

Carbon tetrachloride. Determination of the enthalpy of transition from metastable face-centered cubic carbon tetrachloride to the stable rhombohedral modification

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The heat capacities and enthalpies of fusion of the stable (rhombohedral) and the metastable (face-centered cubic) phases of carbon tetrachloride have been determined.

1. Introduction

Carbon tetrachloride is known to have a metastable face-centered cubic (f.c.c.) modification which transforms spontaneously to a stable rhombohedral phase.^(1, 2) The entropy of transition between these crystal structures has been estimated by Kotake *et al.*⁽³⁾ to be $1.26 \text{ J K}^{-1} \text{ mol}^{-1}$. This value is derived from extrapolation of heat effects in the binary system carbon tetrachloride + *t*-butylchloride. We have determined the enthalpy of transition in a more direct way of measuring the heat capacity and the enthalpy of fusion of the metastable f.c.c. modification and the stable phase.

2. Experimental

MATERIAL

As starting material we employed Merck "Uvasol" carbon tetrachloride which was fractionally recrystallized. The purity of the sample had been determined from the melting curve in a previous experiment to be 99.97 moles per cent. The mass of the sample was 7.4540 g.

THE CALORIMETER

All measurements were made with an adiabatic calorimeter described elsewhere.^(4, 5) The performance of the apparatus was checked by measuring a standard sample of *n*-heptane; the errors were generally within 0.5 per cent. The value for the enthalpy of fusion of the stable phase of carbon tetrachloride obtained in this work is about 0.8 per cent higher than reported before⁽⁴⁾ and about 1.5 per cent higher than reported by Hicks *et al.*⁽⁶⁾ In this experiment a correction for leakage had to be made which can be the cause of the discrepancy first mentioned.

METHOD OF MEASUREMENT

The cooling behaviour of carbon tetrachloride showed the existence of the metastable phase.⁽⁴⁾ First a relative large enthalpy of solidification was measured when the metastable phase was formed; this was followed within a few kelvins by a sharp second effect when the transition to the stable rhombohedral phase occurred. The same observations were made by Kotake *et al.*⁽²⁾ When after the first effect the sample was not allowed to cool down further, it was possible to measure the heat capacity and the enthalpy of fusion of the metastable modification. The sample temperature was kept constant for 1 to 2 h before starting these measurements, in order to assure that solidification was complete. Heat capacities measured in the metastable phase are probably less reliable than those measured in the stable phase, due to the small temperature interval available. Heat capacity and enthalpy of fusion of the stable modification were determined after the sample had been cooled down below the second effect.

3. Results and discussion

The measured heat capacity values and the enthalpies of fusion are given in tables 1, 2, and 3.

The enthalpy of transition between the metastable f.c.c. phase and the stable rhombohedral phase was calculated in the following way. Starting in the metastable phase, two ways are possible to reach the same temperature in the liquid state.

TABLE 1. Measured heat capacities C_p of carbon tetrachloride below and above the melting temperature of the stable phase (250.28 K)

| $\frac{T}{\text{K}}$ | $\frac{C_p}{\text{J K}^{-1} \text{mol}^{-1}}$ | $\frac{T}{\text{K}}$ | $\frac{C_p}{\text{J K}^{-1} \text{mol}^{-1}}$ |
|----------------------|---|----------------------|---|
| 243.16 | 124.0 | 248.67 | 125.5 |
| 244.03 | 124.1 | 251.53 | 132.2 |
| 244.46 | 124.3 | 252.58 | 131.5 |
| 244.77 | 124.3 | 253.84 | 132.2 |
| 245.11 | 123.8 | 256.10 | 131.8 |
| 246.92 | 125.3 | | |

TABLE 2. Measured heat capacities C_p of carbon tetrachloride below and above the melting temperature of the metastable phase (245.70 K)

| $\frac{T}{\text{K}}$ | $\frac{C_p}{\text{J K}^{-1} \text{mol}^{-1}}$ | $\frac{T}{\text{K}}$ | $\frac{C_p}{\text{J K}^{-1} \text{mol}^{-1}}$ |
|----------------------|---|----------------------|---|
| 243.40 | 120.2 | 247.02 | 130.1 |
| 244.26 | 121.4 | 249.26 | 131.6 |
| 244.43 | 122.1 | 251.13 | 131.7 |
| 245.03 | 122.4 | 253.74 | 131.4 |

TABLE 3. Enthalpies of fusion $\Delta H(s)$ of the stable phase and $\Delta H(m)$ of the metastable phase of carbon tetrachloride

| $\Delta H(s)/\text{J mol}^{-1}$ | $\Delta H(m)/\text{J mol}^{-1}$ |
|---------------------------------|---------------------------------|
| 2555 | 1847 |
| 2562 | 1848 |
| 2556 | 1850 |
| mean value: (2558 ± 4) | (1848 ± 2) |

First one can induce the transition between the phases and heat the stable phase to its melting temperature after which the liquid state is reached; the second way is to heat and melt the metastable modification. This leads to:

$$\Delta H(t) = \Delta H(s) - \Delta H(m) - \{T(s) - T(m)\} \{ \langle C_p(l) \rangle - \langle C_p(s) \rangle \} + \{T(m) - T(t)\} \{ \langle C_p(s) \rangle - \langle C_p(m) \rangle \}, \quad (1)$$

where $\Delta H(t)$ is the enthalpy of transition from the rhombohedral state to the f.c.c. modification, $\Delta H(m)$ and $\Delta H(s)$ are the enthalpies of fusion of the metastable and stable phase, respectively, $T(m)$ and $T(s)$ are the melting temperatures of the metastable and stable phases, and $T(t)$ is the varying temperature of transition. The heat capacities in the expression for $\Delta H(t)$ are the mean values in the mentioned temperature intervals; s, m, and l refer to stable solid, metastable solid, and liquid, respectively. Summing the first three terms on the right-hand side of expression (1) leads to:

$$\Delta H(t) = 685 \text{ J mol}^{-1} + \{T(m) - T(t)\} \{ \langle C_p(s) \rangle - \langle C_p(m) \rangle \}. \quad (2)$$

Since the second effect is a transition from a metastable to a stable phase, there does not exist a definite transition temperature in the solid state. The equilibrium must be imagined in the liquid phase and can not be realized. The enthalpy of transition is temperature dependent, which can be seen from expression (2).

The value measured is not in accordance with the value obtained by Kotake *et al.*⁽³⁾ They plotted the entropy of transition from the rhombohedral to the f.c.c. phase in the mixture carbon tetrachloride + *t*-butylchloride against the mole fraction and extrapolated this curve to pure carbon tetrachloride. The estimated value for this transition in pure carbon tetrachloride was about 310 J mol^{-1} . The f.c.c. phase however is metastable with respect to the rhombohedral phase, so the value for pure carbon tetrachloride should have been negative. In our opinion the extrapolation to carbon tetrachloride is not correct and should perhaps be made to pure *t*-butylchloride, also because the enthalpy increases in that direction.

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