Heats of Mixing of Carbon Tetrachloride with Tetrachloroethylene

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Heats of mixing of liquids have been measured and correlated for the binary system carbon tetrachloride–tetrachloroethylene at 25° C.

THIS PAPER reports the experimentally measured heats of mixing values for the binary system carbon tetrachloride–tetrachloroethylene at 25° C.

Brass calorimeters with thermistors as temperature-sensing elements were employed. Before mixing, the two liquids were separated by a tin-foil diaphragm in the two compartments of the calorimeter. The assembled vessel was mounted in a brass jacket, which was evacuated and submerged in a constant temperature bath, controlled at 25° ± 0.01° C. Mixing and stirring were achieved with a gold-plated plunger actuated by a solenoid which was energized in a R-C rectified circuit. As the heat of mixing was endothermic, it was evaluated from the net heat input required for bringing the liquid mixture temperature back to the initial temperature before mixing. A detailed description of the apparatus and the experimental procedure has been reported (*3*). The estimated over-all uncertainty of the measurements is about 1%.

Spectro grade carbon tetrachloride and tetrachloroethylene were supplied by the Matheson, Coleman and Bell Co. and used without further purification. The indicated maximum moisture content for carbon tetrachloride is 0.02% and for tetrachloroethylene is 0.05%. The indicated maximum evaporation residue for both chemicals is 0.0005%. Refractive indices of these chemicals measured at 25° C. (carbon tetrachloride 1.45712, tetrachloroethylene 1.50296) agree well with the literature values (carbon tetrachloride 1.45704, tetrachloroethylene 1.50284) (*1*). Experimental data obtained for this binary are listed in Table I. The three-constant Equation 1 represents the data within an average deviation of 1%.

$$\Delta H = x_1 x_2 \left[62.69 + 20.82\,(x_1 - x_2) + 4.632\,(x_1 - x_2)^2\right] \qquad (1)$$

An attempt was made to predict the heats of mixing values by means of the regular solution equation (*2*),

$$\Delta H = \Delta E = (x_1 V_1 + x_2 V_2)\,(\delta_1 - \delta_2)^2 \phi_1 \phi_2 \qquad (2)$$

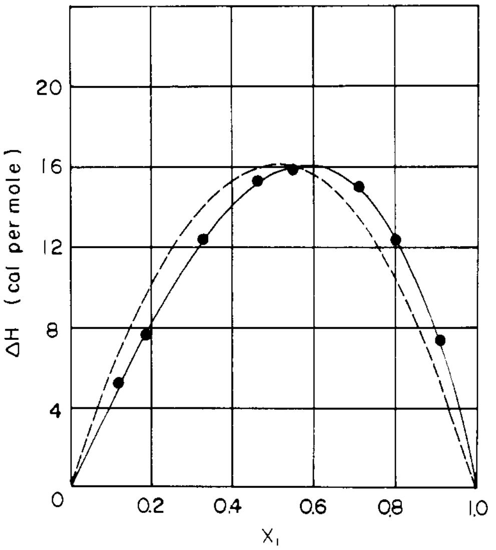

Figure 1. Experimental and predicted ΔH values

Table I. Heats of Mixing Data for the Binary System Carbon Tetrachloride–Tetrachloroethylene at 25° C.

x_1	ΔH, Cal./Mole
0.1188	5.10
0.1803	7.57
0.3226	12.26
0.4556	15.30
0.5474	15.78
0.7091	14.96
0.7987	12.26
0.9040	7.28

In Figure 1, experimental values are compared with that calculated from Equation 2, using $(\delta_1 - \delta_2)^2 = 0.6451$. This value was chosen to obtain the same maximum value of ΔH. The calculated curve as represented by the broken line is much more symmetric, and the maximum difference between the experimental and calculated ΔH values is less than 2 cal. per mole. If δ_1 is taken to be 8.62 (*2*), $\delta_2 = 9.42$, which agrees reasonably well with that calculated from heat of vaporization at 25° C. (*1*), $\delta_2 = 9.30$. The validity of calculating ΔH by means of Equation 2 depends on the magnitude of volume change on mixing, ΔV. In the vicinity of $x_1 = 0.5$ region, ΔV was found to be about 0.02 ml. per mole of the solution in a preliminary study, but the experimental error is of the same magnitude.

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NOMENCLATURE

ΔE = molal energy of mixing, cal./mole
ΔH = heat of mixing (enthalpy of mixing) per mole of solution, cal./mole
V = molal volume, ml./mole
ΔV = volume of mixing per mole of solution, ml./mole
x = liquid mole fraction
δ = solubility parameter, (cal./ml.)$^{0.5}$
ϕ = volume fraction

Subscripts

1 = carbon tetrachloride
2 = tetrachloroethylene

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