A Comparison of Some Physical Properties of Hydrogen and Deuterium Bromides

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The absorption spectra and vapor pressures of the hydrogen and deuterium bromides have
been measured. The frequency difference between the absorption curves of these compounds
is about three times as great as can be accounted for by the zero-point energy differences.
Theoretical reasons for this effect are discussed. The vapor pressures are almost identical.
The application of Trouton's rule to isotopic compounds is discussed and calculated values
for the constant are presented.

INVESTIGATIONS which have been reported
from this laboratory[1] show that the replace-
ment of the hydrogen in hydrogen iodide by
deuterium leads to higher vapor pressures, a
lower melting point and a lower boiling point.
These changes are of the same sign as those
which have been noted by Claussen and Hilde-
brand[2] for the hydrogen fluorides and opposite
to those noted for the corresponding chlorides.[3]
The bromides furnish examples which are inter-
mediate between the chlorides and iodides. The
vapor pressures of deuterium and hydrogen
bromides are practically the same, the boiling
points are almost identical and only in the case
of the triple point is a definite difference noted,
the deuterium bromide having the slightly higher
melting point.

The bromides were prepared by passing a
mixture of bromine and hydrogen or deuterium
over a heated platinum spiral in a manner
similar to that used for the preparation of the

iodides. The halides were each fractionally dis-
tilled three times and the middle fraction was
finally sealed in a unit which included a quartz
cell by means of which the absorption spectra
were ascertained, a quartz spiral manometer for
measurements of the vapor pressure and a cell
in which the halide was condensed and in which
a five-junction copper constantan thermocouple
had been inserted.

A comparison of the absorption spectra of the
hydrogen and deuterium halides gives an insight
into the nature of the energy levels involved.
The continuous absorption of the hydrogen
iodides sets in at a frequency about equivalent
to the energy of dissociation while that of the
bromides begins at a frequency corresponding to
an energy some 10 to 15,000 calories greater than
the dissociation energy, assuming an excited
halogen atom as one of the products. The
striking difference between the absorption spec-
tra of the bromides (Table I and Fig. 1) and
those of the iodides is the persistence for the
bromides of large frequency differences even at
high values of the absorption coefficient, α_r.

In the case of the iodides the separation of the
points of equal absorption began at about 1000

[1] Bates, Halford and Anderson, J. Chem. Phys. **3**, 415
(1935).
[2] Claussen and Hildebrand, J. Am. Chem. Soc. **56**, 1820
(1934).
[3] Lewis, Macdonald and Schutz, J. Am. Chem. Soc. **56**,
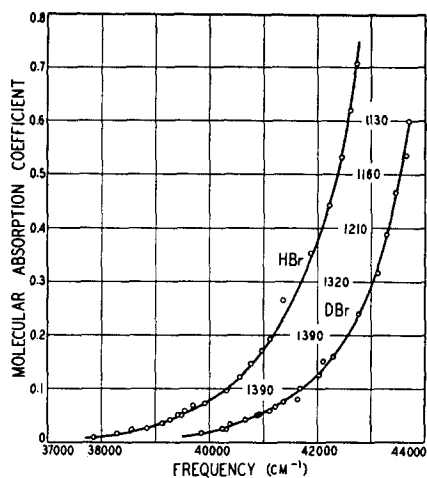494 (1934).

FIG. 1.

TABLE I.

FREQUENCY (mm⁻¹)	LOG MOLE ABS. COEFF.	FREQUENCY (mm⁻¹)	LOG MOLE ABS. COEFF.
Hydrogen bromide			
3785	0.009	4033	0.097
3828	.017	4056	.121
3855	.024	4077	.146
3884	.025	4098	.170
3913	.035	4112	.194
3928	.042	4137	.265
3948	.049	4189	.353
3941	.051	4223	.441
3955	.059	4246	.531
3970	.068	4261	.619
3992	.073	4273	.708
Deuterium bromide			
3985	0.017	4168	0.100
4030	.025	4202	.126
4022	.025	4211	.151
4039	.034	4230	.160
4067	.042	4278	.240
4090	.050	4313	.316
4092	.051	4328	.389
4111	.059	4345	.466
4122	.068	4365	.535
4137	.075	4370	.598
4163	.080		

cm⁻¹ and gradually approached the difference in zero-point energy (340 cm⁻¹) at high values of α_ν. The bromides, however, have a separation of 1100 cm⁻¹, almost three times the zero-point energy difference (374.8 cm⁻¹) at the highest values of α_ν measured. This phenomenon is predictable from the relation of frequency of absorption with the frequency corresponding to dissociation (33,200 cm⁻¹). Absorption to portions of a repulsive upper potential energy curve which lies considerably above the energy of dissociation would always be altered by two factors when hydrogen is replaced by deuterium: first the difference in zero-point energy, and second the contraction of the eigenfunction to smaller values of internuclear separation. The second factor would be practically eliminated in the case where the upper curve is becoming asymptotic to the dissociation level and hence the separation of the absorption curves of the hydrogen and deuterium compounds would tend to approach the zero-point energy difference as was observed in the case of the iodides. The data presented in this paper indicate that the second factor enters to a marked extent in the bromides.

One interesting result of these studies is that it is possible to produce by illumination known amounts of hydrogen atoms in a mixture of hydrogen and deuterium iodides and measure the relative efficiencies of the reactions H+HI and H+DI. Such studies are under way in this laboratory.

THE VAPOR PRESSURES OF HYDROGEN AND DEUTERIUM BROMIDES

The experimental arrangement employed for the measurement of the vapor pressures has already been described. The thermocouple was imbedded in a tube which was sealed into the apparatus in such a way that its lower two inches were immersed directly in the bromide. The cell containing the bromide was in turn immersed in an ether bath in a vacuum flask. Nitrogen cooled by passing through liquid air was directed through a coil of lead tubing immersed in the ether bath. In order to maintain uniform temperature, a rapid stream of cooled air was bubbled through the bath. The required nitrogen stream was sufficiently rapid to permit close regulation of the temperature throughout the period of measurement. With this arrangement, vapor pressures could be obtained with a quantity of the bromide sufficient to permit the measurement of the triple point by means of a heating curve.

The boiling points and triple points are given in Table II.

TABLE II.

	B. p.		Tr. p.
HBr	206.3		186.2
	206.38	Giauque and Wiebe	186.24
DBr	206.3		185.7

TABLE III. *Vapor pressure of hydrogen bromide.*

T	log p (exp.)	log p (calc.)
	liquid	
198.6	2.704	2.703
191.05	2.514	2.515
186.65	2.398	2.398
	solid	
184.9	2.340	2.344
180.3	2.192	2.191
174.15	1.955	1.975

TABLE IV. *Vapor pressure of deuterium bromide.*

T	log p (exp.)	log p (calc.)
	liquid	
205.43	2.861	2.861
202.45	2.792	2.792
197.6	2.675	2.676
192.9	2.556	2.558
189.4	2.468	2.467
186.85	2.399	2.398
	solid	
184.7	2.333	2.334
180.3	2.187	2.188
173.9	1.964	1.963

The experimentally determined vapor pressures are expressed by the following equations:

$$\log p(\text{HBr})(l) = 7.465 - 945.7/T, \quad (1)$$
$$\log p(\text{DBr})(l) = 7.517 - 956.5/T, \quad (2)$$
$$\log p(\text{HBr})(s) = 8.309 - 1103/T, \quad (3)$$
$$\log p(\text{DBr})(s) = 8.306 - 1103/T. \quad (4)$$

The character of the data is shown in Tables III and IV, for the hydrogen and deuterium bromide, respectively, by comparison of the experimental points with the corresponding calculated values, using the above equations.

Eq. (1) agrees, within experimental error, with the equation for liquid hydrogen bromide given in *International Critical Tables*[4] and deviates only slightly from an equation based upon the boiling point and calorimetric measurements of Giauque and Wiebe (Eq. (5)).[5]

$$\log p(\text{HBr})(l)$$
$$= 20.179 - 4.672 \log T - 1338/T. \quad (5)$$

[4] Int. Crit. Tab. 3, 213.
[5] Giauque and Wiebe, J. Am. Chem. Soc. 50, 2193 (1928).

Some difference in the latter comparison is to be expected, because no account has been taken of the deviations from the ideal gas laws.

The new data for solid hydrogen bromide are slightly less satisfactory, and the principal factor in fixing the constants of Eq. (3) has been the necessity for equal vapor pressure of the solid and liquid at the triple point, a factor which apparently was overlooked in deriving the corresponding equation for the *International Critical Tables*. Eq. (3) is also in better agreement with the heat of sublimation given by Giauque and Wiebe, if account is taken of the probable magnitude of deviations from the ideal gas law. Eq. (6), based on the data of Giauque and Wiebe, is included for comparison.

$$\log p(\text{HBr})(s) = 10.488 - 0.004084T$$
$$- 0.2766 \log T - 1250/T. \quad (6)$$

From Eq. (1), the average heat of vaporization of the liquid, assuming the ideal gas law, is 4330 cal. An approximation to the value at the boiling point may be obtained by subtracting the product of half the temperature range by the average heat capacity difference between the vapor and the liquid. The result is 4257 cal. as compared with 4210 cal. found by Giauque and Wiebe.

The heat of vaporization of deuterium bromide is obtained by multiplying 4210 by the ratio of the two values based upon vapor pressure measurements, with 4258 cal. as the result.

TROUTON'S RULE FOR ISOTOPIC SUBSTANCES

The relation between the heat of vaporization and the absolute temperature known as Trouton's rule would be expected to be obeyed by two isotopic substances with greater exactness than by most compounds. However, even a cursory examination of the data obtained to date shows that there exist considerable deviations from the rule even when pairs of isotopic substances are compared. Thus Urey and Teal[6] have shown that the vapor pressure curves of corresponding liquid hydrogen and deuterium compounds intersect at some temperature which is usually not far from the normal boiling point. At the point of intersection, since the heats of

[6] Urey and Teal, Rev. Mod. Phys. 7, 34 (1935).

TABLE V.

SUB-STANCE	a	b	$\Delta H/T_b$	SUB-STANCE	a	b	$\Delta H/T_b$
NH$_3$	8.1616	1266.08	24.179	HF	6.3739	1316.8	20.551
ND$_3$	8.2800	1308.23	24.721	DF	6.2026	1261.6	19.766
H$_2$O	9.1582	2342.5	28.742	HCl	7.6192	891.30	21.696
D$_2$O	9.2854	2399.1	29.325	DCl	7.6125	906.59	21.665
HCN	7.795	1467	22.171	HBr	7.465	945.7	20.397
DCN	7.695	1440	21.728	DBr	7.517	956.5	20.630
				HI			19.869
				DI			19.932

vaporization are not equal, Trouton's rule is not obeyed. To test this further, the constant was calculated for each of a group of substances and these constants are presented in Table V.

The constants a and b are those giving the vapor pressure according to Eq. (7).

$$\log P_{(mm)} = a - b/T \qquad (7)$$

where $b = \Delta H/4.5787$. Correction to constant vapor concentration, as in the Hildebrand[7] modification, produces changes too small to alter the conclusion. For example, the difference between the Trouton's constants for the chlorides is increased in this manner by 0.03.

An interesting observation to be made from Table V is that an isotopic change produces the greatest shift in the value of the constant for those substances which are known to deviate most from Trouton's rule, water and ammonia.

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

Comparison of the Raman Spectra of 1,1,1- and 1,1,2-Trichloroethane

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The Raman frequencies of 1,1,1- and 1,1,2-trichloroethane have been obtained. Comparison with CCl$_4$ indicates that the Cl$_3$C and Cl$_2$HC radicals have tetrahedral symmetry. The frequencies of Cl$_3$C·CH$_3$ and Cl$_2$HC·CH$_2$Cl are compared, and the combination frequencies and modes of vibration of the two molecules indicated.

THE Raman spectra of 1,1,1- and 1,1,2-trichloroethane have been up to the present time unknown. Among the compounds examined by Hanle,[1] are listed the Raman frequencies of Cl$_2$C = CHCl, obviously misnamed trichloroethane. Consequently it has seemed worth while to investigate the Raman spectra of both 1,1,1- and 1,1,2-trichloroethane, and to compare them with those of similar compounds.

Apparatus and experimental technique employed were similar to those described by Wood.[2] In the preliminary investigations a Hilger constant deviation spectrograph was used, having a dispersion of 25A/mm at λ4500. A Cooper-Hewitt Hg arc operated at 750 watts served as light source. The line chosen for excitation was λ4358. A filter consisting of a water solution of NaNO$_2$ was used to eliminate λ4047 and λ4078.

With this apparatus exposures ranged from 30–60 min. In the later work a spectrograph containing two 60° prisms and having a dispersion of 12A/mm at λ4500 was used. Two low pressure Hg arcs operated at 150 watts each served as light source. This apparatus, however, required exposure from 24 to 96 hours. The 1,1,1- and 1,1,2-trichloroethane were purchased from the Eastman Kodak Company and were fractionally distilled before use. The boiling range for the distilled Cl$_3$C·CH$_3$ was 74° to 75.5°C and for the distilled Cl$_2$HC·CH$_2$Cl was 113° to 115°C, both at normal pressure. Both compounds decompose very slowly when exposed to light, necessitating redistillation half-way through each exposure. Measurements were made directly on the spectrograms and also on microphotometer traces (Koch-Goos). A Cu arc spectrum was used for comparison, and wavelengths of the Raman lines were calculated by the Hartmann formula.

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[1] W. Hanle, Ann. d. Physik, [5] **15**, 345 (1932).
[2] R. W. Wood, Phil. Mag. [7] **6**, 729 (1928); Phys. Rev. **36**, 1421 (1930).