in series with a 5V D.C. power supply, a rheostat, and a standard 1Ω resistance. A volt box, which contains two standard resistances of 30KΩ and 100Ω connected in series, is connected in parallel with the heater in order to reduce the potential drop across the heater by a factor of 301 for measurring the voltage of the heater. Before switching over to the calorimeter heater, the D.C. power supply is discharged into a dummy heater for 1 hr to stabilize the voltage output. The heater control switch turns the current from a dummy heater load to the heater and simultaneously activates an electronic timer. The heater power is calculated by measuring the voltages across the standard 1Ω resistance and reduced voltages across the 100Ω standard resistance in the volt box.

The cooling assembly consists of a 1500 mA cooling module (Cambion Thermoionic Corp. Model 3952-1), M, sandwiched between a stainless steel heat sink, N, and a copper cooling plate, O. The 6-mm-diameter copper rod, P, is connected to the copper plate, O, and penetrates through the lid into the mixing vessel. The thermal contact between the components is promoted by a thin film of silicon grease. The upper face of the stainless-steel heat sink is exposed to the water in a thermostatted bath.

The stabilized D.C. power supply, connected in series with a rheostat and with the cooling module, is used to activate the cooling module. The current through the cooling module is fed into a standard resistance in the by-passed circuit and the potential drop across the standard resistance is amplified by a D.C. amplifier in order to get the same sensitivity as the measurement of the heater power, and is monitored on a recorder.

After the calorimeter has been placed over 2 hr in a thermostatted bath controlled to within ±0.001°C, the temperature in the vessel is controlled by means of cooling module to the set temperature of the surroundings within ±0.0002°C. The stirring energy causes the steady temperature in the vessel to be higher than that of the thermostat by $\Delta T \approx 0.01$ °C, so for the endothermic systems the current of the cooling module needs to compensate for only the energy dissipated by the stirrer. On the other hand, for the exothermic systems it needs to remove the energy supplied previously to the calorimeter heater. As soon as the temperature control is obtained, the run begins.

When the run is endothermic, the heater is switched on and the second component is introduced into the calorimeter vessel at such a rate that the contents of the vessel are kept at the set temperature within ±0.003°C. At the end of each injection, the mercury level in the feed tube and in the mercury reservoir is restored before the final addition of energy is made. The equilibrium temperature is restored within 0.0002°C by the manipulation of the burette drive and heater switches.

When the run is exothermic, the heater is turned off so that the thermal energy of mixing is removed from the mixing vessel at a net rate equal to the rate of energy added previously by the heater before mixing. The other procedures in the exothermic run are the same as that in the endothermic run.

Test on Standard Systems

Materials. The systems used for testing the new calorimeter were benzene+cyclohexane, and cyclohexane+*n*-hexane at 25°C as endothermic systems and dichloromethane+benzene at 25°C as an exothermic system. The materials used in the cyclohexane+*n*-hexane system were Phillips Petroleum Company "Research Grade." The specified purity of the two hydrocarbon reagents has 99.98 mol per cent; these materials were used without further purification. The benzene was shaken with sulphuric acid about 10 hr and then washed with water. After drying over calcium chloride about 6 months, the benzene was distilled through a 1.5-meter column over P_2O_5 at a reflux rate of 80: 1. The boiling range was 79.9 to 80.2°C. The cyclohexane used in the cyclohexane+benzene system was shaken with a 10: 50 nitric acid+sulphuric acid mixture about 40 hr and then washed with water. After having been dried over calcium chloride about 6 months, the cyclohexane was distilled through the same column over P_2O_5 at a reflux rate of 80: 1. The boiling range was 80.5 to 80.7°C. The dichloromethane was a commercially-available "special-grade" reagent; it was distilled through the same column at a reflux rate of 80: 1. The boiling range was from 39.6 to 39.8°C. The distilled dichloromethane did not react with mercury. The chromatographic analysis of all the materials showed no impurities.

Results and Discussion. The benzene+carbon tetrachloride system has been used in evaluating the calorimeter performance. This system is suitable for testing the efficiency of stirring because of the large density difference between components, but the study of this system is not well established as a standard. Therefore, we adopted the cyclohexane+*n*-hexane

TABLE 1. EXPERIMENTAL RESULTS FOR THE EXCESS ENTHALPIES OF MIXING

$C_6H_6+C_6H_{12}$ (25°C) H^E/J mol^{-1}			$C_6H_{12}+n\text{-}C_6H_{14}$ (25°C) H^E/J mol^{-1}			$C_6H_6+CH_2Cl_2$ (25°C) H^E/J mol^{-1}		
X_1	(Expt.)	(calc.)	X_1	(Expt.)	(calc.)	X_1	(Expt.)	(calc.)
0.0429	127.5	126.7	0.0287	19.3	19.4	0.0350	−3.2	−3.2
0.1003	280.5	279.9	0.0691	45.4	45.2	0.0703	−8.0	−8.0
0.1747	448.9	449.4	0.1197	75.3	75.4	0.1176	−15.9	−16.1
0.2418	573.5	574.0	0.1738	104.9	104.9	0.1786	−28.2	−28.4
0.2986	658.0	658.2	0.2263	130.7	130.8	0.2369	−41.0	−41.0
0.3594	726.8	727.0	0.2760	152.7	152.7	0.2881	−51.9	−51.7
0.4113	767.8	768.0	0.3352	175.5	175.3	0.3349	−61.0	−60.8
0.4603	791.3	791.7	0.3906	192.9	192.7	0.3794	−68.9	−68.3
0.5053	800.7	800.5	0.4396	204.8	204.9	0.4527	−77.3	−77.8
0.5159	801.6	800.7	0.4930	214.3	214.4	0.4899	−80.5	−81.0
0.5236	801.4	800.5	0.5342	218.4	218.8	0.5315	−82.8	−83.0
0.5289	799.8	800.2	0.5595	220.4	220.2	0.5796	−83.3	−83.3
0.5521	797.1	796.4	0.6064	219.8	219.8	0.6397	−80.6	−80.4
0.5973	779.7	779.5	0.6551	214.8	214.9	0.7171	−71.5	−71.4
0.6511	741.8	742.3	0.6977	206.7	206.6	0.7866	−58.9	−58.8
0.6948	697.3	698.2	0.7446	192.6	192.6	0.8597	−41.6	−41.3
0.7454	630.2	631.0	0.7957	171.0	170.9	0.9197	−24.3	−24.6
0.7949	547.7	547.8	0.8385	147.0	147.0	0.9639	−10.8	−11.3
0.8414	454.0	453.5	0.8778	119.9	120.0			
0.8947	325.5	324.8	0.9194	85.8	85.6			
0.9369	206.5	206.2	0.9547	51.1	51.4			
0.9750	85.8	86.0	0.9814	21.9	22.2			

TABLE 2. VALUES OF COEFFICIENTS FOR Eq. (1) BY METHOD OF LEAST SQUARES

System (25°C)	c_1	c_2	c_3	c_4	σ/J mol^{-1}
$C_6H_6+C_6H_{12}$	3200.51	−180.95	117.97	−59.61	0.53
$C_6H_6+n\text{-}C_6H_{14}$	861.32	−257.76	98.20	−14.82	0.18
$C_6H_6+CH_2Cl_2$	−326.46	116.94	135.62	6.18	0.29

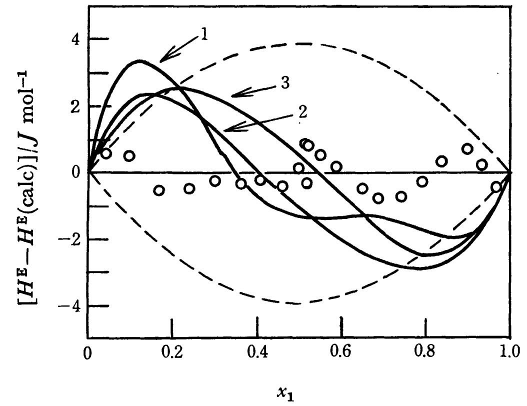


Fig. 2. Deviations of experimental and literature values of excess enthalpies for system benzene+cyclohexane at 25°C where x_1 is the mole fraction of benzene. ○, deviations of our experimental points; 1, data of Lundberg (8); 2, data of Stokes, Marsh and Tomlins (4); 3, data of Murakami and Benson (7); dashed curves represent ±0.5 per cent deviations.

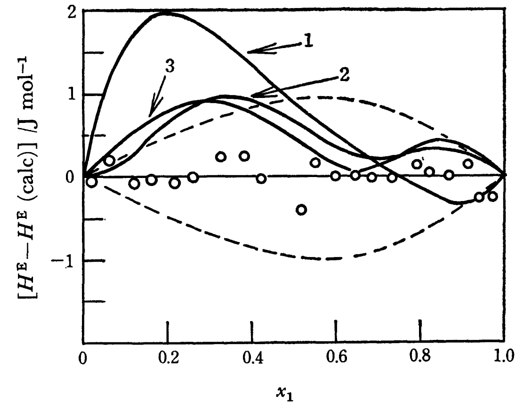


Fig. 3. Deviations of experimental and literature values of excess enthalpies for system cyclohexane+n-hexane system at 25°C where x_1 is the mole fraction of cyclohexane. ○, deviations of our experimental points; 1, data of McGlashan and Stoeckli (9); 2, Marsh and Stokes (10); 3, data of Murakami and Benson (7); dashed curves represent ±0.5 per cent deviations.

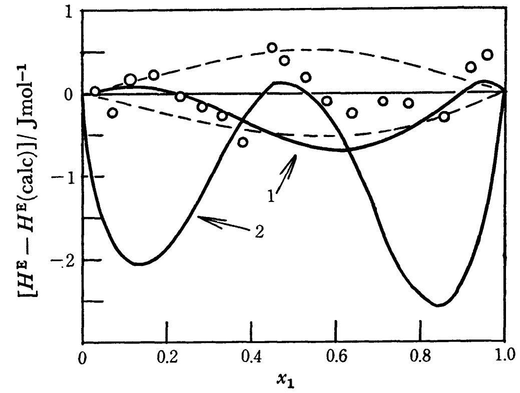


Fig. 4. Deviations of experimental and literature values of excess enthalpies for system benzene+dichloromethane at 25°C where x_1 is the mole fraction of benzene. ○, divations of our experimental points; 1, data of Murakami and Benson (7); 2, Otterstedt and Missen (11); dashed curves represent ±0.5 per cent deviations.

system, which had been suggested as a possible standard by McGlashan.[6]

All three systems used for testing our new calorimeter were measured at 25°C. The results are summarized in Table 1. The experimental points were fitted with the form[12]

$$H^E(\text{calc})/J\,\text{mol}^{-1} = x_1(1-x_1)\sum c_p(1-2x_1)^{p-1} \qquad (1)$$

by the least-squares method, where x_1 is the mole fraction of the (1) component. The coefficients, c_p, adopted are listed in Table 2, along with the corresponding standard deviations. The values of the standard deviations were estimated by means of the following equation:

$$\sigma = [\sum\{H^E - H^E(\text{calc})\}^2/n]^{1/2} \qquad (2)$$

where n is the number of observed points. The deviations of our experimental points from the smoothed function calculated from Eq. (2), $H^E - H^E_{\text{calc}}$, are shown in Figs. 2—4, together with those of other investigators, which are cited so that they can be compared with our results. Our results for the benzene+cyclohexane and cyclohexane+n-hexane systems are in close agreement with those of other investigators,[4,7-10] since the deviations of all sets fall almost entirely within about 0.5 per cent. However, it may be noted that our results appear to be slightly high at a low x_1 value and slightly low at a high x_1 value when compared with the results of other investigators.

At present, there is no suitable exothermic system for the test of a calorimeter. We used the benzene+dichloromethane system as an exothermic system, since the enthalpy of mixing for this system has been measured by several authors and since reliable data seem to have been obtained by using a similar type of calorimeter.[7] In the low-mole fraction of benzene, we observed an endothermic reaction which had too small a heat to be estimated. Our results agree well with those of Murakami and Benson,[7] but the results of Otterstedt and Missen[11] deviate fairly much at x_1=0.15 and 0.85 from ours.

The results obtained with our calorimeter seem to be internally consistent to better than 0.5 per cent, and the accuracy for the measurement of the enthalpy of mixing is believed to be equal to, or better than, that of the calorimeter described previously.

Results have been obtained by using this calorimeter for a number of systems containing polar materials; they will be reported in the near future.

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11) J-E. A. Otterstedt and R. W. Missen, *J. Chem. Eng. Data*, **11**, 360 (1966).

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