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The absorption spectra and vapor pressures of the hydrogen and deuterium iodides have been measured. The absorption of the hydrogen compound occurs at longer wavelengths than does the deuterium iodide. The vapor pressures are only slightly different, the deuterium iodide having a greater value at a given temperature. The theoretical reasons for these differences are discussed, and equations for the vapor pressures are given as determined by this and other work.

THE absorption spectra of the hydrogen halides have been the subject of considerable work.[1] The results have led uniformly to the belief that the absorption occurs from the zero $(v = \frac{1}{2})$ vibrational level of the normal $^1\Sigma$ state to a higher, unstable electronic level whose vibrational states are not quantized, at least in the region to which absorption occurs. The result of such a process would be the continuous absorption with a more or less vague short wave limit which has been observed. If this picture be the true one, the corresponding deuterium halide should show marked deviation in its absorption spectrum, due both to the difference in zero point energy[1a] of the ground states and to the different eigenfunctions characteristic of these levels. The heavier deuterium atom should penetrate less into those regions which are not permitted on classical theory. We have therefore compared hydrogen and deuterium iodides in an effort to discover if the results agree with the commonly accepted theory.

Pure hydrogen iodide was prepared by passing hydrogen and iodine over a heated platinum catalyst, and then distilling the resulting product from a trap in a carbon dioxide snow-acetone mixture to one in liquid air until, after 3 distillations, a colorless product was obtained. In order to avoid possible contamination from hydrogen adsorbed on a catalyst, the deuterium iodide was obtained by heating an excess of iodine with deuterium gas in a 2-liter bulb which

had been previously baked out for some hours in vacuo at 450°C. The bulb was then sealed on and opened into the distillation train in the manner already described by Rittenberg and Urey.[2]

After the distillations the deuterium iodide which was frozen in a liquid air trap, the absorption cell, and the quartz spiral manometer used to measure the pressure were sealed off from the pumps. The gas under measurement thus came into contact only with glass and quartz in a dark room and showed no measurable decomposition even after the illumination necessary to obtain the absorption spectra.

The deuterium gas was more than 99 percent pure as measured by combining a sample with oxygen and determining the refractive index of the water so-formed in an interferometer.

The quantitative absorption spectra were obtained by the use of a Judd-Lewis sector photometer, a Hilger quartz spectrograph (E–3) and the continuous spectrum from a condensed spark between tungsten electrodes under distilled water. The fused quartz absorption cell had a 12.41 cm optical path between the inside faces of the plane parallel ends. Several different pressures of gas were used and at each pressure eight pairs of exposures were made with eight different settings of the comparison beam. The frequency number where each pair of exposures possessed equal intensity was ascertained under a low power comparator. The molecular absorption coefficient was calculated from the equation $\alpha_\nu = (760/P \times L) \cdot e$ where $P$ was the observed pressure in mm, $L$ the length of the gas path in cm, and $e$, the setting of the comparison beam, was the logarithm of the ratio of the intensity of transmitted light to the intensity of the incident

[1] Tingey and Gerke, J. Am. Chem. Soc. **48**, 1838 (1926); Dutta, Zeits. f. Physik **77**, 404 (1932).

[1a] This effect has been found by Franck and Wood in the absorption of the two water vapors in the Schumann region (Phys. Rev. **45**, 667 (1934)). The difficulties of quantitative absorption measurements in this region made it impossible for them to find more than a long wave limit shift, which was qualitatively in agreement with the predicted difference in zero point energies.

[2] Rittenberg and Urey, J. Am. Chem. Soc. **56**, 1885 (1934).

TABLE I.

| Frequency $\times 10^{-2}$ | Mol. abs. coeff. | Frequency $\times 10^{-2}$ | Mol. abs. coeff. |
|---|---|---|---|
| HI | | | |
| 305.6 | 0.012 | 322.5 | 0.109 |
| 309.7 | .024 | 334.7 | .219 |
| 311.6 | .036 | 341.9 | .328 |
| 315.2 | .048 | 346.2 | .437 |
| 316.9 | .061 | 349.5 | .546 |
| 318.6 | .085 | 352.0 | .656 |
| 321.7 | .097 | 355.5 | .765 |
| | | 357.6 | .874 |
| DI | | | |
| 314.6 | 0.008 | 334.8 | 0.125 |
| 318.4 | .016 | 336.8 | .150 |
| 320.8 | .023 | 338.4 | .175 |
| 322.5 | .030 | 340.4 | .200 |
| 323.5 | .038 | 341.2 | .208 |
| 324.8 | .046 | 346.5 | .312 |
| 325.8 | .053 | 350.8 | .416 |
| 326.2 | .050 | 352.9 | .520 |
| 327.2 | .061 | 355.3 | .624 |
| 329.2 | .075 | 358.2 | .729 |
| 332.2 | .100 | 360.3 | .833 |



$$\text{Absorption Coefficient} = \frac{760}{length \times pressure} \times log_{10} \frac{I_0}{I}$$

Fig. 1.

light. The absorption of the empty cell was ascertained and a correction for its absorption was applied to the values obtained for the gases. The temperature of the gas in the absorption cell was approximately 25°.

The value of the absorption coefficient $\alpha_\nu$ is given in Table I for different frequencies and plotted in Fig. 1. The value of $\alpha_\nu$ is seen always to be higher for hydrogen iodide than for deuterium iodide at a given frequency as may be predicted.

In order to obtain a more quantitative comparison between the absorption curves reference should be made to Fig. 2. Here are plotted the potential energy curve of the $^1\Sigma$ state which is the same for HI and DI, treated as an harmonic oscillator, and the two eigenfunctions of the zero vibrational states, as well as a hypothetical completely repulsive upper state. In absorbing radiation of any frequency $\nu$ the molecule in the zero vibrational state is raised to some point on the upper potential energy curve, for which there will be an eigenfunction for every value of the potential energy. A typical example is shown by the dotted line. According to the theory suggested by Franck and worked out in terms of the wave theory by Condon,[3] the probability of a transition will be governed by the probability of a molecule in the ground state being in such a position as to be able to jump to that portion of the upper curve required by the frequency of the radiation, without change
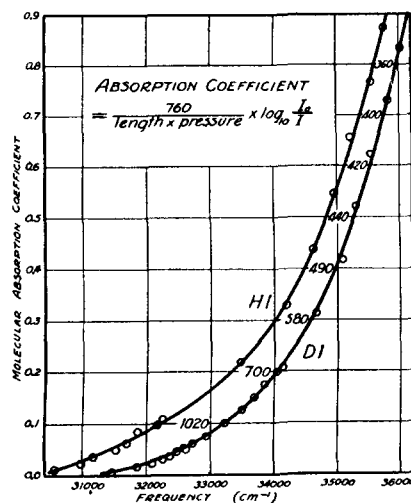
in nuclear separation, $r$. Since the eigenfunction of HI has larger values at greater values of $r$ than has that of DI the absorption of the former should extend to lower frequencies. Further, the absorption curves should at the point of maximum absorption differ by the difference in zero point energies (330 cm$^{-1}$). This can readily be seen to be indicated by the results of Fig. 1.

Stueckelberg and Gibson, Rice and Bayliss[4] have worked out theoretical expressions to indicate the value of $\alpha_\nu$ for cases similar to that under consideration. The resulting expressions have been applied to the continuous absorption of oxygen and iodine with considerable success.

In the present case, however, two important constants are lacking which are necessary for the use of the equations of Gibson, Rice and Bayliss. We do not know the frequency of maximum absorption, nor the total width of the absorption bands. The band of absorption of the halides apparently extends far into the ultraviolet with no indication on our plates of any decreasing absorption on the short wavelength side. This is probably due to factors which make the absorption under consideration different from the case of iodine, which they studied. The reduced mass is much smaller and the upper

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[3] Condon, Phys. Rev. 28, 1182 (1926); 32, 858 (1928).

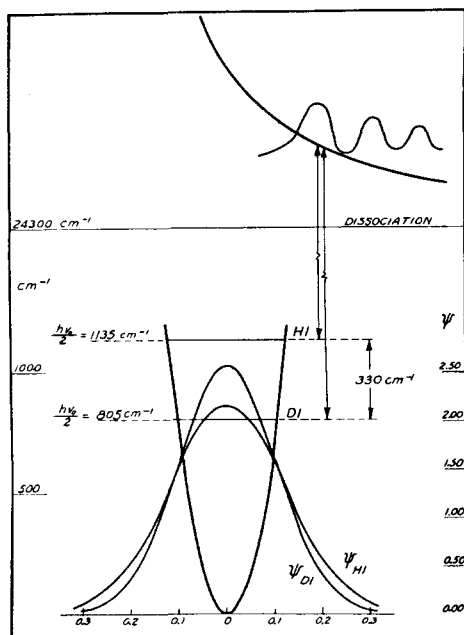[4] Stueckelberg, Phys. Rev. 42, 518 (1932); Gibson, Rice and Bayliss, Phys. Rev. 44, 193 (1933).

curve possibly steeper in the region of strong absorption, giving rise to an unusually broad absorption band.

It is possible to obtain a rough interpretation of our data using the expression of Stueckelberg, though here, too, the lack of the complete curve makes a fit somewhat dubious. The theoretical expression also requires that the upper curve have a constant slope, which is probably not true for an absorption which is occurring to an upper curve when it is approaching the dissociation energy level. A fit of the data for HI gives as a slope of the upper curve $2.3 \times 10^5$ cm$^{-1}$ A$^{-1}$. The same constants applied to DI lead to a value approximately the same, but the requirement that $\nu/c : y$ should give a straight line* is no longer fulfilled. This probably indicates a lack of linearity in the upper potential energy curve. The value of the slope, however, is a very reasonable one, being about 1/5 as large as that found for oxygen.

* Reference 4a, p. 522.

All of the recent work has also supported the picture of the absorption process as given, but there are some points which should perhaps be clarified. Rollefson and Booher[5] have shown that the absorption extends to longer wavelengths than can be accounted for if the decomposition products are an excited iodine atom ($^2P_{\frac{1}{2}}$) and a normal hydrogen atom. They suggest that two separate processes are occurring, the one just mentioned and another giving the two normal $^2P_{3/2}$ and $^2S_{\frac{1}{2}}$ states. It may be shown that the absorption observed by these authors at long wavelengths ($\alpha_\nu \cong 10^{-4}$, assuming that the value of $e$ is about 10 where blackening of the plate is no longer visible) is of the same order of magnitude as the relative populations of the first and the zero vibration levels. Consequently it might appear that absorption might still be due to a single electronic transition giving a $^2P_{\frac{1}{2}}$ iodine atom with the long wave part accounted for by transitions from the level $v = 1$ in the lower state. However the absorption occurs to a wavelength (3900A) which is shorter than could be produced by such a process and the occurrence of a transition to a state giving normal atoms seems to be a necessary conclusion. That the latter is the sole process, and involves a completely repulsive upper state is quite plausible.

In a more recent publication, Dutta and Deb[6] have obtained continuous emission spectra with long wave limits from the hydrogen halides. As has already been pointed out by Urey and Bates[7] this is not the type of spectrum to be expected from such a process, which should have no real long wave limit. The latter investigators looked for such spectra in the hydrogen halogen flames, but decided that those actually observed, having no long wave limit and extending beyond the red, were characteristic of a recombination of two halogen atoms rather than of hydrogen and halogen. This is confirmed by the thermal studies of Kondratjew and Leipunsky.[8] The hydrogen halogen recombination spectra should obviously be similar to these, but extend to shorter wavelengths.

[5] Rollefson and Booher, J. Am. Chem. Soc. **53**, 1728 (1931).
[6] Dutta and Deb, Zeits. f. Physik **93**, 127 (1934).
[7] Urey and Bates, Phys. Rev. **34**, 1541 (1929).
[8] Kondratjew and Leipunsky, Zeits. f. Physik **50**, 366 (1928).

## The Vapor Pressure of Hydrogen and Deuterium Iodide

The pressures were measured with the apparatus described above. A five junction copper-constantan thermocouple, accurate to ±0.1°, was employed for the temperature measurements. In the first series of experiments, with the small amounts of the iodides originally prepared for the study of the absorption spectra, reproducible vapor pressures for both solid and liquid states were obtained, but the triple points could not be determined with sufficient accuracy. With the liquids equilibrium was established very rapidly, but the solids produced reproducible pressures only after standing for considerable lengths of time at constant temperature. At the lowest temperatures, produced by carbon dioxide-acetone mixtures, at least two hours were required. Constant temperatures at other points up to the boiling points of the iodides were maintained by means of a series of freezing baths. In the entire series of measurements the tube which served as the thermocouple well was fixed to the trap containing the hydrogen or deuterium iodide in such a way as to measure the temperature of the bath in the region nearest to the sample.

The triple points were determined by means of heating curves. Larger quantities (about 20 g) of the iodides were prepared and the apparatus was rebuilt so as to effect the direct immersion of the thermocouple well into the hydrogen or deuterium iodide. With this arrangement, the triple points were readily determined, but satisfactory vapor pressures could no longer be obtained.

The new data presented here for liquid hydrogen iodide are in good agreement with values available in the literature.[9] For the solid the agreement is less satisfactory. The results of this and other investigations are perhaps best discussed by comparison with vapor pressures calculated from the boiling point, triple point, and calorimetric data presented by Giauque and

[9] Steele, McIntosh and Archibald, Zeits. f. physik. Chemie 55, 129 (1906); Maas and McIntosh, Proc. and Trans. Roy. Soc. Canada 13, 65 (14); Steele and Bayster, J. Chem. Soc. 97, 2607 (1910); Henglein, Zeits. f. Physik 18, 64 (1924); Miravalles and Moles, Anales soc. españ fis. quim. 23, 509 (1925).

Wiebe[10] for hydrogen iodide. If the various experimental points are placed on a large scale graph showing the logarithm of the pressure as a function of the reciprocal of the temperature, those for the liquid are found to lie on a line slightly above the calculated values, while those for the solid lie almost without exception below the calculated curve. A line drawn through the average of the experimental points for the solid intersects the corresponding line for the liquid at some distance above the triple point. Furthermore, in the 15° temperature range immediately below the triple point, the "experimental curve" shows a curvature opposite to that required by the heat capacity data. Closer agreement between measured and calculated pressures is observed in the neighborhood of the carbon dioxide sublimation point. It is evident, then, that most of the available data for solid hydrogen iodide represent pressures below the true equilibrium values. This is consistent with our experience that reproducible vapor pressures could be obtained with the solid only when constant temperatures were maintained for considerable lengths of time.

We have chosen to express the vapor pressure of hydrogen iodide as a function of the temperature by means of curves with slopes determined by the calorimetric data of Giauque and Wiebe and passing through our measured value of the pressure (log $p = 2.579$) at the triple point (222.3°). The equation thus obtained for the liquid represents the direct experimental data quite accurately. In addition to the assumption that the heat capacity of the vapor is given by $5/2\ R$, the following calorimetric data, taken from the measurements of Giauque and Wiebe, were employed in setting up the equations:

$\Delta H_{237.75}$ (vaporization)

$$= 4724 \text{ cal. (at the boiling point)},$$
$\Delta H_{222.3}$ (fusion) $= 686$ cal. (at the triple point),

$$Cp(l) = 19.11 - 0.021T; \ Cp(s) = 5.72 + 0.029T.$$

The equations follow:

$$\log p(\text{HI}, l) = 26.119 + 0.002293T$$
$$- 7.111 \log T - 1636/T, \quad (1)$$

[10] Giauque and Wiebe, J. Am. Chem. Soc. 51, 1441 (1929).

$$\log p(\text{HI}, s) = 10.493 - 0.003167T$$
$$-0.377 \log T - 1406/T. \quad (2)$$

The corresponding relations for deuterium iodide are obtained by comparing, as shown in Table II, the measured vapor pressures for

Table II. *Vapor pressure of solid and liquid hydrogen and deuterium iodides.*

| $T$ | $\log p(\text{HI})(\text{calc.})$ | $\log p(\text{HI})(\text{exp.})$ | $\log p(\text{DI})(\text{exp.})$ |
|---|---|---|---|
| (a) Liquid | | | |
| 233.9 | 2.813 | 2.816 | 2.823 |
| 226.9 | 2.675 | | 2.685 |
| 222.7 | 2.587 | 2.586 | |
| 219.8 | 2.524 | supercooled liquid 2.535 | |
| (b) Triple point | | | |
| (222.3) | (2.579) | (2.579) | |
| 222.4 | | 2.584 | |
| 221.5 | {2.560(s) | | 2.560, 2.567 |
| | {2.562(l) | | |
| (c) Solid | | | |
| 207.8 | 2.195 | | 2.216 |
| 207.0 | 2.172 | 2.176 | |
| 194.3 | 1.779 | 1.780 | |
| 191.4 | 1.680 | | 1.693 |

deuterium iodide with those calculated for hydrogen iodide at the same temperatures. The table also shows the comparison between measured and calculated values for hydrogen iodide.

In addition to the tabulated results, a number of experiments were performed at temperatures slightly below 200° in which equilibrium was approached from either side. In every case the pressure could be shown to be approaching a value consistent with the above results. For the solid, only the results obtained where constant temperature was maintained for sufficient periods of time are recorded in the table. The measured pressures for deuterium iodide at the triple point, obtained with the 20 g batch of material are obviously low. The true value, by interpolation from the other measurements on the liquid, is 2.572.

Examination of the table shows that the logarithm of the vapor pressure of liquid deuterium iodide may be obtained by adding 0.01 to the calculated value for hydrogen iodide at the same temperature. The corresponding addition for the solid is not so evident from the data, but is set at 0.012 to take account of the difference between solid and liquid hydrogen iodide at the triple point of deuterium iodide. Therefore, for deuterium iodide,

$$\log p(\text{DI}, l) = 26.129 + 0.002293T$$
$$-7.111 \log T - 1636/T, \quad (3)$$
$$\log p(\text{DI}, s) = 10.505 - 0.003167T$$
$$-0.377 \log T - 1406/T. \quad (4)$$

Substituting for $p = 760$ mm in Eqs. (1) and (3) gives for the boiling points most consistent with our experimental data, 237.5° for hydrogen iodide and 237.0° for deuterium iodide. We are at a loss to account for the deviation of our boiling point for hydrogen iodide from that of Giauque and Wiebe (237.75°). Our probable error in temperature measurement is of the order of ±0.1°, the deviation of hydrogen iodide from the ideal gas laws might be expected to operate in the reverse direction, so as to widen the discrepancy, and the correction of our pressures to mm of mercury at 0°C would raise our boiling point only 0.1°.

The conclusion expressed in Eqs. (3) and (4), to the effect that the ratio of the vapor pressures of the two hydrogen iodides is a constant over the entire range for either the solid or the liquid states, can be true only if the heats of vaporization, fusion and sublimation of the two substances are nearly identical at the same temperatures. The difference in heats of vaporization, which play the most important role of the three mentioned, can be estimated in the neighborhood of the boiling point by an application of Trouton's Rule.

Trouton's rule can be applied to the hydrogen iodides with greater confidence than to water or to the other hydrogen halides. The lower electric moment and the numerical value of Trouton's constant, 19.9 for HI, suggest that the iodides should behave as "normal" liquids. The rule is applied in the form suggested by the Hildebrand modification[11] in which the heat temperature quotients at temperatures of equal equilibrium molal volume for the vapors are set equal. From Eq. (4) it is found by approximation that at 269.93° the molal volume of vapor at equilibrium with deuterium iodide is the same as that for hydrogen iodide at its boiling point. Whence, for deuterium iodide,

$$\Delta H_{236.93} \,(\text{vap.}) = 4713 \text{ cal.}$$

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[11] Hildebrand, J. Am. Chem. Soc. **37**, 970 (1915).

and at the boiling point of hydrogen iodide, the value may be estimated from the heat capacity of hydrogen iodide to be 4709 cal. as against 4724 cal. for hydrogen iodide. The effect of this difference upon the vapor pressures is within the limit of accuracy of our measurements. Vapor pressures at the boiling point calculated from a single pressure at the triple point and using, respectively, the two heats of vaporization differing by fifteen calories would be different by 0.7 mm, or the calculated boiling points would differ by 0.05°.

By reference to the summary presented by Claussen and Hildebrand[12] in connection with their vapor pressures of the hydrogen and deuterium fluorides, it is seen that deuterium iodide differs from hydrogen iodide in the same direction as deuterium fluoride from hydrogen fluoride, but to a considerably smaller extent. The greater vapor pressure of the deuterium compounds in these two cases cannot be ascribed to the same cause. The fluoride is known to have properties differing in general from the other halides. This has been supposed to be due to the more ionic nature of the hydrogen fluorine bond. The iodide should according to recent theories be at the other extreme.[13] A possible explanation seems to be that the polarity of the deuterium iodide should be smaller, because of the smaller anharmonicity factor operative in the region of zero point energy.

[12] Claussen and Hildebrand, J. Am. Chem. Soc. 56, 1820 (1934).

[13] Mulliken, J. Chem. Phys. 2, 782 (1934).

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# The Crystal Structure of Lepidocrocite

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The unit of structure, space group symmetry and detailed atomic arrangement of lepidocrocite are determined from x-ray data, and the existence and location of hydrogen bonds in the structure are established from considerations of interatomic distances. The orthorhombic lattice is end centered on (100), and has the axes $a_0=3.87A$, $b_0$ 12.51A, and $c_0=3.06A$. The space group is $V_h^{17}-Amam$. The parameters are determined as $u_{Fe}=-0.332$, $u_O$ $=+0.282$, and $u_{OH}=+0.075$. The structure is described as consisting of iron-centered oxygen octahedra joined by the sharing of edges into two-dimensionally infinite layers, with the successive layers held together by hydrogen bonds. The relationship between the diaspore-goethite structure and the böhmite-lepidocrocite structure is discussed from the standpoint of the coordination theory, and found to depend on two alternative ways of satisfying the electrostatic valence rule.

## INTRODUCTION

LEPIDOCROCITE, FeO(OH), is described by Posnjak and Merwin[1] as forming orthorhombic crystals with the axial ratios 0.64 : 1 : 0.43. The crystals are red and transparent, and form thin plates tabular on (010), slightly striated in the direction of the c-axis.

The monohydrates of iron and aluminum oxide, with the general formula $MHO_2$, exist in two modifications. The structure of the modification corresponding to diaspore, $AlHO_2$, and goethite, $FeHO_2$, is known,[2] but no previous investigation of the structure of the second modification corresponding to lepidocrocite,

[1] E. Posnjak and H. E. Merwin, Am. J. Sci. 47, 311 (1919).

[2] M. Deflandre, Bull. Soc. Franc. Mineral. 55, 140 (1932); K. Takane, Proc. Imp. Acad. Tokyo 9, 113 (1933); S. Goldsztaub, Comptes rendus 195, 964 (1932); F. J. Ewing, J. Chem. Phys. 3, 203 (1935).