

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.

DEPARTMENT OF CHEMISTRY GILBERT N. LEWIS
UNIVERSITY OF CALIFORNIA W. T. HANSON, JR.
BERKELEY, CALIFORNIA

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.

DEPARTMENT OF CHEMISTRY GILBERT N. LEWIS
UNIVERSITY OF CALIFORNIA PHILIP W. SCHUTZ
BERKELEY, CALIFORNIA

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