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The Phase Diagram of the System Carbon Tetrachloride-Cyclohexanone

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The solid-solid and solid-liquid equilibria of the system carbon tetrachloride-cyclohexanone¹ were investigated with an adiabatic calorimeter. The corresponding phase diagram is more complex than the diagram published earlier by Pariaud.² Compound formation in the solid state at the mole fraction $X=0.5$ and solid solution formation in restricted areas of the phase diagram are shown. The result of a model calculation is given.

INTRODUCTION

Both carbon tetrachloride and cyclohexanone belong to the class of plastic crystals³ and as their molar volumes are also practically the same, it can be expected that these substances form solutions in the plastic crystalline state. The solid-liquid diagram for this system, as measured by Pariaud, is that of an equilibrium between a continuous series of solid solutions with liquid solutions, showing a maximum separated by two minima.

As this type of diagram is exceptional, though not a priori impossible (one of us used it as an example in an article about interpreting phase diagrams with the equal-G curve),⁴ we decided to remeasure the system with an adiabatic calorimeter.

MEASUREMENTS

The calorimeter used is described in Ref. 5 and in more detail in Ref. 1. The performance of the apparatus was checked with a standard sample of *n*-heptane⁶

obtained from the National Bureau of Standards in Washington. Divergence of individual specific heat measurements was generally within 0.2%, the overall difference from the values of the Bureau was within 0.5%.

The pure components and nine mixtures were measured quantitatively. First the sample was treated to obtain reproducible results: it was cooled below the lowest transition temperature, then heated till in the transition region and cooled again very slowly. A continuous heating curve was then made with a heating speed of 0.3 to 1.0 K/h. After this, the cooling procedure was repeated and specific heat measurements, including enthalpies of transition and of fusion, were made.

For four additional mixtures only the continuous heating curves were made.

RESULTS

In Table 1 the major enthalpy effects and the temperature range, in which the corresponding transition took place, are given. The entropy of fusion at the mole fraction $X = 0.5$ equals the mean value of the sum of the entropy of transition and fusion of the pure components, as is shown in Table 2.

For more detailed information one is referred to Ref. 1.

CONCLUSIONS

The phase diagram constructed with the thirteen mixtures is given in Figure 1a. Between $X = 0.8$ and $X = 1.0$ it is, in spite of the number of measurements, still somewhat tentative.

The most pronounced features of this diagram, which are supported by the thermal measurements, are:

- a. There is compound formation in the solid state at $X = 0.5$.
- b. This compound does not show a rotational transition.
- c. Solid solution formation is restricted to two mole fraction ranges (between $X = 0$ and $X = 0.2$ and between $X = 0.8$ and $X = 1$).
- d. The transition in the solid solution (from $X = 1$, $T = 220$ K to about $X = 0.8$, $T = 225$ K) may be an indication that the pure components do not have the same crystal structure in the plastic crystalline state. A similar transition occurs in the system carbon tetrachloride-*t*-butylchloride.⁷

MODEL CALCULATION

In order to add significance to the experimental diagram, we give the result of a

TABLE 1

Major enthalpy effects in J mol^{-1} and the corresponding temperature (interval) in degrees K in the system carbon tetrachloride-cyclohexanone

<i>X</i>	Transition 1		Transition 2		Fusion	
	ΔH	T_1 -- T_2	ΔH	T_1 -- T_2	ΔH	T_1 T_2
	J mol^{-1}	K	J mol^{-1}	K	J mol^{-1}	K
0.000	4631	225.28 ---			2536	250.28 ---
0.025	4918	222.9 225.5			2268	--- 247.2
0.098	6741	222.9 224.9			807	229.7 242.9
0.506	207	213.4 ---	60	216 ---	8816	220 234.1
0.694	3913	213.4 ---	1751	218 ---	3312	220 232.4
0.744	4966	213.4 ---				
0.849	7014	213.6 217.6	1098	221.6 ---	795	222 223.6
0.897	7056	213.3 215			1509	220.4 229.3
0.950	7621	213.4 ---	532	224.7 225.2	1074	--- 236.8
1.000	8746	220.6 ---			1357	244.6 ---

TABLE 2

Entropy of transition and of fusion of the components and of the compound in $\text{J mol}^{-1} \text{K}^{-1}$

	Carbon tetrachloride	Compound $X=0.5$	Cyclohexanone
ΔS_{fusion}	10.13	37.91	5.55
$\Delta S_{\text{trans.}}$	20.56	---	39.65
Total	30.69	37.91	45.20
Mean total of the components		37.94	

simple model calculation (see Figure 1b). Omitting the transition in the solid solution, we recognize the following equilibria:

1. Between the liquid solutions (l) and the plastic crystalline solution (p).
2. Between the solid compound (s_c) and liquid solutions.
3. Between solid compound and plastic crystalline solutions.

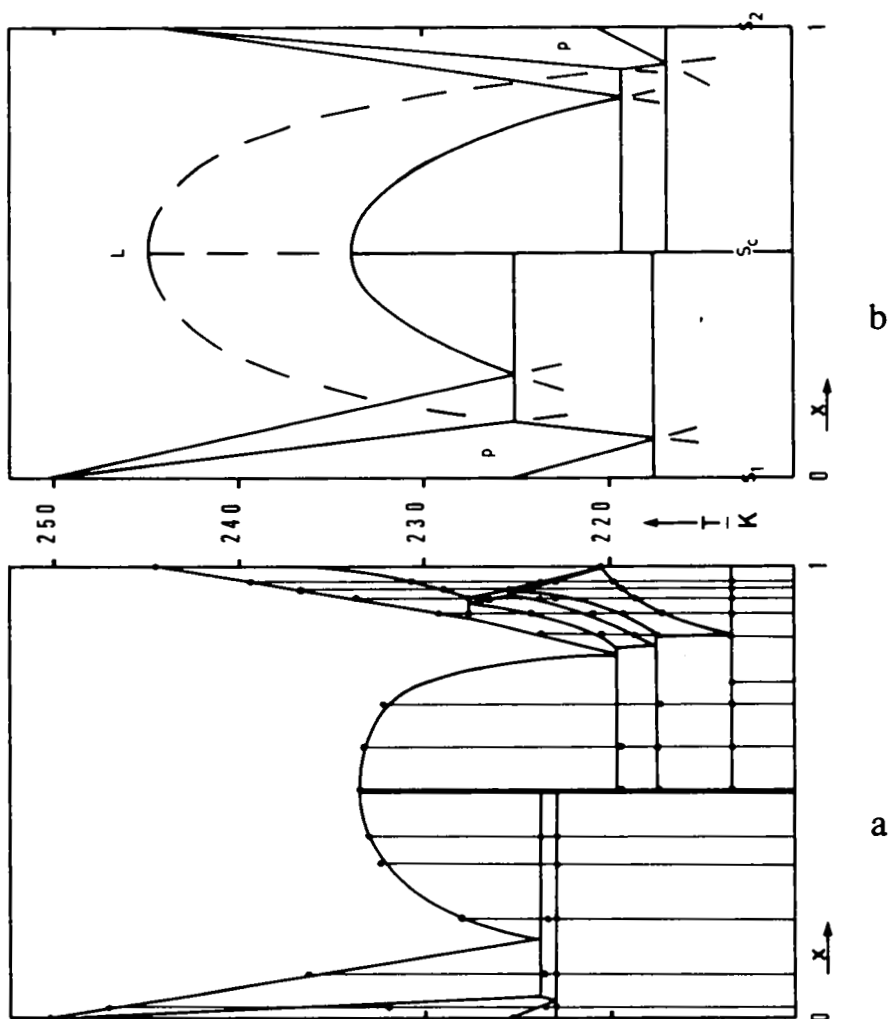


FIGURE 1 The phase diagram measured is given in (a), the result of the model calculation is given in (b).

4. Between the pure low temperature state of component 1 (s_1) and plastic crystalline solutions.

5. Between the pure low temperature state of component 2 (s_2) and plastic crystalline solutions.

The numerical data used for the calculations are summarized in Table 3. Moreover, we made the following assumptions:

a. The liquid solutions are ideal

b. The plastic crystalline solutions on both sides of the diagram belong to one series and can be described by one Gibbs energy function. The excess part of this function is taken independent of temperature and is used in the form $g^E(x) = a \sin \pi X$. The corresponding partial excess quantities are given by:

$$\mu_1^E(X) = a \sin \pi X - a \pi X \cos \pi X$$

$$\mu_2^E(X) = a \sin \pi X + a \pi (1 - X) \cos \pi X$$

Formulas used:

1) The experimental data for the equilibrium between 1 and p reveal, in terms of the EGC method,⁴ the value for the constant a :

$$a = 440 \text{ J mol}^{-1}$$

2) The equilibrium between s_c and 1 is given by:

$$2 \Delta h_c (1/T - 1/T_c) + R \ln 4X(1 - X) = 0$$

TABLE 3

Values used for the model calculation

Used symbols ^a	Explanation	Values
T_1	melting point	250.28 K
T_2	melting point	244.60 K
Δh_1	enthalpy of melting	2535.7 J mol ⁻¹
Δh_2	enthalpy of melting	1357.4 J mol ⁻¹
T_c	melting point	234.0 K
Δh_c	enthalpy of melting	8870 J mol ⁻¹
$T_{tr,1}$	transition temperature	225.28 K
$T_{tr,2}$	transition temperature	220.60 K
$\Delta h_{tr,1}$	enthalpy of transition	4630.8 J mol ⁻¹
$\Delta h_{tr,2}$	enthalpy of transition	8746.1 J mol ⁻¹
R	gas constant	8.31 J mol ⁻¹ deg ⁻¹

^a The index 1 refers to carbon tetrachloride; the index 2 refers to cyclohexanone; the index c refers to the compound formed at $x=0.5$.

3) The equilibrium between s_c and p follows from:

$$\bullet \quad 2\Delta h_c(1/T - 1/T_c) - \Delta h_1^*(1/T - 1/T_1) - \Delta h_2^*(1/T - 1/T_2) + \mu_1^E(X)/T + \mu_2^E(X)/T = 0$$

4 and 5) The equilibria between s_1 and s_2 with p were calculated with:

$$\bullet \quad \Delta h_{tr\ 1}^*(1/T - 1/T_{tr\ 1}) + R \ln(1 - X) + \mu_1^E(X)/T = 0$$

$$\bullet \quad \Delta h_{tr\ 2}^*(1/T - 1/T_{tr\ 2}) + R \ln X + \mu_2^E(X)/T = 0$$

respectively.

References

1. Miltenburg, J. C. van, based upon a thesis entitled: "Construction of an adiabatic calorimeter and measurement of the system carbon tetrachloride-cyclohexanone; Utrecht (1971). Copies available on request to the author.
2. Pinaud, J. C., *Soc. Chim. France Mémoires* T 17, 1239 (1950).
3. Timmermans, J., *J. Phys. Chem. Solids* 18, 1 (1961).
4. Oonk, H. A. J., *Rec. Trav. Chim.* 87, 1345 (1968).
5. Miltenburg, J. C. van, *J. Chem. Thermodynamics* 4, 773 (1972).
6. Douglas, T. B., Furukawa, G. T., McCoskey, R. E. and Ball, A. F., *J. Res. Nat. Bur. Stand.* 53, 139 (1954).
7. Connor, W. P. and Smyth, C. P., *J. Amer. Chem. Soc.* 63, 3424 (1941).