CCXC.—*The Vapour Pressure of Hydrogen Selenide and of Hydrogen Telluride.*

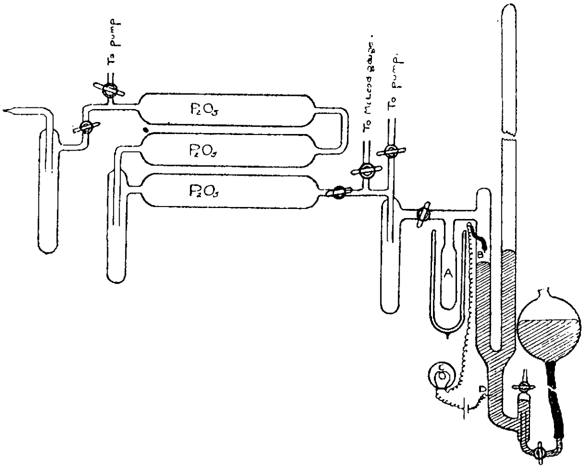
By Norman Oscar Stein.

During a recent investigation of the absorption spectra of the hydrides of the oxygen group carried out in these laboratories (Goodeve and Stein, Faraday Soc. Discussion on Photochemistry, Liverpool, April, 1931), it was found desirable to re-examine the existing data on the vapour pressure of hydrogen selenide and telluride. That of the former has been determined several times (de Forcrand and Fonzes-Diacon, *J. Chim. physique*, 1917, **15**, 576; Bruylants and Dondeyne, *Bull. Acad. roy. Belg.*, 1922, **8**, 387) but that of the latter has apparently been determined only once (Bruylants, *ibid.*, 1920, **6**, 472).

EXPERIMENTAL.

Hydrogen selenide was prepared by the action of water and dilute hydrochloric acid on aluminium selenide, formed by direct combination of the two elements. Hydrogen telluride was prepared in a similar manner. The evolved gases were dried over phosphoric oxide, and condensed in a trap cooled with liquid air. This trap was then sealed to the vapour-pressure apparatus (see Fig. 1). The apparatus was now evacuated, and the hydrides were distilled several times through phosphoric oxide to effect their thorough drying. They were finally condensed in the liquid-air cooled trap A, which was of small volume and was connected by means of a wide-bore tube to a mercury manometer.

FIG. 1.

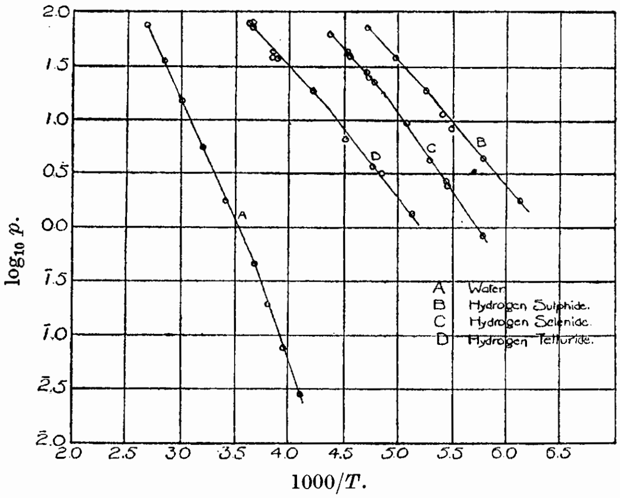


The hydrides were kept at the desired temperature by a jacket of carbon dioxide–alcohol, liquid ammonia, ice–salt mixture, or carbon dioxide–acetone cooled by the addition of liquid air. The temperatures were read on an N.P.L. standard pentane thermometer placed in the cooling agent. The pressures were measured with the aid of a cathetometer reading to 0·01 cm.

The zero level of the mercury was adjusted with the aid of a fine platinum wire B sealed in to a mercury cup which was externally connected to a small 2-volt electric bulb C, the circuit being completed by a platinum wire D, sealed in below the **U** of the manometer. It was thus possible to get accurate zero readings on the low side of the manometer, despite the corrosion of the manometric mercury by the decomposition of hydrogen telluride. Dry hydrogen selenide does not corrode mercury.

For each vapour-pressure reading, successive quantities of the gas were fractionated away until there was no further change in the pressure. The apparatus, with the exception of the manometer, was painted black for the measurements on hydrogen telluride, which, moreover, were made in a darkened room to minimise the photochemical decomposition of the hydrides.

FIG. 2.



The Vapour-pressure Curves.—The values found for the vapour pressures of hydrogen selenide and hydrogen telluride are recorded in Table I. Straight lines are obtained when the logarithms of the vapour pressures (in cm.) are plotted against the reciprocals of the absolute temperatures (see Fig. 2). The corresponding equations are :

$$\begin{aligned} &H_2Se \text{ (liquid) } \log_{10} p = -1030/T + 6{\cdot}27 \\ &\text{,, (solid) } \log_{10} p = -1380/T + 7{\cdot}96 \\ &H_2Te \text{ (liquid) } \log_{10} p = -1005/T + 5{\cdot}53 \\ &\text{,, (solid) } \log_{10} p = -1220/T + 6{\cdot}39 \end{aligned}$$

For comparison, the data of Maass and McIntosh (*Trans. Roy. Soc. Canada*, 1914, **8**, 65) for hydrogen sulphide, and standard data for water, have also been plotted in the same manner.

The curve obtained by plotting the values given by Bruylants and Dondeyne (*loc. cit.*) for hydrogen selenide coincided with that shown in Fig. 2. These investigators, however, did not pursue measurements far below the m. p.

The curves obtained for hydrogen telluride differed somewhat from those plotted from Bruylants's values : whereas the vapour pressures of the liquid phase agreed quite closely, those for the solid phase were slightly higher than those obtained by this investigator. Considerable difficulty was encountered in getting the true vapour pressure of solid hydrogen telluride. The hydrogen resulting from its decomposition is either strongly adsorbed on, or dissolved in, it at low temperatures, since it was always possible, by placing a liquid-air jacket round the tube A (Fig. 1) to bring the levels of the mercury in both arms of the manometer to zero pressure. The measurements must be made rapidly enough to prevent the decomposition from affecting the result, and sufficient time must be allowed to obtain equilibrium. It was necessary to allow at least ½ hour for each pressure measurement : Bruylants allowed considerably less.

TABLE I.

Vapour pressures of hydrogen selenide and telluride.

Hydrogen selenide.				Hydrogen telluride.			
T, Abs.	p (cm.).	T, Abs.	p (cm.).	T, Abs.	p (cm.).	T, Abs.	p (cm.).
173·0°	0·82	212·0°	25·12	195·0°	1·37	257·0°	35·00
183·5	2·45	213·0	27·55	206·5	3·27	260·0	37·92
183·6	2·47	219·5	39·82	209·5	3·67	258·0	43·66
187·5	3·25	220·5	41·92	221·0	6·67	273·0	80·20
197·0	9·45	228·8	63·04	238·0	17·02	273·0	85·90
210·0	23·23			238·0	18·20	273·0	83·20

TABLE II.

			Molecular heats (Cals.) of			
	M. p.	B. p.	vaporisation.	sublimation.	fusion.	Trouton's constant.
H_2O	0·0°	100°	9·67	11·12	1·45	25·9
H_2S	− 83	− 60	4·66	5·33	0·67	21·8
H_2Se	− 66	− 41·5	4·71	6·28	1·57	20·4
H_2Te	− 46	2 ± 2	4·58	5·55	0·97	16·7

The Physical Properties of the Hydrides.—Table II shows some of the physical properties of the hydrides of the oxygen group. The m. p.'s and b. p.'s were obtained from the literature (Bruylants, *loc. cit.*; Paneth and Rabinowitsch, *Ber.*, 1925, **58**, 1138; Dennis and Anderson, *J. Amer. Chem. Soc.*, 1914, **36**, 882). The molecular heats were calculated from the vapour-pressure curves.

It is of interest to compare the slope and position of the curves for water with those for the other hydrides. The values of Trouton's constant indicate no association in the case of these other three hydrides.

In conclusion, the author wishes to thank Mr. C. F. Goodeve for suggesting the research on the hydrides of the oxygen group, and for his kindly criticism and advice.

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