Table IV. Heats of Formation from Elements in Their Standard States at 25° C.

Compound	Molecular Weight	Heat of Formation, $-\Delta H_f^\circ$, Kcal. Mole^{-1} Experimental	Other data (*4*)
Citraconic acid	130.10	197.04 ± 0.35	195.8
Itaconic acid	130.10	201.03 ± 0.14	199.6
α-Ketoglutaric acid	146.10	245.35 ± 0.21	
trans-Aconitic acid	174.11	294.63 ± 0.6	294.2
cis-Aconitic acid	174.11	292.7 ± 1.8	

together in Table III. These averages were used to calculate the data in Table IV for these two compounds. However, the heat of combustion of the two samples of *trans*-aconitic acid were noticeably different. Table I shows that sample A has a lower equivalent weight and lower melting point than does sample B. It seems likely that sample A contains some impurity, and only the data for sample B were used in calculating the heat of formation of *trans*-aconitic acid in Table IV.

The heats of combustion of the two samples of α-ketoglutaric acid are also significantly different. Table I shows that the equivalent weight of sample B is higher than the theoretical value for pure α-ketoglutaric acid. If it is assumed that this high equivalent weight is due to the presence of water in the sample, a correction can be applied to the heat of combustion. This corrected value for sample B is −2946.3 cal. gram^{-1} which differs from sample A by not much more than the calorimetric uncertainty. Therefore this seems to be the correct interpretation and the values listed in Table III as A, B (corr.) were obtained by adding 6.6 to each of the individual values of Sample B and then averaging the values for A and B together. This result was used to calculate the value for α-ketoglutaric acid in Table IV.

Because of its instability, rigorous drying conditions were not used for *cis*-aconitic acid, and it is possible that these samples contained some water. The high equivalent weight shown in Table I indicates this. On this basis, the corrected heat of combustion of *cis*-aconitic acid is −2745.1 cal. gram^{-1}. However, since there was no way to check this result, and since the size of the correction is less than the experimental uncertainty, the original uncorrected value was retained in calculating the value in Table IV. Purity tests described earlier indicate that both the *cis*- and *trans*-aconitic acids were contaminated with the other isomer. However the difference in heats of combustion of these two isomers is only 11 cal. gram^{-1}, and a significant error in the data could be produced only by a large amount of impurity.

The standard state heats of formation at 25° C. which are listed in Table IV were calculated from the experimental data of Table III using the N.B.S. values (*3*) of the heats of formation of carbon dioxide and liquid water with appropriate corrections to the 1961 atomic weight scale. The uncertainties were based on the values of 2σ listed in Table III. The uncertainties for *cis*- and *trans*-aconitic acids were increased by 50% to allow for the possible effect of impurities in these samples. The literature values shown in Table IV for comparison were obtained by recalculating the experiemnntal data of Stohman (*4*) in terms of modern units and atomic weights.

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RECEIVED for review October 12, 1964. Accepted February 8, 1965. This research was supported by Grant **GM-10868** of the National Institutes of Health. A portion of this paper was taken from the M.S. thesis of Imogene Lei. Material supplementary to this article has been deposited as Document No. 8318 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D.C. A copy may be secured by citing the document number and by remitting $1.25 for photoprints or $1.25 for 35 mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

Heats of Mixing of Some Alcohol-Hydrocarbon Systems

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Heats of mixing at 30° and 45° C. are reported for the liquid binary systems made up of ethanol with *n*-hexane and *n*-nonane, *n*-propanol with *n*-heptane, *n*-butanol with *n*-heptane, *n*-pentanol with *n*-hexane, and *n*-octanol with *n*-heptane and *n*-nonane.

AS PART of a continuing and comprehensive study of thermodynamic properties of alcohol-hydrocarbon systems, extensive experimental measurements were made of heats of mixing of the following alcohol-normal hydrocarbon binary systems at 30° and 45° C.: ethanol-*n*-hexane, ethanol-*n*-nonane, *n*-propanol-*n*-heptane, *n*-butanol-*n*-heptane, *n*-pentanol-*n*-hexane, *n*-octanol-*n*-heptane, and *n*-octanol-*n*-nonane. The measurements were made with an isothermal dilution calorimeter similar to that described by Mrazek and Van Ness (*4*). However, many modifications and refinements in detail have been incorporated into the present version of this calorimeter. The purpose here is exclusively the disclosure of data.

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Results obtained with this calorimeter have been compared for various systems with the results of several other investigators. For example, the authors' results for the benzene-carbon tetrachloride, benzene-cyclohexane, and heptane-toluene systems at 25° C. are in excellent agreement with the data of Lundberg (*3*). Figure 1 indicates the agreement of the authors' results with the data of Brown (*1*) for the ethanol-*n*-hexane system at 45° C. The limits of error of the results reported here are believed to be well within ±1%. The materials employed are listed in Table I, and were used in the "as supplied" condition. Further purification was not considered necessary, as experience has been that with high-grade materials the small amounts of impurities present are sufficiently close in nature to the primary material so as not to affect the heats of mixing significantly. Chromatographic analysis showed all materials to have a purity of at least 99 mole %.

The results of this work are presented in Table II. The values of $\Delta H/x_1x_2$ given in this table at even values of alcohol mole fraction were interpolated from the experimental data by machine computation through the use of the spline-fit technique (*2*). In the course of this computational procedure, the second derivative, $\partial^2\Delta H/\partial x_1^2$, determined by the spline-fit was evaluated at each data point. For an occasional point, this calculated second derivative was inconsistent with the general trend. Such points were rejected, and the spline-fit procedure was again applied to the remaining points. The agreement of the curves determined by the spline-fit interpolated values with the experimental data is illustrated in Figure 2.

The values of $\Delta H/x_1x_2$ at $x_1 = 0$ and at $x_1 = 1$ are finite but indeterminate. They also represent $\overline{\Delta H_1}$ and $\overline{\Delta H_2}$ at infinite dilution. Since they must be determined by extrapolation, they are subject to some uncertainty. At $x_1 = 1$ (where component 1 represents the alcohol), this extrapolation is easily made, for the curves in this region are not far from horizontal and exhibit small curvature. Thus values of $\Delta H/x_1x_2$ at $x_1 = 1$ are included in the tables. However, in the vicinity of $x_1 = 0$, the curves of $\Delta H/x_1x_2$ *vs.* x_1 are very steep and rise to high values. An effort was made to establish these curves in this region with some certainty

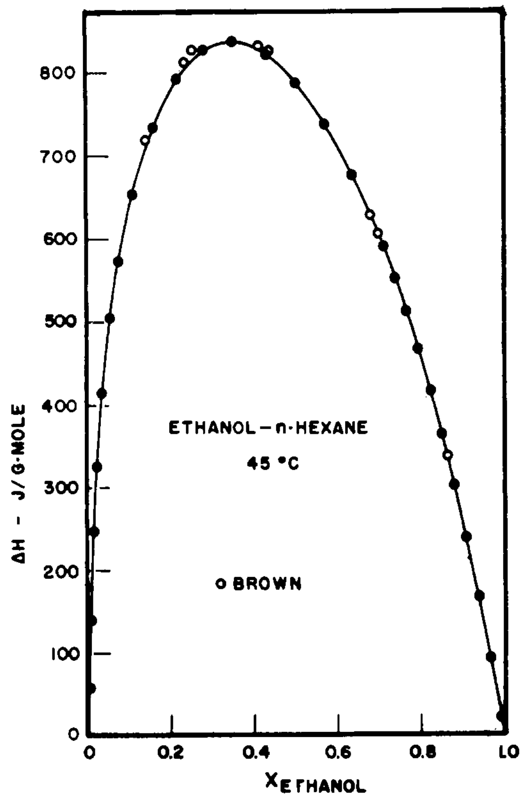

Figure 1. Heat of mixing for the ethanol–*n*-hexane system at 45° C.

Showing comparison of authors' results with those of Brown (*1*)

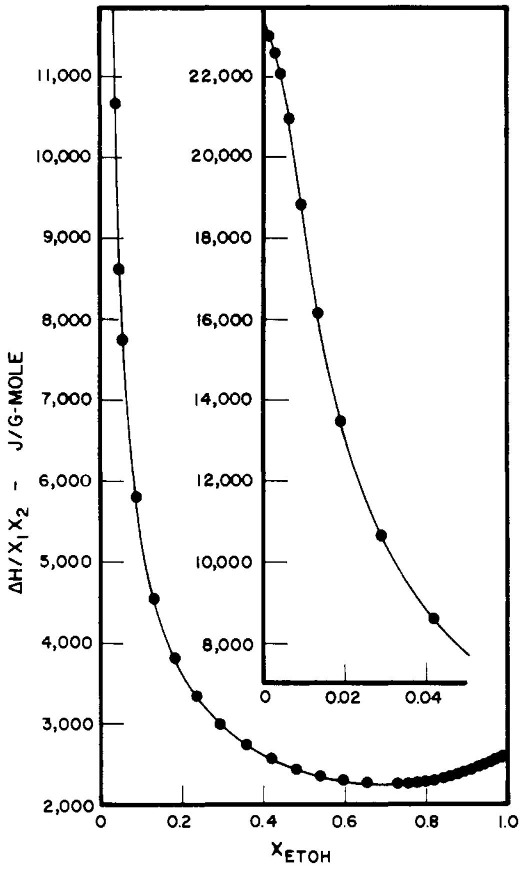

Figure 2. Heat of mixing as $\Delta H/x_1x_2$ for the ethanol–*n*-hexane system at 30° C.

Table I. Materials Employed

Material	Vendor's Specification	Refractive Index at 25° C. Experimental	Refractive Index at 25° C. Literature[a]
Ethanol	Reagent quality, 200 proof, U. S. Industrial Chemicals	1.35920	1.35941
n-Propanol	Certified, Fisher Scientific Co., boiling range, 96.9 – 97.4° C.	1.38337	1.38355
n-Butanol	Certified, Fisher Scientific Co., boiling range, 117.4 – 118.0° C.	1.3974	1.3973
n-Pentanol	Chromatoquality, Matheson Coleman and Bell, 99+ mole %.	1.4078	1.4081
n-Octanol	Certified, Fisher Scientific Co., boiling range, 194.5 – 195.0° C.	1.4273	1.4275
n-Hexane	99+ Mole %, Phillips Petroleum Co.	1.37241	1.37226
n-Heptane	99+ Mole %, Phillips Petroleum Co.	1.38508	1.38511
n-Nonane	99+ Mole %, Phillips Petroleum Co.	1.40312	1.40311

[a] American Petroleum Institute, Research Project 44.

Table II. Heats of Mixing, ($\Delta H/x_1x_2$), Joules/Gram Mole of Solution

Mole Fraction, Alcohol	Ethanol–*n*-Hexane		Ethanol–*n*-Nonane		*n*-Propanol–*n*-Heptane		*n*-Butanol–*n*-Heptane		*n*-Pentanol–*n*-Hexane		*n*-Octanol–*n*-Heptane		*n*-Octanol–*n*-Nonane	
	30° C.	45° C.	30° C.	45° C.	30° C.	45° C.	30° C.	45° C.	30° C.	45° C.	30° C.	45° C.	30° C.	45° C.
0.010	18,010	20,340	19,570	21,020	19,050	20,760	18,390	20,520	17,890	20,300	17,830	19,790	18,610	20,210
0.020	13,060	16,490	14,860	18,140	14,360	17,720	13,960	17,380	13,110	16,570	13,230	16,450	14,360	17,670
0.030	10,420	13,660	12,010	15,490	11,610	15,070	11,380	14,790	10,450	13,740	10,530	13,740	11,630	15,110
0.040	8,830	11,770	10,260	13,520	9,850	13,180	9,720	12,960	8,820	11,850	8,800	11,760	9,890	13,030
0.050	7,760	10,430	9,070	12,080	8,660	11,650	8,560	11,520	7,700	10,500	7,630	10,340	8,650	11,450
0.075	6,150	8,310	7,180	9,720	6,900	9,320	6,740	9,300	6,020	8,250	5,900	8,110	6,730	9,060
0.100	5,220	7,080	6,040	8,280	5,880	8,000	5,720	7,790	5,070	6,910	4,920	6,780	5,620	7,640
0.125	4,620	6,250	5,330	7,320	5,210	7,110	5,050	6,830	4,450	6,050	4,280	5,880	4,900	6,670
0.150	4,190	5,670	4,840	6,640	4,730	6,460	4,580	6,180	4,020	5,460	3,820	5,230	4,380	5,960
0.175	3,860	5,220	4,480	6,110	4,370	5,950	4,230	5,700	3,690	5,010	3,470	4,750	4,000	5,430
0.200	3,610	4,870	4,190	5,700	4,090	5,560	3,950	5,340	3,440	4,650	3,200	4,370	3,700	5,010
0.300	2,960	3,960	3,480	4,670	3,370	4,560	3,270	4,390	2,810	3,740	2,560	3,420	2,970	3,960
0.400	2,620	3,460	3,110	4,130	2,950	3,990	2,860	3,840	2,440	3,240	2,210	2,910	2,590	3,400
0.500	2,410	3,160	2,920	3,820	2,670	3,600	2,570	3,460	2,160	2,880	1,980	2,570	2,350	3,050
0.600	2,310	2,970	2,850	3,670	2,460	3,320	2,330	3,170	1,910	2,580	1,800	2,310	2,130	2,820
0.700	2,270	2,880	2,890	3,650	2,310	3,130	2,130	2,910	1,700	2,320	1,630	2,110	1,970	2,630
0.800	2,300	2,870	3,070	3,760	2,210	2,980	1,960	2,690	1,520	2,080	1,480	1,920	1,820	2,450
0.900	2,430	2,930	3,460	4,090	2,160	2,870	1,810	2,500	1,360	1,870	1,320	1,740	1,670	2,280
1.000	2,660	3,040	4,100	4,740	2,130	2,790	1,700	2,360	1,210	1,690	1,190	1,590	1,550	2,110

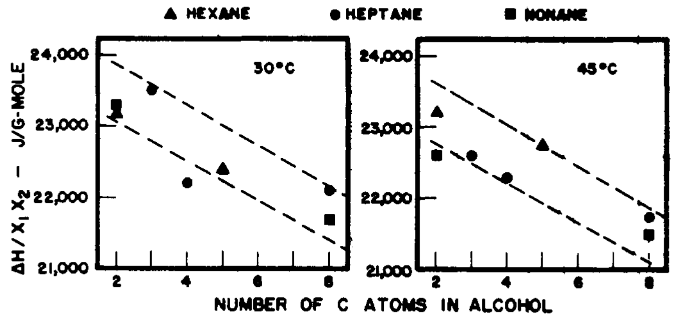

Figure 3. Intercepts of $\Delta H/x_1x_2$ at infinite alcohol dilution as a function of normal alcohol chain length, 30° C. and 45° C.

by making dilution runs for each system. That is, a solution of about 10 mole % in alcohol was mixed with the pure hydrocarbon. This procedure allowed data to be taken at alcohol mole fractions as low as 0.001. Nevertheless, at high dilutions the data become uncertain, and extrapolation with assurance to $x_1 = 0$ is most difficult. For this reason values of $\Delta H/x_1x_2$ at $x_1 = 0$ are not listed in the tables. Accurate determination of these values will be the subject of a separate study at a later date. It should also be remarked that values at $x_1 = 0$ published by Mrazek and Van Ness (*4*) for alcohol-aromatic systems are undoubtedly in error and are certainly too high. The authors' more recent work demonstrates that the curves of $\Delta H/x_1x_2$ change curvature in the concentration range below $x_1 = 0.01$ as shown in Figure 2. Thus very accurate measurements are required at high alcohol dilutions in order to establish values of $\Delta H/x_1x_2$ at $x_1 = 0$.

These intercepts as determined in this work are shown in Figure 3. The true values probably lie within the band width shown, which represents about 4% of the values. This appears to be a reasonable estimate of the uncertainty of these numbers. Certainly, these data are adequate to indicate a general trend with carbon number of the alcohol and with temperature. Thus it is seen that $\Delta H/x_1x_2$ at $x_1 = 0$ decreases consistently as one progresses from ethanol to *n*-octanol at both 30° and 45° C. Moreover, the values at 45° C. average slightly lower than those at 30° C. Since $\Delta H/x_1x_2$ at $x_1 = 0$ is identical with the partial molal heat of mixing of alcohol in an infinitely dilute solution of alcohol, these values are very nearly a direct measure of the hydrogen bond energies of the alcohols. The hydrogen bond energy of ethanol is thus seen to be about 23,500 joules per gram mole or 5.6 kcal. and that of *n*-octanol about 21,800 joules per gram mole or 5.2 kcal. at 30° C. These figures are based on the presumptions that normal hydrocarbons are inert solvents for the alcohols and that the energy for breaking hydrogen bonds is overwhelmingly the primary energy effect of the mixing process. Other heat-of-mixing data which the authors' have taken show conclusively that neither carbon tetrachloride nor aromatic hydrocarbons are inert solvents for alcohols.

The data listed in Table II are adequate to allow the preparation of accurate graphs of $\Delta H/x_1x_2$ *vs.* x_1 over the composition range 0.01 to 1.0. Approximate values at $x_1 = 0$ can be obtained from Figure 3. Accurate values of the partial molal properties $\overline{\Delta H_1}$ and $\overline{\Delta H_2}$ are readily calculated from such graphs by the method described by Van Ness (*5*).

No analytical expression has been found which satisfactorily represents $\Delta H/x_1x_2$ as a function of x_1 for the systems considered here. Attempts to use orthogonal polynomials have proved unsuccessful.

ACKNOWLEDGMENT

This work was supported by National Science Foundation Research Grant **GF-2199**, by a National Science Foundation Postdoctoral Fellowship (awarded to C.G. Savini), and by a National Science Foundation Cooperative Fellowship (awarded to D.R. Winterhalter). The work of W.R. Gustafson and L.H. Kovach in taking much of the data reported here is appreciated.

NOMENCLATURE

ΔH = heat of mixing in joules per gram mole of solution
$\overline{\Delta H}_1$, $\overline{\Delta H}_2$ = partial molal heats of mixing
x_1, x_2 = mole fractions of alcohol and hydrocarbon, respectively

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RECEIVED for review November 2, 1964. Accepted February 26, 1965.

Heats of Mixing for Partially Miscible Systems: Methanol–*n*-Hexane and Methanol–*n*-Heptane

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The use of an isothermal dilution calorimeter to determine the heats of mixing of partially miscible systems provides solubility data at the same time. Data are presented for the methanol–*n*-hexane system at 25°, 30°, 33.7°, 40°, 45°, and 50° C. and for the methanol–*n*-heptane system at 30°, 45°, and 60° C.

THE DATA reported in the preceding paper (*2*) pertained to alcohol-normal hydrocarbon systems which exhibited complete miscibility at room temperature and above. The data presented here were obtained with the same isothermal dilution calorimeter, and demonstrate its advantages for use with partially miscible systems. Not only are heat-of-mixing data determined, but in addition, the compositions representing miscibility limits are readily measured. This is demonstrated here for the methanol-*n*-hexane and methanol-*n*-heptane systems.

The methanol, used as received, was the Certified reagent of the Fisher Scientific Co. The lot analysis specified a boiling range of 64.4° to 65.0° C. and an assay of 99.9%. The *n*-hexane and *n*-heptane were Pure-grade reagents of the Phillips Petroleum Co., specified to have a minimum purity of 99 mole %. Chromatographic analysis showed the *n*-heptane to contain trace impurities only, and it was, therefore, used as received. The *n*-hexane contained measurable amounts of several impurities—nearly 1%—and was, therefore, purified by distillation to 99.9%.

The experimental data are shown in Figures 1 and 2. Some points at very high and very low mole fraction of methanol are omitted for clarity. Smoothed values of ΔH as read from large-scale plots are listed in Tables I and II. The methanol-*n*-hexane data have been smoothed with respect to temperature as well as with respect to composition. All results are believed to be accurate to well within ±1%.

Solubility data for the two systems considered here have been reported by Kiser, Johnson, and Shetlar (*1*). For the methanol-*n*-hexane system, agreement between the two sets of data is not particularly good. For example, at a solubility limit of methanol mole fraction equal to 0.270, the authors' find the temperature to be 25° C., whereas Kiser and coworkers give a value of about 27.5° C., some 2.5° higher.

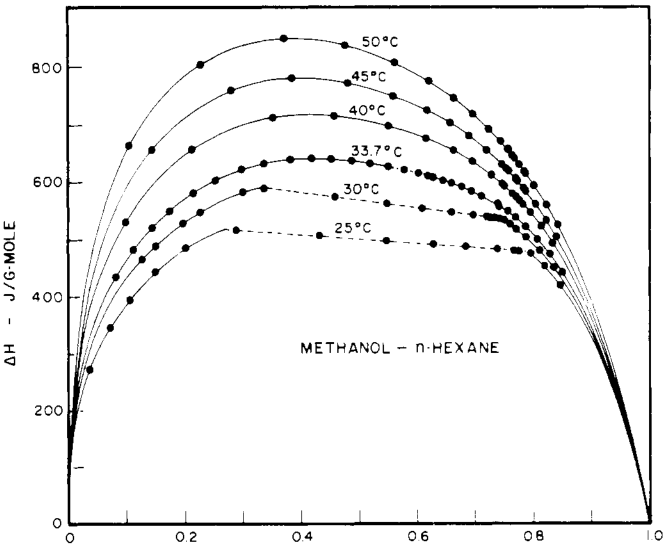

Figure 1. Heats of mixing, methanol–*n*-hexane

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