

that when the mole fraction of H_2 is 0.50 for the liquid, it is about 0.55 for the solid.

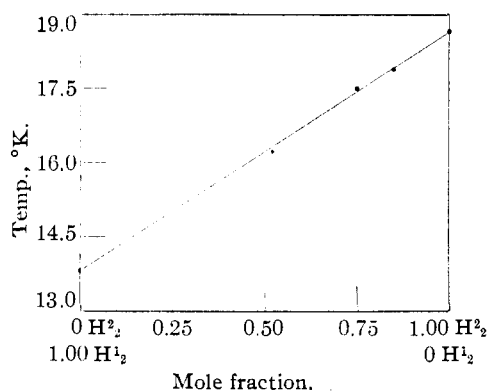


Fig. 2.

All these mixtures contained only the molecules H^1_2 and H^2_2 . One mixture containing equal amounts of these two species was later kept for thirty hours in a bulb containing a hot platinum filament in order to produce the equilibrium amount of H^1H^2 . The vapor pressure of this mixture was then studied. Unfortunately the amount of the mixture was too small for accurate measurements, but there appeared to be no great difference in vapor pressure before and after treatment with the hot wire.

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THE VAPOR PRESSURE OF SOLID AND LIQUID HEAVY HYDROGEN

Sir:

In a series of investigations in which we have been aided by Dr. R. T. Macdonald and Dr. P. W. Schutz, to whom we wish to express our great obligation, we have studied the vapor pressure of pure H^2_2 , and of mixtures of H^2_2 and H^1_2 (accompanying communication). The vapor pressures have been compared at each temperature with that of ordinary hydrogen in the para form, which has served as our thermometer. Our final measurements with pure H^2_2 are shown in the table and the figure. The ratio of p_2 , the vapor pressure of H^2_2 , to p_1 , that of H^1_2 (para), is plotted and tabulated as a function of p_1 . The two large circles in the figure show for comparison provisional values which have just been announced by Brickwedde, Scott, Urey and Wahl [*Bulletin of the American Physical Society*, 9, 16 (1934)].

The centigrade temperature corresponding to each value of p_1 may be obtained from the equation of Keeson, Bilj and van de Horst (Leiden Comm. 217a).

$$t = -260.937 + 1.0270 \log p + 1.7303 \log^2 p$$

Thence we find for $p_1 = 45.40$, corresponding to the triple point of H^2_2 , 18.66°K.

TABLE I

p_1	p_2/p_1	p_1	p_2/p_1	p_1	p_2/p_1
77.00	0.3328	44.94	0.2824	41.01	0.2694
61.17	.3119	44.38	.2810	38.06	.2588
51.21	.2954	44.05	.2795	29.22	.2262
47.27	.2883	43.71	.2782	21.56	.1915
46.27	.2861	42.89	.2761	11.85	.1426
45.26	.2844	42.14	.2731		

The choice of an equation of state for heavy hydrogen, and its use in an exact calculation of the heats of vaporization and the heat of fusion from our data, will be discussed in a later publication, together with our apparatus and method.

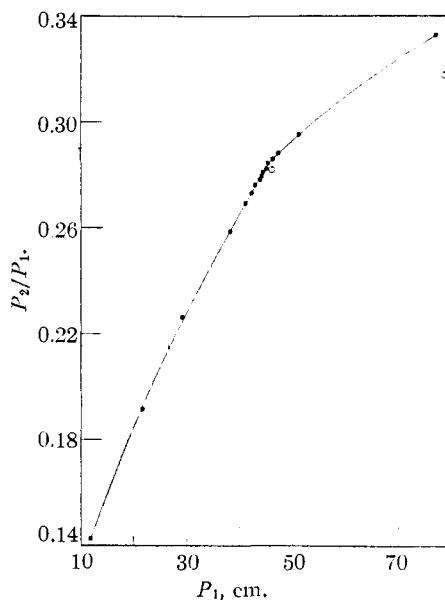


Fig. 1.

The measurements are extremely sensitive to an impurity of light hydrogen. In our first experiment, in which the hydrogen had been produced by the action of heavy water on a fresh sample of sodium, a considerable amount of H^1_2 was found to be present, which undoubtedly came from the sodium. The same sodium was treated again with H^2_2O and the gas still contained 1.5% of H^1 . Finally the same sodium was treated with water in which every effort was made to exclude H^1 . The impurity of 0.1–0.2% remaining in the gas thus produced was finally eliminated by

fractionally distilling at 20°K. After one-half of the liquid had been removed the vapor pressure remained constant to 0.1% upon further fractionation.

After the vapor pressure of pure H₂ was measured it was transferred to another tube containing charcoal, with the expectation of finding a different vapor pressure through the establishment of equilibrium between ortho and para forms of heavy hydrogen. To our surprise the vapor pressure at several temperatures fell exactly upon the curve previously obtained. Whether this is due to failure of the charcoal to promote equilibrium or whether the equilibrium had already been established in the tube which contained no charcoal we cannot say. It is possible also that the difference in vapor pressure between the equilibrium H₂ at high temperatures and the low temperature form is too small to be observed.

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RECEIVED MARCH 22, 1934

THE VAPOR PRESSURE OF LIQUID AND SOLID DEUTOCYANIC ACID

Sir:

In our communication on deutacetic acid [THIS JOURNAL, 56, 493 (1934)] we mentioned the hypothesis that the large difference in vapor pressure between the hydro- and the deuto-forms of such substances as water and ammonia is almost entirely due to the greater strength of the H² bond as compared with the H¹ bond. This hypothesis had already been tested in our experiments on the vapor pressure of hydrochloric and deutochloric acids [Lewis, Macdonald and Schutz, THIS JOURNAL, 56, 494 (1934)]. In that case there is little tendency to form the hydrogen bond and in spite of the low temperature, very little difference in vapor pressure was found.

To test this hypothesis we have chosen hydrocyanic acid, which is a highly abnormal liquid; this abnormality, however, is due not to the hydrogen bond formation but to a high dipole moment. Our measurements show a hardly perceptible difference between the vapor pressure of the two liquids, H¹CN and H²CN, thus furnishing excellent confirmation of our hypothesis.

There is far more hope of securing a theoretical interpretation of the difference in vapor pressure between two isotopic solids than between two

isotopic liquids. For this reason and because in this case the solids have measurable vapor pressures over a considerable range of temperature, we have also studied the two solids.

Our measurements of vapor pressure are given in the accompanying table and can be expressed by the four equations

$$\text{H}^1\text{CN(l)}; \log_{10}p = 7.795 - \frac{1467}{T} \quad (1)$$

$$\text{H}^1\text{CN(s)}; \log_{10}p = 9.372 - \frac{1877}{T} \quad (2)$$

$$\text{H}^2\text{CN(l)}; \log_{10}p = 7.695 - \frac{1440}{T} - \frac{175}{T^2} \quad (3)$$

$$\text{H}^2\text{CN(s)}; \log_{10}p = 9.476 - \frac{1907}{T} \quad (4)$$

TABLE I

T, °K.	H ¹ CN Solid	p, mm.	T, °K.	H ² CN Solid	p, mm.
236.2		27.0	235.3		22.5
241.1		38.5	240.2		34.5
246.7		58.0	245.2		49.0
251.6		82.0	250.5		73.0
256.6		114.0	255.3		101.5
258.4		128.5	260.4		142.5
	Liquid		Liquid		
259.3		136.5	265.8		188.0
264.4		178.0	271.3		242.5
270.2		232.0	274.5		281.0
278.5		338.4	276.8		309.6
283.6		425.5	281.9		386.0
288.7		519.0	288.5		507.0
294.0		638.5	293.5		615.7

The measurements of Perry and Porter on liquid H¹CN [THIS JOURNAL, 48, 299 (1926)] agree within less than 1% with equation (1). For solid H¹CN the agreement between their results and ours is less satisfactory.

The determination of freezing points from measurements of vapor pressure is not accurate. Our equations give 259°K. for the freezing point of hydrocyanic acid and 261°K. for that of deutocyanic acid.

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RECEIVED MARCH 22, 1934

THE IONIZATION CONSTANT OF DEUTACETIC ACID

Sir:

We have measured the conductivity of deutacetic acid in heavy water (97% H₂O) at 25° and at the concentrations 0.0722 M and 0.1444 M, in the same small cell used by Lewis and