

The errors in the total difference quantities are around 0.1 kcal mole<sup>-1</sup>, but errors in the component thermochemical quantities on the right side may be considerably larger. The theoretical rate relations and detailed vibrational frequency assignments for radical and decomposition complexes employed in the calculations are similar in nature to the models previously described and may be found in Refs. 1(e) and 2.

Since the relevant  $\Delta H_{f0}^\circ$  are known,<sup>4</sup> the absolute values,  $E_0^{i55DMH2} = 29.57$  kcal, and  $E_{\min} = 39.85$  kcal, may be calculated from expressions given in Ref. 1(b). The critical energy for the *neo*-pentyl addition to the double bond of *c*B2 relative to *t*B2 is  $E_c(\text{neoP}, \text{cB2}) - E_c(\text{neoP}, \text{tB2}) = 0.55$  kcal mole<sup>-1</sup>. Also, the difference in critical energies for methyl addition to the number 3 C atom of 55DMH2 isomers is

$$E_c(\text{Me}[\text{C}_3], \text{c55DMH2}) - E_c(\text{Me}[\text{C}_3], \text{t55DMH2}) \\ = 0.85 \text{ kcal mole}^{-1}.$$

Previously,<sup>1b,1c</sup> the critical energy difference

$$E_c(\text{R}, \text{cB2}) - E_c(\text{Me}[\text{C}_3], \text{t-2-alkene}) = 0.6 \text{ kcal mole}^{-1}$$

was described for R is ethyl or larger, and *t*-2-alkene is *trans*-2-pentene or larger. Thus, on taking the difference  $\Delta E_c$  in Eq. (3) to be 0.6 kcal mole<sup>-1</sup>, then  $D_0^\circ(\text{Me-H}) - D_0^\circ(\text{neoP-H}) = 3.9$  kcal mole<sup>-1</sup>. Previous competitive reaction studies led to  $D_0^\circ(\text{Me-H}) - D_0^\circ(\text{Et-H}) = 5.70$  kcal mole<sup>-1</sup> so that  $D_0^\circ(\text{neoP-H})$  exceeds  $D_0^\circ(\text{Et-H})$  by 1.8 kcal mole<sup>-1</sup> from our studies (cf. 1.4 kcal mole<sup>-1</sup> from Kerr<sup>5</sup>). Bond dissociation energies,  $D_0(\text{R-H})$ , for R is methyl, ethyl, *n*-propyl, *iso*-propyl, and *neo*-pentyl, have now been fixed by competitive reaction studies at 102.7, 97.0, 96.2, 92.8, and 98.8 kcal mole<sup>-1</sup>, respectively. At 298°K, the corresponding values are 104.3, 98.6, 97.7, 94.3, and 100.3 kcal mole<sup>-1</sup>, respectively. The estimated accuracy of these  $D^\circ$  quantities is within  $\pm 1$  kcal on an absolute basis; the relative errors should be less.

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<sup>1</sup> (a) D. C. Tardy, B. S. Rabinovitch, and C. W. Larson, *J. Chem Phys.* **45**, 1163 (1965); (b) C. W. Larson, B. S. Rabinovitch, and D. C. Tardy, *ibid.*, **47**, 4570 (1967); (c) C. W. Larson, D. C. Tardy, and B. S. Rabinovitch, *ibid.*, **49**, 299 (1968); (d) C. W. Larson and B. S. Rabinovitch, *ibid.*, **50**, 871 (1969); in Eq. (7) the ratio in parenthesis should be inverted and the numbers 2 and 5 in the line below Eq. (7) should be interchanged. (e) See. C. W. Larson, Ph.D. thesis, University of Washington, Seattle, Wash., 1969 for further details.

<sup>2</sup> C. W. Larson, B. S. Rabinovitch, and E. A. Hardwidge (unpublished).

<sup>3</sup> R. A. Marcus and O. K. Rice, *J. Phys. Colloid Chem.* **55**, 894 (1951).

<sup>4</sup> Heats of formation at 298°K were calculated using the technique described in J. D. Rockenfeller and F. D. Rossini, *J. Phys. Chem.* **65**, 267 (1961) and corrected to 0°K using  $H_{298}^\circ - H_0^\circ$  estimated from J. L. Franklin, *Ind. Eng. Chem.* **41**, 1070 (1949). Results are kilocalories mole<sup>-1</sup>:  $\Delta H_{f0}^\circ(\text{c55DMH2}) = -14.65$ ;  $\Delta H_{f0}^\circ(\text{t55DMH2}) = -15.85$ ;  $\Delta H_{f0}^\circ(2,4,4\text{-trimethylhexane}) = -43.71$ ;  $\Delta H_{f0}^\circ(3,5,5\text{-trimethyl-1-hexene}) = -15.70$ . Also,  $\Delta H_{f0}^\circ(\text{neopentene}) = -31.30$  from F. D. Rossini, *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons*

(Carnegie Press, Pittsburgh, Pa., 1953) was used. Using previously adopted or determined values<sup>1d</sup> for the remaining required thermodynamic properties, then  $E_0^{i55DMH2}$  [see Eq. (8), Ref. 1(b)] the critical energy for formation of *i*55DMH2 and  $E_{\min}$  [see Eq. (7), Ref. 1(b)] the minimum energy of the formed vibrationally excited radical (355TMH2\*) were obtained.

<sup>5</sup> J. A. Kerr, *Chem. Rev.* **66**, 465 (1966).

### Heat Capacity of Silver Iodide. III. An Order-Disorder Transition

C. M. PERROTT AND N. H. FLETCHER

*Department of Physics, University of New England,  
Armidale, N.S.W., Australia*

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In the first two papers of this series,<sup>1,2</sup> to be referred to as I and II, we reported measurements of the heat capacity of silver iodide over the range 50°–360°C and proposed a theoretical model to account for the anomalously high heat capacity of stoichiometric  $\alpha$ -AgI. This model was based on the assumption of an order-disorder transition between  $N$  silver ions and  $2N$  silver ion vacancies distributed over the  $3N$  equivalent cluster sites of six interpenetrating simple cubic lattices which may be used to describe the  $\alpha$ -AgI structure. No such transition was observed within the range of the measurements and it was assumed to occur somewhere between 360°C and the melting point, 550°C.

These measurements have now been extended to 480°C and the order-disorder transition has been identified at 430°C. In addition, further information now makes it possible to refine our model for the cluster sites and to make a more significant comparison between theory and experiment.

Our experimental results are summarized in Fig. 1 and show the typical form of an order-disorder transition. At the critical temperature 430°C, however, not only does the heat capacity change discontinuously, but there is a latent heat amounting to  $300 \pm 50$  cal/mole. This implies a discontinuous change in the order parameter at the critical temperature, which was, in fact, a feature of the theory presented in II.

In seeking numerical values for the theory in II, we made the assumption that the lowest energy is associated with the central (*b*) sites in each cluster, the surrounding (*d*) and (*h*) sites having higher energies. It has been pointed out to us by P. D. Greene that this is most unlikely, and recent powder-diffraction data by Burley<sup>3</sup> indicates that the group occupancies of (*b*), (*d*), and (*h*) sites at 430°C are as 2.4:26.4:72. The (*h*) sites thus have lowest energy, with (*d*) and (*b*) sites lying above them by approximately 0.26 and 1.73 kcal/mole, respectively. We have evaluated the contribution to the specific heat of the vibrational motion of silver ions in these cluster wells, using a different approximation for the potential from that in II in order to avoid supernumary wells, and find that it is

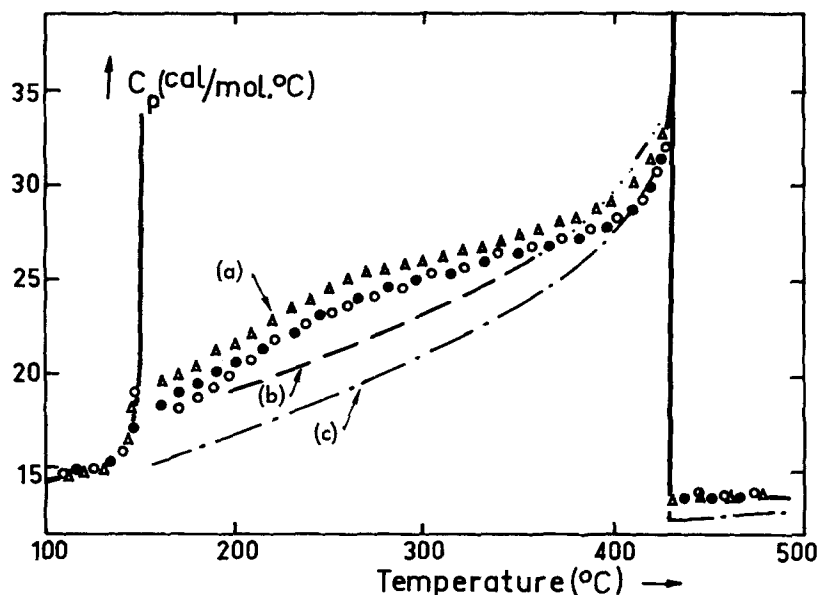


FIG. 1. Molar heat capacity of annealed stoichiometric silver iodide: (a) Typical experimental results, those below 360°C being derived from the previous work<sup>1</sup> and the overlapping results above 300°C representing the present work; (b) results of Lieser<sup>4</sup>; (c) theory for  $\alpha$ -AgI.

less than the normal value  $3R$  by about  $0.70R$  at 200°C,  $0.70R$  at 350°C, and  $0.02R$  at 500°C.

Before presenting the theoretical heat-capacity curve, it is useful to point out that the whole order-disorder problem in  $\alpha$ -AgI can be simplified if the  $3N$  equivalent cluster sites are regarded as comprising not six simple cubic lattices but rather three body-centered cubic lattices. Each such lattice then has the same symmetry as does the iodide ion lattice and it is natural to expect silver ions to occupy just one of these lattices in the ordered state, leaving the other two vacant. It is then no longer necessary to make any special assumptions about the variation of interaction energy with distance because the nearest-neighbor interactions considered always occur over a separation  $\frac{1}{2}a_0$  and the number of nearest neighbors  $z^{ij}$  is constant. On this sublattice model the results are identical with those presented in II but the physical foundations seem more secure.

Finally, to calculate the heat capacity of  $\alpha$ -AgI we obtain the configurational heat capacity in terms of absolute temperature from the correspondence of critical temperatures  $\tau=0.915$  from II and  $T=703^\circ\text{K}$  as observed. This sets the ordering energy  $v=kT/\tau$  as 1.54 kcal/mole. To this we add the vibrational contribution from silver ions referred to above and the normal  $3R$  from iodide ions. The disordering contribution from iodide ions discussed in II is omitted since its existence is uncertain and it is certainly overestimated by the evaluation suggested in II. The final result is shown as curve (c) in Fig. 1, where it is compared with our own measurements (a) and those of Lieser<sup>4</sup> (b), after conversion from  $C_v$  to  $C_p$  as discussed in I.

The agreement between theory and experiment for heat capacity is not at all exact but is reasonably satisfactory in view of the zeroth-order nature of the

order-disorder theory used in the derivation. The calculated value of the latent heat at the transition is 110 cal/mole, which is very much less than the experimental value  $300\pm 50$  cal/mole, but again moderately satisfactory in view of the approximations involved.

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<sup>3</sup> G. Burley, *Acta Cryst.* **23**, 1 (1967).

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### Approximate Hartree-Fock Energies of the $1^1S$ and $2^3S$ States of the Helium Atom Using Three-Parameter Orbitals Generalized from Slater and Gaussian Functions

ROBERT H. CARRIER AND F. L. PILAR

*University of New Hampshire, Department of Chemistry,  
Parsons Hall, Durham, New Hampshire*

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During the course of recent investigations on diatomic molecules we have had occasion to carry out certain calibration calculations on the helium atom using trial wavefunctions constructed from antisymmetrized products of spin orbitals whose spatial portions are of the general form

$$\phi_i(\alpha_i, n_i, m_i) = N\tau^{n_i} \exp(-\alpha_i r^{m_i}), \quad (1)$$