On the Phase Relations of Carbon Tetrachloride below Its Melting Point

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Recent finding by Rudman and Post[1] that the rhombohedral form of carbon tetrachloride is more stable than the previously known face-centered cubic (fcc) form below the melting point has some consequences on our previous paper[2] on the solid solution of *t*-butyl iodide in carbon tetrachloride. We have reexamined our experimental results particularly those of differential thermal analysis (DTA) in the cooling direction and made some additional measurements in order to see if the solid solution also is dimorphous and to be prepared for more thorough calorimetric study.

Figure la shows that in pure CCl_4 an abrupt exotherm directly follows the freezing peak in DTA. The two peaks can well be resolved upon very slow cooling (10°C/ hr) as in Fig. 1b. This indicates that the crystalline phase that forms upon solidification is probably fcc which then transforms into the rhombohedral. The melting point of the fcc phase was found to be 3.86±0.15°C lower than that of the rhombohedral phase. The same behavior has been observed in the solid solution. Therefore, the crystalline phase that was dealt with in our paper[2] corresponds to the rhombohedral structure rather than fcc structure. However, our previous conclusions are hardly affected by such alteration except that the application of Torry's equation becomes less adequate; this does not modify the value of the activation energy of diffusion of CCl_4.

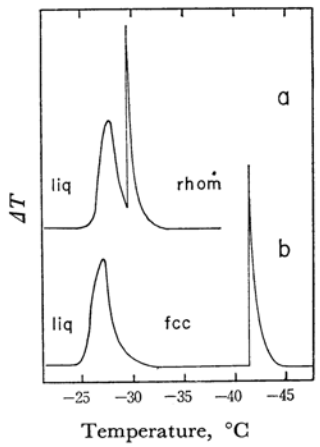

Fig. 1. Cooling DTA curves of pure carbon tetrachloride.

Reexamination of the previous data yielded a freezing point diagram of the binary system as given by open circles in Fig. 2 which is to be compared with the melting point (of the rhombohedral phase) diagram reproduced from Ref. 2. It is important to remark that the DTA curve similar to Fig. 1a was obtained in the *t*-BuI rich region. This suggests that the fcc lattice is a better solid solvent for *t*-BuI than is the rhombohedral lattice.

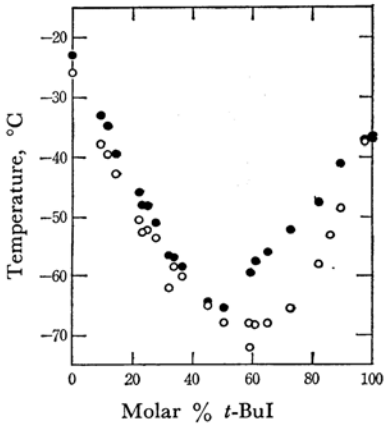

Fig. 2. Melting (●) and freezing (○) diagram of CCl_4-*t*-BuI binary system.

1) R. Rudman and B. Post, *Science*, **154**, 1009 (1966).
2) H. Chihara, M. Otsuru and S. Seki, This Bulletin, **39**, 2145 (1966).