Integral Heats of Mixing of Water and Acetone at 90° C.

D. E. NICHOLSON
Research and Development Division, Humble Oil & Refining Co., Baytown, Tex.

IN CONJUNCTION with the study of thermodynamic properties of systems in the liquid state, the heats of mixing of water and acetone were determined at 90° C. The calorimeter and accessory apparatus used in the current investigation were described previously (*1*, *2*). The apparatus provided for the complete elimination of the vapor space in the calorimeter during the course of experiments. All precautions were taken for an apparatus of high precision: The energy input attributable to stirring, the thermal leakage modulus, and the heat capacity of the calorimeter and contents were evaluated in the course of every set of measurements.

The principal calorimetric results derived from the current study are summarized in Table I. A comparison of the heats of mixing of water with acetone at 90° C. with those of an earlier research (*1*) at 25° C., is given in Figure 1. The significant feature from the comparison is that the deviations from ideality—nonzero heat of mixing—increase with rising temperature over a certain concentration range. The heat effects per mole of mixture are numerically, at 90° C., for high acetone concentrations, larger than at 25° C. Such behavior is to be contrasted with the benzene-cyclohexane, *n*-heptane-*n*-hexadecane, and toluene-cyclohexane systems (*3*) in which the deviation from ideality diminishes as the temperature is raised. Dilute solutions of acetone and water (solvent) at 90° C. are more nearly ideal than at 25° C. The enthalpies of mixing are predominantly endothermic at the higher temperature.

In regular solution theory the energy of mixing is expressed by means of relationships of the type (for a binary)

$$\Delta E^M = (x_1 V_1 + x_2 V_2) \left[\left(\frac{\Delta E_1^V}{V_1} \right)^{1/2} - \left(\frac{\Delta E_2^V}{V_2} \right)^{1/2} \right]^2 \phi_1 \phi_2$$

in which ΔE^M is the energy per mole of mixture, x refers to mole fraction, V to molar volume, ΔE^V to heat of vaporization, and ϕ to volume fraction. This equation and its modifications predict a slight positive temperature coefficient for the energy of mixing of water and acetone. In addition, the calorimetric heats of mixing for nonelectrolytes are usually larger than the theoretical heats of mixing, because the relationship above makes no provision for contributions ot the energy of mixing attributable to dipole forces. For the water-acetone system the theoretical energies of mixing are approximately 10 times as large as the calorimetric energy of mixing at 90° C. The high energy of vaporization of water, existing in an associated or polymeric form, is partly responsible for this result.

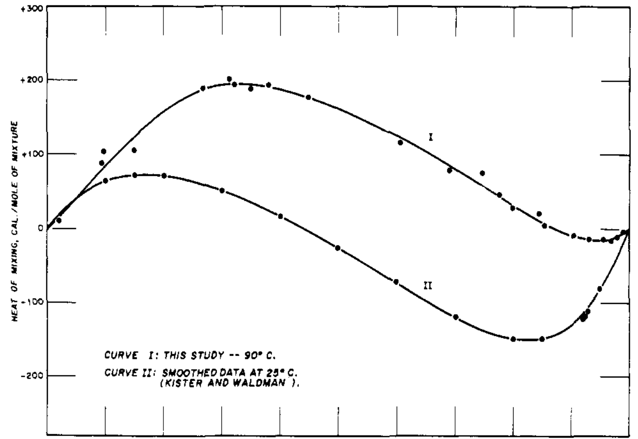

Figure 1. Integral heat of mixing of water and acetone

Table I. Integral Heat of Mixing of Water and Acetone at 90° C.

Mole % Water	Cal./Mole		Mole % Water	Cal./Mole	
	Water	Mixture		Water	Mixture
2.11	519	10.9	74.8	98.7	73.8
9.46	919	87.0	77.7	57.5	44.7
9.55	1083	103.5	79.9	34.2	27.4
12.3	859	106.0	84.4	23.7	20.1
14.8	713	105.5	85.4	4.6	3.9
26.9	703	189	90.4	-11.1	-10.0
31.2	641	200	93.2	-15.8	-14.7
31.9	611	195	95.4	-15.1	-14.4
34.8	542	189	96.7	-14.1	-16.7
37.9	505	192	97.8	-11.3	-11.1
44.9	393	177	99.0	-5.8	-5.7
60.6	190	115	99.1	-5.5	-5.5
69.0	113	78.1			

LITERATURE CITED

(1) Kister, A.T., Waldman, D.C., *J. Phys. Chem.* **62**, 245 (1958).
(2) Nicholson, D.E., J. CHEM. ENG. DATA **5**, 35 (1960).
(3) Papadopoulos, M.M., Derr, E.L., *J. Am. Chem. Soc.* **81**, 2285 (1959).

RECEIVED for review October 12, 1959. Accepted November 19, 1959.

CORRECTION

In "Heats of Mixing of C_4 Hydrocarbons in Water-Acetone Solvent" [D.E. Nicholson, J. CHEM. ENG. DATA **5**, 35 (1960)] the following acknowledgment should have appeared:

The author is indebted to D.C. Ginnings, Heat and Power Division, National Bureau of Standards, Washington, D.C., for several helpful discussions in connection with the initiation of the calorimetric research. In addition, thanks are due to Walter Ruska and Alfred Woelfel, Ruska Instrument Corp., Houston, Tex., for suggestions concerning certain mechanical details involved in the construction of the calorimeter and to Theo Hines for assistance with experimental work.