

It may be noted that ΔS_f corresponds to $R \ln 2.05$, within experimental error to $R \ln 2$.

If any HNO_3 were not intercalated but merely sorbed or condensed onto the specimen used, its presence would be detected in DSC by the readily separable thermal effects associated with its recrystallization (or its melting), which can be induced at different rates of cooling. This would allow any suitable correction to be made to the initial weight uptake. No effects of this kind were recorded with the data illustrated, but they could appear under other conditions. In other forms of calorimetry [7] some of the results recorded may possibly have failed to separate true enthalpies of the intercalate from confusing additions due to other substances such as free HNO_3 , also present in the samples studied.

†Exchange visitor under the programme between the Royal Society and the C.N.R.S. On leave of absence from the Laboratoire de Physico-Chimie des Rayonnements (associé au CNRS), Université Paris Sud—Centre Scientifique d'Orsay, 91405 Orsay (France).

Acknowledgement—Thanks are due to Mr. I. W. Drummond for his kind help. A. Dworkin also thanks the Royal Society for a European Scientific exchange Programme grant.

Department of Chemical Engineering &
Chemical Technology
Imperial College
London SW7 2AZ, England

A. DWORKIN†
A. R. UBBELOHDE

REFERENCES

1. M. J. Bottomley, G. S. Parry and A. R. Ubbelohde, *Proc. Roy. Soc. A* **278**, 291 (1963).
2. D. E. Nixon, G. S. Parry and A. R. Ubbelohde, *Proc. Roy. Soc. A* **291**, 324 (1966).
3. A. R. Ubbelohde, *Proc. Roy. Soc. A* **304**, 25 (1968).
4. I. W. Drummond and A. R. Ubbelohde, to be published, 1978.
5. A. R. Ubbelohde, *J. Chimie Phys.* **66**, 62 (1969).
6. Perkin Elmer DSC2 instructions, pp. 8–14.
7. M. Inagaki, J. C. Rouillon, C. Füg and F. Delhaes, *Carbon* **15**, 181 (1977).

Carbon Vol. 16, pp. 292–293
© Pergamon Press Ltd., 1978. Printed in Great Britain

0008-6223/78/0801-0292/\$02.00/0

Anomalous specific heat due to order-disorder transition in graphite-halogen intercalation compound

(Received 1 December 1977)

The authors have developed an a.c. calorimetric device [1, 2] for studying the λ -transition possibly occurring in some intercalation compounds of graphite [3–5], and made preliminary measurements on compounds with iodine monochloride. Such a device was found to be more sensitive to the specific heat changes than the usual d.c. method by a factor of about ten.

A small sample is periodically heated by chopped light irradiation from a tungsten lamp, which in an appropriate frequency range leads to a temperature oscillation with an amplitude inversely proportional to the heat capacity of the sample. The oscillation is converted to an e.m.f. by a differential Cu–Au–Cu thermocouple whose junctions are attached one to the sample and the other to the heat sink (furnace) and displayed on an x–y recorder using a lock-in amplifier. The ambient temperature is measured by a Cu–constantan thermocouple placed very close to the sample.

The original graphite examined was a compression annealed pyrolytic graphite manufactured by Union Carbide Corporation. A 3 mm square and 0.01 mm thick slab was enclosed in a vessel filled with an ICl-saturated vapor for 48 hr at 100°C. After the reaction, the sample was identified to be a well-ordered second-stage C_{16}ICl compound by means of X-ray diffraction. By assigning the (001) super-structure lines, the lattice period was found to be 10.44 Å in agreement with that obtained by Sasa for C_8Br [6]. C_{16}ICl is not quite stable at room temperature, and the ICl molecules are easily driven out of graphite by heating the sample to 330 K, forming finally a fifth stage compound C_{40}ICl whose lattice period is 20.52 Å.

In Fig. 1 typical results for the specific heat (C_p) vs temperature (T) relationship are given. With elevation of T , data for the C_{16}ICl represented by solid circles show a linearly increasing trend of C_p in the range 290–307 K, and exhibit a large anomalous peak at 309 K as well as its shoulder at 312.5 K. In the range 313.5–323 K, C_p decreases slowly and then returns to a linear increase with further elevation of T . It should be noted, however, that the base line of C_p at $T > 323$ K deviates considerably downward from the extrapolated line from the range 290–307 K. Such a deviation is undoubtedly attributed to the irreversible change of the ICl concentration caused by heating.

In fact, the weight measurements indicate that the composition

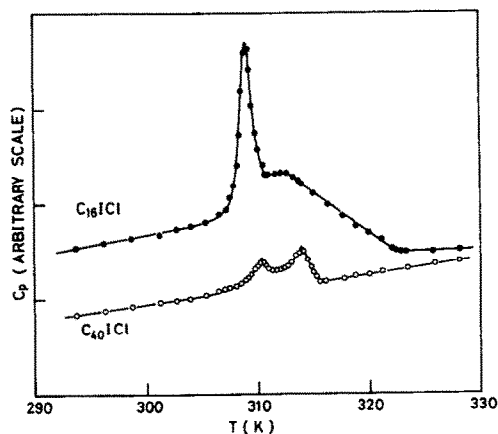


Fig. 1. Specific heat (C_p) plotted against temperature (T). The solid and open circles are for C_{16}ICl and C_{40}ICl respectively.

at $T > 323$ K is nearly C_{40}ICl . Moreover, the second-stage super-structure X-ray diffraction lines were found to decrease in intensity with increasing temperature, finally disappearing at $T > 310$ K. This implies that the ordered alignment of ICl molecules between graphite layers becomes so unstable at 310 K that 60% are driven out and 40% are distributed at random; thence, the large anomalous peak of C_p should partly be ascribed to the evaporation of ICl.

The C_p vs T plot for C_{40}ICl is represented by open circles in Fig. 1, showing two peaks at 310.5 and 314.0 K respectively. These peaks are lower than those of C_{16}ICl , and are shifted by about 1.5 K to the right. As for the reproducibility, C_{40}ICl was found to be fairly stable, not showing any detectable changes in the C_p vs T relationship after repeating the measurements in the range even up to 330 K. Again, the fifth-stage super-structure X-ray diffraction lines are found to disappear at $T > 310$ K; this provides evidence that in C_{40}ICl the order-disorder transition also does take place in about the same temperature range as for C_{16}ICl . The double-peak structure of the anomaly is of much

interest, but more extensive studies will be required for reaching a definite assignment.

College of Medicine
Nihon University
Itabashi-ku
Tokyo, Japan

K. TASHIRO
M. SAITO

College of Science and Technology
Nihon University
Kanda-Surugadai
Chiyoda-ku
Tokyo, Japan

T. TSUZUKU

REFERENCES

1. P. Handler, D. E. Mapother and M. Rayl, *Phys. Rev. Letters* **20**, 356 (1967).
2. D. S. Simons and M. B. Salamon, *Phys. Rev. Letters* **26**, 750 (1971).
3. M. Bottomley, G. S. Parry and A. R. Ubbelohde, *Proc. Roy. Soc. (London)* **A279**, 291 (1964).
4. D. E. Nixon, G. S. Parry and A. R. Ubbelohde, *Proc. Roy. Soc. (London)* **A291**, 324 (1966).
5. K. Kawamura, T. Saito and T. Tsuzuku, *Carbon* **13**, 452 (1975).
6. T. Sasa, Y. Takahashi and T. Mukaibo, *Carbon* **9**, 407 (1971).