Heats of Mixing for Binary Mixtures. The Energy of Hydrogen Bonding between Alcohol and Ketone Molecules

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It is well known that the measurement of the heats of mixing of associated solutions is significant in investigating the interaction energy in a single component and between the different components. In a particular case such as the alcohol-nonpolar solvent system, such thermochemical treatments have already been extensively carried out and have revealed the energy of the intermolecular hydrogen bonding between alcohol molecules.[1] In cases where the associated solutions consist of alcohol and acceptor components, such as ketone, thermochemical data are not ample and detailed enough to allow us to estimate the energy of the intermolecular hydrogen bonding between these pair molecules.

In this paper we shall report the heats of mixing for such alcohol - ketone systems as isopropanol - acetone and *s*-butanol - ethyl methyl ketone systems, as well as those for alcohol - hexane and ketone - hexane systems, and shall estimate the energy of the hydrogen bonding of the $O-H\cdots O=$ type by means of the thermochemical cycle.

Experimental

Materials.—All the samples were purified from commercial products according to the usual method described in the literature,[2] and then they were finally distilled with a Stedman-type column. Considerable attention was devoted to removing the small amount of remaining water; as a result, these fractionated samples did not show a peak for water on a gas chromatogram. Therefore, the water content in these samples was estimated to be 1/100 weight percent or less.

Apparatus and Procedure.—A block diagram of the entire apparatus for measuring heats of mixing is shown in Fig. 1. The calorimeter is of the twin type, shown in Fig. 2, consisting of a mixing vessel and a reference vessel, each held with a vessel holder and fixed in a submarine vessel, installed in a water thermostat at 25°C kept constant to 1/1000°C. The mixing vessel is similar to that described in a previous paper[3] but was modified in some points, as is shown in Fig. 3. For the measurement of dilute solutions, another mixing vessel was used, one which was larger than that one used in the moderate concentration range and which could accomodate about 4 ml. of the liquid sample.

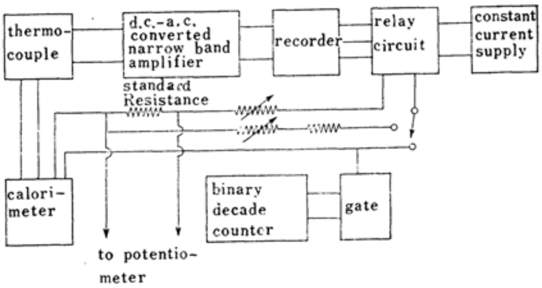

Fig. 1. Block diagram of the apparatus.

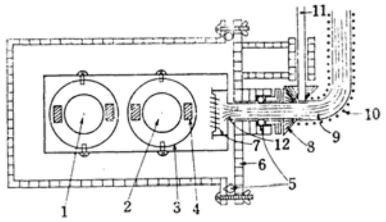

Fig. 2. Calorimeter

1: Reference vessel holder
2: Mixing vessel holder
3: Brass ring
4: Teflon spacer
5: "O" ring rubber packing
6: Submarine vessel
7: Hermetic seal
8: Bebel gear
9: Rubber tube
10: Spring wire
11: Handle
12: Pivot

Before mixing, two components are separated by mercury in the mixing vessel; during mixing, the holder is turned upside down by rotating it around the pivot through the manipulation of the handle from the outside of the submarine vessel.

The temperature change on mixing is detected as the difference in the thermal electromotive force of the thermocouple between the mixing vessel and the reference vessel, which acts as a reference bath for the thermocouple and which contains only mercury. Even a small difference in the electric

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[1] L. Sarolea-Mathot, *Trans. Faraday Soc.*, **49**, 8 (1953); J. A. Barker, *J. Chem. Phys.*, **20**, 1526 (1952).

[2] A. Weissberger and E. S. Proskauer, "Organic Solvents," Interscience Publishers, New York (1955).

[3] K. Amaya, This Bulletin, **34**, 1271 (1961).

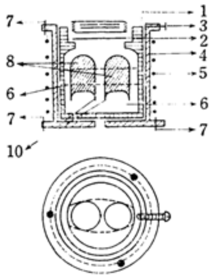

Fig. 3. Cross section and upper side view of vessel holder and mixing vessel.

1 : Stainless steel vessel
2 : Teflon packing
3 : Male screw
4 : Vessel holder
5 : Heater
6 : Mercury
7 : Thermocouple
8 : Sample liquids
9 : Spring steel plates
10 : Glass bells

potential is amplified by the d. c.—a. c. converted narrow band amplifier, the output signal of which is fed to an automatic pen recorder (YEW type E-30). With this amplifier a $\pm 1\times 10^{-8}$ V. change can be detected; the temperature coefficient of one junction of a copper-constantan thermocouple is about 40 μV./°C, so that the sensitivity of our thermometer made of 7 junctions corresponds to about $\pm 3\times 10^{-5}$ deg.

The main construction of the electrical circuit for the automatic thermal compensation is almost the same as that described previously, except that the meter relay is replaced with a microswitch connected to the recorder. The period during which the electric current from the constant current supply passes through the calorimeter heater is automatically registered on the binary decade counter operated with a standard 100 kc. oscillator.

Results and Discussion

The results obtained are given in Tables I, II, III, IV, V and VI and in Figs. 4 and 5, where x_1 is the mole fraction of component 1, and where ΔH^{M} and $\Delta H^{\mathrm{M}}_{x_1}$ are the heats of mixing expressed as cal./mol. of the mixture and those expressed as kcal./mol. of component 1 at mole fraction x_1 respectively.

Plotting $\Delta H^{\mathrm{M}}_{x_1}$ against x_1 and then extrapolating the curve to the infinite dilution ($x_1 \rightarrow 0$) for each system, as is shown in Figs. 4 and 5, we can obtain the heat of mixing per mole of component 1 at the infinite dilution as: 1.76 kcal. for the isopropanol (1) - acetone (2) system, 2.15 kcal. for the acetone (1) - *n*-hexane (2) system, 1.82 kcal. for the *s*-butanol (1) - ethyl methyl ketone (2) system and 1.90 kcal. for the ethyl methyl ketone (1) - *n*-hexane (2) system.

TABLE I. HEAT OF MIXING OF ISOPROPANOL (1) AND ACETONE (2)

Mole fraction of the component 1, x_1	ΔH^{M}, cal./mol. of mixture	$\Delta H^{\mathrm{M}}_{x_1}$, kcal./mol. of the component 1
0.00515	8.97	1.74
0.0143	24.2	1.69
0.0573	91.7	1.60
0.0607	94.0	1.55
0.0803	121.1	1.37
0.128	175.0	1.37
0.134	183.0	1.37
0.225	267.4	1.19
0.398	362.5	0.910
0.438	360.9	0.824
0.451	378.1	0.839
0.489	390.6	0.800
0.613	351.6	0.573
0.724	313.1	0.432
0.800	254.5	0.318
0.879	179.6	0.204

TABLE II. HEAT OF MIXING OF *s*-BUTANOL (1) AND ETHYL METHYL KETONE (2)

x_1	ΔH^{M} cal./mol.	$\Delta H^{\mathrm{M}}_{x_1}$ kcal./mol.
0.1470	225.2	1.532
0.3136	373.0	1.189
0.5073	404.8	0.7980
0.5492	409.1	0.7449
0.6250	387.8	0.6204
0.7606	317.9	0.4178

TABLE III. HEAT OF MIXING OF ACETONE (1) AND *n*-HEXANE (2)

x_1	ΔH^{M} cal./mol.	$\Delta H^{\mathrm{M}}_{x_1}$ kcal./mol.
0.0513	97.9	1.91
0.0671	119.0	1.77
0.0771	136.8	1.78
0.1466	219.1	1.49
0.1748	250.2	1.44
0.3587	362.5	1.01
0.5561	376.6	0.677
0.7357	288.8	0.393
0.8988	131.7	0.147

TABLE IV. HEAT OF MIXING OF ETHYL METHYL KETONE (1) AND *n*-HEXANE (2)

x_1	ΔH^{M} cal./mol.	$\Delta H^{\mathrm{M}}_{x_1}$ kcal./mol.
0.0563	84.7	1.51
0.0819	118.3	1.44
0.1424	164.2	1.15
0.2398	235.2	0.982
0.3305	277.6	0.840
0.4342	302.7	0.697
0.5547	297.4	0.536
0.7525	226.1	0.301

TABLE V. HEAT OF MIXING OF ISOPROPANOL (1) AMD *n*-HEXANE (2)

x_1	ΔH^M cal./mol.	$\Delta H^M_{x_1}$ kcal./mol.
0.1332	133.5	1.00
0.2270	180.1	0.794
0.3052	195.3	0.640
0.4085	191.0	0.468
0.5453	185.8	0.341
0.8005	96.5	0.121
0.8758	50.5	0.058

TABLE VI. HEAT OF MIXING OF *s*-BUTANOL (1) AND *n*-HEXANE (2)

x_1	ΔH^M cal./mol.	$\Delta H^M_{x_1}$ kcal./mol.
0.1655	174.5	1.06
0.2959	216.8	0.733
0.4319	222.2	0.515
0.5823	198.4	0.341
0.7337	158.8	0.216
0.8279	101.2	0.122

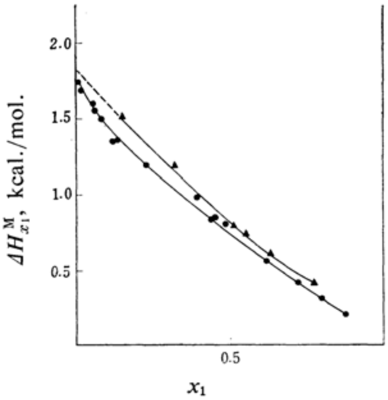

Fig. 4. Heats of mixing, alcohol - ketone systems.

● Isopropanol + Acetone
▲ *s*-Butanol + Ethyl methyl ketone

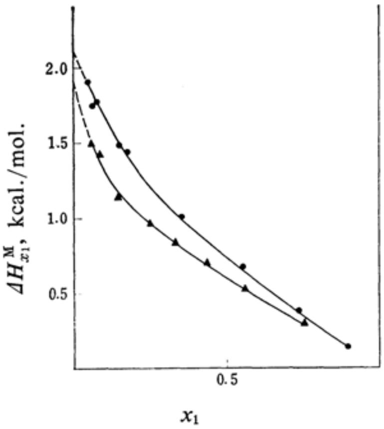

Fig. 5. Heats of mixing, ketone - *n*-hexane systems.

● Acetone + *n*-Hexane
▲ Ethyl methyl ketone + *n*-Hexane

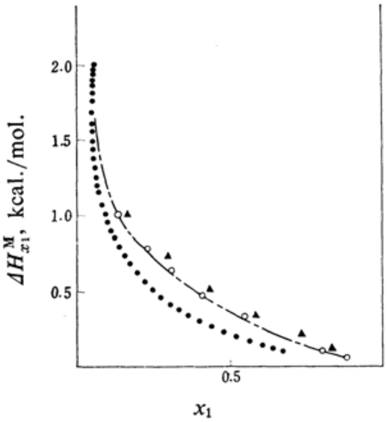

Fig. 6. Heat of mixing, alcohol - *n*-hexane systems.

··· *n*-Alcohol + *n*-Hexane (from Pahlk)
-·- Isopropanol + *n*-Hexane (from Pahlk)
○ Isopropanol + *n*-Hexane
▲ *s*-Butanol + *n*-Hexane

$\lim_{x\to 0} \Delta H^M_{x_1} = 5.8$ kcal. for the dotted curve
$\lim_{x\to 0} \Delta H^M_{x_1} = 5.9$ kcal. for the broken curve

We also measured the heats of mixing $\Delta H^M_{x_1}$ for the isopropanol - *n*-hexane (2) and the *s*-butanol (1) - *n*-hexane (2) systems; the results obtained are plotted in Fig. 6 against x_1, together with the dotted curves for other kinds of alcohol - *n*-hexane systems taken from the literature.[4] As this figure shows, the curves are very steep at small x_1 values, and the extrapolation to $x_1=0$ is apt to produce some errors. The value of $\lim_{x_1\to 0} \Delta H^M_{x_1}$ obtained by Pahlk[4] for the isopropanol-hexane system is 5.90 kcal., and his $\Delta H^M_{x_1}$-x_1 curve coincides with ours in the concentrated range, as is shown in Fig. 6. Therefore, we have adopted 5.90 kcal. for the $\lim_{x_1\to 0} \Delta H^M_{x_1}$ of this system. For the *s*-butanol - hexane system, however, we could not find a $\lim_{x_1\to 0} \Delta H^M_{x_1}$ in the literature. In order to estimate the value for this system, we compared $\Delta H^M_{x_1}$ for the normal alcohol - hexane systems with those for the secondary alcohol - hexane systems. In the former cases, the $\lim_{x_1\to 0} \Delta H^M_{x_1}$ values were reported to be 5.8 kcal.,[4] and for the isopropanol system this value is 5.9 kcal., as has been mentioned above. On the basis of the comparison of these three curves

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[4] Landolt-Börnstein, "Physikalishe-Chemischen Tabellen," Springer, Berlin (1936); G. von Elbe, *J. Chem. Phys.*, **2**, 73 (934).

TABLE VII. PHYSICAL CONSTANTS OE ALCOHOL-KETONE COMPLEXES NECESSARY FOR THE CALCULATION OF Eq. 2, AND CALCULATED VALUES OF ΔG_i AND ΔH_i^{d}

	μ D	t °C	α $\times 10^{-23}$	a^3 $\times 10^{-23}$ cc.	$-\Delta G_{\mathrm{K}}$ kcal./mol.	$-\Delta H_{\mathrm{K}}^{\mathrm{d}}$ kcal./mol.	$-\Delta G_{\mathrm{H}}$ kcal./mol.	$-\Delta H_{\mathrm{H}}^{\mathrm{d}}$ kcal./mol.
Isopropanol-Acetone complex	4.20	15	1.3339	5.9062	2.5428	4.00	0.8800	1.495
		20	1.3342	5.9434	2.5176	3.98	0.8694	1.481
		25	1.3345	5.9806	2.4924	—	0.8588	—
					Average	3.99	Average	1.49
s-Butanol-Ethyl methyl ketone complex	4.08	15	1.6957	7.1489	1.9838	3.08	0.6895	1.15
		20	1.6977	7.1908	1.9648	3.08	0.6815	1.14
		25	1.6997	7.2328	1.9457	—	0.6735	—
					Average	3.08	Average	1.15

Dielectric constant;

t°C	15	20	25
n-Hexane	1.897	1.890	1.883
acetone	(21.7)	21.2	20.7
Ethyl methyl ketone	18.98	18.51	18.07

in Fig. 6, we may estimate $\lim_{x_1 \to 0} \Delta H_{x_1}^{\mathrm{M}}$ to be 6.0 kcal. or a little less for the *s*-butanol - hexane system.

In pure alcohol, all the molecules form hydrogen bondings with each other, while each alcohol molecule in the infinite dilution of alcohol in hexane is surrounded by hexane molecules and the hydrogen bonds are broken. Therefore, the values of about 6 kcal. represent energy sufficient to break the hydrogen bonds of pure alcohol. Similarly, the $\lim_{x_1 \to 0} \Delta H_{x_1}^{\mathrm{M}}$ value for each alcohol - ketone system corresponds to the energy of transfer from the pure alcohol state to one in which each alcohol molecule makes a hydrogen bond with a ketone molecule and in which such complexes are surrounded with a large amount of the ketone medium. Roughly speaking, the difference between the $\lim_{x_1 \to 0} \Delta H_{x_1}^{\mathrm{M}}$ value for the alcohol - ketone system and that for the same alcohol - hexane system, that is about 4 kcal., may correspond to the energy of alcohol - ketone hydrogen bonding.

In order to estimate these hydrogen bond energies in some detail, we have considered the thermochemical cycle shown in Fig. 7, where A, K, H and A-K represent molecules of alcohol, ketone, hexane and alcohol - ketone complexes respectively, and where the hypothetical state IV is assumed. Further, we assume that the whole system contains one mole of A, x mol. of K, and y mol. of H, and that $1 \ll x \ll y$.

Judging from this figure, it is reasonable to consider that the true hydrogen bond energy of the A-K complex is equal to the energy change, ΔH_5, for process 5 from state III to state IV. This energy change is easily given by the thermochemical cycle as:

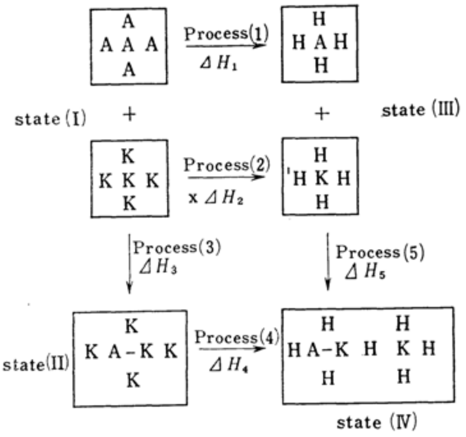

Fig. 7. Thermochemical cycle.

State (I) : One mole of alcohol and x mol. of ketone, both being separated.
State (II) : One mole of A-K complex in the ketone medium, each complex being separated each other.
State (III) : One mole of alcohol, x mol. of ketone in the hexane medium.
State (IV) : One mole of A-K complex and $x-1$ mol. of ketone in the hexane medium.
Process (1) : One mole of alcohol is diluted by a large amount of hexane.
Process (2) : x mol. of ketone are diluted by a large quantities of hexane.
Process (3) : Mixing of alcohol and ketone.
Process (4) : The state (II) is diluted by a large quantities of hexane without breaking A-K complex.

$$\Delta H_5 = -\Delta H_1 - x\Delta H_2 + \Delta H_3 + \Delta H_4 \qquad (1)$$

Since ΔH_1, ΔH_2 and ΔH_3 were measured, it is necessary to estimate the ΔH_4 in process 4 in order to determine ΔH_5.

Two energy changes will contribute to ΔH_4.

The first one, ΔH_4^{KH}, is the heat of the dilution of $(x-1)$ mol. of ketone by large quantities of hexane, which is equal to $(x-1)\ \Delta H_2$. The second one, ΔH_4^d, is due to the difference in the dipolar stabilization enegy of an A-K complex dipole arising from the reaction field by different media, though the van der Waals energy contributes in the latter case to some extent, though this extent is very difficult to estimate and so is disregarded here.

To estimate the energy change for the latter case, we have followed the usual treatment of polar liquids by Onsager,[5] according to which the dipolar stabilization free energy, ΔG_i, is expressed as:

$$\Delta G_i = -(1/2)\mu^2 R/(1-R\alpha)$$
$$R = 2(\varepsilon_i - 1)/(2\varepsilon_i + 1)a^3 \qquad (2)$$

where μ, a and α are the dipole moment, the molecular radius, and the polarizability of the A-K complex, respectively, and where ε_i is the dielectric constant of the medium, i, that is, K or H. Further, the dipolar stabilization energy, ΔH_i^d (i=H or K), is obtained from ΔG_i as:

$$\Delta H_i^d = \frac{\partial(\Delta G_i/T)}{\partial(1/T)}$$

Therefore, the dipolar part of the energy change in process 4 may be given as:

$$\Delta H_4^d = \Delta H_H^d - \Delta H_K^d$$

The data necessary for this calculation and the results obtained are summarized in Table VII. The values of the dipole moment of A-K complexes were determined by the vector addition of those of two component molecules, and the α and a of a complex molecule were assumed to be the sum of those of the two component molecules.

The ΔH_4^d values thus obtained are 2.50 kcal. for the isopropanol - acetone and 1.93 kcal. for the *s*-butanol - ethyl methyl ketone systems. To check the magnitude of these energies, we obtained the difference between the dipolar energy of one mole of ketone in the hexane medium and that of one mole of pure ketone by calculations similar to those described above. The results are as follows: 2.48 kcal. for acetone - hexane and 1.88 kcal. for ethyl methyl ketone - hexane. These values should correspond to the dipolar part of the heats of the dilution of ketone in hexane. Since the measured heats of dilution are 2.15 kcal. and 1.90 kcal. for acetone and ethyl methyl ketone respectively, the calculated dipolar energies are more than or nearly equal to the heats of dilution, indicating that the dipolar energies have been overestimated, particularly in the system containing such small molecules as acetone. Therefore, the ΔH_4^d value of 2.50 kcal. for isopropanol - acetone seems to be overestimated and some correction (at least 0.4 kcal.) may be necessary.

Using ΔH_4^d and other measured values, ΔH_5 is calculated by Eq. 1 as:

for isopropanol - acetone:

$$\Delta H_5 = -5.90 - 2.15\,x + 1.76 + 2.50 + 2.15(x-1)$$
$$= -3.79 \text{ kcal.}$$

for *s*-butanol - ethyl methyl ketone:

$$\Delta H_5 = -6.0 - 1.90\,x + 1.82 + 1.93 + 1.90(x-1)$$
$$= -4.15 \text{ kcal.}$$

Taking account of the overestimation of dipolar energy, the hydrogen bond energy of alcohol - ketone complexes may be estimated to be about 4 kcal. or a little more for the two systems.

Summary

A microcalorimeter of the twin type has been constructed, one which is operated semiautomatically. Using this apparatus, the heats of mixing for alcohol - ketone, alcohol - hexane, and ketone - hexane solutions have been measured. From these heats of mixing, the hydrogen bond energy of the O-H···O= type has been estimated to be about 4 kcal. by means of the thermochemical cycle.

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[5] C. G. Böttcher, "Theory of Electric Polarisation," Elsevier Publishing Co., Houston (1952).