

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.

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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).

We wish to call attention to the fact that their experimental results are not a contradiction of ours, as the conditions were considerably different, and furthermore their results may be interpreted in a manner consistent with our conclusions.

In the first place if we have a group of normal chlorine atoms formed, approximately 2% of them should in time acquire the energy of activation to the 2P_1 state by collisions. These atoms would be capable of forming hydrochloric acid by reaction with hydrogen. If, however, the atoms were destroyed by a reaction such as $ICl + Cl = Cl_2 + I$ before they acquired this energy, there would be no hydrochloric acid formation. Therefore, the most favorable conditions for reaction with hydrogen would be with the hydrogen pressure much higher than the iodine monochloride pressure. Mellor and Iredale had this condition in that they had the hydrogen pressure approximately forty times that of the iodine monochloride, whereas in our experiments of this kind the two pressures were of the same magnitude. Our results were confirmed by Franck and Rabinowitsch,³ who found no reaction between hydrogen and iodine monochloride when they used an electric spark for excitation.

Mellor and Iredale apparently missed the principal point of our argument, namely, that in a given mixture of iodine monochloride, chlorine and hydrogen, light absorbed by the chlorine started a reaction whereas that absorbed by the iodine monochloride did not. That experimental fact is definite proof that the action of light on chlorine gives a product different from that resulting from iodine monochloride. This point is discussed in detail in our previous paper.

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THE REMOVAL OF HYDROGEN HALIDE FROM ORGANIC HALIDES

Sir:

In view of the recent appearance of an article by Semb and McElvain [THIS JOURNAL, 53, 690 (1931)] on the reaction of organic halides with secondary amines, we should like to state that we have been investigating the reaction of organic halides with tertiary amines with the hope of using this reaction to determine the relative ease of removal of hydrogen halide from various organic halides. From the work of Semb and McElvain it is apparent that the usual course of the reaction of organic halides with secondary amines, and in particular with piperidine, is the formation of tertiary amines and that the removal of hydrogen halide takes place to a considerable extent only from tertiary halides. In our work using

³ Franck and Rabinowitsch, *Z. Elektrochem.*, 36, 794 (1930).