

Vapour-Liquid Equilibrium and Thermodynamic Functions for the Liquid System Carbon Tetrachloride + Acetone

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For the system carbon tetrachloride + acetone, we give the results of measurements on the vapour-liquid equilibrium carried out over the entire range of compositions at 20 °C, 25 °C, 30 °C, 35 °C, and 40 °C (17 measurements at 25 °C and 10 measurements at each of the other temperatures). The activity coefficients as well as the molar excess Gibbs function $\bar{G}^E$ for the liquid are derived from these experimental data. The system exhibits an azeotropic point (vapour pressure maximum) at each temperature. For 25 °C there exist published calorimetric data on the molar excess enthalpy $\bar{H}^E$ so that we can compute the molar excess entropy $\bar{S}^E$ for this temperature. While $\bar{G}^E$ and $\bar{H}^E$ are positive, $\bar{S}^E$ is negative. The “symmetry rule” (Haase, 1950) concerning the composition dependence of $\bar{G}^E$ has again been confirmed.

Using an equilibrium still of the Scatchard type [1, 2], we measured vapour pressures and vapour compositions under isothermal conditions for the liquid system carbon tetrachloride + acetone over the whole range of compositions at five temperatures (17 compositions at 25 °C and 10 compositions at 20 °C, 30 °C, 35 °C, and 40 °C). It turns out that the binary system exhibits an azeotropic point (vapour pressure maximum) at each temperature investigated (see Figure 1). The maximum shifts towards the acetone end of the diagram at lower temperatures and probably vanishes at about 15 °C.

We derive the activity coefficients f_1 and f_2 of the components (Fig. 2) and the molar excess Gibbs function $\bar{G}^E$ of the liquid mixture (Fig. 3 and Table 1) in the usual way. These thermodynamic functions (as well as other molar excess functions) practically only depend on the temperature T and on the mole fraction x of one of the components.

For 25 °C there exist calorimetric data [3] for the molar excess enthalpy (molar heat of mixing) $\bar{H}^E$ so that we are able to compute the molar excess

entropy $\bar{S}^E$ ($T\bar{S}^E = \bar{H}^E - \bar{G}^E$) for this temperature (Figure 3). As far as the authors are aware, there are no other published data on the thermodynamic behaviour of the system at hand.

We show part of the details in the figures and in the table. (The complete data are given elsewhere [2].) We see that $\bar{G}^E$ and $\bar{H}^E$ are positive, while $\bar{S}^E$ is negative. We also notice that the symmetry rule [4, 5] again applies: For a given temperature, the

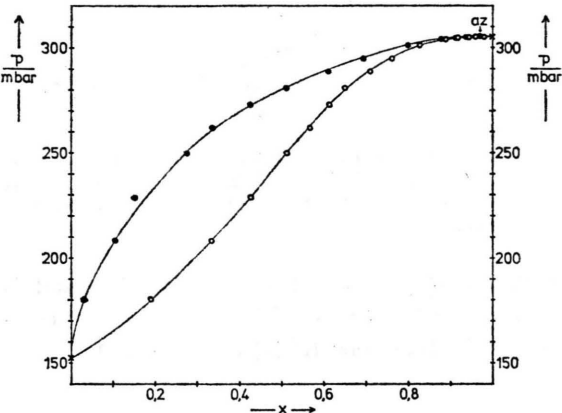


Fig. 1. System carbon tetrachloride + acetone at 25 °C: Vapour pressure p as a function of the mole fraction x of acetone (az denotes the azeotropic point).

Table 1. Liquid system carbon tetrachloride + acetone: Molar excess Gibbs function $\bar{G}^E$ as a function of the mole fraction x of acetone (interpolated values).

x	$\bar{G}^E/\text{J} \cdot \text{mol}^{-1}$				
	20 °C	25 °C	30 °C	35 °C	40 °C
0.05	135	122	150	125	120
0.1	245	240	260	225	220
0.15	328	322	340	310	310
0.2	390	390	395	380	375
0.25	438	442	442	430	430
0.3	475	482	480	475	475
0.35	502	515	510	508	505
0.4	520	535	530	530	530
0.45	530	545	540	545	540
0.5	530	545	540	550	548
0.55	520	530	530	542	540
0.6	490	500	510	520	520
0.65	450	460	480	490	490
0.7	400	420	430	440	442
0.75	350	370	375	380	390
0.8	290	310	315	320	325
0.85	230	240	245	250	255
0.9	160	170	170	180	180
0.95	80	90	90	90	90

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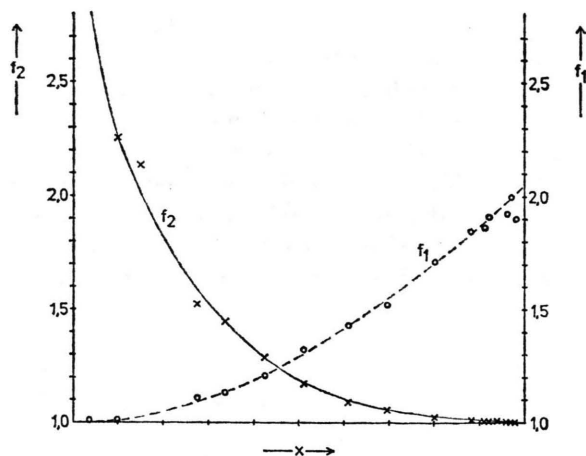


Fig. 2. Liquid system carbon tetrachloride (component 1) + acetone (component 2) at 25 °C: Activity coefficients f_1 and f_2 of the components as functions of the mole fraction x of acetone.

function $\bar{G}^E(x)$ does not change its sign and is nearly symmetric (parabolic), no matter how complicated the functions $\bar{H}^E(x)$ and $\bar{S}^E(x)$ are.

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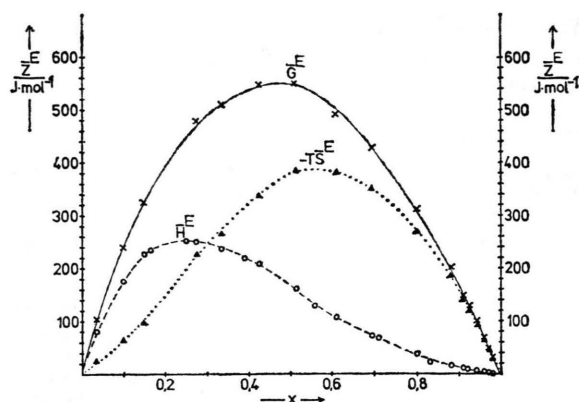


Fig. 3. Liquid system carbon tetrachloride + acetone at 25 °C: Molar excess Gibbs function $\bar{G}^E$, molar excess enthalpy $\bar{H}^E$ (after H. Loiseleur et al. [3]), and product $T\bar{S}^E$ of thermodynamic temperature T and molar excess entropy $\bar{S}^E$ as functions of the mole fraction x of acetone ($T\bar{S}^E = \bar{H}^E - \bar{G}^E$).

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