10. *Determination and Calculation of the Equilibrium Constants for Isotopic Hydrogen Exchange in the Systems* n-*Amyl Alcohol–Water and Ethylthiol–Water. Vapour Pressures and Raman Spectra of* n-*Amyl Deuteralcohol and Ethyldeuterothiol.*

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Determination of the equilibrium constants for protium–deuterium exchange in the gaseous systems

$$n\text{-}C_5H_{11}\cdot OH + HOD \rightleftharpoons n\text{-}C_5H_{11}\cdot OD + HOH \text{ and}$$
$$C_2H_5\cdot SH + HOD \rightleftharpoons C_2H_5\cdot SD + HOH$$

has been made. The values obtained agree well with those calculated from a knowledge of certain energy data of the molecules concerned.

In the course of the work the compounds n-$C_5H_{11}\cdot OD$ and $C_2H_5\cdot SD$ have been prepared in a pure form, and their vapour pressures determined as differences from those of n-$C_5H_{11}\cdot OH$ and $C_2H_5\cdot SH$ respectively. Raman spectra of $CH_3\cdot OH$, $CH_3\cdot OD$, $C_2H_5\cdot SH$, and $C_2H_5\cdot SD$ have been investigated.

Distribution coefficients for protium–deuterium exchange usually differ from unity, because of the different binding energies of these two isotopes. For exchanges between simple molecules, as between hydrogen and the hydrogen halides (Wirtz, *Physikal. Z.*, 1936, **37**, 165; *Z. physikal. Chem.*, 1936, B, **31**, 309), or water and hydrogen sulphide (Small, *Trans. Faraday Soc.*, 1937, **33**, 820), for which spectroscopic data give a fairly complete account of the energy states, the distribution coefficients can be calculated satisfactorily from energy data.

The present work deals with polyatomic molecules containing characteristic atomic groups. We study the exchange reaction between n-amyl alcohol and water,

$$C_5H_{11}\cdot OH + HOD \rightleftharpoons C_5H_{11}\cdot OD + HOH$$

and between ethylthiol and water,

$$C_2H_5{\cdot}SH + HOD \rightleftharpoons C_2H_5{\cdot}SD + HOH$$

using dilute (*ca.* 2%) deuterium water in each case. These particular examples of an alcohol and of a thiol were chosen because, after the establishment of equilibrium, they could be separated from the water without danger of disturbance to the equilibrium isotope distribution (cf. Halford, Anderson, Bates, and Swisher, *J. Amer. Chem. Soc.*, 1935, **57**, 1663; Orr, *Trans. Faraday Soc.*, 1936, **23**, 1033).

The reactants were shaken together at 25·0° until equilibrium was established, and each product was afterwards analysed for deuterium. It was then possible to calculate the equilibrium ratio for the liquid substances, $K_l = [RD]\,[HOH]/[RH]\,[HOD]$,* where RH is either amyl alcohol or ethylthiol. To convert K_l into an equilibrium constant for the gas phase (K_g), it is necessary to evaluate the vapour pressures (at 25°) in the equation $K_g = K_l(p_{RD}{\cdot}p_{HOH}/p_{RH}{\cdot}p_{HOD})$.

Riesenfeld and Chang (*Z. physikal. Chem.*, 1936, *B*, **33**, 120; cf. also Topley and Eyring, *J. Chem. Physics*, 1934, **2**, 217) quote vapour-pressure data for the isotopic water molecules, from which $p_{HOH}/p_{HOD} = 1{\cdot}074$ at 25°.

Although the vapour pressures of *n*-amyl alcohol and ethylthiol are known over a considerable temperature range, similar data are not available for the deuterated molecules, $C_5H_{11}{\cdot}OD$ and $C_2H_5{\cdot}SD$. The latter were therefore prepared in a pure form, and their vapour pressures were determined as differences from those of the respective hydrogen analogues by using differential tensimeters. In each case the heavier molecule had the lower vapour pressure, the ratios at 25·0° being 0·855 for *n*-amyl alcohol and 0·911 for ethylthiol.

TABLE I.

Distribution of Deuterium Between Water and Various Substances.

Exchanging group.	Compound.	*a.*		Exchanging group.	Compound.	*a.*
		Liquid.	Gas.			Liquid.
OH	Ethyl alcohol [1]	1·11	—	NH	Hexamminocobaltic nitrate [8]	*ca.* 0·85
	n-Amyl alcohol [2]	1·09	1·00		Pyrrole [3, 12]	0·88
	Benzyl alcohol [3]	1·10	—		Phenacetin [6]	0·89
	Phenol [3, 4]	1·08	—	CH	Acetone [9]	*ca.* 0·78
	Quinol [5]	1·13	—		Nitromethane [10]	0·78
	Benzoic acid [3, 6]	1·04	—		Acetylene [11]	0·90
SH	Hydrogen sulphide [7]	0·44	0·47		Pyrrole [12]	0·7
	Ethylthiol [2]	0·43	0·42			

[1] Orr, *loc. cit.* [2] This paper. [3] Harada and Titani, *Bull. Chem. Soc. Japan*, 1935, **10**, 554; 1936, **11**, 465. [4] Ingold, Raisin, and Wilson, J., 1936, 1637. [5] Brodskiĭ, *J. Physical Chem., U.S.S.R.*, 1937, **9**, 755. [6] Erlenmeyer, Epprecht, Lobeck, and Gärtner, *Helv. Chim. Acta*, 1936, **19**, 354. [7] Small, *loc. cit.*; the figure is calculated from that obtained at 15°, assuming the temperature coefficient calculated theoretically by this author. [8] Erlenmeyer and Gärtner, *Helv. Chim. Acta*, 1934, **17**, 1009. [9] Klar, *Z. physikal. Chem.*, 1934, *B*, **26**, 335; Halford, Anderson, Bates, and Swisher, *loc. cit.* [10] Reitz, *Z. physikal. Chem.*, 1936, *A*, **176**, 363; *Z. Elektrochem.*, 1936, **42**, 582. [11] Reyerson and Gillespie, *J. Amer. Chem. Soc.*, 1935, **57**, 2250; 1936, **58**, 282. [12] Koizumi and Titani, *Bull. Chem. Soc. Japan*, 1937, **12**, 107.

Using these vapour pressure ratios, we find for amyl alcohol and water $K_g = 0{\cdot}50$, and for ethylthiol and water $K_g = 0{\cdot}21$.

The isotopic distribution coefficients at *ca.* 25°, α, where

$$\alpha = (D/H)_{\mathbf{substance}}/(D/H)_{\mathbf{water}}$$

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* In the derivation of [HOD] from the deuterium content of the water, allowance was made for the small amount of D_2O present. For this purpose the constant $[HOD]^2/[D_2O][H_2O]$ was assumed to have a value of 3·0 at 25° (cf. Topley and Eyring, *loc. cit.*; Jones and Sherman, *J. Chem. Physics*, 1937, **5**, 378).

which are to a close approximation double the equilibrium constants,* are given in Table I along with other data collected from the literature. The selection is intended for comparison with calculated values given later.

Owing to the absence of vapour-pressure data, figures for the gas phase are available in only three cases. Furthermore, in some examples uncertainty attaches to the temperature of experiment, although this is not far removed from 25°. Nevertheless, the approximate constancy of the distribution coefficient for any one characteristic group affords considerable support to the view that the distribution of deuterium is essentially a property of the bonds directly concerned in the exchange.

Calculation of Equilibrium Constants.—Statistical-mechanical theory expresses our equilibrium constants by an equation of the type

$$K = f_{RD} \cdot f_{HOH} / f_{RH} \cdot f_{HOD}$$

where the f's denote the partition functions of the molecules. On the assumption that the partition function for a molecule can be represented as the product of translational, rotational, and vibrational parts, it can be shown that

$$f_{RD}/f_{RH} = (m_{RD}/m_{RH})^{3/2}(\sigma_{RH}/\sigma_{RD})[(ABC)^{1/2}_{RD}/(ABC)^{1/2}_{RH}]e^{(E^0_{RD}-E^0_{RH})/RT}$$

(cf. Jones and Sherman, *loc. cit.*; Urey and Grief, *J. Amer. Chem. Soc.*, 1935, **57**, 321), where m denotes the mass, A, B, and C the three principal moments of inertia, σ the symmetry number, and E^0 the total zero-point energy of the molecule. The symmetry number (σ) is equal to the number of orientations of the molecule which are physically indistinguishable; for instance, $\sigma_{RH} = \sigma_{RD} = \sigma_{HOD} = 1$, $\sigma_{HOH} = 2$. The equation is approximate in that it assumes that the rotational energy is classical and that the vibrational is unexcited.

Molecular zero-point energy (E^0) can be estimated if all the fundamental vibration frequencies of the molecule are known. Unfortunately, for the majority of polyatomic molecules, tables of frequencies are usually incomplete, and hence the energy cannot be accurately calculated. However, for isotopic species the energy difference which has to be substituted in the above equation will depend mainly on those frequencies which are appreciably modified by isotopic substitution. On account of the small mass of a hydrogen atom, the vibrations of the latter are not strongly coupled with those of the rest of the molecule, so the change in zero-point energy can be reckoned approximately as the change in that part of the total molecular zero-point energy which depends on the vibrations of the protium and deuterium atoms. Bending as well as stretching vibrations should be taken into account, although the latter, because of their higher frequency, will make the greater contribution to the zero-point energy. However, we shall at first neglect bending because considerable doubt attaches to the magnitude of the corresponding frequencies in most of the organic molecules under consideration.

Table II gives the constants calculated on the basis of the foregoing approximations, *i.e.*, on the assumption that the only contribution to zero-point energy comes from the hydrogen stretching motion. In addition, the small changes of mass and moment of

TABLE II.

Approximate Calculation of Equilibrium Constants for Exchanges with Water.

Bond.	ν_H (cm.$^{-1}$).	ν_D (cm.$^{-1}$).	ΔE^0 for the reaction (cals.).	$2K$ (25°).
OH	3640 [1]	2650 [2]	−79·6	1·14
SH	2566 [3]	1863 [3]	329	0·57
NH	3320 [4]	2425 [2]	55·5	0·91
CH	2938 [5]	2111 [5]	152	0·77

[1] From infra-red data (see text). [2] Calculated from ν_H. [3] Data for ethylthiol (this paper). [4] Mean of figures for amines given by Kohlrausch ("Der Smekal-Raman-Effekt"). [5] Data for acetic acid (Angus, Leckie, and Wilson, *Proc. Roy. Soc.*, 1936, *A*, **155**, 188).

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* This is because water contains two replaceable hydrogen atoms whereas the organic molecules possess only one. A consideration of the expressions for the equilibrium constant and for the distribution coefficient shows that the 2 : 1 relationship would be strictly true only in the limit of zero deuterium concentration. In our experiments with 2% deuterium water the departure from 2 : 1 is only 0·5%.

inertia resulting from isotopic substitution have been ignored. It will be seen that, even on this basis, there is a fair measure of agreement with the experimental data of Table I.

In the compilation of the table the following considerations dictated the choice of data. For water, the zero-point energy difference term has been derived from the almost pure stretching frequency at 3654 cm.$^{-1}$ which suffers the largest modification on deuterium substitution, becoming 2720 cm.$^{-1}$ in HOD (Borst, Buswell, and Rodebush, *J. Chem. Physics*, 1938, **6**, 61). This modification corresponds with a zero-point energy difference of 1329 cals. With regard to the OH bond in alcohols, the band at 3380 cm.$^{-1}$ was considered until quite recently to represent bond stretching. This frequency has been observed only for the lower aliphatic alcohols as liquids, a fact which is confirmed by its presence in our Raman spectra of the methyl alcohols and its absence from our data for the amyl alcohols. However, it has lately become evident from certain measurements of infra-red absorption (Errera and Mollet, *Compt. rend.*, 1937, **204**, 259; Buswell, Deitz, and Rodebush, *J. Chem. Physics*, 1937, **5**, 501; Fox and Martin, *Proc. Roy. Soc.*, 1937, *A*, **162**, 419) that the band is characteristic of associated molecules. The frequency proper to single molecules is observed when dilute solutions or the vapours of alcohols are studied; it lies at 3640 cm.$^{-1}$. The other frequencies quoted in the table have been taken from the literature, except for the OD and ND bonds, for which in the absence of experimental data, the necessary quantities have been computed from the values of ν_H, unchanged force constants being assumed. In the column headed $2K$, the equilibrium constants have been doubled in order to render them comparable with the distribution coefficients in Table I.

We shall now attempt a more accurate theoretical evaluation of these distribution ratios in the two cases for which we have determined them by experiment.

Consideration of the non-exponential factor in the expression for the equilibrium constant shows that, although for large organic molecules changes of mass and moment of inertia are of no importance, yet they become important for light molecules such as water. Taking the known moments of inertia for this molecule (Mecke *et al.*, *Z. Physik*, 1933, **81**, 313, 445, 465; Herzberg, *ibid.*, 1937, **107**, 549) and allowing for translation, we find a factor 0·55.

We have further to consider the neglected contributions to the zero-point energy. For the water molecules the total molecular zero-point energy is known, since all three fundamental frequencies have been measured. The total frequency shift ($\Delta\Sigma\nu$) on passing from HOH (Plyler and Sleator, *Physical Rev.*, 1931, **37**, 1493; Mecke *et al.*, *loc. cit.*; Bender, *Physical Rev.*, 1935, **47**, 252; Borst, Buswell, and Rodebush, *loc. cit.*) to HOD (Bartholomé and Clusius, *Z. Elektrochem.*, 1934, **40**, 530; Barker and Sleator, *J. Chem. Physics*, 1935, **3**, 660; Borst *et al.*, *loc. cit.*) is computed to be 1110 $\pm$ 30 cm.$^{-1}$. The effect of anharmonicity is quite negligible (Förster, *Z. physikal. Chem.*, 1934, *B*, **27**, 1).

Three of the normal modes of vibration in alcohols and thiols should be associated particularly with the motion of the replaceable hydrogen, and we have already considered one, *viz.*, bond stretching. A second frequency should approximate to a bending motion, and should be of considerably lower frequency. It is unfortunate that no reliable data for this frequency exist for the amyl alcohols. We tried to make good this deficiency but found the spectra were too confused. We have therefore been obliged to take the data from the methyl alcohols, $CH_3{\cdot}OH$ and $CH_3{\cdot}OD$, and to assume that the important frequencies would occur unchanged in the amyl alcohols. We have therefore studied the Raman spectra of $CH_3{\cdot}OH$ and $CH_3{\cdot}OD$. The only line in these spectra which we can assign to the bending motion referred to above is at 1112 cm.$^{-1}$ in light methyl alcohol and 952 cm.$^{-1}$ in the heavy compound. The allocation is tentative, but has also been suggested by other workers (Mizushima, Morino, and Okamoto, *Bull. Chem. Soc. Japan*, 1936, **11**, 698; Halford, Anderson, and Kissin, *J. Chem. Physics*, 1937, **5**, 927). It may be, however, that the frequency is characteristic of associated molecules, and is subject to some modification in the isolated molecule.

Raman spectra of ethyl-thiol and -deuterothiol have likewise been investigated. An inspection of these spectra shows that the only frequency which might represent hydrogen bending is at 507 cm.$^{-1}$ in the deutero-compound. However, there is no corresponding line in the light thiol, but it may be obscured by the strong line at 661 cm.$^{-1}$, which is usually attributed to a vibration of the C–S bond (cf. Donzelot and Chaix, *Compt. rend.*, 1936, **202**, 851).

With one probable exception, considered below, the remaining frequencies of the molecules undergo but a minor modification on isotopic substitution. However, the sum of such shifts is quite appreciable and therefore must be taken into account. Accepting our data for the thiols, supplemented by those of Bartholomé and Sachsse (*Z. physikal. Chem.*, 1935, *B*, **30**, 40) for the methyl alcohols, we can construct the following table showing how the various contributions to the zero-point energy difference arise.

	Frequency modification ($\Delta\Sigma\nu$, cm.$^{-1}$).	
	Methyl alcohol.	Ethylthiol.
Hydrogen stretching	990	703
,, bending	160	~154
Other frequencies	55	48
Total	1205	905

The exception to which reference was made in the foregoing paragraph corresponds with the third degree of freedom of the replaceable hydrogen atom. This may constitute either a low-frequency torsional oscillation (libration) or a free, or almost free, internal rotation (cf. Bartholomé and Sachsse, *loc. cit.*). In either case the effect on the equilibrium constant will appear as a non-exponential factor of approximately $\sqrt{2}$. Even if the motion is of the nature of a restricted rotation (Teller and Weigert, *Nach. Ges. Wiss. Göttingen*, 1933, 218), it is reasonable to assume that the contribution will not vary appreciably.

Finally, the revised values of the equilibrium constants are : $0·5 \times 0·55 \times \sqrt{2} \times 1·26 = 0·49$ for amyl alcohol, and $0·5 \times 0·55 \times \sqrt{2} \times 0·61 = 0·24$ for ethylthiol. In each case the four factors represent symmetry, translation and rotation, internal rotation, and vibration, respectively. Uncertainty in the frequency values introduces a possible error of about 0·04 in the equilibrium constants; nevertheless, agreement with experiment (0·50 and 0·21) is quite satisfactory.*

EXPERIMENTAL.

Exchange with n-*Amyl Alcohol.*—Dry and purified *n*-amyl alcohol (B.D.H.) was shaken at 25·0° with water containing about 2% of deuterium. Supplementary experiments showed that equilibrium was attained within 3 hours. The two layers were then separated. The alcohol, after thorough drying over freshly ignited potassium carbonate, was burnt, and the deuterium content of the combustion water determined by density measurement (Wilson, J., 1936, 1552). The water was passed over red-hot copper oxide and purified by vacuum distillation. The density was then determined, and due allowance was made for the hydrogen introduced by the dissolved alcohol (solubility : 2·7 g./100 g. of solution) in deriving the deuterium content of the water phase at equilibrium.

Results of five experiments are given below. The last row of figures refers to an experiment carried out by starting with light water and partially heavy alcohol. The latter was prepared by shaking amyl alcohol (75 c.c.) and heavy water (20% of deuterium, 3·6 c.c.) for 3 hours. The alcohol was dried with potassium carbonate and distilled.

Exchange of Deuterium between n-*Amyl alcohol and Water at* 25°.

Reactants (g.-mols.).		Time of shaking (hrs.).	D(atom %) in combustion water from		$K_1 = \frac{[\mathrm{AmOD}]\,[\mathrm{HOH}]}{[\mathrm{AmOH}]\,[\mathrm{HOD}]}$.
Water.	Alcohol.		water layer.†	alcohol.	
1·667	0·28	4	1·833	0·1710	0·564
1·667	0·28	24	1·844	0·1652	0·540
1·667	0·28	24	1·845	0·1640	0·537
1·030	0·64	3	1·498	0·1360	0·540
0·545	0·22	6	1·440	0·1318	0·553
					Mean 0·547

† After allowing for the dissolved alcohol.

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* (Note added in proof.) Since the above was written an excellent paper dealing with the exchange between methyl alcohol and water has appeared (Halford and Pecherer, *J. Chem. Physics*, 1938, **6**, 571). Accurate frequency data based on infra-red absorption measurements are quoted (cf. Borden and Barker, *ibid.*, p. 553; Barker and Bosschieter, *bid.*, p. 563) and it is suggested that the third degree of freedom within the hydroxyl group is represented by a low-frequency torsional vibration.

n-*Amyl Deuteralcohol*, $C_5H_{11}{\cdot}OD$.—Complete replacement of the light hydrogen in amyl alcohol was carried out by successive equilibration with pure deuterium oxide. After being shaken, the reactants were cooled to − 10° in order to decrease the mutual solubilities to a minimum and also to freeze the aqueous layer. It was then possible to transfer the upper, alcoholic layer without contact with the atmosphere into a second bulb containing fresh deuterium oxide. Treatment with four successive portions (each 3 equivs. of replaceable hydrogen) of water containing 99·6% of deuterium was followed by two equilibrations with water containing 99·95% of deuterium. Finally, the alcohol was dried over strongly ignited potassium carbonate followed by aluminium amalgam.

The optimum drying procedure was chosen as a result of trial experiments in which the water content of test samples of light alcohol was followed by density measurement (for information on the desiccation process see Brunel, Crenshaw, and Tobin, *J. Amer. Chem. Soc.*, 1921, **43**, 561). *n*-Amyl deuteralcohol was distilled in a vacuum and analysed for deuterium (Found: $C_5H_{11}{\cdot}OD$, 99·9%).

Comparison of the Vapour Pressures of the n-*Amyl Alcohols*.—Determination of the difference in vapour pressure between the light and the heavy form of *n*-amyl alcohol was made by using a simple U-tube differential tensimeter containing mercury as indicating liquid (cf. Wilson, J., 1935, 494). From the results, given below, it may be deduced that $p_{\text{AmOD}}/p_{\text{AmOH}} = 0{\cdot}855$ at 25°.

t	25°	30°	40°	60°	80°	100°	110°	120°	130°	140°
$p_{\text{AmOH}} - p_{\text{AmOD}}$ (mm. Hg)	0·6	0·7	1·5	4·1	8·0	13·6	18·1	22·2	32·7	38·2
p_{AmOH}* (mm. Hg)	4·13	5·5	10·6	34·1	95·1	233·1	350·3	512·3	730·8	—

* International Critical Tables, Vol. III, p. 220.

Methyl Deuteralcohol (cf. Redlich and Pordes, *Sitzungsber. Akad. Wiss. Wien*, 1936, **145**, 67; Bartholomé and Sachsse, *loc. cit.*).—Magnesium was dissolved in absolute methyl alcohol, and the magnesium methoxide produced was dried in a vacuum at 100°. Less than 1 equiv. of deuterium oxide (99·95% of deuterium) was then added, and after the mixture had been kept and shaken for some time the methyl deuteralcohol was removed by warming to 60° in a vacuum. Analysis showed that the material contained 99·2% of CH_3OD.

Raman Spectra of the Methyl Alcohols.—A Hilger E 3 spectrograph was employed having a dispersion of about 20 A. per mm. The frequencies observed are listed below; the figures in parentheses are relative intensities.

$CH_3{\cdot}OH$: 3376(2b), 3128(1), 2948(9), 2833(9), 1850(5), 1458(3), 1112(1), 1031(5).
$CH_3{\cdot}OD$: 2946(9), 2837(9), 2568(2b), 2216(2), 1853(4), 1452(4), 1032(5), 952(1) (cf. Wagner, *Z. physikal. Chem.*, 1938, B, **40**, 50; Redlich and Pordes, *loc. cit.*; Mizushima, Morino, and Okamoto, *loc. cit.*; Halford, Anderson, and Kissin, *loc. cit.*).

Exchange with Ethylthiol.—The procedure was similar to that employed for amyl alcohol. Equilibrium was attained within ten hours. The thiol layer was dried with potassium carbonate and for the combustion the first foot of the copper oxide filling in the hot tube was replaced by granular lead chromate wrapped in copper gauze. Ethylthiol has a solubility in water at 25° of 1·3 g./100 g. of solution.

The results are given in the table below: the last experiment was carried out with light water and partly deuterated thiol.

Exchange of Deuterium between Ethylthiol and Water at 25°.

Reactants (g.-mols.).		Time of shaking (hrs.).	D(atom %) in combustion water from		$K_1 = \dfrac{[\text{EtSD}][\text{HOH}]}{[\text{EtSH}][\text{HOD}]}$.
Water.	Thiol.		water layer.*	thiol.	
1·41	0·48	72	1·715	0·1236	0·215
1·98	0·48	18	1·790	0·1291	0·215
1·73	0·28	24	0·836	0·0596	0·214
					Mean 0·215

* After allowance for the dissolved thiol.

Ethyldeuterothiol, $C_2H_5{\cdot}SD$.—Sodium (3 g.) and dry ethylthiol (20 c.c.) gave the sodium derivative, which was treated with excess deuterium oxide and dry carbon dioxide. Ethyldeuterothiol was caught in a trap immersed in carbon dioxide–acetone, dried over potassium carbonate, and distilled in a vacuum. Analysis showed that the material contained 93·0% of $C_2H_5{\cdot}SD$, the rest being $C_2H_5{\cdot}SH$. However, for the purpose in hand the thiol was sufficiently pure.

Comparison of the Vapour Pressures of the Ethylthiols.—The measurements were carried out with the 93% material (above). The technique has already been described.

t	0°	10°	20°	25°	30°	40°
$p_{\text{EtSH}} - p_{\text{EtSD}}$ (mm. Hg)	22·5	30·2	39·2	43·8	49·2	61·0
p_{EtSH}* (mm. Hg)	—	—	—	540	—	—

* Interpolated from data given by Berthoud and Brum, *J. Chim. physique*, 1924, **21**, 143.

A linear relation being assumed between the vapour-pressure difference and deuterium content, it follows that at 25° for isotopically pure compounds, $p_{\text{EtSD}}/p_{\text{EtSH}} = 0{\cdot}911$.

Raman Spectra of the Ethylthiols.—The Raman measurements were made as before. The results were :

$C_2H_5{\cdot}SH$: 2965(4), 2931(9), 2872(3), [2751(3)], 2566(9), 1444(6), 1272(3), 1063(2), 982(2), 661(8).
$C_2H_5{\cdot}SD$: (93% pure) : 2971(5), 2928(10), 2861(5), 2573(3), 1863(8), 1441(6), 1248(5), 1057(2), 968(2), 668(6), 507(2).

The frequency at 2573 cm.$^{-1}$ in the deutero-compound is due to the thiol present. The results for the latter agree with those of Venkateswaran (*Indian J. Physics*, 1930, **5**, 219).

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