Raman Spectrum of Solid H2S

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The Gaseous Equilibrium of 1,2-Diiodobutane, Butene-1 and Iodine

Of the equilibria between iodine and gaseous olefines only that involving ethylene has been studied previously.[1,2] From the temperature coefficient of the equilibrium constants the heat of reaction was calculated to be 13.4 ± 0.5 Cal.

It seemed to be worth while to study other equilibria of this type, primarily to determine whether the heats of iodination follow regularities found to apply to the heats of hydrogenation of the olefinic hydrocarbons.[3]

For the present investigation butene-1 was chosen because it happened to be available in a state of high purity and because, by analogy with the hydrogenation processes, it was hoped that the equilibrium would not be so much displaced towards olefine and iodine as to prevent its quantitative study. 1,2-diiodobutane has been prepared by Forbes and Nelson[4] by photoiodination of butene-1 at low temperatures in Freon solution.

The method employed was in most essentials that described by Cuthbertson and Kistiakowsky,[2] but the reaction flask was placed now in a liquid thermostat and instead of an outside pump to mix the gases a long iron-cored sealed glass tube was rolled on the bottom of the 40 cm long and 75 mm wide reaction tube by a pulsating magnetic field. For the determination of iodine the fraction of light absorbed in passage through the length of the reaction flask was measured, but instead of the phototronic cells previously used two vacuum phototubes connected in a differential circuit to the Penick[5] amplifier were employed. This increased the sensitivity of the apparatus so much that a better monochromatized and a geometrically better defined light beam could be used. The stability of the system was improved also. The scale of the rotary Nicol prism was calibrated in terms of the iodine pressure by introducing sealed capillary tubes with weighed amounts of iodine into the evacuated reaction vessel and breaking them magnetically.

The same procedure was employed in the equilibrium determinations and the pressure of iodine was usually followed for about two days, after which time it invariably reached a constant value. Butene was introduced through stopcocks into the evacuated vessel, but the reaction system was sealed off from the stopcocks and from the rest of the apparatus before the iodine tubes were broken. The total pressure was read on a quartz spiral manometer. Thus enough data were available to calculate the equilibrium pressures of all constituents.

Because of condensation of the constituents at lower temperatures and of the too unfavorable position of equilibrium at higher ones, only a small temperature range could be investigated. At 67.1°C five determinations gave $K = 1.36 \pm 0.06$ atmos. and at 80.7°C three determinations gave 2.74 ± 0.08 atmos.

From these data ΔH of the reaction is computed to be -12.0 ± 1.5 Cal., which is to be compared with the corresponding figure for the iodination of ethylene, -13.4 ± 0.5 Cal. Although due to the large experimental errors it is impossible to make a definite statement, the iodination

of butene is apparently less exothermic, and this is made probable also by the observation that the free energy change in the reaction is more positive, by about 0.9 Cal. There seems to be, therefore, the same trend as in the heats of hydrogenation, but if we may draw more inferences than are strictly justified by the accuracy of the data, we are inclined to think that the change in the heat of iodination from ethylene to butene-1 is smaller than in the heats of corresponding hydrogenations, which amounts to about 2.5 Cal.

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Raman Spectrum of Solid H₂S

The Raman spectrum of solid H_2S was studied by the present writers and four Raman lines with $\Delta\nu$ respectively equal to 80 cm⁻¹, 2523 cm⁻¹, 2547 cm⁻¹ and 2558 cm⁻¹ were reported.[1] Recently Murphy and Vance have repeated the investigation[2] and have failed to observe the lines at 80 cm⁻¹ and 2558 cm⁻¹. We want to point out in this connection that the lines 2547 and 2558 cm⁻¹ lie very close to each other and these two lines excited by the Hg line 4046A were just resolved by the Fuess glass spectrograph used by us. This spectrograph has a dispersion of about 18A per mm in the region mentioned above. Probably the spectrograph used by Murphy and Vance was unable to resolve these two lines 2547 and 2558 cm⁻¹ and that may be the reason why these authors have observed one line having a frequency almost intermediate between those of the two lines observed by us. As regards the line at 80 cm⁻¹ it may be pointed out that this line is a broad band and may not be detected with a spectrograph, which cannot produce lines free from coma. The origin of this band is different from that of the other three lines as discussed previously.

As regards the statement of the above authors that they have recorded the anti-Stokes Raman line at 2523 cm⁻¹ of solid H_2S in one hour, we want to point out that it is impossible to record this line at the temperature of liquid air ($-180°C$) whatever be the efficiency of the experimental arrangement. The ratio of the intensity of the anti-Stokes to that of the Stokes line, according to theoretical calculations, is of the order $1 : 10^{18}$. If the anti-Stokes line is recorded in 1 hour, the Stokes line ought to have been recorded in less than 10^{-14}th of a second. Evidently some mistake has been made by the above authors in the assignment of the line.

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