Enthalpy Concentration Diagram of the System Carbon Tetrachloride–Chloroform

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VAPOR-LIQUID EQUILIBRIA for the system carbon tetrachloride–chloroform have been determined at 760 mm. of Hg, using a conventional adiabatic Othmer still (*7*), and used together with published data on specific heats, latent heats of vaporization, and heats of mixing (*2, 3, 4, 6*) to construct the enthalpy-concentration diagram of the system. Compositions of the liquid and vapor phases were determined through their refractive indices and the data indicated in Table I.

In order to test the thermodynamic consistency of the experimental values, the vapor pressure of chloroform in the range 50° to 75° C. had to be determined. A slightly modified isotenciscope method was used, and the data were fitted with the following equation that predicts the experimental results with a relative error of less than 0.5%:

$$\log P = 6.418 - \frac{859.3}{181.9 + t}$$

A similar equation is given in the literature (*1*) for carbon tetrachloride:

$$\log P = 6.859 - \frac{1197}{222.1 + t}$$

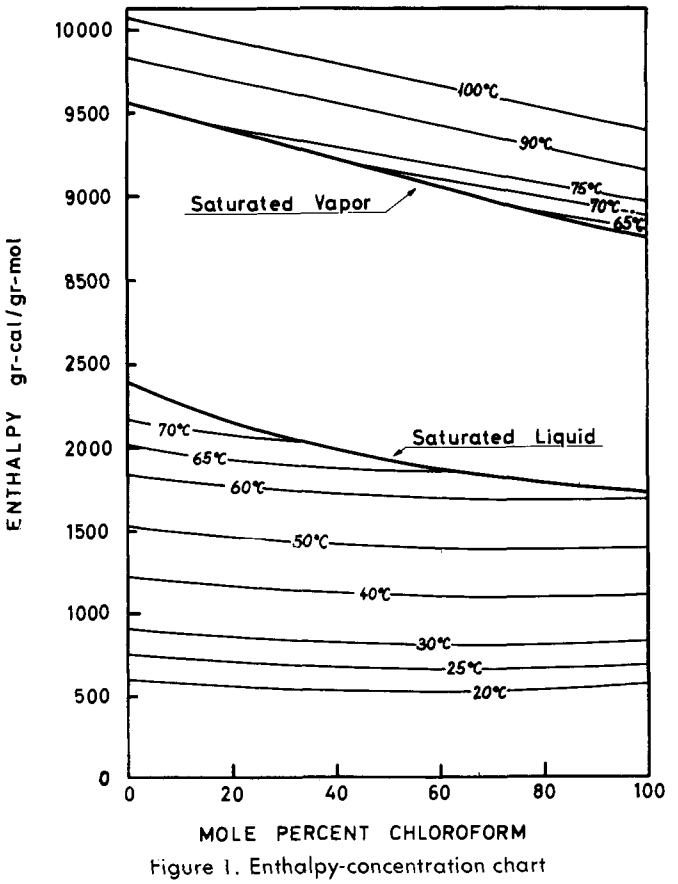

Figure 1. Enthalpy-concentration chart

Activity coefficients were calculated and found to be 1.00 + 0.01. This fact indicates that in spite of the dipole moment of chloroform the behavior of solutions of carbon tetrachloride and chloroform is near ideal, as has been indicated elsewhere (*5*).

The calorimetric data are summarized in Table II and Figure 1, based on the reference states of pure liquids at 0° C. and their vapor pressure.

Table I. Refractive Indices of Mixtures of of CCl_4 and $CHCl_3$ at 20° C.

x_{CCl_4}	n	x_{CCl_4}	n
0.00	1.4600	0.75	1.4489
0.10	1.4586	0.90	1.4470
0.25	1.4563	1.00	1.4459
0.50	1.4526		

Table II. Enthalpies of the System CCl_4 – $CHCl_3$

Temp.	Mole Fraction Chloroform						
°C.	0.00	0.10	0.25	0.50	0.75	0.90	1.00
	LIQUID PHASE						
20	606	577	548	519	517	530	562
25	759	731	698	665	658	670	681
30	914	879	846	811	802	810	820
40	1224	1187	1148	1106	1091	1091	1105
50	1537	1494	1450	1405	1383	1386	1392
60	1854	1804	1757	1708	1683	1680	1683
65	2017	1961	1911	1861	...	...	...
70	2177	2113	2063	...	...	...	...
75	2339	...	...	...	...	...	...
	SATURATED LIQUID CURVE						
	2390	2266	2112	1925	1796	1470	1725
	LATENT HEAT OF VAPORIZATION.						
	7170	7209	7327	7208	7129	7070	7020
	SATURATED VAPOR CURVE.						
	9560	9475	9349	9133	8925	8810	8745
	VAPOR PHASE.						
65	...	...	...	...	8928	8852	8801
70	...	...	...	9149	9003	8936	8884
75	...	...	9384	9245	9106	9023	8968
90	9839	9768	9664	9497	9326	9225	9155
100	10050	9982	9884	9721	9555	9456	9391

LITERATURE CITED

(1) Barker, J.A., Brown, I., Smith, F., *Discussions Faraday Soc.* **15**, 143 (1953).
(2) Chessman, G.H., Whitaker, B., *Proc. Roy. Soc. (London), Ser.* **A212**, 406 (1952).
(3) International Critical Tables, McGraw-Hill, New York, 1927.
(4) Kobe, K.A., Long, E.G., *Petrol, Refiner* **29**, (3), 157 (1950).
(5) McGlashan, M.L., Pure, J.E., Sainsbury, J., *Tran. Faraday Soc.* **50**, 1284 (1954).
(6) Nat. Bur. of Sts., "Selected Values of Thermodynamic Properties," (U. S.) 1953.
(7) Othmer, D.F., Gilmont, R., Conti, J., *Ind. Eng. Chem.* **52**, 625 (1960).

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