The minimum in furfural solubility in the water-rich phase also occurs at 35° C. The minimum is less pronounced, however, probably owing to the greater thermal energy of the system at the higher temperature. The minimum appears to be shifted to a slightly lower acid-to-water ratio, but the effect is not pronounced.

ACKNOWLEDGMENT

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Endothermic Heats of Mixing by Isothermal Dilution Calorimetry

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An evaluation is presented of an isothermal dilution calorimeter for the measurement of endothermic heats of mixing. Results accurate to well within ±1% are obtained routinely and rapidly. Both integral and partial molal heats of mixing may be measured, and data may be taken at mole fractions as low as 0.001.

THE PRINCIPLE of operation of the heat-of-mixing calorimeter discussed here was first described by Mrazek and Van Ness (4) in 1961. Subsequent refinement of this calorimeter has led to the development of a highly versatile instrument which lends itself to the rapid and routine production of data.

For a truly isothermal calorimeter, the only data necessary from which to calculate heats of mixing of endothermic systems are the masses of the constituents mixed and the electrical energy added to the system for maintenance of isothermal conditions. Such measurements lend themselves to high precision. The temperature of the calorimeter and the temperature of its surroundings must not only be the same, but must be held constant within very close limits. The practicality of the basic idea was demonstrated by Mrazek and Van Ness (4) with their publication of data on alcohol–aromatic hydrocarbon systems. Because of hydrogen bonding between alcohol molecules, these systems exhibit wide departures from ideality. In particular, a large heat addition is necessary to maintain isothermal conditions when a small quantity of alcohol is mixed with a relatively large amount of pure hydrocarbon. The calorimeter design of Mrazek and Van Ness (4) did not permit accurate determination of this important measurement. The new design allows measurements of integral heats of mixing to be made to mole fractions as low as 0.001, and at the same time provides means for the direct determination of partial molal heats of mixing. Two recent papers (5) have reported extensive data taken with the newly designed calorimeter for alcohol–n-hydrocarbon systems, but its description and evaluation are reserved to this paper.

APPARATUS

The general mode of operation of the calorimeter can be visualized by reference to the schematic diagram of Figure 1. The primary element of the calorimeter is a 150-ml. Dewar flask, A. One of the components to be mixed is weighed into this flask and is then sealed by the plug, B; all air is vented in the process. The second component, to be added to the one contained in the Dewar flask, is stored in the feed bulb, C, of about 100-ml. capacity. Small-bore tubing leads from the top of the

feed bulb, through plug B, into the interior of the Dewar flask, where its open end is submerged in mercury contained in a small cup, E. Mercury is initially drawn up into the tubing to a fiducial mark at D. The feed component in C is stored over mercury, which is introduced into the bottom of the feed bulb through a length of glass tubing leading upward to a 150-ml. mercury-storage reservoir, G. The mercury level is initially adjusted so that it just touches a probe in the neck at H as indicated by a neon bulb in a sensing system. This probe is located about 70 cm. above the bottom of the feed bulb, C. When the stopcock, I, is open, this head of mercury pressurizes the system.

The side-arm assembly, J, is used for loading and draining mercury from reservoir G. A rubber stopper, K, holding a line leading to a vacuum system, can be inserted into the top of reservoir G, allowing vacuum to be applied to draw mercury up into the reservoir from the feed bulb. This is used during the loading operation, as it is necessary to flush the feed bulb thoroughly and then fill it with the second component of the system to be studied. Flushing and loading are accomplished before the Dewar flask is placed on its closure plug. The cup, E, is removed from the end of the feed tube, and an extension is placed on the feed tube to allow it to dip into a beaker containing the second component. The feed bulb is flushed and then filled by appropriate use of the vacuum system. A small amount of mercury is then drawn into the end of the feed tube and the mercury-filled cup, E, is returned to position. The O-ring joints at L require no grease, nor does the stopcock, I, with its Teflon plug. Thus grease is never introduced into the system.

The entire apparatus shown in Figure 1 is mounted on a portable rack. For loading, this rack is fastened over a laboratory bench; for running, it is lowered into a constant-temperature bath, F, so that the Dewar flask and feed bulb are submerged. The plug, B, is held firmly in a fixed position, but the Dewar flask, A, is fastened to a movable frame that can be raised or lowered by turning a threaded rod. The mixing process is carried out by lowering the Dewar flask. This draws material from the feed bulb into the feed line so that it bubbles up through the mercury in cup E into the Dewar flask. The head of mercury from reservoir G, is the driving force for the process,

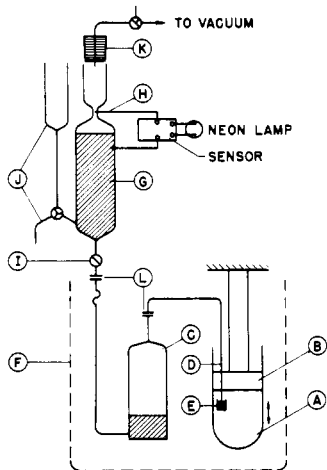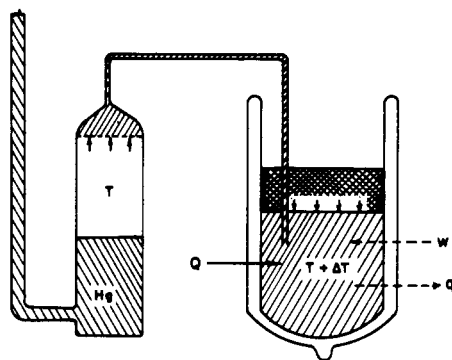Figure 1. Schematic diagram
of calorimeter

Figure 2. Dewar flask and feed bulb,
showing energy effects on the system
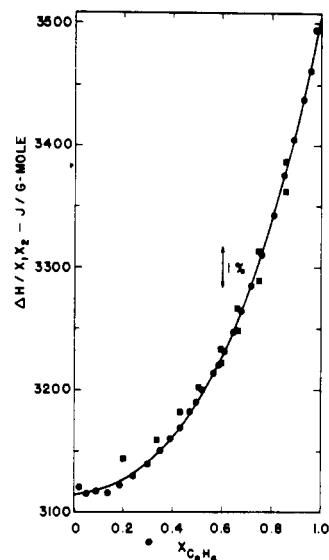during a mixing step

Figure 3. Benzene-cyclohexane
system at 25° C.

●This work ■ Lundberg (3) Equation of
curve is $\Delta H/x_1x_2$ = 3114.2 + 24.4x_1 +
136.3x_1^2 + 230.0x_1^3 The root mean-
square percentage deviation of the authors'
points from the curve is 0.084%

which may be interrupted at will for the recording of data. When the mixing process is stopped, the Dewar flask is raised slightly to force mercury from cup E up into the feed tube to the mark at D. Mercury is then weighed from a container into reservoir G, to restore the level in that reservoir to the probe at H. Knowledge of the mass of mercury added to the system allows calculation of the quantity of feed component introduced into the Dewar flask and, hence, of the composition of the solution in the Dewar flask. This process is continued until the plug, B, reaches the top of the Dewar flask. The amount of the first component initially weighed into the Dewar flask is chosen so that the volume of material in the Dewar flask at least doubles during a run. A second run is, of course, necessary with the components switched between feed bulb and Dewar flask.

A magnetically driven paddle provides sufficient stirring to ensure complete mixing throughout a run. Energy is supplied by electrical resistance heating to keep the temperature in the Dewar flask essentially constant during mixing. Precise measurements of potential drop and current through the heater and of time allow direct calculation of the heat added to maintain isothermal conditions. Temperature sensing is accomplished by a thermistor in a Wheatstone bridge circuit, and bath temperature is controlled throughout a run to ±0.001° C. A detailed description of the calorimeter, its auxiliary equipment, and of operating procedures is available (1).

RESULTS

Direct association of the measured electrical energy input with the heat of mixing takes no account of any secondary effects which may enter during the mixing process. These are now examined with reference to Figure 2. This figure shows the Dewar flask and the feed bulb. The thermodynamic system is taken as the contents of the Dewar flask and the portion of constituent 2 in the feed bulb which will be injected into the Dewar flask during a mixing step. Pressure forces are exerted on the system by the closure plug of the Dewar flask and by the remaining liquid in the feed bulb. These forces move during the mixing process and do work on the system. However, if they move slowly, their work effects essentially cancel.

The quantity, w, shown entering the system in Figure 2 represents the work of stirring. During the equilibration period before the start of a run the steady input of stirring work gradually raises the temperature in the Dewar flask above that of the constant-temperature bath and hence above that of the component stored in the feed bulb. If the bath temperature is T, eventually the Dewar temperature reaches a stable value T + ΔT such that ΔT is just large enough as a heat transfer driving

force so that q, the rate of heat transfer from the Dewar flask to the bath, balances the energy input of stirring. Thus the equilibrium temperature of the Dewar flask is higher by ΔT than the equilibrium temperature in the feed bulb, and these are the temperatures maintained during a run. Since the energy input of stirring is just balanced by the energy lost by heat transfer, no direct account need be taken of the stirring energy. However, during mixing the energy supplied by the calorimeter heater, Q, must not only balance the heat of mixing, but must also provide the sensible heat required to raise the temperature of the feed component from T to T + ΔT.

The energy input of stirring at constant stirrer speed is directly proportional to the density of the liquid in the Dewar flask, and ΔT is thus also directly proportional to density. For the vast majority of systems run, the density has been in the range 0.65 to 0.85 grams per cc. In this case, ΔT amounts to no more than 0.02° C. Liquid heat capacities for these same systems are about 0.5 cal./gram-°C. Injection of 50 grams of feed (which is about the norm for a full run) requires a sensible heat of about (0.5) (50) (0.02) = 0.5 cal. For highly nonideal systems, such as alcohol-hydrocarbon, the total heat, Q, for a full run is about 300 to 400 cal. Thus the correction for the sensible heat effect amounts to something less than 0.2%, and need not, therefore, be made with great exactness.

No other secondary effect of any significance is normally encountered in running the calorimeter. To test this conclusion, a series of experiments was conducted in which the calorimeter was run in the normal fashion except that the same liquid was placed in the feed bulb as in the Dewar flask. The measured heat was then the result of secondary effects only. The measured heats were accounted for within ±5% by the sensible heat requirements of raising the feed temperature to that of the Dewar flask.

During development of the calorimeter, the benzene-cyclohexane binary at 25°C. has been used as the test system. Data taken with the present calorimeter are shown in Figure 3, where they are also compared with recent data of Lundberg (3). Agreement between the two sets of data is within ±0.5%. The authors' data are well correlated by the line shown. With all the modifications and refinements made on the apparatus since the original design of Mrazek and Van Ness (4), the change in results has been no more than 1.5%. Figure 4 again compares
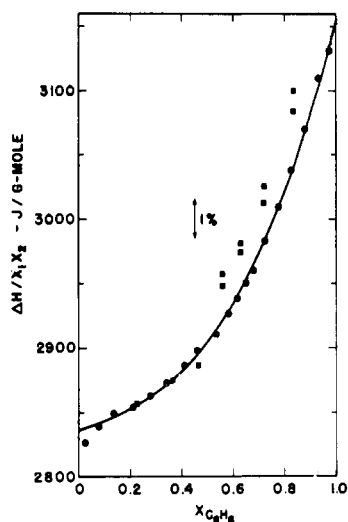
Figure 4. Benzene-cyclohexane system at 50° C.

●This work ■ Lundberg (3) Equation of curve is $\Delta H/x_1 x_2 = 2835.9 + 74.3x_1 + 12.2x_1^2 + 231.6x_1^3$ The root mean-square percentage deviation of the authors' points from the curve is 0.132%
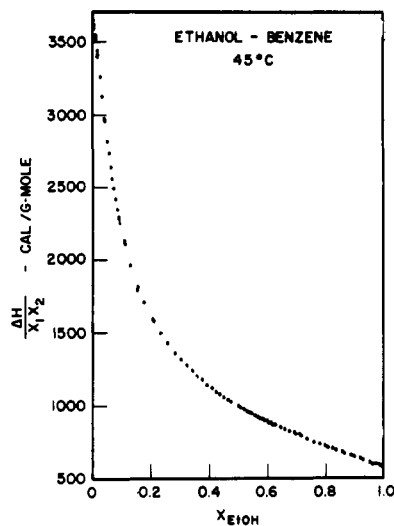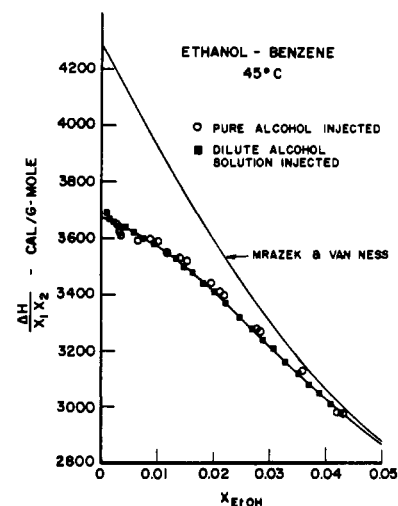

Figure 5. Ethanol-benzene system at 45° C.

Figure 6. Ethanol-benzene system at 45° C.

Region of high alcohol dilution, showing compari son with extrapolation of Mrazek and Van Ness (4)

the authors' results with those of Lundberg for the same benzene-cyclohexane system, but at 50° C.

An example of the extensive data taken with the calorimeter for alcohol-hydrocarbon systems is shown in Figure 5 where the results of several runs on the ethanol-benzene system at 45° C. are included. The reproducibility of the data is evident, and the runs made starting from opposite ends of the composition range overlap in the mole fraction range of 0.5 to 0.6.

Alcohol-hydrocarbon systems are highly nonideal, exhibit large endothermic heats of mixing, and show unsymmetric curves of ΔH vs. x, primarily as a result of the hydrogen-bonding characteristics of the alcohols. When the data are plotted as $\Delta H/x_1 x_2$ vs. x_1, the resulting curves rise steeply to very high values at high alcohol dilutions. The intercepts on such a graph represent the partial molal heats of mixing at infinite dilution, and these values are of considerable theoretical interest. However, $\Delta H/x_1 x_2$ becomes indeterminate as either x_1 or x_2 approaches zero. Hence, the intercepts on this type of plot must be obtained by extrapolation. Because of the steepness of these curves at low alcohol concentrations, extrapolation to zero alcohol concentration is uncertain unless measurements are made accurately at very low alcohol concentrations. The validity of such measurements depends on one's ability to determine accurately the masses of small amounts of alcohol injected into the Dewar flask. A practical method of accomplishing this is to use a dilute solution of alcohol in the hydrocarbon as feed material. The heat of mixing of this feed solution must be previously established. By this procedure measurements have been made to an alcohol mole fraction of 0.001.

A line representing the data of Figure 5 reverses curvature at an alcohol mole fraction of about 0.02. This is better illustrated in Figure 6 where an expanded view of the dilute alcohol region is shown. Data points obtained both by direct mixing of the pure components and by injecting a dilute alcohol solution are included. The present data are in excellent agreement with those reported by Mrazek and Van Ness (4) at mole fractions above 0.05. However, their extrapolation into the dilute-alcohol region was in error, as shown in Figure 6.

Figure 7 illustrates how well data taken with the calorimeter fulfill the requirements of thermodynamic consistency. The smooth curves on this plot represent the partial molal heats of mixing for the ethanol-benzene system at 45° C., as determined from the integral heat-of-mixing measurements represented in Figure 5. The precise calculation of partial molal heats of mixing from a plot of $\Delta H/x_1 x_2$ is described by Van Ness and Mrazek (6, 7). Superimposed on Figure 7 are points representing

directly measured values of partial molal heats of mixing. These values are determined by measurement of the energy required to maintain isothermal conditions in the calorimeter when a very small amount of feed component is introduced into the Dewar flask.

An examination of the benzene–carbon tetrachloride system, studied so extensively by Larkin and McGlashan (2), is of particular interest. Results are also reported by Lundberg (3). This system presents a severe test of the calorimeter, for it exhibits small heats of mixing and the two components have very different densities.

The density of carbon tetrachloride at 25° C. is about 1.58 grams per cc. and when equilibrated in the Dewar flask, its temperature rises about 0.04° C. above the bath temperature. Benzene has a density of about 0.87 gram per cc., and for it, ΔT is about 0.02° C. This large density difference creates an added problem, for during a run, as mixing takes place, density changes occur in the liquid in the Dewar flask. Since the power input of the stirrer at constant speed depends directly on density, the rate of energy input from the stirrer either increases or decreases during a run, depending on which component is initially placed in the Dewar flask. However, the temperature of the Dewar flask is held at the initial equilibrium value, and hence the heat-loss rate, controlled by ΔT, is constant. Thus heat is lost at a rate greater than the work-energy input when benzene is injected into carbon tetrachloride and the work-energy input rate becomes greater than the heat-loss rate when carbon tetrachloride is injected into benzene. This effect is superimposed on that of the sensible-heat requirement, adding to it in the one case and counteracting it in the other. If these effects are ignored, they can cause errors of 3 or 4%, since the heat of mixing for this system is, at most, only 28 cal. per gram mole.

It is not difficult to determine ΔT as a function of density of the liquid in the Dewar flask, and such experiments confirm the direct proportionality of this relation. Moreover, the heat-loss rate as a function of ΔT is readily established by experiment by energizing the heater at a low voltage and letting the temperature in the Dewar flask rise until the heat-loss equals the electrical energy input. Such experiments with the present calorimeter give a value for heat-loss rate of about 100 cal./hour-° C. From this value and a knowledge of the ΔT's caused by stirring alone, one can compute the rate of energy input caused by stirring as a function of ΔT or as a function of density of the liquid in the Dewar flask. With these figures in hand, corrections to Q, the measured electrical energy input, can be
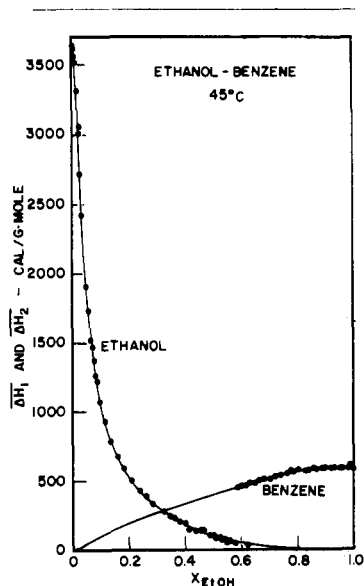
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Figure 7. Ethanol-benzene
system at 45° C.

Comparison of directly measured partial molal
heats of mixing with values determined from
integral heats of mixing

Figure 8. Benzene–carbon
tetrachloride system at 25° C.

O Uncorrected results from runs with full
stirrer speed. Δ Uncorrected results from run
at half stirrer speed. ● Corrected values from
runs at full stirrer speed. The equation of the
curve is $\Delta H / x_1 x_2 = 506.18 - 173.54 x_1 + 159.93 x_1^2 - 19.82 x_1^3$. The root mean-square
percentage deviation of the corrected data
points from the curve is 0.188%

Figure 9. Benzene–carbon
tetrachloride system at 25° C.

Comparison of results with those of Lundberg
(3), shown by dashed curve, and with those of
Larkin and McGlashan (2) as shown by the
solid squares. The solid line is the same as that
shown in Figure 8.

made, because the density of the liquid in the Dewar flask can
be calculated at each data point, and the known time of
operation is multiplied by the heat-loss rate. The effect of these
corrections is seen in Figure 8. The solid curve represents what,
in the authors' judgment, is the best correlation of the corrected
data.

As an added experiment, the benzene–carbon tetrachloride
system was rerun with the stirrer speed in the Dewar flask at
half the usual value—i.e., at 100 r.p.m. rather than 200 r.p.m.
Since energy input from stirring is proportional to the cube of
the stirrer speed, this decreased the work input and hence the
ΔT's and all corrections by nearly an order of magnitude,
making the corrections almost negligible. The run made by
injecting carbon tetrachloride into benzene was entirely
successful, and the data taken, uncorrected for any secondary
effects, are shown as open triangles on Figure 8. These data
agreed well with the earlier results. Attempts to run the other
half of the curve by injecting benzene into carbon tetrachloride
were unsuccessful because of inadequate stirring. This problem
arises only when the lighter component is injected into the
heavier, as in this instance the light component rises to the top
of the Dewar flask, forming a layer just below the closure plug.
Mixing occurs primarily at this layer, lowering its temperature
below that of the rest of the liquid in the Dewar flask, and since
heat transfer with the bath occurs almost entirely through the
plug, this has the effect of lowering measured values of Q.
Fortunately, this problem can always be detected, for it affects
only one of the two runs necessary for a system, and the two
halves of the heat-of-mixing curve fail to meet. Data are never
accepted unless the two half curves join within a small fraction
of 1%.

Results for the benzene–carbon tetrachloride system are
compared with those of Lundberg (3) and those of Larkin and
McGlashan (2) in Figure 9. Lundberg gives only an equation
for this system, but states that his data are fitted with a
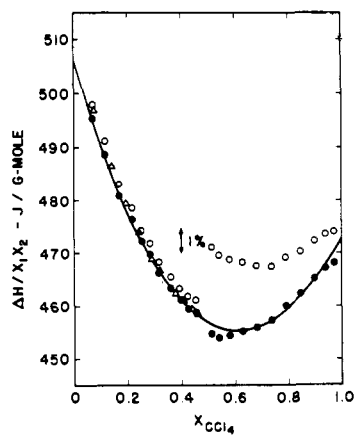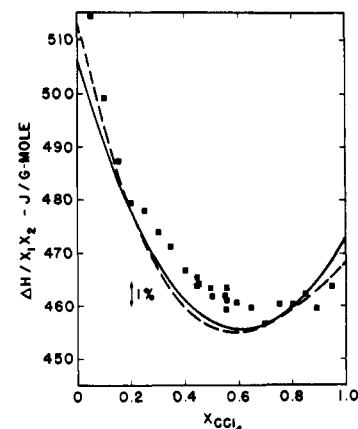standard error of 0.1%. The agreement between Lundberg's

equation and the present results is good. The Larkin and
McGlashan data differ in a systematic way. The reason for this
is not apparent. Like Lundberg, the authors made no effort to
achieve extreme purity of the components, and it is possible
that this is the source of the discrepancy. However, Lundberg's
materials were obtained from different suppliers. Fisher
certified reagents were used in this work for both components.
The lot analyses specified the maximum water content of the
benzene as 0.02% and of the carbon tetrachloride as 0.01%. In
any event, the agreement among the three sets of data is quite
satisfactory when one considers the delicacy of the measure-
ments and the fact that three different types of calorimeter
were employed.

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