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Excess enthalpies from displacement calorimetry
Excess enthalpies for 1,1,1- trichloroethane+carbon tetrachloride and 2-chloro-2-methylpropane+carbon tetrachloride at 298.15 K

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Excess enthalpies H^E are reported for the 1,1,1–trichloroethane+carbon tetrachloride and 2-chloro-2-methylpropane+carbon tetrachloride systems. The results are fitted to the formula $H^E = x(1-x)\Sigma_i a_i(1-2x)^i$.

1. Introduction

Binary systems composed of methylchloromethanes seem to be promising for testing theories of liquid mixtures. Furthermore, as the components belong to the class of plastic crystals and the mixtures often form solid solutions, it is probable that the solid state may be used for further development of the theory of molecular interaction.

One of us is studying the phase diagrams of 1,1,1-trichloroethane + carbon tetrachloride by means of adiabatic calorimetry.[1] Vapour-pressure measurements of this mixture have been reported previously.[2] The combination of the thermodynamic properties of the liquid state (G^E, H^E, and S^E) with the results of adiabatic calorimetry (C_p^E H^E_{fusion}) will enable us to calculate the thermodynamic properties of the solid solutions.

In this paper we present excess enthalpies of two mixtures in the liquid state at 298.15 K and compare them with the results published by Das, Diaz Peña, and McGlashan.[3]

2. Experimental

MATERIALS

Carbon tetrachloride (Merck Uvasol) and 2-chloro-2-methyl-propane (Fluka puriss) were used as received. 1,1,1-Trichloroethane (Baker Chemicals, Grade) was distilled in a Fisher column that had an equivalent of 40 theoretical plates. The purity of carbon tetrachloride and 1,1,1-trichloroethane as determined by g.l.c. was better

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than 99.9 moles per cent. 2-Chloro-2-methylpropane is not very stable and the g.l.c. after the measurements indicated a purity of 99.6 moles per cent. All liquids were degassed by sublimation under vacuum and transferred to the calorimeter without any contact with air.

APPARATUS

The calorimeter used has been described in detail.[4] For 2-chloro-2-methylpropane + carbon tetrachloride a few liquid injections resulted in an exothermic effect. Our calorimeter is not suited for measuring exothermic effects; in this case, however, since the effects were very small, they could be determined by comparing them with a known energy input. We used the exponential extrapolation method as described by Stout.[5]

3. Results

Molar volumes from the literature were used in the calculations.[6,7] We need the excess volumes of the mixtures at about $x = 0.5$ in order to check the buret volume and to make sure that no leakage has occurred. These were also taken from literature.[8]

The experimental values of H^E for 1,1,1-trichloroethane + carbon tetrachloride and 2-chloro-2-methylpropane + carbon tetrachloride are reported in table 1. The

TABLE 1. Molar excess enthalpy H^E at 298.15 K

x	H^E/J mol^{-1}	x	H^E/J mol^{-1}	x	H^E/J mol^{-1}	x	H^E/J mol^{-1}
			$(1-x)Cl_3CCH_3+xCCl_4$ [a]				
0.00466	1.45	0.33623	88.00	0.52041	109.31	0.75081	93.85
0.00927	2.87	0.36554	92.98	0.53162	109.74	0.78956	85.38
0.01409	4.37	0.39536	97.48	0.55111	110.23	0.83252	73.73
0.05806	17.99	0.42010	100.70	0.57365	110.41	0.86752	62.15
0.10259	31.51	0.44275	103.30	0.59626	110.05	0.90652	46.83
0.14304	43.28	0.46587	105.51	0.62117	109.17	0.94868	27.61
0.17882	53.01	0.48539	107.03	0.64873	107.46	0.99334	3.82
0.22427	64.51	0.49660	107.71	0.67903	104.64	0.99658	1.96
0.26358	73.59	0.50873	108.39	0.71148	100.55	0.99918	0.47
0.30370	81.97						
			$(1-x)CH_3CCl(CH_3)CH_3+xCCl_4$ [b]				
0.00966	−0.25	0.35779	24.33	0.53000	52.34	0.80263	71.97
0.06360	−0.52	0.38843	28.95	0.57377	58.97	0.84347	66.39
0.08655	−0.23	0.41743	33.53	0.59726	62.17	0.87606	59.02
0.11960	0.70	0.44270	37.78	0.62444	65.71	0.90798	48.99
0.16422	3.05	0.46575	41.83	0.64265	67.87	0.95294	29.27
0.19670	5.46	0.48866	45.47	0.67662	71.06	0.98182	12.39
0.24474	9.88	0.50603	48.09	0.69909	72.74	0.98860	8.00
0.28627	14.55	0.52198	50.61	0.73003	74.15	0.99298	5.03
0.32365	19.43	0.53563	52.93	0.76485	74.29	0.99644	2.51

[a] Coefficients of the smoothing equation $H^E/\text{J mol}^{-1} = x(1-x)\Sigma_i a_i(1-2x)^i$: $a_0 = 432.25$; $a_1 = -122.66$; $a_2 = 32.6$; $a_3 = -12.33$; $a_4 = -12.70$; standard deviation: 0.08; maximum deviation: 0.18.
[b] Coefficients of the smoothing equation $H^E/\text{J mol}^{-1} = x(1-x)\Sigma_i a_i(1-2x)^i$: $a_0 = 188.87$; $a_1 = -329.0$; $a_2 = 144.0$; $a_3 = -47.6$; $a_4 = 18.4$; standard deviation: 0.10; maximum deviation: 0.28.

coefficients at the bottom of the tables are the values found by fitting the results to the formula: $H^E = x(1-x)\Sigma_i a_i(1-2x)^i$, where x is the mole fraction of the component with the greater molar mass, in this case always carbon tetrachloride. The standard deviations and the maximum deviations are also given.

In table 2 we compare our results at $x = 0.5$ with the values given by Das, Diaz Peña, and McGlashan.[3] As they presented their other results as a graph further

TABLE 2. Molar excess enthalpies $H^E(x = 0.5)$

	this work	Das, Diaz Peña, and McGlashan[3] H^E/J mol^{-1}
$(1-x)Cl_3CCH_3+xCCl_4$	108.1	103
$(1-x)CH_3CCl(CH_3)CH_3+xCCl_4$	47.2	49

comparison cannot be made. Their measurements vary between $0.1 < x < 0.9$, which is the reason that no exothermic effect was given for 2-chloro-2-methylpropane + carbon tetrachloride; we found the exothermic effect to be restricted to within $x = 0$ and $x = 0.095$.

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