

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 H<sub>2</sub> 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 H<sub>2</sub> at high temperatures and the low temperature form is too small to be observed.

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#### 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 H<sup>2</sup> bond as compared with the H<sup>1</sup> 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, H<sup>1</sup>CN and H<sup>2</sup>CN, 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 <sup>1</sup> CN Solid p, mm.	T, °K.	H <sup>2</sup> 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 H<sup>1</sup>CN [THIS JOURNAL, 48, 299 (1926)] agree within less than 1% with equation (1). For solid H<sup>1</sup>CN 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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#### THE IONIZATION CONSTANT OF DEUTACETIC ACID

*Sir:*

We have measured the conductivity of deutacetic acid in heavy water (97% H<sub>2</sub>O) at 25° and at the concentrations 0.0722 M and 0.1444 M, in the same small cell used by Lewis and

Doody [THIS JOURNAL, 55, 3504 (1933)]. The specific conductivities were respectively 1.83 and  $2.59 \times 10^{-4}$ , both giving for the ionization constant the value  $0.59 \times 10^{-5}$ . Unfortunately the heavy water used had a specific conductivity of  $2.3 \times 10^{-3}$  and in ignorance of the nature of its impurity it is difficult to apply the proper correction. If the whole conductivity of the water is subtracted from the conductivity of the acid the dissociation constant will be lowered by 20%. In any case we have the striking result that the ionization constant is less than one-third as great as that of acetic acid in common water,  $1.84 \times 10^{-5}$ . We hope to repeat this experiment with a purer solvent and also with a stronger acid

(monochloroacetic) in order to obtain more accurate ionization constants.

This enormous shift of equilibrium in going from a hydro- to a deuto-compound shows again how much more tenaciously a deuteron is held by a pair of electrons of another atom than is a proton. For although the ionization of an organic acid undoubtedly involves the addition of solvent molecules to the un-ionized acid and to the ions, still the main phenomenon is the separation of  $H^{1+}$  or  $H^{2+}$  from a pair of electrons of a carboxyl oxygen.

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## NEW BOOKS

**Goethe als Chemiker und Techniker.** (Goethe as Chemist and Technologist.) By PAUL WALDEN. Verlag Chemie, G. m. b. H., Corneliusstrasse 3, Berlin W 10, Germany, 1932. 87 pp.  $12 \times 15.5$  cm. Price, Mk. 2.

In the flood of books about Goethe which were published in 1932, occasioned by the centenary of his death, it is not surprising that there should have been one dealing with Goethe's relationship to chemistry—particularly when one recalls how many-sided was Goethe's genius.

The extent of Goethe's interests and activities in chemistry will, however, I think surprise most readers of this small volume. Joh. Philipp Fresenius, grandfather of Carl Remigius Fresenius, one of the great names in the history of our science, was Goethe's godfather; as an impressionable young man, Goethe's life was saved by the ministrations of an alchemical physician; the chemists Buchholz in Weimar, Götting, Wackenroder and particularly Döbereiner in Jena, and later the great Berzelius, were Goethe's intimate friends.

At Ilmenau we find Goethe busied with the development of the reverberatory furnace for the better smelting of lead, with the reopening of the coal mines and with the various textile industries practised in that vicinity. In 1799, with Götting, Goethe studied the extraction of sugar, and ten years later, with Döbereiner, the production of sugar and alcohol from beets.

In 1783-1784 we find Goethe deeply engrossed with the invention and perfection of the air balloon, only to be narrowly anticipated by Charles and Montgolfier in Paris.

Throughout his life, Goethe's notebooks are replete with descriptions and sketches of innumerable chemical and manufacturing establishments which he visited and inspected; the smelters at Rammelsberg, Clausthal, Andreasberg, etc., the porcelain and munition plants at Potsdam, the optical works at Stuttgart, the knife factory at Bad Pyrmont, the sulfur springs at Berka, the tanneries

at Ingelheim, the jewelry and textile factories at Hanau and a host of others.

These and many other interesting facts and observations showing the important role that chemistry played in Goethe's life are skilfully told in this small brochure, which is a reprint of a lecture delivered by Professor Paul Walden before the Verein Deutscher Chemiker in Berlin in connection with the Goethe Memorial Celebration in that city on March the 14th, 1932.

Chemistry is scorned by some humanists as the preoccupation of lesser minds; here we find it a life-long interest and a continual inspiration to perhaps the greatest poet, writer and philosopher of modern times.

ARTHUR B. LAMB

**Säure-Basen-Indicatoren, ihre Anwendung bei der colorimetrischen Bestimmung der Wasserstoffionenkonzentration.** (Acid-Base Indicators, and their Application in the Colorimetric Determination of Hydrogen-Ion Concentration.) By DR. I. M. KOLTHOFF and DR. HARRY FISCHGOLD. Fourth edition of "Der Gebrauch von Farbindicatoren." Verlag von Julius Springer, Linkstrasse 23-24, Berlin W 9, Germany, 1932. xi + 416 pp. 26 figs.  $14 \times 22$  cm. Price, RM. 18.60; bound, RM. 19.80.

This is a very complete survey of the theory and the practical use of acid-base indicators, especially valuable for its treatment of recent developments. Notable in this respect is the discussion of the use of indicators in non-aqueous solutions and in highly acid systems and of the so-called salt and alcohol errors in indicator measurements.

In an ideal educational world one would object to the devotion of more than one-quarter of a book on indicators to a perfectly general discussion of the modern theory of electrolyte solutions. This material ought to be so universally accepted a part of even an elementary chemical