

produce the type of oscillation suggested. At sufficiently low temperatures this oscillation should cease. One would expect, therefore, small "humps" in the heat capacity curves of all benzene derivatives (unless oscillation is prevented by external forces), similar to those found⁸ for certain of them which have been attributed⁷ to rotation of CH₃ groups.

Another alternative is to assume easy (not necessarily frequent) oscillation and that the orientation of the puckering in a particular molecule in crystalline C(CH₃)₆ does not depend on the orientations in surrounding molecules.

The "anomalous" isomerism found among biphenyl derivatives may perhaps be due to non-oscillating puckered rings, rather than to a lack of free rotation about the bond joining them.

X-Ray studies have revealed no cases of two mutually perpendicular planes of symmetry passing through benzene ring centers (as would be expected if the rings were plane), although in several cases a center of symmetry has been found.⁹ X-Ray evidence also definitely favors models with equivalent atoms at or oscillating about the corners of a regular hexagon. A satisfactory model must account, moreover, for the synthesis of benzene derivatives, first by methods indicating 1,4-linkages and second, by simple ring closure of a conjugated system.¹⁰ The writer knows of no model, other than that proposed here, which meets these requirements.

From this model one would predict that "electron density" calculations from accurate x-ray intensity data by the method of Fourier Series summations¹¹ would show the carbon atom "peaks" to be considerably elongated normal to the "plane of the ring."

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY
STANFORD UNIVERSITY, CALIFORNIA
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MAURICE L. HUGGINS

GRADUAL TRANSITION IN CRYSTALLINE SODIUM NITRATE¹

Sir:

Some interest has been elicited in recent years in gradual transitions in crystalline solids. In these transitions the heat capacity of the crystal alters abnormally over an extended range of temperatures, with a more or less well-defined temperature at which the heat capacity reaches a maxi-

⁸ Huffman, Parks and Daniels, *THIS JOURNAL*, 52, 1547 (1930).

⁹ See, for instance, Hendricks, *Chem. Rev.*, 7, 431 (1930).

¹⁰ Ingold, *J. Chem. Soc.*, 121, 1143 (1922).

¹¹ Duane, *Proc. Nat. Acad. Sci.*, 11, 489 (1925); Havighurst, *ibid.*, 11, 502 (1925); Compton, "X-Rays and Electrons," D. Van Nostrand Co., Inc., New York, 1926, p. 151; W. L. Bragg, *Proc. Roy. Soc. (London)*, A123, 537 (1929).

¹ Abstract of a presentation made at the February meeting of the Washington Section of the American Chemical Society, Washington, D. C.

mum, but there is no sharply defined finite discontinuity in the total heat absorbed. All the examples quoted in the literature (see, *e. g.*, the work of F. Simon on ammonium salts, Giauque and Wiebe on hydrogen bromide and iodide, K. Clusius on crystalline nitrogen, oxygen, methane, etc.) occur in the region of very low temperatures, and are for this reason difficult to examine for changes in other physical properties. There exists accordingly some uncertainty as to the exact behavior of a crystal during these apparent inversions, and doubt has been expressed [A. Smits, *Physik. Z.*, (1930)] as to whether the experimental conditions do not account for the anomaly. It is also clear that theoretical explanations of this type of transition [L. Pauling, *Phys. Rev.*, August (1930)] cannot be fully accepted for all cases until our knowledge is more complete.

Sodium nitrate exhibits a gradual transition which ends at approximately 275°. We have examined the changes in heat capacity as shown by differential heating and cooling curves, thermal expansion, the solubility of the salt to its melting point in water, and the x-ray diffraction patterns at various temperatures. Further work on other properties is in progress. The results obtained indicate that the properties of sodium nitrate crystals alter reproducibly over a range of temperatures rather than suddenly at a definite transition point. The expansion coefficient is nearly constant to about 150°, then it gradually increases to a peak value near 275°, followed by a rapid decrease to a normal value beyond 280°. The heat absorption on heating likewise gradually increases to a maximum at 275.5°, while on cooling the heat evolution begins at about 278°. Hysteresis phenomena are completely absent. The change in x-ray patterns is definite but small, and optical examination with a heating microscope shows that the crystals remain optically uniaxial up to the melting point. The solubility curve undergoes a small, but apparently real, change in the transition region. The detailed results of the experimental work will be communicated in the near future.

THE GEOPHYSICAL LABORATORY
CARNEGIE INSTITUTION OF WASHINGTON
WASHINGTON, D. C.
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F. C. KRACEK
E. POSNJAK

THE PHOTO-REACTION BETWEEN HYDROGEN AND IODINE MONOCHLORIDE

Sir:

In a note on the reaction between iodine monochloride and hydrogen, D. P. Mellor and T. Iredale¹ have presented some experiments which they believe are contrary to conclusions presented by us in a recent paper.²

¹ Mellor and Iredale, *Nature*, 127, 93 (1931).

² Rollefson and Lindquist, *THIS JOURNAL*, 52, 2793 (1930).