1403 (1956).
111. T. G. Andronikashvili, Soobshch. Akad. Nauk Gruz. SSR, 19, 273 (1957).
112. V. A. Sokolov and T. G. Andronikashvili, Trudy. Inst. Nefti Akad. Nauk SSSR, No. 10, 101 (1957).
113. V. A. Sokolov, "Metody Analiza Gazov" (Methods for the Analysis of Gases), Gostoptekhizdat, 1958.
114. A. T. James and A. J. P. Martin, J. Appl. Chem., 6, 105 (1956).
115. A. Zlatkis, Analyt. Chem., 30, 332 (1958).
116. S. Dal Nogare and L. W. Safranski, Analyt. Chem., 30, 894 (1958).
117. S. Dal Nogare and J. C. Harden, Analyt. Chem., 31, 1829 (1959).
118. J. L. Ogilvie, M. C. Simmonds, and G. P. Hinds Jnr., Analyt. Chem., 30, 25 (1958).
119. J. A. Rodgway and W. Schoen, Ind. Eng. Chem., 51, 1023 (1959).
120. D. H. Lichtenfels, S. A. Fleck, and F. H. Burow, Analyt. Chem., 27, 1510 (1955).
121. W. L. Podbielniak and S. T. Petrol, Ref., No. 35, 215 (1956).
122. D. A. Vakhirev and L. E. Reshetnikova, Trudy po Khim. i Khim. Tekhnol., Gor'kii, No. 2, 339 (1958).
123. A. N. Korol', Zavod. Lab., 26, 151 (1960).
124. W. D. Betts, F. Popper, and R. I. Silsby, J. Appl. Chem., 7, 497 (1957).
125. W. J. Hendricks, R. M. Soemantri, and H. I. Waterman, J. Inst. Petroleum, 43, 228 (1957).
126. J. Janák and M. Hřivnač, J. Chromatog., 3, 297 (1960).
127. R. A. Baxter and R. T. Keen, Analyt. Chem., 31, 475 (1959).
128. A. Reuter, K. O. Gohne, and J. Lieb, Z. analyt. Chem., 164, 335 (1958).
129. G. H. Beaven, A. T. James, and E. A. Johnson, Nature, 179, 490 (1957).
130. A. Zlatkis, L. O'Brien, and P. R. Scholly, Nature, 180, 1794 (1958).
131. D. H. Desty, A. Goldup, and W. T. Swanton, Nature, 183, 107 (1959).
132. M. A. Hughes, D. White, and A. L. Roberts, Nature, 184, 1796 (1959).
133. S. H. Langer, C. Zahn, and G. Pantazoplos, Chem. and Ind., 1145 (1958).
134. J. Franc and J. Jokl, Coll. Czech. Chem. Comm., 24, 144 (1959).
135. A. Zlatkis, Su-Yu Ling, H. R. Kaufman, Analyt. Chem., 31, 945 (1959).
136. L. Blom and L. Edelhausen, Analyt Chim. Acta, 15, 559 (1956).
137. E. A. Johnson, J. Chem. Soc., 4155 (1957).
138. R. M. Soemantri and H. I. Waterman, J. Inst. Petroleum, 43, 94 (1957).
139. B. Smith, Acta Chem. Scand., 13, 877 (1959).
140. F. A. Fabrizio, R. W. King, C. C. Cerato, and J. W. Loveland, Analyt. Chem., 31, 2060 (1959).
141. B. Smith and R. Ohlson, Acta Chem. Scand., 13, 1253 (1959).
142. L. J. Sullivan, J. R. Lotz, and C. B. Willingham, Analyt. Chem., 28, 495 (1956).
143. E. Gil-Av, J. Herling, and J. Shabtai, J. Chromatog., 1, 508 (1958).
144. J. Shabtai, J. Herling, and E. Gil-Av., J. Chromatog., 2, 406 (1959).
145. E. Gil-Av, J. Herling, and J. Shabtai, Chem. and Ind., 1483 (1957).
146. E. A. Dahmen and J. D. van der Laarse, Z. analyt. Chem., 164, 37 (1958).
147. R. L. Clements, Science, 128, 899 (1958).
148. R. A. Berhard, J. Assoc. Offic. Agric. Chemists, No. 40, 915 (1957).
149. W. J. Zubyk and A. Z. Conner, Analyt. Chem., 32, 912 (1960).
150. V. Lukeš, R. Komers, and V. Herout, J. Chromatog., 3, 303 (1960).
151. M. J. E. Golay, "Gas Chromatography 1958" (Edited by D. H. Desty), Butterworths, London, 1958, p. 36.
152. W. A. Wiseman, Nature, 185, 841 (1960).
153. A. Zlatkis and J. E. Lovelock, Analyt. Chem., 31, 620 (1959).
154. D. H. Desty, A. Goldup, and B. H. F. Whyman, J. Inst. Petroleum, 45, 287 (1959).
155. R. D. Condon, Analyt. Chem., 31, 1717 (1959).
156. F. T. Eggertsen, S. Groennings, and J. J. Holst, Analyt. Chem., 32, 904 (1960).
157. "Otchet Laboratorii No. 15 Novokuibyshevskogo Filiala NIISS po Teme 100/56 za 1961" (Laboratory Report No. 15, Novokuibyshev Section, Scientific Research Institute for Synthetic Alcohols and Organic Products, on Theme 100/56, 1961).

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ISOTOPE EFFECT IN VAPOUR PRESSURE

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A. EXPERIMENTAL DATA

The vapour pressure of isotopic substances has attracted much attention from investigators mainly in connection with the use of fractional distillation as a method for separating isotopes. Keesom and van Dijk[1,2] were the first to achieve by this means a partial separation of the isotopes of neon. A year later Urey *et al.*[3] distilled hydrogen and increased its deuterium content by a factor of 25; this led to their discovery of deuterium. The same method was used[4] to prepare 50% deuterium (enrichment by a factor of 3200). The industrial production of deuterium by the low-temperature fractionation of hydrogen has now been achieved in the USSR[5] and in Western Germany[6] with the aim of preparing heavy water, for which purpose the fractionation of water itself is employed in the USA[7]. Highly efficient columns have been designed for this process, and it has been shown that, economically, it is especially suitable for the final concentration of the heavy water, starting from about 1% solutions[8].

Twenty years ago Brodskii *et al.*[9] and Huffman and Urey[10] were able to increase the content of heavy oxygen in water severalfold by fractionation. Recently Zhavoronkov and his coworkers have described the preparation by this means of water having $H_2{}^{18}O$ contents of 24.5%[11,12] and 60%,[13] while Dostrovsky and Raviv[14] have given an account of a column producing 99.8% $H_2{}^{18}O$ (490-fold enrichment).

Atmospheric helium contains only $(1.2-1.3)\times 10^{-4}$ at.% of ^3He, but Esel'son and Lazarev[15] fractionated ordinary helium until it contained 1.5% of the light isotope, and only three years later 99% ^3He was obtained in this way[16]. The same method has been used to separate the isotopes of argon[17].

Recently Tikhomirov and Tunitskii[18] have reported the enrichment of carbon monoxide by fractionation to a content of 37 at.% ^{13}C and 4.5% ^{18}O, while London[19] has described a column in which it is possible to obtain small quantities of CO containing 60–70 at.% of ^{13}C (~60-fold enrichment) and 5–6% of ^{18}O (~27-fold enrichment).

Zhavoronkov and his colleagues were the first to achieve a high concentration of the light isotope of boron, up to 57 at.% by the fractionation of BCl_3[12,20] and up to 86–96 at.% of ^{10}B by fractionating BF_3.[21]

Clusius and Schleich[22] have recently enriched nitric oxide with the ^{15}N isotope severalfold and have shown the advisability of the industrial production of heavy nitrogen by this method.

At the present time, research is being vigorously pursued in various countries to extend the use of fractionation for separating isotopes, and columns are being constructed for the industrial development of processes which have already been studied[14,21]. In the USSR investigations on these lines were started by Brodskii[9,23-25], and are being carried on by Zhavoronkov, Malkov, Tunitskii, and other scientists.

In order to settle the question of the usefulness of fractionation and to design columns, data are required on the relative volatility factor α, which is approximately equal to the ratio of the vapour pressures of the pure components at the given temperature, provided that the departure of the system from an ideal solution can be neglected. Because of this, and also in view of the theoretical interest attaching to the effect of isotopes on physicochemical properties, data have been obtained during the course of thirty years' investigation on the effect of isotopic composition on the vapour pressures of sixty substances of various chemical types.

When it was possible to work with concentrated isotopic compounds, the difference in their vapour pressures was measured directly, by means of differential manometers. When the content of one isotope was small, the mixtures were regarded as ideal and the ratio of the vapour pressures of the components was taken as α, which was determined directly from the composition of the equilibrium phases, by the Raleigh distillation method, or, in the last resort, from operating data for fractionating columns. These methods have been described in detail[25-27].

In the present review the vapour pressure of isotopic compounds is usually expressed in the form of empirical $\log P = f(T)$ equations, where P is the pressure in mm Hg. Values are also given for the ratio P_h/P_l, where the subscripts denote the heavy and the light forms of the molecules†. In the cases of helium and hydrogen, with which the isotopic effect is exceptionally large, numerical values of the vapour pressures are also given.

† The inverse ratio is often quoted in the literature. This originated in the fact that, with several substances which are liquid at comparatively low temperatures and which were investigated earlier than the others, $P_h < P_l$, while the ratio of these quantities was chosen to be such that it would exceed unity. However, the relationship $P_h > P_l$ is more general, as is shown in the account below, and for polyatomic isotopic compounds several workers[12] employ the quantity P_h/P_l. In order to compare the isotope effect in the vapour pressure of different classes of substances, this effect is always expressed in the same way in the present paper – by means of the ratio P_h/P_l. It is also preferable because with the vast majority of substances described – isotopic compounds of H, O, C, and N – the light variety is the usual form, and in expressing a new quantity in terms of one which is already known it is more logical to take the latter as unity.

1. VAPOUR PRESSURE OF MONATOMIC ISOTOPIC SUBSTANCES

The isotope effect proved particularly large in the vapour pressure of helium. For example, a 0.16% enrichment of ordinary helium with its light isotope at 1.5 °K produces an increase in vapour pressure of 6%.[28] The vapour pressure of pure ^{3}He formed by the decay of tritium has been studied[29-34]. The light helium isotope used by Abraham *et al.*[30] contained only 0.03% of ^{4}He. These results are evidently most accurate, and the corresponding data[35] for ^{4}He are given in Table 1, where the temperature has been measured on the 1955 T_E scale[35,36]. The exact variation of the vapour pressure of ^{3}He with temperature over the range 1.0°–3.3 °K is represented by the equation[30]:

$$\log P_{mm} = -\frac{0.97796}{T} + 2.5 \log T + 0.000302 T^3 + 1.91594, \qquad (1)$$

where T is measured on the 1948 scale[37] with Kistemacker's corrections[38].

The isotope effect decreases sharply with rise in temperature: at 1 °K the vapour pressure of ^{3}He exceeds the vapour pressure of ^{4}He by a factor of 72, but at 3.3 °K this factor has become only 3. Sydoriak and Roberts[39] were able to make very accurate measurements of the vapour pressure of ^{3}He below 1 °K (from 0.45° to 1.0°), their results being represented by the equation

$$\log P_{mm} = \frac{1.1037}{T} + 2.3214 \log T + 2.0936 - 0.08976\,T + 0.03756\,T^2 - 0.004T^3, \qquad (2)$$

where the temperature is measured on the 1955 T_E scale.

The normal boiling point of ^{4}He exceeds that of ^{3}He (3.195 °K) by 1.021°. The data[30] in Table 2 on the heat of evaporation ΔH_e of ^{3}He have been calculated by means of the Clausius–Clapeyron equation, and are accurate to a few tenths of a calorie per mole.

Similar calculations have been carried also by Kerr[40] for the range 1.0°–3.3° and by Roberts and Sydoriak[41] between 0.54° and 1.25 °K. At 1.5 °K a calorimetric method[42] has given a value for ΔH_e (^{3}He) of 10.39 ± 0.02 cal mole^{-1}, which is quite close to the corresponding calculated value. The values given in Table 2 for ^{4}He are calorimetric, and are accurate to a few hundredths of a calorie per mole.

Interesting results have also been obtained[45-51] for the vapour pressure of solutions of ^{3}He in ^{4}He, Fig. 1 showing the corresponding diagrams for this system[47]. The curve of vapour pressure against liquid composition diverges markedly from the corresponding straight line representing Raoult's law‡.

The isotope effect is much smaller with liquid neon than with helium, but it is still considerable. As early as 1935 Keesom and Haantjes[57] measured the vapour pressure of a series of mixtures of neon isotopes having mean atomic weights between 20.04 and 21.16, and obtained by extrapolation the data for the pure isotopes given in Table 3§. It was found graphically that the temperature of the triple point for ^{22}Ne was 0.134° higher than that for ^{20}Ne (24.6 °K).

With argon the isotopic difference in vapour pressures is only a few tenths of 1%. The following results were obtained by Clusius and Meyer[17] for the isotopes having atomic weights of 40, 38, and 36 from data on the fractionation of natural argon (^{36}Ar 0.307, ^{38}Ar 0.060%) at temperatures near the triple point (83.8 °K):

$$0.995 > P_{40}/P_{36} > 0.993,$$
$$0.997 > P_{40}/P_{38} > 0.996.$$

TABLE 1. Vapour pressure of isotopes of helium on T_E temperature scale.

T, °K	P, mm Hg ^{4}He[35]	P, mm Hg ^{3}He[30]	$P_{^4He}/P_{^3He}$	T, °K	P, mm Hg ^{4}He[35]	P, mm Hg ^{3}He[30]	$P_{^4He}/P_{^3He}$
1.0	0.12170	8.564	0.0142	2.2	40.703	212.28	0.1917
1.1	0.29956	13.384	0.0224	2.3	51.266	248.52	0.2062
1.2	0.63253	19.765	0.0320	2.4	63.589	288.60	0.2203
1.3	1.2220	27.913	0.0433	2.5	77.793	332.71	0.2338
1.4	2.1776	38.03	0.0573	2.6	94.046	381.02	0.2468
1.5	3.6336	50.30	0.0722	2.7	112.438	433.73	0.2594
1.6	5.7414	64.91	0.9885	2.8	133.214	491.09	0.2713
1.7	8.663	82.06	0.1056	2.9	156.419	553.01	0.2829
1.8	12.565	101.93	0.1233	3.0	182.226	619.92	0.2940
1.9	17.607	124.69	0.1412	3.1	210.776	691.88	0.3046
2.0	23.930	150.55	0.1590	3.2	242.196	769.04	0.3149
2.1	31.625	179.68	0.1760	3.3	276.624	851.50	0.3249

TABLE 2. Heat of evaporation of isotopes of helium.

T, °K	ΔH_e, cal mole^{-1} ^{4}He[43,44]	ΔH_e, cal mole^{-1} ^{3}He	References for ^{3}He
1.0	18.8	9.1	30
1.5	21.40	10.6	
2.0	22.20	11.3	
2.5	22.05	10.8	
3.0	22.42	7.9	40
3.3	23.00	3.4	

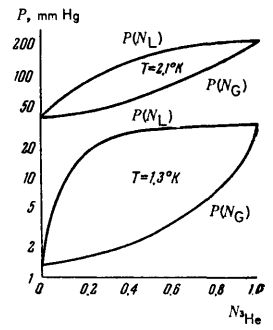


Fig. 1. Vapour pressure–composition diagrams for solutions of ^{3}He in ^{4}He. N = mole fraction; N_L = mole fraction of ^{3}He in liquid; N_G = mole fraction of ^{3}He in vapour.

‡ Melting-point curves for ^{3}He and ^{4}He up to 3500 kg cm^{-1} have been described by Mills and Grilly[52]. The method of measuring vapour pressure and additional data on the properties of ^{3}He and its solutions in ^{4}He have been given[53-55]. For the separation of the isotopes of helium see Kuznetsov[56].

§ Recently Roth and Bigeleisen[58] confirmed the data of Keesom and Haantjes using a specimen of neon containing 77.2% ^{22}Ne.

TABLE 3. Isotope effect in the vapour pressure of neon[57].

T, °K	$P_{^{22}Ne}/P_{^{20}Ne}$ expt.	calc. from Eqns. (85)	calc. from Eqns. (92), (93)	T, °K	$P_{^{22}Ne}/P_{^{20}Ne}$ expt.	calc. from Eqns. (85)	calc. from Eqns. (92), (93)
	Solid state				Liquid state		
20	0.924	0.935	0.925	25	0.957		
21	0.930	0.942		26	0.960		
22	0.935	0.946	0.936	27	0.962		
23	0.940	0.950					
24	0.944	0.954	0.945				

A differential manometer has been used[59] to measure differences in vapour pressure for two specimens of krypton differing in atomic weight by 1.74 units, and two specimens of xenon differing by 2.95 units. In the case of krypton the specimen enriched with the heavy isotope had a vapour pressure which was the smaller by 0.3% over the range 0–760 mm Hg¶; and with the isotopic mixtures of xenon the difference in vapour pressures over the same range already lies within the limits of error (0.02 mm Hg) of the measurements. Such a small isotope effect explains the absence of appreciable separation of isotopes in the experiments of Clusius[60] on the fractionation of xenon in a column equivalent to 25 theoretical plates at temperatures around the ternary point (161.36°K, 612.2 mm Hg)†. Another monatomic substance which has been investigated is mercury. Grigor'ev *et al.*[61] found by Rayleigh distillation and by other methods that ^{204}Hg has a lower vapour pressure than has ^{198}Hg, the difference not exceeding 0.2% at 253°K, and 0.08% at 453°K.

2. VAPOUR PRESSURE OF DIATOMIC ISOTOPIC SUBSTANCES

(a) Isotopes of Hydrogen

Only two years after the discovery of deuterium Scott *et al.*[62] made careful direct measurements of the vapour pressure of a specimen of this substances obtained from heavy water and containing only 0.1 at.% of the light isotope of hydrogen. Later such measurements were made by several investigators on deuterium of normal (*n*) ortho–para composition (high-temperature equilibrium mixture)[63-74], on the *e* composition (in equilibrium at 20.4°K)[69-71,74-76] and also hydrogen deuteride‡[69,73-75,77]. Data were obtained for the solid and liquid states of these substances right up to the critical temperature.

In 1942 only a rough calculation was possible[78] of the vapour pressure of tritiohydrogen HT from the radioactivity of the gaseous distillate of a 10^{-9} M solution of this substance in ordinary hydrogen. But Grilly[72] has subsequently made direct measurements on tritium containing only ~0.5% of light hydrogen.

More recent data on the vapour pressures of the isotopic modifications of hydrogen of identical ortho–para composition differ among themselves by only tenths of 1%, and these discrepancies are explained mainly by a difference in the temperature scales employed. The experimental results for isotopes of *n* composition can be represented by the following equations (in these and subsequent equations P = vapour pressure in mm Hg, and T = temperature in °K).

For the solids:

H_2 [74] $$\log P = 4.56488 - \frac{47.2059}{T} + 0.03939T, \quad (3)$$

HD [74] $$\log P = 4.70260 - \frac{56.7154}{T} + 0.04101T, \quad (4)$$

D_2 [72] $$\log P = 6.2100 - \frac{77.077}{T} + 28.8\times10^{-4}(T - 16.5)^2, \quad (5)$$

T_2 [72] $$\log P = 6.4773 - 88.002/T. \quad (6)$$

For the liquids:

H_2 between 14° and 20°K [74]
$$\log P = 3.66687 - \frac{44.9569}{T} + 0.020537T,$$
H_2 between 19.5° and 24.5°K [72]
$$\log P = 5.5567 - \frac{54.650}{T} + 10.9\times10^{-4}(T - 22)^2, \quad (3')$$

HD [74] $$\log P = 5.04964 - \frac{55.2495}{T} + 0.01479T, \quad (4')$$

D_2 [72] $$\log P = 5.8404 - \frac{70.044}{T} + 4.59\times10^{-4}(T - 23)^2, \quad (5')$$

T_2 [72] $$\log P = 6.0334 - \frac{78.925}{T} + 2.0\times10^{-4}(T - 25)^2. \quad (7)$$

The isotope effect is clear from Table 4. Both the results and the values obtained by calculation based on Eqns. (3)–(7) are accurate to within 0.01 mm Hg for pressures up to 10 mm, and to within 0.1 mm for higher pressures.

TABLE 4. Vapour pressure of isotopic variation of hydrogen*.

T, °K	P, mm Hg: *n*-T_2	*n*-D_2	HD	*n*-H_2	$\frac{P(T_2)}{P(H_2)}$	$\frac{P(D_2)}{P(H_2)}$	$\frac{P(T_2)}{P(D_2)}$	$\frac{P(HD)}{P(H_2)}$
			Solid state					
10		0.05	0.23	1.7		0.03		0.16
11		0.20	0.99	5.1		0.04		0.19
12	0.14	0.73	2.94	12.7	0.011	0.057	0.19	0.23
13	0.51	2.14	7.46	27.9	0.018	0.07	0.24	0.27
14	1.55	5.44	16.8				0.285	
15	4.08	12.3	34.4				0.332	
16	9.49	25.4	65.2				0.374	
17	20.0	48.6					0.412	
18	38.8	87.2					0.445	
19	70.1							
20	119.5							
			Liquid state					
19		145.1	264.2	490.8		0.296		0.538
20		219.9	382.0	675.7		0.325		0.565
21	170.1	322.2	534.9	906.4	0.188	0.355	0.528	0.590
22	252.5	458.5	728.5	1189.0	0.212	0.386	0.551	0.613
23	362.4	636.2	969.0	1529.6	0.237	0.416	0.570	0.633
24	505.1		1262.3					

* Data for T_2 calculated by means of Eqns. (6) and (7); published data were taken for H_2 and D_2,[74] and for HD.[75]

¶ According to Grigor'ev and Rudenko's data ["V Soveshchanie po Fizike Zhidkogo Sostoyaniya, Tezisy Dokladov" (Fifth Congress on the Physics of the Liquid State, Abstracts of Papers), Kiev University, 1961, p. 6], the vapour pressure of ^{86}Kr at the normal boiling point (120°K) is lower than that of ^{82}Kr by $(4.6 \pm 0.7) \times 10^{-2}$%.

† For argon see G. Boato, G. Scoles, and M. E. Vallauri, Nuovo Cim., 14, 735 (1959).

‡ *n*-H_2 contains 0.2500 para + 0.7500 ortho, and *n*-D_2 0.3333 para + 0.6667 ortho, modifications; *e*-H_2 consists of 0.979 para + + 0.021 ortho, and *e*-D_2 of 0.022 para + 0.978 ortho, modifications. Hydrogen deuteride is prepared by the reaction $LiAlH_4 + 4D_2O = LiOD + Al(OD)_3 + 4HD$.[79,80]

Above the boiling point the vapour pressure is about 3.5% lower with n-H_2 than with e-H_2, the corresponding difference for n-D_2 and e-D_2 being 0.5%. These percentage differences are somewhat greater below the boiling point[69,75].

Values of P_h/P_l for the different pairs of isotopic hydrogen molecules at the same temperature approach unity as the corresponding M_h/M_l approaches unity, where M is the molecular weight, and the subscripts h and l denote the heavy and the light varieties respectively, an increase in one of these ratios corresponding to a decrease in the other. However, the isotope effect is not a simple or direct function of the mass of the molecule. In particular, it is interesting that, in spite of the identical molecular weight of HT and D_2, the vapour pressure of the former is considerably greater than that of the latter: at 20.3°K, for example, the difference is ~45%§.[82] With the isotopic pairs T_2–D_2 and DH–H_2, which have the same value of M_h/M_l, however, the values of P_h/P_l at the same temperature differ by only 2%.

Tables 5 and 6 give the temperatures and the heats of the phase transformations of the hydrogen isotopes. Values of the latter calculated from the general form of the Clausius–Clapeyron equation agree with available calorimetric data to within a few calories per mole¶. No departure from Raoult's law was observed[81] for mixtures of hydrogen and deuterium. Hoge and Arnold[75], however, found from measurements of the dew points of such mixtures that their vapour pressures exceed by approximately 3% the values calculated on the assumption that such systems are ideal. In agreement with this, it has been shown[80] that the experimental plots of P and T against composition (N) for mixtures of H_2 and D_2 deviate by a few per cent from the plots based on Raoult's law.

(b) Diatomic Substances Differing in Isotopic Composition with Respect to Carbon, Nitrogen, Oxygen, Hydrogen, and Chlorine

Several investigations have been made[87-93] of the varieties of carbon monoxide $^{13}C^{16}O$ and $^{12}C^{16}O$. Johns[89,91] used a differential manometer to measure the difference in vapour pressure between a standard specimen of normal carbon monoxide (1.1 at.% of ^{13}C) and each of five specimens of the oxide containing between 14 and 73 mole % of $^{13}C^{16}O$. He found that, within the limits of experimental error, the vapour pressure of both liquid and solid phases varies linearly with the mole fraction of the heavy variety, and this enabled him to extrapolate the experimental results to the corresponding values for pure $^{13}C^{16}O$ and $^{12}C^{16}O$. Over the range investigated, 57°–81°K, the heavy oxide had the lower vapour pressure, the isotope effect decreasing with rise in temperature. The P_h/P_l ratio changes from 0.9795 to 0.9820 between 57.2° and 61.7°K, and from 0.9891 to 0.9930 over the range 68.3°–81.1°K. The following relation was found for the solid phase over the range 61.6°–68.1°K:

$$\log(P_h/P_l) = 0{,}16/T - 36/T^2; \quad (8)$$

while for the liquid phase between 68.2° and 81.2°K

$$\log(P_h/P_l) = 0.171/T - 33.9/T^2. \quad (8')$$

The error in the determination of $\log(P_h/P_l)$ was 1–2%.

It has been calculated that the melting point of $^{13}C^{16}O$ exceeds that of $^{12}C^{16}O$ by 0.061°. Results obtained by Groth *et al.*[90], who investigated only the liquid–vapour equilibrium, give values of $\log P_h/P_l$ which are 5% greater than those found by Johns. Although they also carried out[90] direct measurements of the differences in vapour pressures, they used an oxide containing only 10 at.% of ^{13}C, so that their extrapolation[90] might entail a greater error than that in the work of Johns[89,91].

Devyatykh *et al.*[92,93] employed Rayleigh distillation of ordinary carbon monoxide to investigate the vapour pressure of $^{13}C^{16}O$ relative to that of $^{12}C^{16}O$. The isotopes were analysed in a mass spectrograph. For temperatures between the normal melting and boiling points they obtained the equation

$$\log(P_h/P_l) = 0.0024 - 0.387/T. \quad (8'')$$

TABLE 5. Triple points and boiling points of isotopes of hydrogen.

Substance	Triple point T, °K	Triple point P, mm	B.p., °K (760 mm)	Ref.
n-H_2	13.96	54.0	20.39	72
e-H_2	13.81	52.8	20.28	75
HD	16.60	92.8	22.14	75
n-D_2	18.73	128.6	23.67	72
e-D_2	18.69	128.5	23.64	75
n-T_2	20.62	162.0	25.04	72

TABLE 6. Heats of phase transformations of hydrogen isotopes (from different published sources), in cal mole^{-1}.

Substance	ΔH_f at triple point: calorimetric	$\Delta H_{sublimation}$ at triple point: calc.	$\Delta H_{sublimation}$ at triple point: calorimetric	ΔH_e at b.p. (760 mm): calc.	ΔH_e at b.p. (760 mm): calorimetric
n-H_2	28[83]	247[72]	246[83]	219[86] 216[72]	219[84] 216[83]
p-H_2	28[84,85]				215[84]
HD	38[74]				257[74]
n-D_2	47[71]	346[72]	349[71]	293[72]	294[76]
e-D_2	47[76]			294[76]	
n-T_2		393[72]		333[72]	

§ According to Libby and Barter[78], HT and D_2 have identical vapour pressures. These results, however, obtained by Rayleigh distillation of a 10^{-9} M solution of HT in H_2, are evidently much less accurate than those of Bigeleisen and Kerr[82], which were calculated from the radioactivity of the phases in equilibrium with 10^{-8} M solutions. Pure HT cannot be investigated because of its thermodynamic instability.

¶ White *et al.*[232] report a calorimetric investigation of the heats of evaporation of ortho-deuterium and para-hydrogen from their boiling points up to the critical points.

It follows from Eqn. (8″) that P_h/P_l changes from 0.9876 at 68.3° to 0.9896 at 81.1°K, the vapour pressure of the heavy oxide thus being 1.24–1.04% lower than that of the light oxide, whereas according to Johns [89,91] the corresponding difference is 1.09–0.70%. This discrepancy is apparently due to the less accurate character of experiments involving Rayleigh distillation of a mixture having a low content of one of the isotopes, compared with the direct determination of the relative vapour pressure of a greatly enriched isotopic mixture.

Kirschenbaum [94] used a differential manometer to measure the difference in vapour pressure between ordinary nitrogen and its equilibrium isotopic mixture, the latter containing 12 at.% of $^{15}N_2$ and 45% of $^{15}N^{14}N$. By extrapolating his results on the basis of Raoult's law, Kirschenbaum and Urey [95] obtained the following relation for the pure liquid isotopes

$$\log [P(^{15}N_2)/P(^{14}N_2)] = 0.00582 - 0.7230/T. \quad (9)$$

Johns [96] compared the vapour pressures of natural nitrogen and of two mixtures, containing $^{15}N_2$ 81.6, $^{15}N^{14}N$ 16.9 at.%, and $^{15}N_2$ 35.1, $^{15}N^{14}N$ 47.9 at.%. The isotopic difference in pressure was proportional to the ^{15}N content, which confirms the applicability of Raoult's law to this case. It follows also from these results [96] that the law of the geometric mean is observed [97]

$$P^2(^{15}N^{14}N) = P(^{15}N_2) \times P(^{14}N_2), \quad (10)$$

or approximately

$$2[P(^{14}N_2) - P(^{15}N^{14}N)] = P(^{14}N_2) - P(^{15}N_2).$$

Clusius and Schleich [98] measured the vapour pressure of isotopically almost pure specimens of $^{15}N_2$ and $^{15}N^{14}N$ and obtained results close to those which follow from Eqns. (9) and (10), namely

$$\log [P(^{15}N_2)/P(^{14}N_2)] = 0.00691 - 0.7974/T, \quad (9')$$

$$\log [P(^{15}N^{14}N)/P(^{14}N)_2] = 0.00343 - 0.3985/T. \quad (11)$$

According to Eqn. (9′) the vapour pressure of heavy nitrogen is lower than that of ordinary nitrogen, by 1.3% at 63.3°K and by 0.8% at 77°K. In comparison with $^{14}N_2$, the $^{15}N_2$ variety has a higher melting point (63.19° compared with 63.14°K), boiling point (77.39° against 77.32°K), and heat of evaporation (1336.5 against 1333.0 cal mole^{-1}) [95,98].

An unexpectedly large isotope effect has been observed [98,99] with nitric oxide, and is represented by the equation

$$\log (P_h/P_l) = 0.01340 - 3.0230/T, \quad (12)$$

where the subscripts h and l refer to $^{15}N^{16}O$ and $^{14}N^{16}O$ respectively.

It follows from Eqn. (12) that in this case, too, the molecular species containing heavy nitrogen has the lower vapour pressure. However, the corresponding isotopic difference for $^{15}N^{16}O$ decreases from 3.1% at 111° to 2.7% at 120°K, whereas for $^{15}N^{14}N$ this difference is ~0.5% at pressures up to 1 atm. Yet the difference in mass between heavy and light molecules is approximately the same in the two cases. The relative volatility for $^{15}N^{16}O$ and $^{14}N^{16}O$ is according to Kuhn *et al.* [100,101] rather lower than would follow from Clusius and Schleich [98]. It must be assumed, however, that, since Clusius and Schleich carried out direct measurements of the vapour pressure of isotopically almost pure substances†, whereas Kuhn *et al.* employed the Rayleigh distillation of ordinary nitric oxide (0.36 at.% ^{15}N), the results obtained by the former investigators are the more accurate‡.

The relative vapour pressure of the isotopic varieties of molecular oxygen have been studied [87,91,102–107]. The most accurate results have apparently been obtained by Johns [91] by using oxygen which had been considerably enriched with heavy isotopes and by employing a method of direct differential measurements. Two specimens of oxygen containing 13.85 and 42.71 mole% $^{16}O^{18}O$ were compared with a standard specimen containing 0.45% of this isotopic variety (the $^{16}O^{17}O$ content was always calculated as $^{16}O^{18}O$). Extrapolation to 100% was based on the assumption that the isotopic difference in vapour pressure was proportional to the mole fraction of $^{16}O^{18}O$. The following relation was obtained for the range 65°–89.2°K:

$$\log (P_h/P_l) = 0.124/T - 30/T^2, \quad (13)$$

where the subscripts h and l denote $^{16}O^{18}O$ and $^{16}O_2$ respectively. It follows from Eqn. (13) that at 73.8°K the vapour pressure of $^{16}O^{18}O$ is 0.90% lower than that of $^{16}O_2$, while at 90.1°K a slight extrapolation gives a difference of 0.54%. The corresponding values obtained by Kronberger [87] by Rayleigh distillation were 0.84% and 0.62%. Thode and Smith [105] found by the same method that at 90.1°K the difference between P_h and P_l is 0.65%. The data obtained by Johns also agree well with results [106] on the fractionation of oxygen, according to which the ratio P_h/P_l changes from 0.987 at 63.1° to 0.991 at 74.0°K, the heavy variety being, as above, $^{16}O^{18}O$.

Devyatykh and Zorin [107] used their data on the Rayleigh distillation of natural oxygen to calculate the relative vapour pressures of pure $^{18}O_2$. They postulated that the rule of the geometric mean [97] was applicable in this case, *i.e.* that

$$P(^{16}O^{18}O) = [P(^{18}O_2) \times P(^{16}O_2)]^{1/2}.$$

In this way the following relation was obtained from the experimental data for the range 66.07°–99.13°K:

$$\log (P_h/P_l) = 0.00019 - 0.367/T, \quad (14)$$

where the subscripts h and l denote $^{18}O_2$ and $^{16}O_2$ respectively. Hence it follows that at 90°K the vapour pressure of $^{18}O_2$ is 0.89% lower than that of $^{16}O_2$, which is comparatively close to the corresponding value of 1.08% calculated from Johns' data. The difference between the results of Devyatykh and Zorin [107] and Johns [91] becomes somewhat larger at lower temperatures§.

Carbon monoxide containing heavy oxygen has been studied [91,107,108]. According to Devyatykh and Zorin's results [107], obtained by Rayleigh distillation of ordinary carbon monoxide, the ratio of the vapour pressures of $^{12}C^{18}O$

† The heavy nitric oxide contained $^{15}N^{16}O$ 98.00, $^{15}N^{18}O$ 0.20, $^{14}N^{16}O$ 1.80%.

‡ For the relative volatility factors for varieties of nitrous oxide containing different isotopes of nitrogen and oxygen, and also of nitrogen dioxide isotopic with respect to nitrogen, see section 3a.

§ Clusius *et al.* Helv. Chim. Acta., 44, 98 (1961), have measured the vapour pressure of 99.64% $^{18}O_2$ relative to that of ordinary oxygen. For pure $^{18}O_2$ and $^{16}O_2$ between 63.5° and 90°K they obtained $P_T/P_{\pi} = -(57.285/T^2) + (0.145/T) + 0.661 \times 10^{-3}$.

and $^{12}C^{16}O$ changes from 0.9848 to 0.9957 over the range 71.3° – 82.1°K, corresponding to the equation:

$$\log (P_h/P_l) = 0.0265 - 2.35/T. \quad (15)$$

According to Johns[91] the percentage difference in vapour pressures of these isotopic oxides is less by a factor of about 1.5–2.0 than would follow from Eqn. (15): between 69° and 77°K the ratio P_h/P_l changes from 0.9921 to 0.9941, and is represented by the equation

$$\log (P_h/P_l) = 0.132/T - 25.3/T^2. \quad (16)$$

Below the melting point we have for the β form of the solid phase

$$\log (P_h/P_l) = 0.13/T - 27/T^2. \quad (17)$$

The melting point of $^{12}C^{18}O$ is 0.047° higher than that of $^{12}C^{16}O$, while the α–β transition temperature is 0.11° higher. Direct differential measurements are reported[91], but only one specimen of the oxide, containing ~20 mole % of $^{12}C^{18}O$, was studied, and the results were extrapolated to 100% on the hypothesis that the isotopic difference in vapour pressure was proportional to the ^{18}O content.

It follows[96] from Johns' data that $^{12}C^{18}O$ occupies an intermediate position between $^{12}C^{16}O$ and $^{13}C^{16}O$ with respect to vapour pressure, although it has the largest molecular weight, so that the rule of the geometric mean[97] is not applicable here.

Clusius and Schleich[98] determined the vapour pressure of nitric oxide containing 100 at.% of heavy oxygen, their results being expressed as

$$\log (P_h/P_l) = 0.02103 - 4.4684/T, \quad (18)$$

where the subscripts h and l denote $^{14}N^{18}O$ and $^{14}N^{16}O$. It follows from Eqn. (18) that the isotope effect is somewhat greater for these varieties of the molecules than for the oxides described above, which were isotopic with respect to nitrogen. At about 111°K the vapour pressure of $^{14}N^{18}O$ is 4.3% lower than that of $^{14}N^{16}O$, and at 120°K 3.6% lower. Complete replacement of ordinary by heavy oxygen in nitric oxide produces increases of 0.14° in the melting point, 0.31° in the boiling point, and 20.5 cal mole^{-1} in the heat of evaporation.

The effect on the vapour pressures of hydrogen chloride, bromide, and iodide produced by replacing the hydrogen by deuterium is interesting. The following equations have been obtained[109] for DCl and HCl:

$$\log (P_h/P_l) = 0.075 - 15.4/T \quad (19)$$

for the liquid state, and

$$\log (P_h/P_l) = -0.387 + 57.7/T \quad (19')$$

for the solid state.

The vapour pressures of liquid DBr and HBr are represented[110] by equations of the type

$$\log P_{mm} = A - B/T, \quad (20)$$

values of the constants A and B being given in Table 7. The following equations have been obtained[111] for DI and HI:

$$\left.\begin{aligned} \log P_{mm}\ (HI) &= 26.119 - 0.002293T - 7.111 \log T - 1636/T; \\ \log P_{mm}\ (DI) &= 26.129 + 0.002293T - 7.111 \log T - 1636/T, \end{aligned}\right\} \text{liquid state} \quad (21), (22)$$

$$\left.\begin{aligned} \log P_{mm}\ (HI) &= 10.493 - 0.003167T - 0.3771 \log T - 1406/T, \\ \log P_{mm}\ (DI) &= 10.505 - 0.003167T - 0.3771 \log T - 1406/T. \end{aligned}\right\} \text{solid state} \quad (21'), (22')$$

Values of P_h/P_l for the liquid state calculated from Eqns. (19)–(22) are plotted against temperature in Fig. 2.

TABLE 7. Constants in Eqn. (20).

Substance	A	B	Substance	A	B
Liquid state			Solid state		
HBr	7.465	945.7	HBr	8.309	1103
DBr	7.517	956.5	DBr	8.306	1103

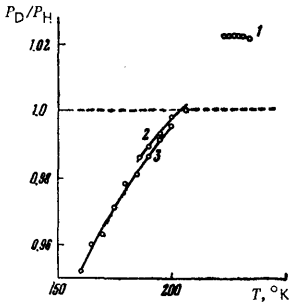


Fig. 2. Isotope effect in vapour pressure of liquid hydrogen halides:
1) DI/HI; 2) DBr HBr; 3) DCl/HCl.

TABLE 8. Phase transformations of isotopic hydrogen iodides[110].

Property	HI	DI
Triple point, °K	222.4	221.5
B.p., °K	237.05	237.00
ΔH_e at b.p., cal mole^{-1}	4725	4710

With hydrogen and deuterium chlorides P_h/P_l increases from 0.952 to 0.995 between 160° and 200°K, with HBr and DBr this ratio increases from 0.986 at 186° to 1.000 at 206°K, and in the case of HI and DI the ratio is 1.025 between 223° and 234°K. Comparison of the isotope effects for all three hydrogen halides in the liquid state shows that the ratio P_h/P_l, which is less than unity up to 200°K, increases with rise in temperature and becomes greater than unity¶.

The behaviour of solid hydrogen chloride is peculiar. With solid DBr and HBr the ratio P_h/P_l is 0.993 over the range 150° – 185°K, while for solid DI and HI it is 0.972–0.975 over the range 191° – 220°K, so that in both cases, as with the corresponding liquid phases, $P_h < P_l$. With solid DCl and HCl however, the value of P_h/P_l decreases[109] from 1.55 to 1.005 between 100° and 162°K. In the case of DCl the isotope effect in the vapour pressure of the solid phase is opposite in sign to the effect for the liquid phase, and a minimum is observed in the ratio at the melting point. As will be shown below, a similar phenomenon has been found to occur with heavy water.

Fractional distillation of hydrogen chloride on a column at 185°K has yielded[112] a value of 0.9992–0.9990 for the ratio P_h/P_l for $H^{37}Cl$ and $H^{35}Cl$. Zhavoronkov *et al.*[113]

¶ The vapour pressure of DF is discussed in section 4b.

established by the more accurate method of Rayleigh distillation that this ratio changes from 0.9978 to 0.9986 for these isotopic substances between 167° and 181°K.

Recently Matveev *et al.*[130] have carried out the Rayleigh distillation of molecular chlorine. Regarding the mixture of its isotopic varieties as ideal, they found that the ratio $P(^{37}Cl_2)/P(^{35}Cl_2)$ changes from 0.9827 to 0.9999 between the normal melting and boiling points (172° and 238.6°K). With both HCl and Cl_2 at vapour pressures of a few hundred mm Hg, the separation factor differs from unity by at most 0.2%. Consequently it is useless to employ fractionation of these substances to obtain pure isotopes of chlorine[113,114,130].

3. POLYATOMIC ISOTOPIC SUBSTANCES NOT ASSOCIATED BY HYDROGEN BONDS (COMPOUNDS ISOTOPIC WITH RESPECT TO HYDROGEN, BORON, CARBON, NITROGEN, SILICON, CHLORINE, AND GERMANIUM)

(a) Negative Isotope Effect

With all the monatomic and diatomic molecules described above, other than hydrogen iodide, the heavier isotopic variety has the lower vapour pressure. Several polyatomic molecules are also known with which a similar effect is observed, which will be termed a negative isotope effect in vapour pressure. Thus Kuhn *et al.*[101] found by Rayleigh distillation that with the isotopic pairs $^{15}N^{14}N^{16}O$–$^{14}N_2{}^{16}O$ and $^{15}N_2{}^{18}O$–$^{15}N_2{}^{16}O$ at about 184°K and $^{15}N^{16}O_2$–$^{14}N^{16}O_2$ at about 293°K the values of P_h/P_l are 0.9988, 0.9982, and 0.9973 respectively.

Several papers have shown that a decrease in vapour pressure takes place also when light carbon is replaced by heavy carbon in methane, ethylene, and ethane. Johns[91] measured directly the vapour pressure of three specimens of methane containing between 28 and 71 at.% $^{13}CH_4$, and extrapolated the results to a 100% content on the assumption that the isotopic difference in vapour pressure is proportional to the content of heavy carbon. He found that the ratio P_h/P_l changes from 0.9946 at 91.0° to 0.9965 at 104.8°K, corresponding to the equation

$$\log (P_h/P_l) = 0.191/T - 36.8/T^2. \qquad (23)$$

The equation obtained for the solid phase was

$$\log (P_h/P_l) = 0.10/T - 30/T^2. \qquad (23')$$

Groth *et al.*[90] made direct measurements of the difference in vapour pressure between natural methane and a specimen containing 10 at.% ^{13}C, over the range 90.7–96.0°K. Values of $\log P_h/P_l$ obtained by them are 5% smaller than the corresponding values derived from Eqn. (23). Clusius and Bühler[115] compared the vapour pressure of $^{13}CH_4$ containing only 0.2 mole % $^{12}CH_4$ with that of natural methane (1.1% $^{13}CH_4$) at the ternary point of the latter, obtaining a value of P_h/P_l = 0.996. Recently Clusius *et al.*[116] have made direct measurements on 99.05% $^{13}CH_4$ relative to ordinary methane between 91.17° and 110.44°K. Their results give a P_h/P_l ratio changing from 0.9945 to 0.9969 over this range, in good agreement with Johns' results †.[91]

† According to Clusius *et al.*[116] the melting and boiling points (at 760 mm Hg) are respectively 90.70° and 111.70°K for $^{13}CH_4$, and 90.67° and 111.66° for $^{12}CH_4$. The heat of evaporation is greater with $^{13}CH_4$ than with $^{12}CH_4$, by 3.20 cal mole^{-1} at the melting point and 2.52 cal mole^{-1} at 100°K.

Results obtained by the Rayleigh distillation of natural methane have shown[107] that the ratio P_h/P_l for $^{13}CH_4$ and $^{12}CH_4$ changes from 0.9893 to 0.9902 between 97.55° and 111.8°K, and also[117] that over the same temperature range this ratio increases from 0.9900 to 0.9932. Thus direct differential measurements between the normal melting and boiling points indicate that the difference in vapour pressure between $^{13}CH_4$ and $^{12}CH_4$ is ~0.5%, while investigations based on Rayleigh distillation of natural methane indicate the difference to be about twice as great.

Ordinary ethylene and ethane have also been subjected to Rayleigh distillation[117], the following relations having been obtained. For $^{13}C^{12}CH_4$ and $^{12}C_2H_4$ over the range 120.0–169.3°K:

$$\log (P_h/P_l) = 0.0945/T - 0.00136; \qquad (24)$$

for $^{13}C^{12}CH_6$ and $^{12}C_2H_6$ over the range 130.0–184.5°K:

$$\log (P_h/P_l) = 0.00213 - 0.3958/T. \qquad (25)$$

It follows from Eqns. (24) and (25) that $P_h < P_l$, but the difference between these quantities does not exceed 0.2%. With the ethanes the isotope effect diminishes rapidly with rise in temperature, and at the normal boiling point it has already reached zero within the limits of experimental error. It has been calculated that the heat of evaporation is greater with $^{13}CH_4$ than with $^{12}CH_4$, and greater with $^{13}C^{12}CH_6$ than with $^{12}C_2H_6$, by several calories per mole[118].

(b) Positive Isotope Effect and Mixed Cases

It was considered for a long time that a negative isotope effect in vapour pressure was a general phenomenon. However, a considerable majority of the polyatomic molecules, not associated by a hydrogen bond, which have been investigated exhibit a positive isotope effect — an increase in vapour pressure on replacement of a light by a heavy isotope — or else a negative effect at some temperatures and a positive effect at others. A positive isotope effect is observed also with compounds which show association by hydrogen bonds, provided that the hydrogen atom forming this bond is not substituted, or when the molecules remain associated in the gas phase.

Hydrocarbons and their derivatives. Let us begin with those cases in which the lighter molecules have the higher vapour pressure at comparatively low temperatures, while the opposite is true at elevated temperatures. The behaviour of the deuteromethanes is typical in this respect and has formed the subject of several papers[119–121], the most complete and accurate work being that of Armstrong *et al.*[121] They represented the isotope effect in vapour pressure by equations of the type

$$T \log (P_D/P_H) = A - B/T, \qquad (26)$$

values of the constants A and B being given in Table 9 ("H" in this equation denotes CH_4).

The following equations are given for CH_4:

between 54° and 90.66°K (over the solid)

$$\log P_{mm} = 6.7838 - 477.46/T + 0.00469/T, \qquad (27)$$

between 90.66° and 112°K (over the liquid)

$$\log P_{mm} = 7.55073 - 483.22/T - 0.0030686T.$$

Values of P_h/P_l for molecules with a successively increasing number of deuterium atoms approximately form a

TABLE 9. Constants in Eqn.(26).

Substance	A	B	Substance	A	B
	Solid state			Liquid state	
CH_3D	1.260	110.2	CH_3D	1.328	129.5
CH_2D_2	2.694	222.2	CH_2D_2	2.671	245.4
CHD_3	4.452	351.7	CHD_3	3.969	343.8
CD_4	5.529	410.5	CD_4	5.159	421.1

TABLE 10. Triple points of deuteromethanes[121].

Substance	P, mm Hg	T, °K
CH_4	87.5	90.66
CH_3D	84.5	90.41
CH_2D_2	82.0	90.17
CHD_3	80.2	89.96
CD_4	79.1	89.79

TABLE 11. Vapour pressure ratios for isotopic methanes.

T, °K	CH_3D/CH_4	CH_2D_2/CH_4	CHD_3/CH_4	CD_4/CH_4	T, °K	CH_3D/CH_4	CH_2D_2/CH_4	CHD_3/CH_4	CD_4/CH_4
		Solid state					Liquid state		
55	0.969	0.945	0.922	0.922	91	0.997	0.999	1.005	1.014
60	0.978	0.962	0.948	0.951	95	0.999	1.002	1.009	1.018
70	0.989	0.984	0.981	0.989	100	1.001	1.005	1.012	1.022
80		0.998	1.002	1.012	105	1.002	1.007	1.015	1.026
85	0.999	1.002	1.009	1.019	111	1.003	1.010	1.018	1.029

geometric progression. The departure of mixtures of the isotopic methanes from ideal behaviour is insignificant. Curves for the temperature dependence of P_D/P_H of all four deuterated methanes pass through the value unity (Fig.3), and the temperature at which this occurs is lower the greater the number of hydrogen atoms which have been replaced by deuterium. With tetradeuteromethane at 110°K the vapour pressure is already approximately 3% greater than with ordinary methane‡.

Similar behaviour to that of the deuteromethanes is observed when hydrogen in the silanes is replaced by deuterium. Stokland[123] determined the vapour pressures of monosilane, disilane, and their deutero-derivatives containing ~99 at.% of deuterium. The results were expressed in the form of equations of the type

$$\log P_{mm} = A/T + 1.75\log T + BT + C, \qquad (28)$$

values of the constants A, B, and C being given in Table 12.

It follows from Eqn.(28) that the vapour pressure *vs.* temperature curves for isotopic monosilanes intersect at 132.5°K: *i.e.* below this temperature replacement of

‡ Monodeuterotetramethylmethane (deuteroneopentane) boils at a lower temperature than ordinary neopentane[122], from which it follows that in this case, too, the deuterohydrocarbon has a greater vapour pressure than its hydrogen analogue near the normal boiling point (282.7°K).

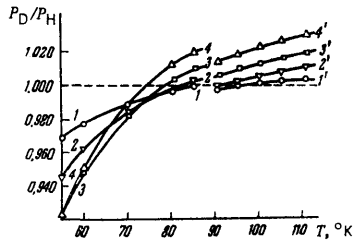


Fig.3. Isotope effect in vapour pressure of deuteromethanes, subscript H denotes CH_4; D: 1,1′) CH_3D; 2,2′) CH_2D_2; 3,3′) CHD_3; 4,4′) CD_4; 1–4) solid state; 1′–4′) liquid state.

TABLE 12. Constants in Eqns.(28) and boiling points of isotopic silanes.

Substance	−A	-10^7B	C	B.p., °K	Substance	−A	-10^7B	C	B.p., °K
SiH_4	740.0	79 701	4.87448	161.95	Si_2H_6	1380.2	69 309	5.78216	259.00
SiD_4	773.0	94 026	5.31421	161.80	Si_2D_6	1394.3	71 510	5.91428	257.80

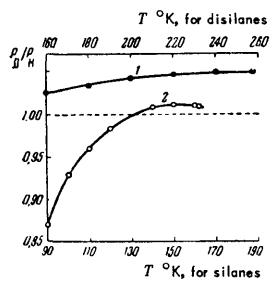


Fig.4. Isotope effect in vapour pressure of deuterosilanes: 1) Si_2D_6/Si_2H_6; 2) SiD_4/SiH_4.

hydrogen by deuterium in silane causes a decrease in vapour pressure, but above this temperature an increase is observed. In the case of disilane, replacement of hydrogen by deuterium causes an increase in vapour pressure over the whole temperature range between the normal melting and boiling points (Fig.4). In another paper[124] Stokland showed that liquid Si_3D_8 and Si_4D_{10} also have higher vapour pressures than their ordinary analogues Si_3H_8 and Si_4H_{10} respectively.

Zeltmann and Fitzgibbon[125] determined the vapour pressures of mono-, di-, and tri-germane in which 99.6% of the hydrogen had been replaced by deuterium, the results being expressed in the form of equations of the type

$$\log P_{mm} = -\frac{\Delta H_e}{4.575\,T} + B, \qquad (29)$$

applicable to vapour pressures between 10 and 800 mm Hg.

Values of ΔH_e and the constant B are given in Table 13, which includes also the melting points determined experimentally to within 0.2°, and the boiling points calculated from Eqn. (29). Unfortunately, the ordinary germanium hydrides were not studied at the same time as the deuterides in this work[125], and it is necessary to use the results of other work[126] for their vapour pressures, which diminishes the accuracy of the calculated isotope effect. The temperature variation of the ratios P_D/P_H calculated from the data given by Zeltmann and Fitzgibbon[125] and by Stull[126] is plotted in Fig. 5. With regard to the sign of the isotope effect, it is clear that the situation observed with the isotopic methanes and silanes is repeated.

The isotopic pentaboranes also show a greater vapour pressure with the heavy variety. According to Shapiro and Ditter[127] Eqns. (30) and (31) apply to these compounds between 250° and 320°K, the latter equation relating to 99.5 at.% of deuterium

$$\log P_{mm}(B_5H_9) = 9.49191 - 0.0028956T - 1881.29/T, \quad (30)$$

$$\log P_{mm}(B_5D_9) = 9.46916 - 0.0028783T - 1870/T. \quad (31)$$

The P_h/P_l ratios calculated from these equations are given in Table 14. The equations together with the Clausius–Clapeyron equation show that replacement of the hydrogen in pentaborane by deuterium depresses the boiling point by 1° (332.2° instead of 333.2°K) and decreases the heat of evaporation by 40 cal mole^{-1} (7390 instead of 7430).

A positive isotope effect on the vapour pressure is exhibited in the liquid phase, two cyclic hydrocarbons which have been studied in this connection being deuterobenzene C_6D_6 [128,129] and deuterocyclohexane C_6D_{12}.[129] The temperature dependence of the vapour pressure of these deuterated hydrocarbons and their hydrogen analogues is given by equations of the type

$$\log P_{mm} = A - B/(T-C); \quad (32)$$

values of the constants A, B, and C are given in Table 15, and the P_h/P_l ratios in Table 16.

The vapour pressure is increased, and the boiling point and the heat of evaporation are decreased, when hydrogen is replaced by deuterium in the methyl halides[132], chloroform[134], and chloropropyne[133], for which substances the following equations have been obtained

$$\log P_{mm}(CH_3Cl) = -1590.72/T - 3.97770\log T + 18.7955, \quad (33)$$

$$\log P_{mm}(CD_3Cl) = -1593.76/T - 4.06144\log T + 19.02286, \quad (34)$$

$$\log P_{mm}(CH_3Br) = -1696.01/T - 3.36805\log T + 17.23566,$$
$$\log P_{mm}(CD_3Br) = -1683.89/T - 3.28743\log T + 17.00870, \quad (35)$$

$$\log P_{mm}(CH_3I) = -1476.2/T + 7.5549, \quad (36)$$

$$\log P_{mm}(CD_3I) = -1471.9/T + 7.5613, \quad (37)$$

$$\log P_{mm}(CH_3C{\equiv}CCl) = -1480/T + 7.740, \quad (38)$$

$$\log P_{mm}(CD_3C{\equiv}CCl) = -1487/T + 7.782. \quad (39)$$

The isotope effect is indicated by the data in Table 17, which have been calculated by means of Eqns. (33)–(39).

It is interesting that the ratio P_h/P_l decreases for the methyl halides, but increases for chloropropyne, with rise in temperature over the same range in the two cases. It is seen from Figs. 3 and 4 that an increase in the ratio with rise in temperature occurs also with methane and the silanes. With other deuterohalogenohydrocarbons the vapour pressure has not been investigated, but typical data[134] are available on the effect of replacement of hydrogen by deuterium on the boiling point of dibromoethane (Table 19). Compared with the ordinary form of

TABLE 13. Temperatures of phase transformations and constants in Eqn. (29) for germanium deuterides[125].

Substance	M.p., °K	B.p., °K	ΔH_e, cal mole^{-1}	B
GeD_4	107.0	184.0	3744	7.327
Ge_2D_6	165.3	301.6	6483	7.579
Ge_3D_8	172.9	383.7	7876	7.367

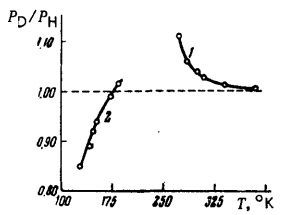


Fig. 5. Isotope effect in vapour pressure of deuterogermanes:
1) Ge_3D_8/Ge_3H_8; 2) GeD_4/GeH_4.

TABLE 14.

T, °K	$P_{B_5D_9}/P_{B_5H_9}$	T, °K	$P_{B_5D_9}/P_{B_5H_9}$
250	1.057	300	1.042
260	1.053	310	1.039
270	1.048	320	1.037
280	1.047	329	1.035
290	1.044		

TABLE 15. Constants in Eqn. (32), boiling points, and heats of evaporation of isotopic benzenes and cyclohexanes[129].

Substance	A	B	C	B.p., °K	ΔH_e at 353 °K, cal mole^{-1}
C_6H_6	6.9121	1214.64	51.96	353.26	7395
C_6D_6	6.8886	1196.38	53.96	352.47	7370
C_6H_{12}	6.8450	1203.53	50.30	353.90	7215
C_6D_{12}	6.8704	1203.29	48.72	351.58	7150

TABLE 16. Vapour pressure ratios for isotopic benzenes and cyclohexanes[129].

T, °K	$\frac{C_6D_6}{C_6H_6}$	$\frac{C_6D_{12}}{C_6H_{12}}$	T, °K	$\frac{C_6D_6}{C_6H_6}$	$\frac{C_6D_{12}}{C_6H_{12}}$
283	1.024	1.093	323	1.026	1.081
293	1.025	1.090	333	1.025	1.077
303	1.026	1.088	343	1.025	1.074
313	1.026	1.084	353	1.025	1.072

TABLE 17. Vapour pressure ratios for isotopic halogenated derivatives.

T, °K	$\frac{CD_3Cl}{CH_3Cl}$	T, °K	$\frac{CD_3Br}{CH_3Br}$	T, °K	$\frac{CD_3I}{CH_3I}$	T, °K	$\frac{CD_3C\equiv CCl}{CH_3C\equiv CCl}$
183	1.055	203	1.040	273	1.055	230	1.030
193	1.048	213	1.040	283	1.055	240	1.032
203	1.044	223	1.040	293	1.052	250	1.032
213	1.042	233	1.037	303	1.052	260	1.035
223	1.040	243	1.036	315	1.048	270	1.037
233	1.037	263	1.033			280	1.040
243	1.035	273	1.032			290	1.040
249	1.032	277	1.032				

TABLE 18. Heat of evaporation and boiling point of isotopic halogenated derivatives[131].

Substance	B.p., °K (760 mm Hg)	ΔH_e at b.p. of H cpd., cal mole^{-1}	Substance	B.p., °K (760 mm Hg)	ΔH_e at b.p. of H cpd., cal mole^{-1}
CH_3Cl	249.4	5310	CD_3Br	276.0	5900
CD_3Cl	248.6	5280	CH_3I	316.0	6750
CH_3Br	276.8	5910	CD_3I	314.6	6730

TABLE 19. Normal boiling points of dibromodeuteroethanes.

Substance	B.p., °C	Substance	B.p., °C
CH_2Br-CH_2Br	131.55	CH_2Br-CD_2Br	130.90
$CHDBr-CH_2Br$	131.25	$CHDBr-CD_2Br$	130.50
$CHDBr-CHDBr$	130.90	CD_2Br-CD_2Br	130.15

this substance, the deuterated derivatives boil at a lower temperature the greater the number of deuterium atoms in the molecule, the decrease per hydrogen atom replaced being 0.35°. The melting points of the deuterated compounds, however, lie above that of ordinary dibromoethane.

Compounds isotopic with respect to boron and silicon. Zhavoronkov and his coworkers[12,13,21,135] used Rayleigh distillation to determine the isotope effect in the vapour pressure of boron trichloride and trifluoride. With the $^{11}BCl_3-^{10}BCl_3$ system it was found that $P_h < P_l$ below 211.5°K, but the opposite is true above this temperature (Fig. 6). The isotope effect between 188° and 286°K is described by the equation

$$\log(P_h/P_l) = 0.00483 - 1.00757/T, \quad (40)$$

where h and l denote $^{11}BCl_3$ and $^{10}BCl_3$ respectively. At the normal boiling point (285.9°K) the value of P_h/P_l is 1.003. Earlier work[136] had given a value of 1.002 at the same temperature, but this value had been calculated from results for the fractionation of BCl_3, which would be less accurate than those obtained by Rayleigh distillation. The positive isotope effect in the vapour pressure of boron trifluoride is almost three times as great. The following equation has been given[21,137] for the $^{11}BF_3-^{10}BF_3$ system:

$$\log(P_h/P_l) = 0.01903 - 2.6796/T, \quad (41)$$

from which it follows that the ratio P_h/P_l increases with rise in temperature, as in the case of boron trichloride. At the normal boiling point (171.5°K) the ratio is 1.0075.

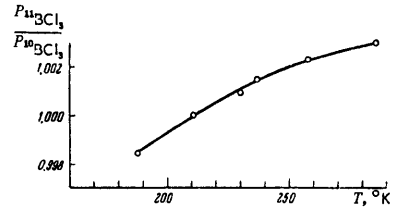


Fig. 6. Temperature dependence of vapour pressure ratio of isotopic boron trichlorides.

The same value was obtained by Nettley *et al.*[138], but values of 1.0082[139] and 1.0091[140] have also been obtained at the boiling point.

Zel'venskii *et al.*[141] have established that carbon disulphide $^{13}C^{32}S_2$ is more volatile than its isotopic analogue $^{12}C^{32}S_2$.

A positive effect on the vapour pressure has been established by Orlov and Zhavoronkov[142] also for the isotopes ^{30}Si, ^{29}Si, and ^{28}Si in silicon tetrachloride. Prolonged fractionation of the ordinary material resulted in a slight enrichment of the vapour with the heavy isotopes.

It is clear from the experimental results described above that the sign of the isotope effect in vapour pressure depends on the temperature range, the complexity of the molecule, and the relative difference in mass between its isotopic varieties. The nature of the isotopes themselves is also important in this connection[143]. When chloroform and carbon tetrachloride are distilled, heavy carbon (^{13}C) accumulates in the distillate, as in the case of benzene, but heavy chlorine (^{37}Cl) is concentrated in the residue. The distillation was carried out at 34.6° in columns having a large number of theoretical plates and with a very high reflux ratio. Analysis was carried out with a mass spectrograph. The relative difference in vapour pressure was calculated by means of Fenske's equation

$$(P_h - P_l)/P_l = (R_r/R_d)^{1/n} - 1, \quad (42)$$

where P_h and P_l are the vapour pressures of the pure heavy and light varieties, differing isotopically only with respect to a given atom, at the temperature of distillation; R_r and R_d are the concentration ratios of the light to the heavy isotope in the still pot and in the distillate respectively; and n is the number of theoretical plates. By approximate integration of the Clausius–Claypeyron equation on the assumption that the integration constants are identical for isotopic analogues and also by the use of Trouton's rule, an expression was obtained from Eqn. (42) for the isotopic difference in boiling points:

$$T_h - T_l = -(T^2/10.7 \times T_b n)\ln(R_r/R_d). \quad (43)$$

Here T_h and T_l are the absolute boiling points of the pure heavy and light varieties at the pressure at which the distillation was carried out, and T and T_b are the boiling points of the substance of normal isotopic composition at the same pressure and at 1 atm respectively. Results of the calculations are given in Table 20.

The results[143] represent two cases in which a given substance shows an isotope effect in the vapour pressure which is positive with respect to one element and negative with respect to another at the same temperature. It is noteworthy, however, that the percentage difference in vapour

TABLE 20. Data[143] for isotopic fractionation at 307.8°K.

System	P_h/P_l	$T_h - T_l$*
$^{13}CHCl_3 - {}^{12}CHCl_3$	1.0008	−0.02
$CH^{37}Cl^{35}Cl_2 - CH^{35}Cl_3$	0.9999	+0.003
$^{13}CCl_4 - {}^{12}CCl_4$	1.0013	−0.033
$C^{37}Cl^{35}Cl_3 - C^{35}Cl_4$	0.99997	+0.001
$^{13}C^{12}C_5H_6 - {}^{12}C_6H_6$	1.00025	−0.006

* T_h and T_l are the boiling points of the heavy and the light varieties at the pressure under which the given substance of normal isotopic composition boils at 307.8°K.

pressure is 10–40 times as great in substances which are isotopic with respect to carbon as in those which are isotopic with respect to chlorine, whereas the corresponding percentage differences in mass between the isotopic molecules or atoms are comparatively close to one another.

4. POLYATOMIC ISOTOPIC MOLECULES ASSOCIATED BY HYDROGEN BONDS

(a) Compounds Showing Little or No Association in the Gas Phase (Alcohols, Ammonia, Amines, Water, and Hydrogen Cyanide)

The work considered above[143] included also an investigation of the separation of the isotopes of carbon and oxygen by the fractionation of methanol, in which isotope effects of opposite sign were found. Heavy carbon accumulated in the distillate, as had been observed in the distillation of chloroform, carbon tetrachloride, and benzene, but heavy oxygen was concentrated in the residue (Table 21). However, whereas in the distillation of CCl_4 and $CHCl_3$ the percentage positive isotope effect due to ^{13}C exceeds the percentage negative effect due to ^{37}Cl by a factor of several tens, the percentage negative isotope effect due to ^{18}O in the distillation of methanol was nearly ten times as great as the positive effect due to ^{13}C.

Comparison of isotope effects in the vapour pressure of $^{12}CH_3{}^{18}OH$ and $^{14}CH_3{}^{16}OH$ is still more revealing, since these varieties of methanol show an almost identical relative increase in both the mass of the molecule and the mass of the isotopic atoms, compared with $^{12}CH_3{}^{16}OH$. Table 23 gives results obtained[141] in the fractionation of ordinary methanol to which $^{14}CH_3{}^{16}OH$ had been added. It was found, in agreement with Baertschi *et al.*[143], that heavy carbon accumulates in the distillate, and heavy oxygen in the residue. When the same isotope of oxygen is present, molecules containing ^{14}C are more volatile than those containing ^{13}C, which in turn are more volatile than molecules containing ^{12}C. The percentage accumulation of ^{18}O in the residue is about seven times as great as that of ^{14}C in the distillate. Enrichment of the residue with heavy oxygen when methanol is distilled has also been observed in other work[144,145]. It has also been established with methanol that deuterium accumulates to a considerable extent in the residue[141], and that this is due to a change in isotopic composition of the hydroxyl hydrogen[146]. Enrichment of the residue with deuterium has been observed during the fractionation of ethanol[147].

TABLE 21. Relative difference in vapour pressure and difference in boiling point for isotopic methanols*.

Heavy molecule (h)	P_h/P_l from ref. 143	P_h/P_l from ref. 141	T_h/T_l, deg, from ref. 143
$^{13}CH_3{}^{16}OH$	1.002	1.0043	$-5.5\cdot10^{-3}$
$^{14}CH_3{}^{16}OH$		1.001	
$^{12}CH_3{}^{18}OH$	0.997	0.9971	0.07

* Calculated from results of fractionation. The light molecule (l) is in all cases $^{12}CH_3{}^{16}OH$; T = b.p. at 200 mm Hg.

Beersmans and Jungers[148] prepared the isotopic methanols CD_3OH, CH_3OD, and CD_3OD, and measured the difference between the vapour pressure of each of these compounds and that of ordinary methanol (Fig. 7). Over the range 0°–60°C it was found that replacement of the three methyl hydrogen atoms by deuterium produced an increase in vapour pressure of about 0.7%. If only the hydroxyl hydrogen was substituted, a negative effect about seven times as great was produced, the diminution in vapour pressure being from 3% (at 60°) to 6% (0°). Replacement of all the hydrogen atoms in the methanol molecule by deuterium also causes a fall in the vapour pressure, but by a few tenths of 1% smaller than in the previous case, this being the resultant of the first two effects.

With respect to replacement of the methyl hydrogen by deuterium, methanol behaves like the hydrocarbons and halogenated derivatives, disilane, digermane, and pentaborane described above. For substitution of hydrogen in the hydroxyl group, however, a large negative isotope effect is observed, as with the monatomic and diatomic molecules at comparatively low temperatures. The vapour pressure of the isotopic varieties of methanol can be represented to within ~2 mm Hg by equations of the type

$$\log P_{mm} = A + B/T + C \log T. \qquad (44)$$

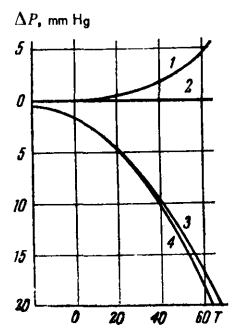


Fig. 7. Difference in vapour pressure P for isotopic methanols.
$\Delta P = P$ (D-alcohol) − P (CH_3OH):
1) CD_3OH; 2) CH_3OH; 3) CD_3OD; 4) CH_3OD.

TABLE 22. Boiling points, heats of evaporation, and constants in Eqn. (44) for isotopic methanols.

Substance	D, at %	B.p., °K	ΔH_e at b.p., cal mole^{-1}	A	$-B$	$-C$	Ref.
CH_3OH	0	338.0	9010	16.36638	2348.68	2.58414	149
CD_3OH	98	337.8	9005	16.87022	2372.83	2.75386	148
CH_3OD	92	338.7	9105	17.20687	2408.54	2.85113	148
CD_3OD	98 in CD 97 in OD	338.6	9120	16.42088	2372.75	2.58178	148

TABLE 23. Constants in Eqn. (46) for ethanol and the propanols (over the range 20°–70°) and for the butanols (20°–80°).

Alcohol	A	$-B$	$-C$	Alcohol	A	$-B$	$-C$
C_2H_5OH	24.1146	2898.10	5.1000	$CH_3(CH_2)_3OH$	30.6838	3648.5	7.1166
C_2H_5OD	24.5030	2932.60	5.2209	$CH_3(CH_2)_3OD$	31.1884	3695.4	7.2691
$CH_3(CH_2)_2OH$	35.5791	3670.60	8.8750	$(CH_3)_2CHCH_2OH$	31.6340	3631.40	7.4415
$CH_3(CH_2)_2OD$	36.2509	3706.10	9.1110	$(CH_3)_2CHCH_2OD$	31.5004	3634.70	7.3871
$(CH_3)_2CHOH$	25.8692	3079.70	5.6153	$C_2H_5CHOHCH_3$	33.5817	3628.5	8.1468
$(CH_3)_2CHOD$	26.0250	3121.00	5.6348	$C_2H_5CHODCH_3$	34.3629	3488.7	8.8160

Values of the constants A, B, and C are given in Table 22. Differentiation of Eqn. (44) with respect to temperature and comparison with the Clausius–Clapeyron equation leads to the expression

$$\Delta H_e = -4.574B + 1.986CT. \qquad (45)$$

Heats of evaporation calculated from Eqn. (45) and the normal boiling points calculated from Eqn. (44) are also given in Table 22.

On the basis of calorimetric data[150] the heat of evaporation of CH_3OD at 273°K is 9385 ± 20 cal mole^{-1}, compared with 9205 ± 20 cal mole^{-1} for CH_3OH, agreeing in the sign and the order of magnitude of the isotope effect with data given by Beersmans and Jungers[148]. In addition, CH_3OD has a lower heat of fusion and a lower melting point than CH_3OH, 726 ± 3 compared with 755 ± 3 cal mole^{-1}, and 173.5° as against 175.4°K.[150]

Rabinovich *et al.*[151] investigated the effect of replacing the hydrogen by deuterium in the hydroxyl groups of methyl, ethyl, propyl, isopropyl, butyl, isobutyl, and s-butyl alcohols on their vapour pressures. The results for the isotopic methanols agree to within 1 mm Hg with those reported above[148]. The vapour pressures of other alcohols are represented by equations of the type of (46), the constants A, B, and C in which are given in Table 23

$$\log P_{mm} = A + B/T + C \log T. \qquad (46)$$

All the deuteroalcohols investigated (95–98% D in the hydroxyl) have a lower vapour pressure than their hydrogen analogues. The isotope effect amounts to several per cent. Its dependence on the composition and the structure of the alcohol and on the temperature can be seen from Fig. 8.

A decrease in vapour pressure when the hydrogen is replaced by deuterium in the –OH of pentanol and in the –SH of ethanethiol has been reported by Hobden *et al.*[153]. However, the numerical values which they give for P_D/P_H, 0.85 for the pentyl alcohols and 0.91 for the ethanethiols at

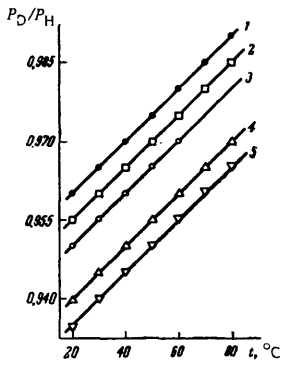


Fig. 8. Effect of replacement of hydroxyl hydrogen by deuterium on vapour pressure of alcohols (experimental values of P_D/P_H rounded off to 0.5%):
1) s-butanol; 2) isobutanol; 3) methanol; 4) ethanol and isopropanol; 5) propanol and n-butanol.

25°, are evidently much too low, since it is improbable that the percentage isotopic difference in vapour pressure in these cases would be several times larger than that for CH_3OD and almost the same as for D_2O (see Table 25).

A large reduction in the vapour pressure is produced by replacing the three hydrogen atoms in ammonia by deuterium[95,154]. According to the direct measurements made by Kirschenbaum and Urey[95] the data for ND_3 (subscript h) containing 98 at.% of D and ordinary NH_3 (l) are represented by

$$\text{solid state } \log (P_h/P_l) = 0.1305 - 49.69/T, \qquad (47)$$
$$\text{liquid state } \log (P_h/P_l) = 0.14003 - 46.45/T.$$

The heat of evaporation of deuteroammonia is greater, and its boiling point higher, than for ordinary ammonia, by 212 cal mole^{-1} and 2.37° respectively. The corresponding differences in the heat of fusion and the temperature of the ternary point are 15 cal mole^{-1} and 3.11° in the same direction. Replacement of ^{14}N by ^{15}N in ammonia[155–157] also produces isotopic effects in the same direction as with deuterium. Thode[155] made direct measurements on liquid ammonia containing 70.6% $^{15}NH_3$ (h) compared with ordinary NH_3 containing 0.38% $^{15}NH_3$ (l), the following equation being obtained for the vapour pressure

$$\log (P_h/P_l) = 0.00325 - (0.9593/T). \qquad (48)$$

TABLE 24. Vapour pressure ratio for isotopic varieties of ammonia.

T, °K	ND_3/NH_3* solids[95]	T, °K	ND_3/NH_3* liquids[95]	T, °K	$^{15}NH_3/^{14}NH_3$** liquids[155]
180	0.715	202	0.815	198	0.994
185	0.728	210	0.831	209	0.996
190	0.740	220	0.851	228	0.997
195	0.751	230	0.869	240	0.998
		236	0.880		

* 98% deuterium.
** 100% heavy nitrogen – extrapolated.

It was calculated by extrapolation assuming additivity that complete replacement of ^{14}N by ^{15}N in ammonia would increase in the heat of evaporation, the boiling point, and the temperature of the triple point of 6.25 cal mole^{-1}, 0.055°, and 0.118° respectively.

Even before the work on deuteroammonia, it had been shown[158] that the vapour pressure is lowered on substitution of deuterium for hydrogen in methylamine. In this case the ratio P_D/P_H for 99 at.% D varies from 0.92 at 223° to 0.95 at 263°K. The melting point of ND_2CH_3 (184.0°) is 3.9° higher than that of NH_2CH_3.

Another amine which has been investigated is aniline. With this compound, too, replacement of the hydrogen in the amino-group by deuterium results in a lower vapour pressure[151]. In this case the isotope effect decreases comparatively rapidly with rise in temperature, being 3.5% for $C_6H_5ND_2$ at 50°, but only 0.5% at 80°. This is apparently explained by the comparatively rapid decrease in the degree of association of aniline with rise in temperature.

The isotope effect in vapour pressure has been subjected to particularly detailed investigation in the case of heavy water. Very accurate results have been obtained for deuterium oxide in several papers[159-167], mostly by direct measurement of the pressure. Table 25 gives values of P_h/P_l for liquid D_2O (99.7–99.8 at.%) and H_2O obtained by Kirschenbaum[162] by graphical averaging of experimental data[163-166], and also the corresponding results of the most recent precision measurements by Combs *et al.*[167] and Oliver and Grisard[161]. Two interesting facts are the comparatively large decrease in the vapour pressure of water over the range 0°–50° produced by substitution of deuterium for hydrogen, and the change in sign of the isotope effect in the vicinity of 225°. $P(D_2O) < P(H_2O)$ up to this temperature, but above it $P(D_2O) > P(H_2O)$, so that 225° is the point of intersection of the vapour pressure–temperature curves for heavy and ordinary water[165,166] (for brevity this point will be termed the "crossover temperature"). The following equation (in which the temperature is t°C) is accurate to ~0.5% over the range 20°–100°, and to within 0.1% between 100° and 370°

$$\log [P(D_2O)/P(H_2O)] = 0.0306605 - 9.14056/(75.753 + t)\ \S.$$

Combs and Smith[168] found that for ~0.1 M solutions of some electrolytes the value of $P(D_2O)/P(H_2O)$ is increased by several per cent and the crossover temperature lowered by tens of degrees (Table 26, Fig.9). Comparatively small ions such as Li^+ and F^- have a weaker effect than have large ions such as I^- and PO_4^{3-}. These workers[168] suggest that this effect can be used to enrich water with deuterium by extractive distillation above the crossover temperature, since with ~0.15 M LiI or ~0.10 M K_3PO_4 a separation factor can be achieved of

$$\alpha = [P(D_2O)/P(H_2O)]^{1/2} = 1.035\ ¶.$$

Unexpected results were obtained by Johannin-Gilles and Johannin[160] for the difference in vapour pressure between heavy and ordinary ice at 273°–240°K: as the temperature fell over this range, the ratio P_h/P_l increased, and at

TABLE 25. Vapour pressure ratios of isotopic varieties of water.

t, °C	$\frac{HT^{16}O}{H_2^{16}O}$ ref. 179	$\frac{D_2^{16}O}{H_2^{16}O}$ ref. 167	$\frac{D_2^{16}O}{H_2^{16}O}$ ref. 162	$\frac{HD^{16}O}{H_2^{16}O}$ ref. 162	$\frac{H_2^{18}O}{H_2^{16}O}$ ref. 26	$\frac{H_2^{17}O}{H_2^{16}O}$ ref. 170
0			0.79_7	0.89_3		
10		0.836	0.84_6	0.92_0		
20		0.854	0.86_7	0.93_1	0.9912	
30	0.80_0	0.871	0.88_0	0.93_9	0.9918	
40	0.85_5	0.885	0.89_1	0.94_4	0.9926	
50	0.97_6	0.899	0.903	0.051	0.9933	
60	0.88_5		0.914	0.956	0.9940	0.9970
70	0.89_5		0.926	0.962	0.9947	0.9975
80			0.934	0.966	0.9954	
90			0.943	0.971	0.9961	
100			0.951	0.975	0.9968	

t, °C	$\frac{D_2^{16}O}{H_2^{16}O}$ ref. 162	$\frac{HD^{16}O}{H_2^{16}O}$ ref. 162	t, °C	$\frac{D_2^{16}O}{H_2^{16}O}$ refs. 161, 162	$\frac{HD^{16}O}{H_2^{16}O}$ ref. 162	t, °C	$\frac{D_2^{16}O}{H_2^{16}O}$ ref. 161
110	0.957	0.978	180	0.989	0.995	260	1.007
120	0.963	0.981	190	0.992	0.996	280	1.010
130	0.969	0.984	200	0.995	0.997	300	1.012
140	0.974	0.987	210	0.997	0.998	320	1.014
150	0.978	0.989	220	0.999	1.000	340	1.017
160	0.982	0.991	230	1.001	1.000	360	1.019
170	0.986	0.993	240	1.004	1.002	370	1.021

TABLE 26. Effect of electrolytes on temperature of intersection of $P-T$ curves for D_2O and H_2O.[168]

Electrolyte	Concn., mole fraction	Depression of temp. of intersection, deg	Electrolyte	Concn., mole fraction	Depression of temp of intersection, deg
AgF	0.100	12	LiI	0.150	114
KF	0.100	30	LiI	0.100	50
KCl	0.110	74	LiI	0.0005	0
KBr	0.010	68	ZnI_2	0.100	46
KI	0.103	81	Na_2SO_4	0.100	0
NaI	0.092	67	K_3PO_4	0.100	137

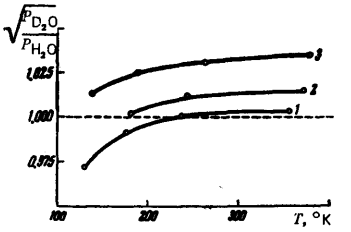


Fig.9. Temperature dependence of $\alpha = [P(D_2O)/P(H_2O)]^{1/2}$ for solutions of LiI at concentrations (in mole fractions) of: 1) 0.005; 2) 0.100; 3) 0.150.

§ C.B.Willingham *et al.*, J.Res.Nat.Bur.Stand., 35, 219 (1945); E.W.Walley, in "Proceedings of the Joint Conference on the Thermodynamic and Transport Properties of Fluids, 1957", Institution of Mechanical Engineers, London, 1958, p.15.

¶ It is assumed here that at low D contents $\alpha = P(HDO)/(H_2O)$ and that Eqn.(50) is valid.

about 249°K $P_h = P_l$. Hence there is a point of crossover at about 249°K of the vapour pressure–temperature curves for the solid state in addition to the above crossover point at about 498°K for liquid D_2O and H_2O. The vapour pressure of heavy ice over the range 240°–273°K is described[160] by the following equation

$$\log P_{mm} = -2886.9/T - 1.0327 \log T - 0.199156\,T + 0.000368\,T^2 + 40.5677 \quad (49)$$

the ice containing 99.5 at.% of D. Earlier data[171] for heavy ice between 273° and 275°K also agree with Eqn. (49). Fig. 10 shows the temperature dependence of P_D/P_H for heavy and ordinary water over the whole range studied, 240°–625°K.

The vapour pressure of HDO cannot be measured directly, since the following equilibrium is rapidly established

$$D_2O + H_2O \rightleftarrows 2HDO.$$

It follows from the equilibrium constant[25] of this reaction, for example, that with 50 at.% of deuterium at 25° the mixture contains ~48 mole % of HDO and 26% each of D_2O and H_2O. Some investigators, however, postulate[172,173] that the following relation holds

$$P(HDO) = [P(H_2O) \cdot P(D_2O)]^{1/2}, \quad (50)$$

i.e. that the rule of the geometric mean based on the masses of the molecules[97] is applicable in this case. Wahl and Urey[164] used Rayleigh distillation to determine the vapour pressure of HDO. They assumed that solutions of the isotopic varieties of water behave ideally, and hence that with a small deuterium content, when the concentration of D_2O is low, the separation factor α is approximately equal to the ratio of the vapour pressures of HDO and H_2O. Values of P(HDO) calculated from Eqn. (50) and from the experimental value of α were found to agree within the limits of error involved in determining the latter. Schutz[174], by carrying out a single distillation at 100° of water containing 1 at.% deuterium (1.98% HDO + 0.01% D_2O), determined α directly from experimental data on the composition of the phases in equilibrium It was found that $P(HDO)/P(H_2O)$ = = 0.971 at 100°, whereas the corresponding value calculated from Eqn. (50) is 0.975. According to Combs *et al.*[167], who used the same method, the difference between the values of α obtained experimentally and calculated from Eqn. (50) reaches 0.6% over the range 10°–50°, this being two or three times as great as the experimental error. The explanation is evidently that solutions of the isotopic varieties of water depart slightly from ideal behaviour.

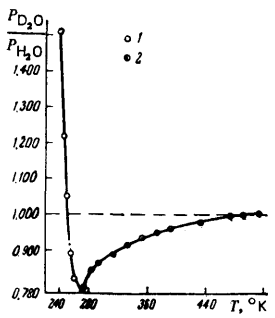


Fig. 10. Isotope effect in vapour pressure of heavy water: 1) solid, $P(D_2O)$ calculated from Eqn. (49). $P(H_2O)$;[233] 2) liquid[182].

Several papers have described investigations of the ratio $P(H_2{}^{18}O)/P(H_2{}^{16}O)$ using fractionating columns[170,172,175–177], Rayleigh distillation[26,164,165], and direct determination of the composition of the equilibrium phases[26]. The results of some of these investigations, however, do not agree sufficiently well. At about 80°, for example, values have been found of 0.9936,[176] 0.9951,[165] 0.9954,[26] and 0.996,[172]. The most detailed and apparently most accurate results are given by Zhavoronkov *et al.*[26] Water enriched to 1.1–1.4 mole % with $H_2{}^{18}O$ was used and, in addition to Rayleigh distillation, it was distilled in an apparatus equivalent to one theoretical plate, the composition of the equilibrium phases then being determined. Results obtained by the two methods agreed well. They can be represented by the following equation:

$$\log P(H_2{}^{18}O)/P(H_2{}^{16}O) = 0.00781 - 3.4492/T, \quad (51)$$

which also reproduces satisfactorily the data of Riesenfeld and Chang[165]. With heavy-oxygen water over the range investigated (10°–100°), as with heavy-hydrogen water, the vapour pressure is lower than that of ordinary water, and the corresponding relative difference diminishes with rise in temperature, the isotope effect for $H_2{}^{18}O$ being considerably less than that for D_2O (Table 25), as expected. Baertschi[178] found that the quantity $[1 - P(D_2{}^{18}O)/P(D_2{}^{16}O)]$ is about 20% smaller than $[1 - P(H_2{}^{18}O)/P(H_2{}^{16}O)]$†.

The ratio $P(H_2{}^{17}O)/P(H_2{}^{16}O)$ has been determined by means of a fractionating column[170] to be approximately 0.9969 at 58° and 0.9974 at 67°. The corresponding values of $P(H_2{}^{18}O)/P(H_2{}^{16}O)$ are 0.9939 and 0.9945. If allowance is made for the error of 0.0002 in the data of Thode *et al.*[170], it follows that the rule of the geometric mean with respect to molecular mass[97] holds approximately for the vapour pressures of $H_2{}^{18}O$, $H_2{}^{17}O$, and $H_2{}^{16}O$.

The vapour pressure of HTO has been investigated by Price[179], who used a standard sample of tritiated water to prepare solutions in H_2O having activities of 5–25 $\mu c\ ml^{-1}$, and measured the activities of their saturated vapours at a series of temperatures between 25° and 75°. He found that at a given temperature the ratio of the activities of the equilibrium phases is constant, from which it follows that Henry's law is applicable to this case. Since the solutions of HTO were very dilute, it is easy to show by the application of Raoult's and Dalton's laws that the ratio of the activity of the vapour to that of the liquid is approximately equal to the ratio $P(HTO)/P(H_2O)$. Values of this ratio determined in this way and averaged graphically are given in Table 25. Although the ratios of the molecular weights $M(HTO)/M(H_2O)$ and $M(D_2O)/M(H_2O)$ are very close to one another, the ratio $P(HTO)/P(H_2O)$ is about 9% smaller than the ratio $P(D_2O)/P(H_2O)$ over the range 25°–40°: *i.e.* the isotope effect is greater with HTO than with D_2O.

The most accurate value of the boiling point of D_2O is apparently 101.431° ± 0.003° obtained by Stokland[180]. The values given elsewhere[159,165] differ from this value by only 0.01° and 0.03° respectively. It has been established[181] that the elevation of boiling point of solutions of D_2O in H_2O relative to pure H_2O is proportional to the mole fraction of heavy water.

† For the $H_2{}^{16}O/H_2{}^{18}O$ and $D_2{}^{16}O/D_2{}^{18}O$ separation factors, see P. Baertschi and M. Thürkauf, Helv. Chim. Acta, 43, 80 (1960).

Determinations of the heat of evaporation of D_2O are described[61,165,166,182,183], and most of the results have been summarised[162]. At 3.82° $\Delta H_e(D_2O) = 11\,109 \pm 20$ cal mole^{-1}, its value at 25° being 10 846 ± 20 cal mole^{-1}: *i.e.* at the two temperatures it is respectively 407 and 331 cal mole^{-1} greater than $\Delta H_e(H_2O)$. This isotopic difference in heat of evaporation decreases steadily as the temperature rises, being 208, 143, and 105 cal mole^{-1} at 100°, 160°, and 220° respectively. Golik *et al.*[184] give data for the heat of evaporation of solutions of D_2O in H_2O which show that such solutions depart from ideal behaviour.

The same temperature of 3.82° was obtained for the melting point of D_2O in several investigations[185-187,189]; other determinations have been made[159,180,188]. The pressure corresponding to the triple point is 5.06 mm Hg. The derivative dT/dP for D_2O, which measures the variation of its melting point with pressure, is about 93% of the corresponding value for H_2O.[185,187,190] The following formula is given by LaMer and Baker[191,192] for the freezing point of solutions of D_2O in H_2O.

$$t_s(°C) = 39.42\ \Delta\rho_{25}^{25} - 38.8\,(\Delta\rho_{25}^{25})^2, \qquad (52)$$

where $\Delta\rho_{25}^{25} = \rho_{25}^{25} - 1$, ρ_{25}^{25} being the density of the solution at 25° relative to H_2O at the same temperature.

According to Price[179], the mean values of ΔH_e over the range 25°–75° are 10 900, 10 600, and 10 300 cal mole^{-1} for HTO, D_2O, and H_2O respectively, the uncertainty being ±100 cal mole^{-1} in every case.

Libby and Cornog[193] concluded from their data on the vapour pressure of solutions of HTO in H_2O (numerical values of which are not given in the paper) that the normal boiling point of pure HTO is lower than that for H_2O. However, in view of the facts that (as shown by Price[179]) at about 70° the vapour pressure of HTO is 10% lower, and its heat of evaporation 600 cal mole^{-1} greater, than those of H_2O, and also in the light of the isotope effect and its temperature dependence in the vapour pressure of D_2O, the above conclusion[193] must evidently be regarded as erroneous.

It has been calculated[26] from the vapour pressure that, compared with $H_2{}^{16}O$, the boiling point of $H_2{}^{18}O$ is 0.09° higher and its mean heat of evaporation between 15° and 100° is 16 cal mole^{-1} greater; similar results have been obtained elsewhere[164,165]. From data on the separation of $H_2{}^{18}O$ and $H_2{}^{16}O$ by the fractional crystallisation of water, the melting point of the former is 0.05° ± 0.008°.[194]

Giguère[183] made calorimetric measurements of heats of evaporation over a wide range of concentrations in the systems heavy water–deuterium peroxide and ordinary water–hydrogen peroxide. Extrapolation of the curves to 100% peroxide showed that the heat of evaporation of D_2O_2 at 25° (12 510 ± 50 cal mole^{-1}) is greater than the corresponding quantity for H_2O_2 by 170 cal mole^{-1}.

The isotope effect in the vapour pressure of deuterium cyanide appears[195] to be somewhat unusual. The following equations were suggested[195] (P in mm Hg):

$$\log P(HCN_L) = 7.795 - 1467/T, \qquad \log P(HCN_S) = 9.372 - 1877/T. \qquad (53)$$

$$\log P(DCN_L) = 7.695 - 1440/T - 175/T^2, \qquad \log P(DCN_S) = 9.476 - 1907/T. \qquad (54)$$

It appears from Eqns. (53) and (54) that the ratio P_D/P_H for the solid state increases from 0.93 at 225°K to 0.97 at 258°K, but for the liquid state, on the other hand, the ratio decreases from 1.01 at 261°K to 0.93 at 298°K. Consequently there should be a maximum ratio at about the melting point, which according to Lewis and Schutz[196] is approximately 259°K for HCN and 261°K for DCN.

(b) Isotopic Compounds Which Are Strongly Associated in Both Liquid and Gaseous Phases (Hydrogen Fluoride, Carboxylic Acids)

It is clear from the above account that, in the case of liquids in which the association complexes decompose completely or almost completely on evaporation (water, alcohols, ammonia, etc.)‡, substitution of deuterium for hydrogen forming a hydrogen bond causes a decrease in the vapour pressure. At the same time, several papers have shown that the opposite isotope effect is observed when association persists in the gas phase. As early as 1934 Claussen and Hildebrand[196] represented the vapour pressure of the liquid isotopic hydrogen fluorides over the range 5–760 mm Hg by the equations:

$$\log P_{mm}(HF) = 7.3739 - 1316.79/T, \qquad \log P_{mm}(DF) = 7.2026 - 1261.16/T. \qquad (55)$$

It follows from Eqn. (55) that the ratio $P(DF)/P(HF)$ is greater than unity and decreases steadily from 1.150 at 240° to 1.040 at 290°K, the boiling points being 293.07° for HF and 291.81°K for DF.

Lewis and Schutz[197] who were the first to study the vapour pressure of deuteroacetic acid CH_3COOD, found that at 50° it is 7.5%, and at 90° 3% greater than the vapour pressure of CH_3COOH§. The vapour pressure of CD_3COOH is 2–4% greater (at 35°–85°)[235] than that of CH_3COOH. Since this isotopic substitution has practically no influence on the association, the isotope effect observed has the same sign as in the replacement of hydrogen by deuterium in the methyl group of methanol or in unassociated compounds at moderate temperatures. The difference in vapour pressure between CD_3COOD and CH_3COOH should equal the sum of the positive isotope effects produced by substitution in the methyl and in the hydroxyl groups. Among experimental investigations of the effect of the complete deuteration of acetic acid on its vapour pressure[199-201], Wilson[200] described his data by the equation

$$\log P(CD_3COOD)/P(CH_3COOH) = 3.94/T + 0.0106, \qquad (56)$$

from which it follows that P_h/P_l decreases steadily from 1.06 at 20° to 1.05 at 100°. Halford and Anderson[201] show the isotope effect to be considerably lower, but Wilson's results[200] were confirmed within the limits of error of their measurements by Potter and Ritter[199], who give the following equations for the vapour pressure of the two isotopic acids:

$$\log P_{mm}(CH_3COOH) = 7.4275 - 1558.03/(T - 48.37), \qquad (57)$$

$$\log P_{mm}(CD_3COOD) = 7.4397 - 1556.17/(T - 48.34).$$

The most accurate value for the melting point of CD_3COOD is apparently 15.92°,[199] which is 0.68° below the melting point of CH_3COOH.

‡ In the vapours of alcohols, for example, only a few per cent of the molecules are associated[152].

§ No exchange was detected[197] between the hydrogen of the carboxyl and of the methyl groups in CH_3COOH. Such an exchange was shown later[198,199] to be possible, but it is very slow[199] even at 100°.

Rabinovich *et al.*[151] investigated how vapour pressure is affected by the substitution of deuterium for hydrogen in the carboxyl group of acetic, butyric, isobutyric, and isovaleric acids. Over the temperature ranges investigated (Fig.11) all four acids showed a positive isotope effect P_D/P_H, but an interesting feature was observed with acetic and butyric acids, for the curves showing the temperature dependence of the ratio passed through maxima. Since with the other two acids the ratio increases with rise in temperature over the ranges investigated, it can be supposed that at higher temperatures a maximum in the vapour pressure ratio will be observed in these cases too. The numerical values of the vapour pressures of the acids are represented by equations of the type

$$\log P_{mm} = A + B/T + C \log T, \qquad (58)$$

the constants in which are given in Table 27. According to our results the isotope effect amounts to a few per cent, and for CH_3COOD in particular it is about half the value found previously[197].

It is interesting that, as Dawber and Wyatt[202] have shown, the vapour pressure at 0° of deuteronitric acid DNO_3 (84.37% of N_2O_5 in D_2O) is 7% higher than that of HNO_3. Since this effect is opposite in sign to the isotope effects with D_2O, ND_3, and CH_3OD, but the same as that with CH_3COOD, these results[202] may perhaps mean that at about 0° nitric acid is associated to a considerable extent even in the gas phase.

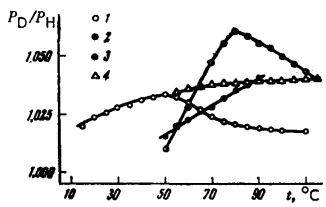


Fig.11. Effect of replacement of carboxyl hydrogen by deuterium on vapour pressure of: 1) acetic acids; 2) butyric acids; 3) isobutyric acids; 4) isovaleric acids.

TABLE 27. Constants of Eqns.(58) (H = ordinary acid; D = its analogue containing 99% D in the carboxyl).

Acid	A	$-B$	$-C$	Temp. range, °C
Acetic-H	15.5817	2480.4	2.4528	
Acetic-D	16.9093	2542.0	2.9016	20—118
Butyric-H	12.0505	2828.0	1.0168	
Butyric-D	12.0505	2821.8	1.0154	50—115
Isobutyric-H	8.8195	2532.7	0.0068	
Isobutyric-D	9.9223	2615.0	0.3379	50—90
Isovaleric-H	11.6256	2972.1	0.7826	
Isovaleric-D	12.1938	2982.6	0.8621	50—110

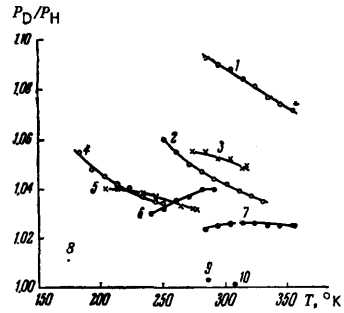


Fig.12. Positive isotope effect in vapour pressure of non-associated substances (hydrogen bonds absent): 1) C_6D_{12}/C_6H_{12}; 2) B_5D_9/B_5H_9; 3) CD_3I/CH_3I; 4) CD_3Cl/CH_3Cl; 5) CD_3Br/CH_3Br; 6) $CD_3C{\equiv}CCl/CH_3C{\equiv}CCl$; 7) C_6D_6/C_6H_6; 8) $^{11}BF_3/^{10}BF_3$; 9) $^{11}BCl_3/^{10}BCl_3$; 10) $^{13}CCl_4/^{12}CCl_4$.

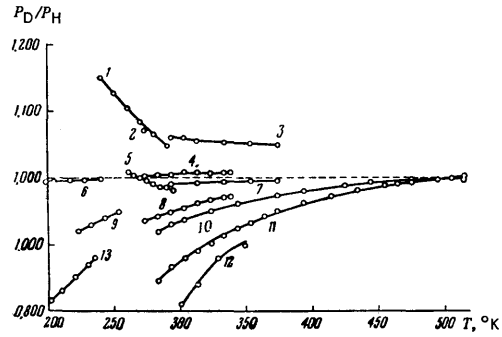


Fig.13. Isotope effect in vapour pressure of substances which are associated by hydrogen bonds: 1) DF/HF; 2) DNO_3/HNO_3; 3) CD_3COOD/CH_3COOH; 4) CD_3OH/CH_3OH; 5) DCN/HCN; 6) $^{15}NH_3/^{14}NH_3$; 7) $H_2{}^{18}O/H_2{}^{16}O$; 8) CH_3OD/CH_3OH; 9) ND_2CH_3/NH_2CH_3; 10) HDO/H_2O; 11) D_2O/H_2O; 12) HTO/H_2O; 13) ND_3/NH_3.

Fig.12 summarises the experimental data on the positive isotope effect in the vapour pressure of unassociated substances, and Fig.13 illustrates the effect on vapour pressure of replacing hydrogen by deuterium in various cases of association involving a hydrogen bond.

B. CALCULATIONS AND INTERPRETATION OF THE ISOTOPE EFFECT IN VAPOUR PRESSURE

1. INTRODUCTION

From the point of view of classical mechanics, the forces of interaction between isotopic atoms or molecules are identical. We therefore find that, to the degree of

approximation of classical statistics[203], the chemical potentials of isotopic substances should differ only by a constant multiplied by the temperature

$$\mu_h - \mu_l = -\frac{3}{2} kT \ln \frac{M_h}{M_l}, \quad (59)$$

where μ is the chemical potential for a single molecule, M is its mass, the subscripts h and l refer to the heavy and the light isotopic varieties respectively, and k is the Boltzmann constant. When the phases are in equilibrium we have

$$\mu_h^c(P_h, T_h) = \mu_h^g(P_h, T_h), \quad (60)$$

$$\mu_l^c(P_l, T_l) = \mu_l^g(P_l, T_l), \quad (61)$$

where the superscript c and g denote the condensed and gas phases respectively. Further, if the vapours obey the ideal gas laws, we also have

$$\mu_h^g(P_h\ T_h) = \mu_h^{g,0}(T_h) + kT \ln P_h, \quad (62)$$

$$\mu_l^g(P_l, T_l) = \mu_l^{g,0}(T_l) + kT \ln P_l, \quad (63)$$

where $\mu^{g,0}$ is the part of μ^g which depends only on the temperature. Since the chemical potential of the condensed phase is little affected by pressure, substitution of Eqns.(62) and (63) in (60) and (61), with $T_h = T_l = T$, yields

$$\ln \frac{P_h}{P_l} = \frac{(\mu_h^c - \mu_l^c) - (\mu_h^{g,0} - \mu_l^{g,0})}{kT}. \quad (64)$$

Since the difference (59) is the same for all phases of a given substance, and since for the gas phase this difference is represented by the difference between $\mu_h^{g,0}$ and $\mu_l^{g,0}$, it follows from Eqn.(64) that $P_h = P_l$. Thus within the limits of classical statistical mechanics, isotopic substances have the same vapour pressure. The incompatibility of this conclusion with the experimental data is a result of quantum-mechanical effects. Quantum statistics would lead to an isotopic difference in vapour pressure even if the intermolecular forces in the isotopic substances were equal. This difference cannot in general be calculated for any given substance, but approximate solutions are available for the simplest cases. Thus in the case of a monatomic substance we have according to Landau and Lifshits[203]

$$\mu^c = \mu^c_{\text{class}} + \frac{h^2}{24MkT} \overline{F^2}, \quad (65)$$

including terms of the order of h^2, where h is Planck's constant, and

$$\overline{F^2} = \overline{\left(\frac{\partial U}{\partial x}\right)^2} + \overline{\left(\frac{\partial U}{\partial y}\right)^2} + \overline{\left(\frac{\partial U}{\partial z}\right)^2} \quad (66)$$

is the mean square force in the condensed phase exerted on one atom by the remaining atoms, U is the potential energy, and x, y, z are coordinates. For a gas the chemical potential retains its classical value, since interaction between the particles can be neglected in this case. Substituting Eqn. (65) in (64), we therefore obtain

$$\ln \frac{P_h}{P_l} = \frac{h^2 \overline{F^2}}{24 (kT)^2} \cdot \left(\frac{1}{M_h} - \frac{1}{M_l}\right), \quad (67)$$

or in the case of a small difference in pressure ($\Delta P/P \ll 1$),

$$\Delta P_{\text{iso}} = P_h - P_l = P_{\text{class}} \frac{h^2 \overline{F^2}}{24 (kT)^2} \cdot \left(\frac{1}{M_h} - \frac{1}{M_l}\right), \quad (68)$$

where P_{class} is the common classical value of P_h and P_l. In order to calculate ΔP_{iso} from Eqn. (68) it is necessary to know how $\overline{F^2}$ depends on the temperature. However, this formula explains qualitatively the lower vapour pressure of the heavier isotope in the cases of monatomic substances described above.

Lifshits and Stepanova[204] have suggested an approximate formula for the isotopic difference in vapour pressure of monatomic solids which can be used for actual calculations. They started from Eqn. (64) and employed the quantum expressions for thermodynamic functions derived from the Debye theory of solids. Introduction of $\varphi = \mu_h - \mu_l$ converts Eqn. (64) into

$$\ln \frac{P_h}{P_l} = \frac{\varphi^c - \varphi^{g,0}}{kT}. \quad (69)$$

The quantity φ is expressed in terms of the classical relation (59), so that for a small difference in isotopic masses ($\Delta M/M \ll 1$) we have

$$\varphi^{g,0} = -\frac{3}{2} kT \frac{\Delta M}{M}. \quad (70)$$

The free energy of a solid whose atoms perform small oscillations about an equilibrium position is

$$F = NU_0 + \sum_a \left[\frac{h\nu_a}{2} + kT \ln (1 - e^{-h\nu_a/kT})\right], \quad (71)$$

where NU_0 is the interaction energy of all the atoms in the solid in the equilibrium position and ν_a is a characteristic frequency of their oscillations. If the isotopes are assumed to have the same value of U_0, the isotopic difference in free energy in the solid phase will then be

$$\Delta F = \Delta \sum_a \left[\frac{h\nu_a}{2} + kT \ln\left(1 - e^{-h\nu_a/kT}\right)\right] = -\frac{\Delta M}{2M} U, \quad (72)$$

where

$$U = \sum_a h\nu_a \left[\frac{1}{2} + \frac{1}{e^{h\nu_a/kT} - 1}\right], \quad (73)$$

and

$$-\frac{\Delta M}{2M} \simeq \ln \left(\frac{M_h}{M_l}\right)^{-1/2} = \ln \frac{\nu_{a,h}}{\nu_{a,l}} \simeq \frac{\Delta \nu_a}{\nu_a}. \quad (74)$$

The inverse proportionality between ν_a and $M^{1/2}$ arises from the assumption that the oscillations of the atoms in the lattice are harmonic. In Debye's approximation the energy U is represented by the formula

$$U = 3NkT\left[\frac{3}{8}\frac{\theta}{T} + U_D\left(\frac{\theta}{T}\right)\right], \quad (75)$$

where $\theta = h\nu_D/k$ is the characteristic temperature, ν_D the Debye (maximum) frequency of the atomic oscillations, and $U_D(\theta/T)$ is the Debye function

$$U_D(Z) = \frac{3}{Z^3} \int_0^Z \frac{t^3}{e^t - 1} dt. \quad (76)$$

From Eqns. (72) and (75) we have

$$\varphi^c = \left(\frac{\partial \Delta F}{\partial N}\right)_{p,v} = -\frac{3}{2}\frac{\Delta M}{M} kT\left[\frac{3}{8}\frac{\theta}{T} + U_D\left(\frac{\theta}{T}\right)\right]. \quad (77)$$

Hence, using Eqn. (70) we find that

$$\varphi^c - \varphi^{g,0} = -\frac{3}{2}\frac{\Delta M}{M} kT \varphi\left(\frac{\theta}{T}\right), \quad (78)$$

where

$$\varphi(Z) = \frac{3Z}{8} - 1 + U_D(Z). \quad (79)$$

Substituting Eqn. (78) in (69), we obtain for small isotopic differences in vapour pressure

$$\frac{\Delta P}{P} = -\frac{3}{2}\frac{\Delta M}{M}\varphi\left(\frac{\theta}{T}\right). \quad (80)$$

It is interesting that, with the monatomic substances discussed above, Eqn. (80) gives a qualitatively correct result for the liquid–gas equilibrium as well.

2. CALCULATIONS OF THE ISOTOPE EFFECT IN VAPOUR PRESSURE AT THE TRIPLE POINT BY LINDEMANN'S METHOD

(a) Monatomic Substances

By a different approach Lindemann[205] arrived at a relation fundamentally similar to Eqn. (80) as early as 1919, when he was examining the difference in vapour pressure of the isotopes of lead. Keesom and Haantjes[57] applied Lindemann's method to the isotopes of neon, and Clusius and Meyer[17] to argon. These workers also employ Debye's approximate theory of solids, but start from the Clausius–Clapeyron equation instead of the relations (60)–(64). The approximate form of this equation is used, in which the volume of the condensed phase is neglected, and the heat of evaporation ΔH_e is expressed, according to Kirchhoff's equation, in terms of its value at the absolute zero $\Delta H_{e,0}$ and the heat capacities of the vapour C_g and the solid C_s. Integration of the appropriate expressions for the isotopic substances yields

$$\ln\frac{P_h}{P_l} = -\frac{(\Delta H_{0,h} - \Delta H_{0,l})_e}{RT} - \frac{1}{R_0}\int_0^T\frac{dT}{T^2}\int_0^T(C_{s,h} - C_{s,l})\,dT + \\ + (i_h - i_l) + (a_h - a_l), \quad (81)$$

where i is the vapour pressure constant and a is a correction for the deviation of the vapour from ideal behaviour.

Further, the isotopic difference in heat of evaporation can be written

$$(\Delta H_{0,h} - \Delta H_{0,l})_e = -(U_{0,h} - U_{0,l}) - (E_{0,h} - E_{0,l}),$$

where U_0 is the potential energy of interaction between the atoms at $T = 0$, and E_0 is the zero-point (kinetic) energy of the atomic oscillations. It is also postulated that $U_{0,h} = U_{0,l}$. The zero-point energy is expressed, after Debye, in terms of the characteristic temperature: $E_0 = 9R\theta/8$, the term $(i_h - i_l)$ in Eqn. (81) is replaced by $1.5 \ln M_h/M_l$, and the difference $(a_h - a_l)$ is neglected. In addition, the heat capacity at constant pressure C_p is introduced into Eqn. (81). It is related to the heat capacity at constant volume C_v by the well-known formula

$$C_p = C_v + \frac{\alpha^2 TV}{\beta}, \quad (82)$$

where V is the atomic volume, α the (volume) coefficient of thermal expansion, and β the isothermal compressibility. On the hypothesis that the van der Waals forces are equal in isotopic substances, the latter are assumed to have identical values of V as well as of β, and very similar values of α. Under these conditions the isotopic difference in the second term on the right-hand side of Eqn. (82) can be neglected, so that we find that

$$C_{p,h} - C_{p,l} = C_{v,h} - C_{v,l}. \quad (83)$$

In view of this, we can introduce into Eqn. (81) the Debye function representing the free energy

$$\int_0^T\frac{dt}{T^2}\int_0^T C_s\,dT = -\frac{F_D}{T}. \quad (84)$$

Hence we finally obtain

$$\ln\frac{P_h}{P_l} = \frac{9}{8T}(\theta_h - \theta_l) + \frac{1}{RT}(F_{D,h} - F_{D,l}) + \frac{3}{2}\ln\frac{M_h}{M_l}. \quad (85)$$

The value of F_D/T for a given value of θ/T is found from tables of Debye functions[206]. Since it is accepted that characteristic temperatures are inversely proportional to the corresponding values of $M^{1/2}$, the value of θ for one of the isotopic varieties is sufficient to calculate the ratio P_h/P_l by means of Eqn. (85). It is easily shown that Eqns. (80) and (85) differ only in the presence in the latter of the additional term $9(\theta_h - \theta_l)/8T$, which represents the isotopic difference in zero-point energy of the atomic oscillations.

Table 3 gives a comparison of experimental results obtained by Keesom and Haantjes[57] on the isotopic effect in the vapour pressure of solid neon with values which they calculated by means of Eqn. (85) using the value of $\theta_l = 63.0°$ found by Clusius[207]. According to the experimental data, the vapour pressure of ^{22}Ne between 20° and 24°K is 7.5–5.5% less than that of ^{20}Ne, while the calculated difference is 6.5–4.5%. Thus, in spite of the number of approximations introduced into the calculation, the results in this case show satisfactory agreement with experiment.

For the argon isotopes ^{40}Ar and ^{36}Ar, Clusius and Meyer[17] obtained a value between 0.9916 and 0.9950 for P_{40}/P_{36} at the triple point using Eqn. (85), while their experimental results gave 0.993–0.995.

With xenon, however, calculation gives an incorrect result. As mentioned above, two isotopic mixtures of xenon differing in atomic weight by 3 units of mass have identical vapour pressures (to within 0.02 mm Hg)[57] at the triple point (161.4°K), whereas according to calculation they should differ by several tenths of a millimetre¶.

(b) Calculations for the Isotopes of Hydrogen

With the aim of obtaining a rough approximation, Urey *et al.*[3] used the Debye theory of specific heat to calculate the isotope effect in the vapour pressure of hydrogen. The solid–vapour equilibrium is considered at the temperature of the triple point of ordinary hydrogen (13.95°K), and the following postulates are made.

1) Hydrogen molecules are capable of free rotation in the crystal; the energy of this rotation and that of the atomic oscillations remain unchanged during evaporation, and are therefore disregarded.

¶ For calculations on the isotopes of Ne, Ar, Kr, and Xe, see G. Casanova, R. Fieschi, and N. Terri, Nuovo cim., 18, 837 (1960).

2) In the equation for the free energy of the vapour G_g:

$$G_g = U_g + PV_g - TS_g, \quad (86)$$

the internal energy U_g and the entropy S_g are represented by the corresponding expressions for an ideal monatomic gas.

3) The free energy of isotopic substances in a real solid is calculated on the basis of the Debye theory. The following expression is used for the free energy G_S:

$$G_s = E_0 + T(F_D/T) + PV_s, \quad (87)$$

where, as above, E_0 is the zero-point energy, and F_D/T is the Debye function for the free energy. Further, since a phase equilibrium is being considered, the right-hand sides of Eqns. (86) and (87) are equal. The term PV_S is neglected, since it is small compared with PV_g, and the latter is replaced by RT. Hence we obtain for the vapour pressure

$$\ln P = \frac{9\theta}{8T} + \frac{F_D}{RT} + \frac{3}{2}\ln M + \frac{5}{2}\ln T - \frac{\Delta H_0'}{RT} + \text{const.} \quad (88)$$

Here $\Delta H_0'$ is the heat of evaporation at $T = 0$ when the translational energy of the molecules in the vapour and the zero-point energy of their vibrations in the solid are ignored. Under these conditions the heat of evaporation is a measure of the van der Waals interaction energy, which is regarded as identical for isotopic substances. The constant in Eqn. (88) is independent of the molecular mass. Hence it follows from Eqn. (88) that, with the approximations made by Urey *et al.*[3], Eqn. (85) can be applied to the isotopes of hydrogen at the temperature of the triple point. With $\theta_1 = 91°$,[83] calculation based on Eqn. (85) for HD and H_2 at 13.95 °K indicates that $P_h/P_l = 0.45$, the corresponding experimental value[74,75] being ~0.30.

Several refinements were introduced into the above calculation by Scott *et al.*[62], but make no fundamental difference to the calculations, which remain, as before, in the nature of an extremely rough approximation. Thus the value of P_h/P_l calculated by these authors for D_2 and H_2 at 13.95 °K is 0.30, whereas the corresponding experimental value is ~0.09†.

(c) Calculations for Some Complicated Substances

The above principles for calculating the isotope effect in vapour pressure at the triple point have also been applied as approximations to some more complicated substances, it being assumed that various rotational terms should be introduced in addition to the terms for vibrational motion. In calculating the P_h/P_l ratios for $^{13}C^{16}O$–$^{12}C^{16}O$, $^{12}C^{18}O$–$^{12}C^{16}O$, and $^{13}CH_4$–$^{12}CH_4$, therefore, Johns[91] introduced the following additional postulates: (1) the heat capacity is the sum of the corresponding Debye and Einstein terms; and (2) the frequencies of rotation, and consequently also the Einstein characteristic temperature, are inversely proportional to the square root of the moment of inertia of the molecule. On this basis the following equation was obtained[91]:

$$\ln\frac{P_h}{P_l} = -\frac{E_{g,h} - E_{g,l}}{RT} + \frac{1}{T^2}\left[\frac{3}{40}\theta_{D,l}^2\left(\frac{M_l}{M_h} - 1\right) + \sum\frac{n_E}{24}\theta_{E,l}^2\left(\frac{I_l}{I_h} - 1\right)\right], \quad (89)$$

where E_g is the energy of mutual attraction of the molecules, θ_D the Debye characteristic temperature, n_E the number of possible rotational and torsional degrees of freedom, θ_E the corresponding Einstein characteristic temperatures, M and I are the masses and moments of inertia of the molecules, and the subscripts h and l denote the heavy and the light isotopic substances. Although the isotopic difference in the van der Waals energy is shown here, in actual calculations the corresponding term in Eqn. (89) is omitted, since no data are available for estimating this difference. For $^{13}C^{16}O$–$^{12}C^{16}O$ the calculated numerical values of $(P_h - P_l)/P_l$ are about 20% smaller than the corresponding experimental values obtained by the same investigator[91]; with $^{12}C^{18}O$–$^{12}C^{16}O$, on the other hand, the calculated values are 35% greater than the experimental; while in the case of $^{13}CH_4$–$^{12}CH_4$ the calculated are about double the experimental results.

Kirschenbaum[208] calculated the vapour pressures of $^{15}N_2$ and $^{14}N_2$ for several possible models of solid nitrogen. The best approximation to the experimental data was obtained with a model in which the molecules undergo oscillations corresponding to restricted rotations.

Devyatykh[209] employed the principle of Lindemann's method to calculate the isotope effect in the vapour pressure of $^{13}C^{16}O$, $^{12}C^{18}O$, $^{13}CH_4$, $^{12}CD_4$, $H_2{}^{18}O$, and $D_2{}^{16}O$ at the temperature of the triple point; together with Shavarin[210] he made a similar calculation for ND_3 and NT_3. This work was based on the chemical potential of a given isotopic variety being the same in the solid and gas phases at equilibrium, the potential being expressed in terms of components due to the different forms of motion. Introduction of the approximations characteristic of the method and also of several other assumptions resulted in the equation

$$\ln\frac{P_h}{P_l} = \frac{3}{2}\ln\frac{M_h}{M_l} + \frac{1}{2}\ln\frac{(ABC)_h}{(ABC)_l} - \frac{h}{2kT}\sum_i(\Delta\nu_{i,h} - \Delta\nu_{i,l}) + \frac{9}{8}\frac{\theta_{k,h} - \theta_{k,l}}{T} + \frac{1}{RT}(F_{k,h} - F_{k,l}) + \frac{9}{8}\frac{\theta_{B,h} - \theta_{B,l}}{T} + \frac{1}{RT}(F_{B,h} - F_{B,l}), \quad (90)$$

where A, B, and C are the principal moments of inertia of the molecule, $\Delta\nu_i$ is the change in the ith frequency when a molecule passes from the vapour into the crystalline phase, θ_k and F_k are the characteristic temperature and the free-energy function describing the lattice vibrations

TABLE 28. Comparison of calculated and experimental values of P_h/P_l at the temperature of the triple point.

Isotope molecules	Temp. of triple point of light variety, °K	$-100(P_h - P_l)/P_l$			
		calc.	ref.	expt.	ref.
$^{13}CH_4$–$^{12}CH_4$	90.7	0.7	209	0.5	91
				1.1	107
$^{13}C^{16}O$–$^{12}C^{16}O$	68.1	1.2		1.1	91
				1.2	93
$^{12}C^{18}O$–$^{12}C^{16}O$	68.1	1.6		1.3	91
				1.9	107
$H_2{}^{18}O$–$H_2{}^{16}O$	273.2	1.2		1.1	26
$^{12}CD_4$–$^{12}CH_4$	90.5	–0.4		–1.3	121
$^{14}ND_3$–$^{14}NH_3$	195.4	21.1	210	24.8	95
$^{14}NT_3$–$^{14}NH_3$	195.4	25.6		*	
$D_2{}^{16}O$–$H_2{}^{16}O$	273.2	15.3	209	20.3	162

† It has been shown[74] that experimental data on the heat capacity C_v for H_2 and D_2 give values of $\theta_l = 105°$ and $\theta_h = 97°$. Hence it follows that the postulated proportionality between θ and $M^{-1/2}$ is incorrect for the isotopes of hydrogen.

* No experimental data. It follows from the relation $P(ND_3) = [P(NT_3) \times P(NH_3)]^{1/2}$ that $P(NT_3)/P(NH_3) = 0.566$.

of the molecules, and θ_B and F_B are the corresponding quantities for the librations of the molecules in the lattice.

The most representative quantity for judging the agreement between calculated and experimental results is evidently $(P_h - P_l)/P_l$, the values of which based on calculations[209,210] differ, in most cases in Table 28, by 10–30% from the corresponding experimental values. With tetradeuteromethane, which shows a positive isotope effect, the calculated value of this ratio is less than one-third of the experimental value.

3. CALCULATION BASED ON EVALUATION OF THE PARTITION FUNCTION BY HENKEL'S METHOD

Johns[211] has obtained good results in calculating the isotope effect in the vapour pressure of solid neon by using Henkel's method[212] for calculating the partition function Q of a solid. This method is a variant of the Einstein treatment of the crystal lattice in which allowance is made for the anharmonic character of the atomic vibrations. Henkel assumed that the potential energy of an atom with respect to another, identical atom at a distance r is of the form

$$U = \frac{A}{r^n} - \frac{B}{r^6}, \qquad (91)$$

and he expressed the partition function Q as a function of r, n, A, and B. Agreement between calculated and experimental values is governed by suitable choice of values for the last three quantities. For neon Johns took the values: $n = 14$, $A = 0.373 \times 10^{-119}$ erg cm^{14}, and $B = 0.90 \times 10^{-59}$ erg cm^6, which are close to values used earlier[213]. The procedure for calculating the partition function has been set out in detail[211,212], and will be omitted here. The free energy at constant volume A of a solid is calculated from this function by means of the well-known formula

$$A = -RT \ln Q. \qquad (92)$$

The solid–vapour equilibrium was then considered by Johns[211], the isotopic difference in free energy at constant pressure for the solid phases being put equal to the corresponding difference for the vapours. It was then postulated that the deviation of the vapours from ideal gas behaviour can be neglected, and that the difference in free energy at constant pressure for the solids can be replaced by the corresponding difference in free energy at constant volume. The isotope effect in the vapour pressure is then calculated from the equation

$$\ln \frac{P_h}{P_l} = \frac{F_h - F_l}{RT} + \frac{3}{2} \ln \frac{M_h}{M_l}. \qquad (93)$$

It is seen from Table 3 that results obtained in this way for the isotopes of neon agree far better with the experimental data than do values calculated by Lindemann's method. However, the Henkel–Johns method is applicable only to monatomic solids, and moreover its application is very restricted owing to the absence of data on the quantities n, A, and B in the Lennard-Jones expression, Eqn.(91), for the potential.

4. DE BOER'S METHOD

Another interesting, semi-empirical method of calculation has been developed by de Boer on the basis of his quantum theory of corresponding states[214-216], and used by him to predict the vapour pressure of the light isotope of helium. According to this theory, the field of two molecules is described by a somewhat modified Lennard-Jones potential[217]

$$\varphi(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \qquad (94)$$

where r is the distance between the molecular centres, ϵ the absolute interaction energy at the minimum on the potential-energy curve, and σ the intermolecular distance when $\varphi = 0$. The quantities ϵ and σ are used to express the thermodynamic variables in "molecular units": temperature in the form ϵ/k, pressure as ϵ/σ^3, and molar volume as $N\sigma^3$, where N is the Avogadro number and k the Boltzmann constant. Dimensionless reduced values of the temperature, pressure, and volume are then introduced, these being the ratios of the ordinary values to the corresponding values in molecular units

$$T^* = T/(\varepsilon/k), \quad P^* = P/(\varepsilon/\sigma^3), \quad V^* = V/(\sigma^3 N). \qquad (95)$$

An additional dimensionless quantity is introduced to take care of quantum effects — the reduced de Broglie wavelength

$$\lambda^* = \lambda/\sigma = h/(\varepsilon M)^{1/2},$$

where M is the molecular mass. The reduced equation of state is of the form

$$f(P^*, V^*, T^*, \lambda^*) = 0. \qquad (96)$$

This function is assumed to apply to all substances having the same intermolecular force law. Since, however, its form is unknown, theoretical calculation of vapour pressure by means of Eqn. (96) is impossible, and a semi-empirical method is therefore used. Values of P^* are plotted against λ^* at constant V^* and T^* for a number of substances with known vapour pressures having the same intermolecular force law as the test material. The value of P^* for the test material is then found graphically from the known value of λ^*, and finally P is determined from P^*. In this way de Boer was able, by using plots of P^* against λ^* for the inert gases, to calculate the vapour-pressure curve and the boiling point of ^{3}He a year before the first work on its liquefaction. The experimental vapour pressures obtained later[29] lay on the theoretical curve within the limits of error of the measurements.

Hammel[218] used the same method to predict the vapour pressure of tritium, but in this case the calculated and subsequent experimental[72] values differed by 25%. Maslan[219] and also Devyatykh[209] attempted to employ de Boer's method to calculate the isotope effect in the vapour pressure of oxygen, nitrogen, methane, carbon monoxide, and several other substances, but obtained poor results. Evidently this method can be used satisfactorily only in the simplest case of the inert gases.

Friedman *et al.*[220] remark that de Boer's method cannot be applied to the isotopes of hydrogen, since their molecules are not spherical, and hence cannot be compared in thermodynamic properties with the inert gases. A still more specialised empirical method was employed[220] to calculate the vapour pressures of HD and HT, based on the hypothesis that the phase transformation temperatures for all the isotopic varieties of hydrogen are inversely proportional to the square roots of the molecular weights. Appropriate graphs plotted from experimental data for H_2, D_2, and T_2 were used to determine the melting and boiling points of HD and HT, and equations of the type $\log P = A + B/T$ were set up based on these values. Since the molecular weights of HT and D_2 are identical, identical values were

obtained for the corresponding phase transformation temperatures and vapour pressures. As, however, subsequent experimental results [82] showed that at ~20°K the vapour pressure of HT is about 45% greater than that of D_2, the method of calculation employed by Friedman *et al.*[220] is evidently unsound.

According to Babloyantz[221] the difference in thermodynamic properties between HT and D_2 is due to the fact that, while the total mass is identical, its distribution between the two atoms is different. Quantum-mechanical calculation shows that the energy of the ground state is greater for ensembles of heteronuclear molecules than for those of homonuclear molecules, so that the corresponding equations of state are different.

5. INTERPRETATION OF THE NATURE OF THE ISOTOPE EFFECT

The calculations of the isotope effect in vapour pressure by Lindemann's method discussed above also make clear the corresponding interpretation of the nature of this effect with monatomic solids. Since $M_h > M_l$ and $\theta_h/\theta_l = (M_l/M_h)^{1/2}$, the term in Eqn. (85) representing the isotopic difference in zero-point energies is negative, while the integral involving the difference in heat capacities and the logarithmic term in the equation are positive. Hence according to Eqn. (85) a lower vapour pressure of the heavy compared with the light substance is due to the effect of the isotopic difference in zero-point energy and heat capacity on the ratio P_h/P_l predominating over the direct effect of the difference in mass. In other words, a negative isotope effect in the vapour pressure of a monatomic solid is explained by a lower zero-point energy and a greater heat capacity, and thus a greater heat of evaporation of the heavy substance, the zero-point energy being the principal factor at low temperatures.

As mentioned above, calculations by Lindemann's method gave to a first approximation a correct result for the vapour pressure of the isotopes of neon. Corresponding principles and approximations proved to be applicable also to some complicated substances in the solid state, such as varieties of methane and carbon monoxide isotopic with respect to carbon and oxygen. With deuterium and hydrogen at the temperature of the triple point of the latter, however, calculation led to a value of P_h/P_l which was about three times as great as the experimental value. Calculation also proved unsatisfactory for methane and tetradeuteromethane (Table 28), an example of a positive isotope effect. It is therefore clear that some important factors have been ignored in the above explanation of the difference in vapour pressure between isotopic substances.

An original interpretation of a positive isotope effect has been suggested by Bradley[222]. He starts from the dependence of vapour pressure on the entropy and the heat of evaporation, and considers only the translational entropy S_{tr} of the molecules in the vapour. The quantity $(S_h - S_l)$ is then positive, since $M_h > M_l$. The difference in heats of evaporation $(\Delta H_h - \Delta H_l)_e$ is also positive, since it is equated to the corresponding difference in zero-point energies of the quasi-oscillations in the liquid state with the opposite sign $[-(E_{0,h} - E_{0,l})]$. Hence it follows from the equation

$$\ln(P_h/P_l) = (\Delta S^0_h - \Delta S^0_l)_e /R - (\Delta H_h - \Delta H_l)_e /RT, \qquad (97)$$

where S^0 is the entropy when $P = 1$, that P_h can be either greater than or less than P_l depending on the ratio of the absolute magnitudes of the entropy and enthalpy terms.

Bradley further assumes that the zero-point energy considered here can be represented as a sum of zero-point energies of the quasi-oscillations corresponding to interaction between different pairs of atoms in two neighbouring molecules. He also introduces the idea that, with complicated molecules having a central atom, such as CCl_4, $CHCl_3$, and CH_3OH, the intermolecular interaction is governed mainly by the outer atoms, since the central atom is screened by them. Therefore replacement of the central atom by a heavy analogue, *e.g.* substitution of ^{13}C for ^{12}C in the above substances, produces an increase in entropy of the vapour, but does not affect the intermolecular interaction. In such a case the isotopic difference in zero-point energies of the quasi-vibrations should, in Bradley's opinion, be disregarded, so that the difference in heat of evaporation between heavy and light varieties will be zero, with the result that $P_h > P_l$.

In cases of the substitution of a peripheral atom by its heavy analogue, for example, in the replacement of ^{36}Cl by ^{37}Cl in $CHCl_3$ or CCl_4, however, the enthalpy term in Eqn. (97) will, according to Bradley, be numerically greater than the entropy term, so that $P_h < P_l$. The relative difference between these quantities is greater the lighter the peripheral atom which is replaced and the stronger the intermolecular interaction. An explanation on these lines has been given[222] for the experiments of Baertschi *et al.*[143] on the fractionation of CCl_4, $CHCl_3$, C_6H_6, and CH_3OH reported above, in which a positive isotope effect was observed with respect to carbon, but a negative effect with respect to chlorine and oxygen.

However, Bradley's treatment evidently cannot be regarded as satisfactory. Firstly, it does not agree with the experimental results for a number of substances. Thus the postulated decrease in vapour pressure when peripheral atoms are replaced by their heavy analogues contradicts the facts of an increase in vapour pressure when hydrogen is replaced by deuterium in methane, silanes, germanes, halogenated hydrocarbons, and the methyl group of methanol; the assumed increase in vapour pressure when the central atom is replaced by its heavy isotope does not agree with the decrease in vapour pressure accompanying replacement of ^{12}C by ^{13}C in methane, ethylene, and ethane, nor with the similar effect of substituting ^{15}N for ^{14}N in ammonia. Moreover, in the case of substitution of the central atom, when according to the above treatment $(\Delta H_h - \Delta H_l)_e = 0$, it follows from Eqn. (97) that the sign of the isotope effect is independent of the temperature. According, however, to published results[135], the vapour pressure of $^{11}BCl_3$ is lower than that of $^{10}BCl_3$ below 211.5°K, whereas above this temperature the opposite effect is observed.

Secondly, neglect of the isotopic difference in entropy of the liquid, and also of the isotopic difference in zero-point energies of the quasi-oscillations on substitution of the central atom, has no theoretical basis. Finally, as will be shown below, the difference in heats of evaporation of heavy and light varieties of molecules cannot be reduced solely to a difference in the zero-point energies of the quasi-oscillations.

Since the electron shells of isotopes are identical, it is usually considered that the molecular interaction between isotopic molecules is identical. In particular, this assumption has been made in Lindemann's method of calculating

the isotope effect in vapour pressure described above. However, as has been shown[114,223-228], the isotopic difference in the energy of intermolecular dispersion forces is substantial. Baertschi and Kuhn[114] consider that the dispersion energy should be smaller for heavy than for light molecules, since the former show lower infra-red frequencies for the intramolecular vibrations involving isotopic atoms.

According to London[230] the energy of dispersion interaction E_d between two molecules of different type is given by the formula

$$E_d = -\frac{3}{2}\frac{h}{r^6}\sum_{i,k}\alpha_{1,i}\alpha_{2,k}\frac{\nu_{1,i}\ \nu_{2,k}}{\nu_{1,i}+\nu_{2,k}}, \qquad (98)$$

where $\nu_{1,i}$ and $\nu_{2,k}$ are the frequencies of the absorption bands, and $\alpha_{1,i}$ and $\alpha_{2,k}$ the corresponding polarisability components, for molecules 1 and 2. Only absorption bands in the visible and ultra-violet regions are usually considered, since the contribution of other frequencies to the interaction energy is much smaller. We therefore use the simpler formula

$$E_d = -\frac{3}{2}\frac{\alpha_{1,0}\alpha_{2,0}}{r^6}h\frac{\nu_{1,0}\ \nu_{2,0}}{\nu_{1,0}+\nu_{2,0}}, \qquad (99)$$

where $\nu_{1,0}$ and $\nu_{2,0}$ are the mean sums of the optical frequencies, the products $h\nu_0$ being roughly equal to the ionisation potentials of the given molecules, and $\alpha_{1,0}$ and $\alpha_{2,0}$ are the sums of the static polarisabilities associated with the optical frequencies.

Baertschi and Kuhn[114] assume that both these frequencies and the corresponding electron polarisabilities have very similar values in heavy and light varieties of molecules, and can be regarded as identical. It is, however, necessary to take into account the difference in infra-red frequencies if isotopic atoms take part in the corresponding vibrations. When such an infra-red frequency $\nu_{2,R}$ is present in one of the interacting molecules, corresponding to a polarisability $\alpha_{2,R}$, Eqn. (99) is replaced by

$$E_d = -\frac{3}{2}\left[\frac{\alpha_{1,0}\alpha_{2,0}}{r^6}h\frac{\nu_{1,0}\ \nu_{2,0}}{\nu_{1,0}+\nu_{2,0}} + \frac{\alpha_{1,0}\ \alpha_{2R}h}{r^6}\frac{\nu_{1,0}\ \nu_{2,R}}{\nu_{1,0}+\nu_{2,R}}\right]. \qquad (100)$$

Since $\nu_{2,R} \ll \nu_{1,0}$ the second term on the right-hand side of Eqn. (100) is proportional to $\nu_{2,R}$. When the two interacting molecules are identical and have an infra-red absorption which is identical in frequency and intensity, we obtain to a first approximation:

$$E_{h,d} = -\frac{3h}{4}\frac{\alpha_{1,0}^2}{r^6}\left[1+4\frac{\nu_{h,R}\ \alpha_{1,R}}{\nu_{1,0}\ \alpha_{1,0}}\right] \qquad (101)$$

Here $E_{h,d}$ is the energy of dispersion interaction between two heavy molecules, and $\nu_{h,R}$ is their infra-red vibration frequency in question; the corresponding polarisability $\alpha_{h,R}$ for the heavy molecule is regarded as equal to the value $\alpha_{1,R}$ for the light molecule. For two light molecules having an interaction energy of $E_{1,d}$ the quantity $\nu_{h,R}$ in Eqn. (101) is replaced by $\nu_{1,R}$. It is further assumed that the difference in the forces of attraction of heavy and light molecules affects the equilibrium intermolecular distance, and that this causes a difference in the energy of repulsion. The isotopic difference in the quantity E_d is equated, with suitable correction, to the isotopic difference in absolute magnitude of the heats of evaporation, yielding after some rearrangement

$$(\Delta H_h - \Delta H_l)_e = 8(\Delta H_l)_e \cdot \alpha_{1,R}(\nu_{h,R} - \nu_{1,R})/\nu_{1,0}\ \alpha_{1,0}. \qquad (102)$$

It is then assumed[114] that at temperatures well above the Debye characteristic temperature ($\theta = h\nu_D/k$) the effects on the value of P_h/P_l of all factors other than the isotopic difference in dispersion energy cancel out, and this ratio is evaluated from the formula:

$$\ln(P_h/P_l)_R = -(\Delta H_h - \Delta H_l)_e/RT. \qquad (103)$$

Calculated and experimental values of $(P_h - P_l)/P_l$ differ by a factor of 1.5–2. This discrepancy must be explained by the crude approximations made in the calculations, in particular the neglect of the isotopic difference in zero-point energy of the molecular oscillations in the liquid lattice. However, the fact that calculated and experimental results agree in sign and order of magnitude is evidently an important justification for the view that the main reason for the higher vapour pressure of the heavy compared with the light varieties of molecules is the smaller energy of dispersion interaction with the former (Table 29).

It is assumed[114] that above the Debye characteristic temperature a negative isotope effect caused by the difference in zero-point energy of the molecular vibrations decreases as T^{-2}, whereas a positive effect, caused by a difference in van der Waals interaction, decreases as T^{-1} at temperatures below $h\nu_{1,R}/k$. Thus over the range $\theta < T < h\nu_{1,R}/k$ the positive effect decreases with rise in temperature more slowly than does the negative effect, which explains several cases of a change in sign of the isotopic difference in vapour pressure.

According to the treatment of Baertschi and Kuhn[114], the polarisabilities of isotopic substances are identical, which applies to both atom and electron polarisabilities. However, this does not agree with experiment. A difference between α_h and α_l in gases was observed long ago by Larsen[231], and a similar effect has been established for liquids by Rabinovich and Volokhova[224].

The idea of a difference in the dispersion interaction of heavy and light molecules has been developed by us[223-228] using a different theoretical approach to the problem from that of Baertschi and Kuhn[114], and we have been the first to provide a broad experimental basis for this isotopic effect. In particular, we have established that the decrease in dispersion interaction when hydrogen is replaced by deuterium is responsible for the accompanying decrease in electron polarisability[224] and the critical temperature[225] and the increase in compressibility[227].

TABLE 29. Results of calculations based on Eqns. (102) and (103).

Isotope substances	$100(P_h - P_l)/P_l$ at normal b.p.		
	calc. from ref. 114	expt.	ref.
$^{13}CCl_4/^{12}CCl_4$	0.28	0.13	143
$^{13}CS_2/^{12}CS_2$	0.16	0.1	114
$^{11}BCl_3/^{10}BCl_3$	0.6	0.3	135
$^{11}BF_3/^{10}BF_3$	1.2	0.8	13
C_6D_6/C_6H_6	3.5	2.5	129

The present reviewer has suggested the following interpretation of the isotope effect in the vapour pressure of liquids, which, although qualitative, does explain a number of fundamental characteristics of this phenomenon.

It follows from the fact that the free energies of the liquid (L) and the vapour (G) are equal that:

$$\log(P_h/P_l) = -\frac{1}{RT}(\Delta H_h - \Delta H_l)_e + \frac{1}{R}[(S_h^0 - S_l^0)_G - (S_h^0 - S_l^0)_L], \quad (104)$$

where the difference in enthalpy between the equilibrium phases has been replaced by the heat of evaporation ΔHe, and S^0 is the entropy at $P = 1$. The heat of evaporation can be regarded as the sum of the work of expansion and the energy of intermolecular interaction (in absolute magnitude) less the zero-point energy of the quasi-oscillations of the molecules in the liquid phase $E_{0,q}$. However, the work of expansion is approximately RT for both substances, and is eliminated from Eqn. (104). The interaction energy, in its turn, is the sum of the dispersion, orientation, and polarisation energies and in some cases also the energy of association by means of a hydrogen bond (U_{ass}). As a result, Eqn. (104) becomes

$$\ln(P_h/P_l) = \frac{1}{RT}[\underset{(1)}{(E_{0,h} - E_{0,l})_q} \underset{(2)}{- K'(\alpha_h^{3/2} r_h^{-6} - \alpha_l^{3/2} r_l^{-6})} \underset{(3)}{- K''(r_h^{-6} - r_l^{-6})} - \underset{(4)}{K'''(\alpha_h r_h^{-6} - \alpha_l r_l^{-6})} \underset{(5)}{- (U_h - U_l)_{ass}}] + \frac{1}{R}[\underset{(6)}{(S_h^0 - S_l^0)_G - (S_h^0 - S_l^0)_L}]. \quad (105)$$

Here the dispersion energy (*2*) is expressed by the Slater–Kirkwood formula[229], with $K' = (3eh/8\pi)(n/m)^{1/2}$, h being Planck's constant, e and m the charge and the mass of the electron, n the total number of valency electrons belonging to all the atoms in the molecule, α the static electron polarisability, and r the distance between the molecules. Isotopic differences in the orientation (*3*) and polarisation (*4*) energies are expressed by means of the appropriate well-known formulae of Keesom and of Debye and Falkenhagen: $K'' = -2d_l^4/3kT$ and $K''' = -2d_l^2$, where d is the dipole moment, it being assumed that to a first approximation $d_h = d_l$‡. The individual terms in Eqn. (105) have the following effects on the ratio P_h/P_l.

(a) The Quantity $(E_{0,h} - E_{0,l})_q$

This quantity is always negative, which depresses P_h relative to P_l. The effect of the van der Waals interaction energy – terms (*2*)-(*4*) in Eqn. (105) – depends on the isotopic difference in polarisability and the intermolecular distance.

(b) Isotopic Difference in Polarisability[224]

Since replacement of a light by a heavy isotope involves a decrease in the zero-point energy of the atomic vibrations E_0, whereas the electronic potential energy curve and the force constants of the bonds (f) remain practically unchanged[25,237], the polarisability is diminished. Thus in the simplest case of a diatomic molecule it is found by making certain approximations that the lowering of the vibrational levels in the electronic spectra causes an increase in energy of the electronic transitions (E^e) from the ground (0) to an excited (i) level. By neglecting the difference in electronic energy between light and heavy compounds at the same i levels, and also disregarding the difference in rotational energy, since its absolute magnitude is small compared with the difference in vibrational energy, we obtain

$$\Delta E^e = (E_h^e)_{0,i} - (E_l^e)_{0,i} = (E_{0,l} - E_{0,h})_0 - (E_{0,l} - E_{0,h})_i. \quad (106)$$

For the isotopic difference in E_0 we have approximately, omitting terms of higher order[25,237]:

$$E_{0,l} - E_{0,h} = {}^1/_2 h\nu_{0,l}(1-\zeta) - {}^1/_4 h\nu_{0,l} x_0 (1-\zeta^2) = \frac{h}{4\pi}\mu_l^{-1/2} f^{1/2}[(1-\zeta) - \frac{x_0}{2}(1-\zeta^2)], \quad (107)$$

where μ is the reduced mass, x_0 the anharmonicity constant, and $\zeta = (\mu_l/\mu_h)$. Hence it follows from Eqn. (106) that:

$$\Delta E^e = \frac{h}{4\pi}\mu^{-1/2}(f_0^{1/2} - f_i^{1/2}) \cdot [(1-\zeta) - \frac{x_0}{2}(1-\zeta^2)]. \quad (108)$$

Since $f_0 > f_i$, $(1-\zeta)$ and $(1-\zeta^2)$ are positive and of the same order of magnitude, and x_0 is of the order 0.01,[25,237] we have from Eqn. (108):

$$\Delta E^e > 0 \text{ or } \nu_{i,h}^e > \nu_{i,l}^e, \quad (109)$$

where ν_i^e is the frequency of the electronic transition. The relations (109) are probably valid also for a polyatomic molecule. This opinion was apparently held by Ingold *et al.*[128], since they used fundamentally the same arguments as given above for a diatomic molecule, but in a cruder form, to explain the decrease in the polarisability of benzene observed when hydrogen is replaced by deuterium. Urey and Teal[238] explained the smaller polarisability of heavy water compared with ordinary water also by the inequality $\nu_{i,h}^e > \nu_{i,l}^e$. This relation is supported also by spectroscopic data[239-243]. The electron polarisability is given by the formula[244]

$$\alpha = \frac{2}{h}\sum \frac{\nu_i^e P_i^2}{(\nu_i^e)^2 - \nu^2}, \quad (110)$$

where P_i^2 are the probabilities of electron transitions, and ν is the frequency of the incident light. Since the electron shells of isotopic molecules are identical, $P_{i,h}^2 \simeq P_{i,l}^2$. From Eqn. (110) we obtain for the polarisability α_i at level i:

$$\frac{\alpha_{i,h}}{d_{i,l}} = \frac{\nu_{i,l}^e - \nu^2/\nu_{i,l}^e}{\nu_{i,h}^e - \nu^2/\nu_{i,h}^e}. \quad (111)$$

Since $\nu_{i,l}^e < \nu_{i,h}^e$, and for colourless substances $\nu_i^e > \nu$, it follows from Eqn. (111) that $\alpha_{i,h} < \alpha_{i,l}$. In view of this, it is probable that in general

$$\alpha_h < \alpha_l. \quad (112)$$

This has been confirmed experimentally: it has been shown that replacement of hydrogen by deuterium in hydrocarbons and their nitro- and halogeno-derivatives, water, alcohols, and acids, produces a decrease in the electron polarisability of a few tenths of 1%, depending on the number of atoms substituted[224].

(c) and (d) Isotopic Difference in Intermolecular Distances[226]

The decrease in the zero-point energy of the molecular vibrations on replacement of a light isotope by a heavy iso-

‡ The isotopic difference in the energy of repulsion of the molecules is neglected.

tope causes a decrease in molar volume, *i.e.* in the intermolecular distance r. This has been proved rigorously by London[245] for monatomic and diatomic substances in the solid phase, and also by Schäfer[246] for solid hydrogen in particular. The effect has been observed experimentally with the pairs H_2-D_2,[74] $^6Li-^7Li$,[247] $^6LiF-^7LiF$,[248] NaH–NaD, KH–KD, and LiH–LiD.[249] An increase in mass of the particles should cause a decrease in molar volume in the liquid phase as well, since here, too, vibrations play the main part in molecular motion. The isotopic change in r should be especially large for substances of low molecular weight at low temperatures, *e.g.* for helium and hydrogen, with which the zero-point energy of the quasi-oscillations and also its isotopic difference form a large fraction of the total energy of these vibrations§. According to the experimental data, the molar volume of ^4He at 2°K is 29% less than that of ^3He, and with D_2 at 20°K the molar volume is 17% lower than with H_2.[250] On the other hand, since intermolecular dispersion forces depend on the electron polarisability, it may be supposed from Eqn. (112) that these forces will become weaker when a light isotope is replaced by a heavy one, and this will increase the distance between the molecules. However, the isotopic increase in r evidently predominates over its decrease only at elevated temperatures, when the influence of the zero-point energy of the quasi-vibrations of the molecules is insignificant. Thus at about 300°K the molar volumes (V) of C_6D_6 and C_6D_{12} are still 0.2–0.3% smaller than those of C_6H_6 and C_6H_{12} respectively[251].

With substances which are associated by hydrogen bonds an additional factor enters into the isotopic change in r. As pointed out by Samoilov[253,254], even in solids, when the closeness of packing of the atoms is low it can be increased by introducing some disorder into their arrangement. Such a phenomenon is especially probable with molecular liquids. In them, formation of a lattice or other ordered arrangement is evidently associated with increasing deviations from the closest packing of the molecules, and consequently with some expansion. Water represents a clear example of such behaviour. Because of this, an increased degree of association when the hydrogen forming the hydrogen bond is replaced by deuterium can cause some increase in the mean intermolecular distance. This is supported by the experimental results: such substitution produces an increase in molar volume in water[162], hydrogen peroxide[255], methanol[256], and other alcohols[226] even in the vicinity of 300°K, far below the corresponding critical temperatures.

(e) Isotopic Difference in Energy of Association[236]

Substitution of deuterium for hydrogen forming a hydrogen bond produces a decrease in the zero-point energy of the vibrations corresponding to this bond. With a characteristic frequency of 175 cm^{-1}, for the OH ... O bond[257], for example, an approximate calculation shows that $\Delta E_0 = E_{0,H} - E_{0,D} = 3 \times 10^{-16}$ erg per molecule. Further, very roughly:

$$\bar{n}_D/\bar{n}_H = e^{(U_H - U_D)/kT} = e^{-\Delta E_0/kT}, \qquad (113)$$

where n is the number of molecules remaining unassociated and U the energy of the bond. According to data of Oster and Kirkwood[258], the mean number of hydrogen bonds linking a molecule in a chain is about 1.4 for monohydric alcohols from methanol to pentanol; in the three-dimensional network of water at about 300°K each molecule has on the average ~2 hydrogen bonds[259,260]. Assuming that the number of "unruptured" bonds exceeds the number of "ruptured" bonds by a factor of at most a few units¶, we find that replacement of hydrogen by deuterium produces an increase in the energy of association of a few tens of calories per mole. On the basis of Swain and Bader's work[252] it can be supposed that in several cases a considerably greater difference in the intermolecular energy of isotopic associated substances can be caused by a difference in the rotational frequencies of their molecules. Statistical calculation[252] has shown that the difference in libration frequencies of the molecules H_2O (three frequencies each of 667 cm^{-1}) and D_2O (483 cm^{-1}) corresponds to a difference in enthalpy between these substances of several hundred calories per mole. This is confirmed by the fact that the heat of evaporation is about 100 cal $mole^{-1}$ greater with monohydric deuteroalcohols than with their hydrogen analogues[148,150,151] and it is 330 cal $mole^{-1}$ greater with heavy water than with ordinary water (at 25°)[162]. An increase in the degree of association of alcohols on replacement of the hydroxyl hydrogen by deuterium has been shown also by cryoscopic measurements[263], by data on the isotope effect in viscosity[236], and by spectroscopic data[262].

(f) Entropy Component

The component entropies due to the various forms of motion in the vapour and the liquid are increased when a light isotope is replaced by a heavy isotope, since both the masses and the moments of inertia of the molecule are increased, and the frequencies of the atomic and molecular vibrations are decreased. However, entropy terms relating to atomic vibrations can, to a first approximation, be eliminated from Eqn. (105) if the difference in frequencies between identical atoms in the vapour and in the liquid is neglected. In view of this, it can be supposed that the isotopic difference in entropy of motion of the molecules in the liquid has been subtracted from the corresponding difference for the vapour phase in term (6) of Eqn. (105). It is possible that, to a first approximation, these differences have similar values, and practically balance one another, as has been assumed[114]. However, it is also probable that the isotopic difference in entropy is appreciably greater for the vapour than for the liquid, and this, according to Eqn. (105), will cause some increase in P_h relative to P_l.

The joint influence of the above factors (a)–(f), with their varying dependence on the temperature, the nature of the substance, the mass of the molecule, and the number and mass of the isotopic atoms, results in the isotope effect in vapour pressure manifesting itself in a variety of ways. With substances of low molecular (atomic) weight at low temperatures, when r_h is considerably smaller than r_l, the decrease in intermolecular distance on substitution of a light by a heavy isotope affects the dispersion energy

§ The zero-point energy of liquid ^4He is about 50–70 cal $mole^{-1}$, while its actual thermal energy at the critical temperature (5.2°K) is only ~10 cal $mole^{-1}$. The rather lower value of r_h compared with r_l is probably due to the fact that the vibrations are less anharmonic with the heavy than with the light molecules.

¶ In water, for example, 10–15% of the hydrogen bonds have already been ruptured on melting[254,261], and the number of ruptured bonds increases with rise in temperature.

to a greater extent than does the decrease in polarisability†. Therefore the terms (2)–(4) in Eqn. (105) are positive and, like term (1), cause a decrease in P_h relative to P_l.

If the entropy term in Eqn. (105) is assumed to be small compared with the enthalpy terms, a comparatively large negative isotope effect in the vapour pressure ($P_h < P_l$) should be observed with a low molecular weight at low temperatures. This is confirmed experimentally in the cases of hydrogen and helium (Tables 1 and 4). This also explains the negative isotope effect with other non-associated substances at comparatively low or reduced temperatures.

Since at an absolute temperature of a few hundred degrees $r_h \simeq r_l$ or $r_h > r_l$,[226] it follows from Eqn. (112) that the terms (2) and (4) in Eqn. (105) are negative, while term (3) is negative or close to zero. Hence the terms (2)–(4) and perhaps also (6) in Eqn. (105) cause an increase in P_h relative to P_l, whereas term (1), as before, affects the vapour pressure in the opposite direction. Consequently, at such temperatures the sign of the isotope effect in the vapour pressure of non-associated substances depends on the relative absolute magnitudes of terms (2)–(4) and (1) in Eqn. (105), and both $P_h > P_l$ and $P_h < P_l$ are possible. Since the role of vibrations in the thermal motion of molecules in a liquid diminishes rapidly with rise in temperature‡, the relation $P_h < P_l$ should be observed at lower temperatures than $P_h > P_l$, with respect to the same isotopes in the same substance. Every substance should have a temperature above which $P_h > P_l$, provided that this transition does not lie above the critical point. As has been shown in section A of the present review, all this has been established experimentally for a number of substances.

The above treatment of the isotopic difference in vapour pressure can be used to give a qualitative explanation of the occurrence of opposite effects for different isotopic substitutions in the same substance, such as the cases of chloroform and carbon tetrachloride described above, in which $P_h > P_l$ with respect to ^{12}C–^{13}C but $P_h < P_l$ with respect to ^{35}Cl–^{37}Cl (Table 20). With these substances, isotopic substitution of a chlorine atom produces a change in the zero-point energy of one atomic vibration, but substitution of carbon affects four such vibrations, each of them being associated with a greater change in E_0 than in the case of the chlorine isotopes. In view of Eqns. (106)–(111) it can be assumed that replacement of ^{12}C produces a greater decrease in electron polarisability, and hence a greater reduction in the intermolecular dispersion energy, a factor which tends to raise the vapour pressure. On the other hand, the decrease in zero-point energy of the quasi-oscillations of the molecules, a factor tending to lower the vapour pressure, is greater on isotopic replacement of ^{35}Cl than when ^{12}C is replaced.

In another case, that of isotopic substitutions in liquid methane, the experimental results relate to temperatures of 90°–110°K, which are considerably lower than in the cases of CCl_4 and $CHCl_3$. Therefore the decrease in the zero-point energy of the quasi-oscillations of the molecules plays a greater part with methane, and replacement of ^{12}C by ^{13}C still produces a decrease in vapour pressure, but this effect diminishes with rise in temperature. When, however, a hydrogen atom is replaced by deuterium, the decrease in zero-point energy of the corresponding atomic vibration is much greater, while the decrease in zero-point energy of the quasi-oscillations of the molecules is the same as for the isotopic replacement of carbon, and $P_h < P_l$ up to about 97°K, whereas above this temperature $P_h > P_l$. When all four hydrogen atoms are replaced by deuterium, the relation $P_h > P_l$ is already observed above 75°, up to the melting point (Table 11 and Fig. 3).

It has been shown above that the energy of association, term (5) in Eqn. (105), is increased by substitution of deuterium for the hydrogen forming a hydrogen bond by which a substance is associated in the liquid phase, while its vapour is monomeric, and the heat of evaporation is thereby increased by tens of calories per mole. This effect is opposite in sign to the isotopic change in van der Waals interaction energy, and can be shown to be several times greater than the latter in absolute magnitude. In this way term (5) affects the vapour pressure in the same direction as term (1) and, taking into account the above remarks on the role of the entropy term in Eqn. (105), we find that $P_h < P_l$ over the temperature range within which association persists in the liquid phase. This explains the decrease in vapour pressure when hydrogen is replaced by deuterium in water, ammonia, the hydroxyl groups of alcohols, the amino-group of aniline, and in other similar cases (Fig. 13). This interpretation is confirmed by the fact that substitution of deuterium for the methyl hydrogen in methyl alcohol produces the opposite effect — an increase in vapour pressure[148].

With rise in temperature the degree of association decreases and consequently the influence of association on the isotope effect should also diminish. This will explain the fact that with heavy and ordinary water $P_h < P_l$ only up to 225°, whereas the opposite relation is observed above this temperature. It is evident that above 225° water is hardly, if at all, associated. Similar temperatures at which $P_h > P_l$ as with non-associated substances, can probably be found for alcohols and amines in which the hydrogen forming a hydrogen bond is replaced by deuterium. Bernal and Fowler[265] have shown that in a number of cases the dissolution of electrolytes in water has a similar effect on its structure to that of a rise in temperature. It is now clear[254] that such electrolytes produce a decrease in the activation energy for the passage of molecules from one equilibrium position to another, which is equivalent to an increase in the number of hydrogen bonds ruptured. Solutions of these substances in ordinary and heavy water should therefore have a lower temperature of intersection of the vapour pressure curves than have the pure solvents. In other words, dissolution of appropriate electrolytes should lower the temperature above which the relation $P_h > P_l$, characteristic of non-associated substances at moderate and elevated temperatures, is observed for D_2O and H_2O. Phenomena which confirm this experimentally[168] have been described in section A of the present review. In cases in which hydrogen forming a hydrogen bond is replaced by deuterium in compounds which show considerable association in the gas phase as well, consideration

† As Schäfer[246] has shown, owing to the greater distance between H_2 molecules compared with D_2 molecules, the interaction energy at $T = 0$ is −460 cal mole^{-1} for H_2, whereas it is −520 cal mole^{-1} for D_2 (its value at the potential-energy minimum is −560 cal mole^{-1}). If the zero-point energy of $9R\theta_D/8$, ~ 235 cal mole^{-1} for H_2 and ~ 215 cal mole^{-1} for D_2, is added to the above energy, almost correct values are obtained for the heats of sublimation at $T = 0$; 225 and 305 cal mole^{-1} for H_2 and D_2 respectively.

‡ According to Frenkel'[264], $\tau = \tau_0 U/kT$, where τ is the duration of the vibrations of the molecule between two transitions from one position of equilibrium to another, τ_0 is the period of the vibrations, and U the activation energy of the transition.

must be given to the combined effects of two factors: (1) an increase in the energy of rupture of the hydrogen bond, and (2) a decrease in the proportion of associated complexes which decompose on evaporation. The first of these factors, by increasing the heat of evaporation, produces a decrease in vapour pressure; whereas the second factor, which is a consequence of the first, by decreasing the heat of evaporation produces an increase in vapour pressure. Since the proportion of aggregates decomposed depends exponentially on the bonding energy, the effect of the second factor should predominate. This is confirmed by experiment: with carboxylic acids containing deuterium in the carboxyl and with hydrogen fluoride it is found that $P_h > P_l$ at all the temperatures investigated. The fact that the curve showing the variation with temperature of the ratio P_h/P_l for acids passes through a maximum (Fig. 11) can be explained by the temperature dependence of the degree of association in the vapour§.

Such a treatment of the isotope effect in carboxylic acids is also supported by the fact that, as Potter *et al.*[268] have calculated from experimental data on the temperature dependence of vapour density, the heat of dimerisation of CD_3COOD is about 300 cal mole^{-1} greater than that of CH_3COOH, while the dimerisation constant in the vapour at 120° is 1.17 times greater in the former than in the latter compound.

§ The strengthening of a hydrogen bond when the hydrogen is replaced by deuterium, and also the reason for the accompanying change in vapour pressure of alcohols and acids, were first pointed out by Lewis and his coworkers[266,267].

1. W. N. Keesom and H. van Dijk, Proc. Acad. Amsterdam, 34, 42 (1931).
2. W. N. Keesom, H. van Dijk, and J. Haantjes, Proc. Acad. Amsterdam, 36, 248 (1933).
3. H. C. Urey, F. C. Brickwedde, and G. M. Murphy, Phys. Rev., 39, 164, 864 (1932); 40, 1 (1932).
4. R. B. Scott and F. G. Brickwedde, Phys. Rev., 48, 483 (1935).
5. M. P. Malkov, A. G. Zel'dovich, A. V. Fradkov, and I. V. Danilov, "Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958" (Translated into Russian), "Doklady Sovetskikh Uchenykh" (Papers by Soviet Scientists), Izd. Glav. Upr. Ispol'z. Atom. Energ. Moscow, 1959, Dokl. No. 2323.
6. A. Klemm, Atomwirtschaft, 3, 341 (1958); Chem. Ind., 10, 712 (1958).
7. M. Benedict, "Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1955"(Translated into Russian), Vol. 8, Metallurgizdat, 1958, p. 435.
8. P. Baertschi and W. Kuhn, "Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1955" (Translated into Russian), Vol. 8, Metallurgizdat, 1958, p. 180.
9. A. I. Brodskii, O. K. Skarre, and V. A. Aleksandrovich, Zhur. Fiz. Khim., 10, 538 (1937).
10. J. P. Huffman and H. C. Urey, Ind. Eng. Chem., 29, 531 (1937).
11. O. V. Uvarov, V. A. Sokol'skii, and N. M. Zhavoronkov, Khim. Prom., No. 7, 404 (1956).
12. N. M. Zhavoronkov, O. V. Uvarov, and S. I. Babkov, in the Symposium, "Trudy Vsesoyuznoi Nauchno-tekhnicheskii Konferentsii po Primeneniyu Radioaktivnykh i Stabil'nykh Izotopov i Izluchenii v Narodnom Khozyaistve i Nauke" (Proceedings of the All-Union Scientific and Technical Conference on the Application of Radioactive and Stabilised Isotopes and of Radiations in the National Economy and in Science), Izd. Akad. Nauk SSSR, Moscow, 1958.
13. N. N. Sevryugova, O. V. Uvarov, S. I. Babkov, G. N. Chernykh, V. A. Sokol'skii, and N. M. Zhavoronkov, "8 Mendeleevskii S'ezd, Referaty Dokladov i Soobshchenii" (Eighth Mendeleev Congress, Abstracts of Papers and Communications), Izd. Akad. Nauk SSSR, Moscow, 1958, No. 12.
14. L. Dostrovsky and A. Raviv, in "Proceedings of the International Symposium on Isotope Separation", North-Holland Publishing Co., Amsterdam, 1958.
15. B. N. Esel'son and B. G. Lazarev, Zhur. Eksper. Teor. Fiz., 20, 742 (1950).
16. W. M. Fairbank, W. B. Ard, H. G. Dehmelt, W. Gordy, and S. R. Williams, Phys. Rev., 92, 208 (1953).
17. K. Clusius and H. Meyer, Helv. Chim. Acta, 36, 2045 (1953).
18. M. V. Tikhomirov and N. N. Tunitskii, Zhur. Prikl. Khim., 32, 531 (1959).
19. H. London, in "Proceedings of the International Symposium on Isotope Separation", North-Holland Publishing Co., Amsterdam, 1958.
20. N. N. Sevryugova, O. V. Uvarov, and N. M. Zhavoronkov, in Symposium "Bor. Trudy Konferentsii po Khimii Bora i Ego Soedinenii" (Boron. Transactions of the Conference on the Chemistry of Boron and Its Compounds), Goskhimizdat, Moscow, 1958; Dokl. Akad. Nauk SSSR, 126, 1044 (1959).
21. N. M. Zhavoronkov, Khim. Nauka i Prom., 4, 487 (1959).
22. K. Clusius and K. Schleich, Helv. Chim. Acta, 42, 232 (1959).
23. A. I. Brodskii, Uspekhi Khim., 6, 152 (1937); Uspekhi Fiz. Nauk, 20, 153 (1938); Zhur. Prikl. Khim., 13, 663 (1940).
24. A. I. Brodskii and O. K. Skarre, Zhur. Fiz. Khim., 13, 453 (1939).
25. A. I. Brodskii, "Khimiya Izotopov" (The Chemistry of Isotopes), 2nd Edition, Izd. Akad. Nauk SSSR, Moscow, 1957.
26. N. M. Zhavoronkov, O. V. Uvarov, and N. N. Sevryugova, in Symposium "Primenenie Mechenykh Atomov v Analiticheskoi Khimii" (Application of Tracer Atoms to Analytical Chemistry), Izd. Akad. Nauk SSSR, Moscow, 1955.
27. A. Weissberger (Editor), "Physical Methods in Organic Chemistry" (Translated into Russian), Vol. 2, Inostr. Lit., Moscow, 1952, pp. 349–455.
28. H. A. Fairbank, C. A. Reynolds, C. T. Lane, B. B. McInteer, L. T. Aldrich, and A. O. Nier, Phys. Rev., 74, 345 (1948).
29. S. G. Sydoriak, E. R. Grilly, and E. F. Hammel, Phys. Rev., 75, 303 (1949).
30. B. M. Abraham, D. W. Osborne, and B. Weinstock, Phys. Rev., 80, 336 (1950).
31. J. G. Daunt, Phil. Mag. Suppl., 1, 209 (1952).
32. T. C. Chen and F. London, Phys. Rev., 89, 1038 (1953).
33. B. Weinstock, B. M. Abraham, and D. W. Osborne, Phys. Rev., 89, 787 (1953).
34. D. ter Haar, Phys. Rev., 91, 1018 (1953).
35. H. van Dijk and M. Durieux, in Symposium "Conférence de Physique des Basses Températures", Paris, 1955.
36. H. van Dijk and M. Durieux, Physica, 22, 760 (1956).
37. H. van Dijk and D. Shoenberg, Nature, 164, 151 (1949).
38. J. Kistemacker, Physica, 12, 272 (1946).
39. S. G. Sydoriak and T. R. Roberts, Phys. Rev., 106, 175 (1957).
40. E. C. Kerr, Phys. Rev., 96, 551 (1954).
41. T. R. Roberts and S. G. Sydoriak, Phys. Rev., 98, 1672 (1955).
42. D. W. Osborne and B. Weinstock, in Symposium "Kammerlingh Onnes Conference on Low Temperature Physics", Leyden, 1958.

43. W. H. Keesom, "Helium" (Translated into Russian), Inostr. Lit., 1949.
44. J. Kistemaker, Physica, 12, 281 (1946).
45. B. N. Esel'son, B. G. Lazarev, and N. E. Alekseevskii, Zhur. Eksper. Teor. Fiz., 20, 1055 (1950).
46. B. Weinstock, D. Osborne, and B. Abraham, Phys. Rev., 77, 400 (1950).
47. H. S. Sommers, Phys. Rev., 88, 113 (1952).
48. B. N. Esel'son, Zhur. Eksper. Teor. Fiz., 26, 744 (1954).
49. J. G. Daunt and T. P. Tseng, in Symposium "Conférence de Physique des Basses Températures", Paris, 1955.
50. B. N. Esel'son and N. G. Bereznyak, Zhur. Eksper. Teor. Fiz., 30, 628 (1956).
51. V. P. Peshkov and V. N. Kachinskii, Zhur. Eksper. Teor. Fiz., 31, 720 (1956).
52. R. L. Mills and E. R. Grilly, in Symposium "Conférence de Physique des Basses Températures", Paris, 1955.
53. J. G. Daunt, Adv. Phys., 1, 209 (1952).
54. R. A. Chentsov, Uspekhi Fiz. Nauk, 55, 49 (1955).
55. V. P. Peshkov and K. N. Zinov'eva, Uspekhi Fiz. Nauk, 67, 193 (1959).
56. V. M. Kuznetsov, Zhur. Eksper. Teor. Fiz., 32, 1001 (1957); Candidate's Thesis, Institute of Physical Problems of the Academy of Sciences of the USSR, 1957.
57. W. H. Keesom and J. Haantjes, Physica, 2, 986 (1935).
58. E. G. Roth and J. Bigeleisen, J. Chem. Phys., 32, 612 (1960).
59. W. Groth and P. Harteck, Z. Elektrochem., 47, 167 (1941).
60. K. Clusius, Z. phys. Chem., 50B, 403 (1941).
61. V. N. Grigor'ev, Ya. S. Kan, N. S. Rudenko, and B. G. Safonov, Zhur. Eksper. Teor. Fiz., 33, 576 (1957).
62. R. B. Scott, F. C. Brickwedde, H. C. Urey, and M. H. Wahl, J. Chem. Phys., 2, 454 (1934).
63. G. N. Lewis and W. T. Hanson, J. Amer. Chem. Soc., 56, 1001, 1687 (1934).
64. H. C. Urey, Angew Chem., 48, 315 (1935).
65. H.C. Urey and C. K. Teal, Rev. Mod. Phys., 7, 34 (1935).
66. E. Bartholomé, Z. phys. Chem., 33D, 387 (1936).
67. H. D. Megaw and P. Simon, Nature, 138, 244 (1936).
68. K. Schaeffer, Z. phys. Chem., 42B, 380 (1939).
69. F.G.Brickwedde and R.B.Scott, J.Chem.Phys., 3, 653 (1935).
70. F. G. Brickwedde, R. B. Scott, and H. C. Taylor, J. Res. Nat. Bur. Stand., 15, 463 (1935).
71. K. Clusius and E. Bartholomé, Z. phys. Chem., 30B, 257 (1935).
72. E. R. Grilly, J. Amer. Chem. Soc., 73, 843 (1951).
73. R. B. Newman and L. C. Jackson, Trans. Faraday Soc., 54, 1481 (1958).
74. H. W. Woolley, R.B. Scott, and F. G. Brickwedde, J. Res. Nat. Bur. Stand., 41, 379 (1948).
75. H. J. Hoge and R. D. Arnold, J. Res. Nat. Bur. Stand., 47, 63 (1951).
76. E. C. Kerr, E. B. Rifkin, H. L. Johnston, and J. T. Clarke, J. Amer. Chem. Soc., 73, 282 (1951).
77. R. B. Scott and F. G. Brickwedde, Phys. Rev., 48, 483 (1935).
78. W. F. Libby and C. A. Barter, J. Chem. Phys., 10, 184 (1942).
79. A. Tookson, P. Pomerantz, and E. H. Rich, J. Res. Nat. Bur. Stand., 47, 449 (1951).
80. R. B. Newman and L. C. Jackson, Trans. Faraday Soc., 54, 1481 (1958).
81. G. N. Lewis and W. T. Hanson, Jnr., J. Amer. Chem. Soc., 56, 1000 (1934).
82. J.Bigeleisen and E.C.Kerr, J.Chem.Phys., 23, 2442 (1955).
83. F. Simon and F. Lange, Z. Physik, 15, 312 (1923).
84. H. L. Johnston, J. T. Clarke, E. B. Rifkin and E. C. Kerr, J. Amer. Chem. Soc., 72, 3933 (1950).
85. K. Clusius and K. Hiller, Z. phys. Chem., 4B, 158 (1929).
86. D. White, A. S. Friedman, and H. L. Johnston, J. Amer. Chem. Soc., 72, 3927 (1950).
87. H.Kronberger, Thesis, Birmingham University, 1948. Quoted in ref. 90.
88. T. F. Johns and H. London, A.E.R.E. Report, Harwell, 1951. Quoted in ref. 17.
89. T. F. Johns, Proc. Roy. Soc., 66B, 808 (1953).
90. W. Groth, H. Ihle, and A. Murrenhoff, Naturforsch., 9a, 805 (1954).
91. T.F.Johns, in "Proceedings of the International Symposium on Isotope Separation", North-Holland Publishing Co., Amsterdam, 1958.
92. N. N. Tunitskii, G. G. Devyatykh, M. V. Tikhomirov, A. D. Zorin, and N. I. Nikolaev, in Symposium "Trudy Vsesoyuznoi Nauchno-tekhnicheskii Konferentsii po Primeneniyu Radioaktivnykh i Stabil'nykh Izotopov i Izluchenii v Narodnom Khozyaistve i Nauke" (Proceedings of the All-Union Scientific and Technical Conference on the Application of Radioactive and Stabilised Isotopes and of Radiations in the National Economy and in Science), Izd. Akad. Nauk SSSR, Moscow, 1958.
93. G. G. Devyatykh, A. D. Zorin, and N. I. Nikolaeva, Zhur. Prikl. Khim., 31, 368 (1958). See also ref. 61.
94. I. Kirschenbaum, J. Chem. Phys., 9, 660 (1941).
95. I. Kirschenbaum and H. C. Urey, J. Chem. Phys., 10, 706 (1942).
96. T. F. Johns, Proc. Phys. Soc., 71, 701 (1958).
97. J. Bigeleisen, J. Chem. Phys., 23, 2264 (1955); in "Proceedings of the International Symposium on Isotope Separation", North-Holland Publishing Co., Amsterdam, 1958.
98. K. Clusius and K. Schleich, Helv. Chim. Acta, 41, 1342 (1958).
99. K. Clusius, M. Vecchi, A. Fischer, and U. Piesbergen, Helv. Chim. Acta, 42, 1975 (1959).
100. W. Kuhn, A. Narten and M. Türkauf, Helv. Chim. Acta, 41, 1342 (1958).
101. W. Kuhn, A. Narten and M. Türkauf, Helv. Chim. Acta, 42, 1433 (1959).
102. R. Klar and A. Krauss, Naturwiss., 22, 119 (1934).
103. E. R. Smith, J. Chem. Phys., 2, 298 (1934).
104. D. F. Stedman, Canad. J. Res., 13, 114 (1935).
105. H. G. Thode and S. R. Smith, Nat. Res. Co., Canada, Report Mc. Mc-45 (1944). Quoted in ref. 96.
106. W. Groth, H. Ihle and A. Murrenhoff, Angew. Chem., 68, 644 (1956).
107. G. G. Devyatykh and A. D. Zorin, Zhur. Fiz. Khim., 30, 1133 (1956). See ref 92.
108. T. F. Johns, H. Kronberger, and H. London, "Mass Spectrometry", Institute of Petroleum, London, 1952.
109. J. R. Bates, J. O. Halford, and L. C. Anderson, J. Chem. Phys., 3, 531 (1935).
110. J. R. Bates, J. O. Halford, and L. C. Anderson, J. Chem. Phys., 3, 415 (1935).
111. G. N. Lewis, R. T. Macdonald, and P. W. Schutz, J. Amer. Chem. Soc., 56, 494 (1934).
112. I. G. Gverdtseteli, T. A. Gagua, and Yu. V. Nikolaev, Atomnaya Energiya, 4, 24 (1958).
113. K. I. Matveev, O. V. Uvarov, and N. M. Zhavoronkov, Dokl. Akad. Nauk SSSR, 125, 580 (1959).
114. P. Baertschi and W. Kuhn, Helv. Chim. Acta, 40, 1084 (1957). See ref. 14.
115. K. Clusius and H. H. Bühler, Naturforsch., 9a, 775 (1954).
116. K. Clusius, F. Endtinger, and K. Schleich, Helv. Chim. Acta, 43, 1267 (1960).
117. G. A. Yagodin, O. V. Uvarov, and N. M. Zhavoronkov, Dokl. Akad. Nauk SSSR, 111, 384 (1956).
118. G. A. Yagodin, Candidate's Thesis, Mendeleev Institute of Chemical Technology, Moscow, 1956.
119. A. Frank and K. Clusius, Z. phys. Chem., 42B, 395 (1939); K. Clusius and L. Popp, Z. phys. Chem., 46B, 63 (1940).

120. G.T. Armstrong, F.G. Brickwedde, and R.B. Scott, J. Chem. Phys., 21, 1293 (1953).
121. G.T. Armstrong, F.G. Brickwedde, and R.B. Scott, J. Res. Nat. Bur. Stand., 55, 39 (1955).
122. F.C. Whitmore, C.H. Fleming, D.H. Rank, E.R. Bordner, and K.D. Larsen, J. Amer. Chem. Soc., 56, 749 (1934).
123. K. Stokland, Kgl. norske Videnskab. Selskabs Forh., 12, 122 (1940); Chem. Zentr., II, 314 (1940).
124. K. Stokland, Kgl. norske Videnskab. Selskabs Forh., 12, 126 (1940); Chem. Zentr., II, 314 (1940).
125. A.H. Zeltmann and G.C. Fitzgibbon, J. Amer. Chem. Soc., 76, 2021 (1954).
126. D.R. Stull, "Tables of the Vapour Pressures of Pure Substances" (Translated into Russian), Inostr. Lit., Moscow, 1949. [Probably a translation of D.R. Stull, Ind. Eng. Chem., 39, 517, 540 (1947) (Ed. of Translation)].
127. I. Shapiro and J.F. Ditter, J. Chem. Phys., 26, 798 (1957).
128. G.K. Ingold, G.G. Raisin, and C.L. Wilson, J. Chem. Soc., 915 (1936).
129. R.T. Davis, Jnr., and R.W. Schiessler, J. Phys. Chem., 57, 966 (1953).
130. K.I. Matveev, O.V. Uvarov, and N.M. Zhavoronkov, Zhur. Fiz. Khim., 34, 2123 (1960)[Russ. J. Phys. Chem., 1007(1960)].
131. W.T. Ziegler and D.H. Andrews, J. Amer. Chem. Soc., 64, 2482 (1942).
132. J. Beermans and J.C. Jungers, Bull. Soc. chim. belges, 56, 238 (1947).
133. A.T. Morse and L.C. Leitch, Canad. J. Chem., 32, 500 (1954).
134. J. Verhulst and J.C. Jungers, Bull. Soc. chim. belges, 58, 73 (1949).
135. N.N. Sevryugova, O.V. Uvarova, and N.M. Zhavoronkov, Atomnaya Energiya, No.4, 113 (1956).
136. M. Green and G.R. Martin, Trans. Faraday Soc., 48, 416 (1952).
137. N.N. Sevryugova, O.V. Uvarov, and N.M. Zhavoronkov, Zhur. Fiz. Khim., 34, 1004 (1960) [Russ. J. Phys. Chem., 477 (1960)].
138. P.T. Nettley, D.K. Cartwright, and H. Kronberger, in ref. 14.
139. Yu.K. Myulenfordt, G.G. Zivert, and T.A. Gagua, in ref. 12.
140. K. Zühlke, in "Proceedings of the International Symposium on Isotope Separation", North-Holland Publishing Co., Amsterdam, 1958.
141. Ya.D. Zel'venskii, V.E. Sokolov, and V.A. Shalygin, Nauch. Dokl. Vys. Shkoly, Khim. i. Khim. Tekhnol., No.2, 388 (1958).
142. V.Yu. Orlov and N.M. Zhavoronkov, Zhur. Prikl. Khim., 29, 959 (1956).
143. P. Baertschi, W. Kuhn, and H. Kuhn, Nature, 171, 1018 (1953).
144. J. Roberts and H.C. Urey, J. Amer. Chem. Soc., 60, 2391 (1938).
145. H.C. Urey, A. Mills, J. Roberts, H.G. Thode, and J.R. Huffman, J. Chem. Phys., 7, 138 (1939).
146. I. Dostrovsky, E.D. Hughes, and D.R. Llewellyn, Bull. Res. Council Israel, 1, 133 (1951); Chem. Abs., 46, 5917d (1952).
147. A.H. Widiger and W.G. Brown, J. Amer. Chem. Soc., 61, 2453 (1939).
148. J. Beersmans and J.C. Jungers, Bull. Soc. chim. belges, 56, 72 (1947).
149. E.F. Fiock, D.C. Ginnings, and W.B. Holton, J. Res. Nat. Bur. Stand., 6, 818 (1931).
150. L.A.K. Staveley and A.R. Gupta, Trans. Faraday Soc., 45, 50 (1949).
151. I.B. Rabinovich, N.A. Sokolov, and P.A. Artyukhin, Dokl. Akad. Nauk SSSR, 105, 762 (1955).
152. O.R. Foz, J.F.G. Banda, and A.P. Masià, Z. Elektrochem., 56, 569 (1952).
153. F.W. Hobden, E.F. Johnston, L.H.P. Weldon, and C.L. Wilson, J. Chem. Soc., 61 (1939).
154. J.M.A. de Bruyne and C.F. Smith, J. Amer. Chem. Soc., 57, 1203 (1935); H.S. Taylor and J.F. Jungers, J. Amer. Chem. Soc., 55, 5057 (1933).
155. H.G. Thode, J. Amer. Chem. Soc., 62, 581 (1940).
156. M.H. Wahl, I.F. Hoffman, and J.A. Hipple, J. Chem. Phys., 3, 435 (1935).
157. H.C. Urey and A.H.W. Aten, Phys. Rev., 50, 575 (1936).
158. H.J. Emeléus and H.V.A. Briscoe, J. Chem. Soc., 128 (1937).
159. G.N. Lewis and R.T. MacDonald, J. Amer. Chem. Soc., 55, 3057 (1933).
160. A. Johannin-Gilles and P. Johannin, Compt. rend., 239, 1470 (1954).
161. G.D. Oliver and J.W. Grisard, J. Amer. Chem. Soc., 78, 561 (1956).
162. I. Kirschenbaum, "Heavy Water" (Translated into Russian), Inostr. Lit., Moscow, 1953.
163. K. Bartholomé and K. Clusius, Z. phys. Chem., 28B, 175 (1935).
164. M.H. Wahl and H.C. Urey, J. Chem. Phys., 3, 411 (1935).
165. E.H. Riesenfeld and T.L. Chang, Z. phys. Chem., 33B, 120 (1936).
166. F.T. Miles and A.W.C. Menzies, J. Amer. Chem. Soc., 58, 1067 (1936).
167. R.L. Combs, J.M. Googin, and H.A. Smith, J. Phys. Chem., 58, 1000 (1954).
168. R.L. Combs and H.A. Smith, J. Phys. Chem., 61, 441 (1957).
169. A.H. Price, Nature, 181, 262 (1958).
170. H.G. Thode, S.R. Smith, and F.O. Walking, Canad. J. Res., 22B, 127 (1944).
171. K. Niwa and E. Shimazaki, J. Fac. Sci. Hokkaido Imp. Univ., Ser., 3, 35 (1940). Quoted in ref. 160.
172. G.N. Lewis and R.E. Cornish, J. Amer. Chem. Soc., 55, 2616 (1933).
173. B. Toplay and H. Eyring, J. Chem. Phys., 2, 217 (1934).
174. P.W. Schutz, SAM Report 595A, 1943. Quoted in ref. 162.
175. H.E. Watson, J. Appl. Chem., 3, 556 (1953).
176. I. Dostrovsky, J. Gillis, D.R. Llewellyn, and B.H. Vromen, J. Chem. Soc., 3517 (1952).
177. S. Sakata and N. Morita, Bull. Chem. Soc. Japan, 30, 254 (1957).
178. P. Baertschi, in "Proceedings of the International Symposium on Isotope Separation", North-Holland Publishing Co., Amsterdam, 1958, in discussion on paper by Dostrovsky and Raviv.
179. A.H. Price, Nature, 181, 262 (1958).
180. K. Stokland, Kgl. norske Videnskab. Selskabe Forh., 10, 145 (1937); Chem. Abs., 32, 6121 (1938).
181. E.R. Smith and M. Wojciechowski, J. Res. Nat. Bur. Stand., 17, 841 (1936).
182. F.D. Rossini, J.W. Knowlton, and H.L. Johnston, J. Res. Nat. Bur. Stand., 24, 369 (1940).
183. P.A. Giguère, B.C. Morisette, A.W. Olmos, and O. Knop, Canad. J. Chem., 33, 804 (1955).
184. O.Z. Golik, S.D. Ravikovich, and V.E. Baranovskii, Dopovidi Akad. Nauk Ukrain. RSR, No.2, 210 (1958).
185. E. Bartholomé and K. Clusius, Z. phys. Chem., 28B, 167 (1935).
186. H.S. Taylor and P.W. Selwood, J. Amer. Chem. Soc., 56, 988 (1934).
187. J. Timmermans, M. Hennawt-Roland, and D. Rozental, Compt. rend., 202, 1061 (1936); J. Timmermans and L. Deffet, Compt. rend., 200, 1661 (1935).
188. A. Eucken and K. Schaefer, Z. anorg. Chem., 225, 319 (1935).
189. E.A. Long and J.D. Kemp, J. Amer. Chem. Soc., 58, 1829 (1936).
190. P.W. Bridgman, J. Chem. Phys., 3, 597 (1935).
191. V.K. LaMer and W.N. Baker, J. Amer. Chem. Soc., 56, 2641 (1934).

192. V.K.LaMer, W.C.Eichelberger, and H.C.Urey, J.Amer. Chem.Soc., 56, 248 (1934).
193. W.F.Libby and R.Cornog, Phys.Rev., 60, 171 (1941).
194. W.Kuhn and M.Thürkauf, Helv.Chim.Acta, 41, 938 (1958).
195. G.N.Lewis and P.W.Schutz, J.Amer.Chem.Soc., 56, 1002 (1934).
196. W.H.Claussen and J.H.Hildebrand, J.Amer.Chem.Soc., 56, 1820 (1934).
197. G.N.Lewis and P.W.Schutz, J.Amer.Chem.Soc., 56, 493 (1934).
198. R.C.Herman and R.Hofstadter, J.Chem.Phys., 6, 538 (1938).
199. A.E.Potter, Jnr., and H.L.Ritter, J.Phys.Chem., 58, 1040 (1954).
200. C.L.Wilson, J.Chem.Soc., 492 (1935).
201. J.O.Halford and L.C.Anderson, J.Amer.Chem.Soc., 58, 736 (1936).
202. J.G.Dawber and P.A.H.Wyatt, J.Chem.Soc., 3636 (1958).
203. L.Landau and E.L.Lifshits, "Statisticheskaya Fizika" (Statistical Physics), Gos.Izd.Tekh.Teoret.Lit., Moscow–Leningrad, 1951.
204. I.M.Lifshits and G.I.Stepanova, in the Symposium, "Problemy Kinetiki i Kataliza" (Problems of Kinetics and Catalysis), Vol.9, Izd.Akad.Nauk SSSR, Moscow, 1957; Zhur. Eksper.Teor.Fiz., 30, 938 (1956).
205. F.A.Lindemann, Phil.Mag., 38, 173 (1919).
206. Landolt-Börnstein, "Physikalisch-Chemische Tabellen", 5th Edn., Eg.1, 703, Berlin, 1927.
207. K.Clusius, Z.phys.Chem., 4B, 1 (1929).
208. I.Kirschenbaum, J.Chem.Phys., 10, 717 (1942).
209. G.G.Devyatykh, Zhur.Fiz.Khim., 31, 1445 (1957); Trudy Khim. i Khim.Tekhnol., Gor'kii, No.2, 239 (1958).
210. G.G.Devyatykh and Yu.Ya.Shavarin, Trudy Khim. i Khim. Tekhnol., Gor'kii, No.2, 229 (1959).
211. T.F.Johns, Phil.Mag., 3, 229 (1958).
212. J.H.Henkel, J.Chem.Phys., 23, 681 (1955).
213. I.J.Zucker, J.Chem.Phys., 25, 915 (1956).
214. J.de Boer, Physica, 14, 139 (1948).
215. J.de Boer and B.S.Blaisse, Physica, 14, 149 (1948).
216. J.de Boer and R.J.Lundbeck, Physica, 14, 510, 520 (1948).
217. J.E.Lennard-Jones and A.F.Devonshire, Proc.Roy.Soc., 163A, 53 (1937).
218. E.F.Hammel, J.Chem.Phys., 18, 228 (1950).
219. F.Maslan and E.Aberth, J.Chem.Phys., 19, 658 (1951).
220. A.S.Friedman, D.White, and H.L.Johnston, J.Chem.Phys., 19, 126 (1951).
221. A.Babloyantz, Mol.Phys., 2, 39 (1959).
222. D.C.Bradley, Nature, 173, 260 (1954); 174, 323 (1954).
223. I.B.Rabinovich, V.I.Kucheryavyi, and P.N.Nikolaev, Zhur. Fiz.Khim., 32, 1499 (1958).
224. I.B.Rabinovich and Z.B.Volokhova, Dokl.Akad.Nauk SSSR, 122, 844 (1958).
225. I.B.Rabinovich and V.A.Gorbushenkov, Dokl.Akad.Nauk SSSR, 120, 566 (1958).
226. I.B.Rabinovich, in the Symposium, "Stroenie Veshchestva i Spektroskopiya" (Structure of Matter and Spectroscopy), Izd.Akad.Nauk SSSR, Moscow, 1960.
227. I.B.Rabinovich, Zhur.Fiz.Khim., 34, 423 (1960) [Russ.J. Phys.Chem., 198 (1960)].
228. I.B.Rabinovich, A.A.Lobashov, and V.I.Kucheryavyi, Zhur. Fiz.Khim., 34, 2202 (1960) [Russ.J.Phys.Chem., 1046 (1960)].
229. J.C.Slater and J.G.Kirkwood, Phys.Rev., 37, 682 (1931).
230. F.London, Z.Physik, 63, 245 (1930); Uspekhi Fiz.Nauk, 17, 421 (1937).
231. T.Larsen, Z.Physik, 100, 543 (1936).
232. D.White, Jih Heng Hu, and H.L.Johnston, J.Phys.Chem., 63, 1181 (1959).
233. "Spravochnik Fiziko-Khimicheskikh i Tekhnologicheskikh Velichin, Prilozhenie k Tekhnicheskoi Entsiklopedii" (Handbook of Physical, Chemical, and Engineering Data, Supplement to Technical Encyclopaedia), Vol.5, Izd.Sovetskaya Entsiklopediya, Moscow, 1930.
234. I.B.Rabinovich and P.N.Nikolaev, Zhur.Fiz.Khim., 34, 2289 (1960) [Russ.J.Phys.Chem., 1087 (1960)].
235. J.O.Halford and L.C.Anderson, J.Amer.Chem.Soc., 58, 736 (1936).
236. I.B.Rabinovich, V.I.Murzin, and L.S.Zhilkin, Zhur.Fiz. Khim., 34, 1973 (1960) [Russ.J.Phys.Chem., 937 (1960)].
237. G.Herzberg, "Spectra and Structure of Diatomic Molecules" (Translated into Russian), Inostr.Lit., Moscow, 1949.
238. H.C.Urey and C.K.Teal, Rev.Mod.Phys., 7, 34 (1935).
239. C.K.Ingold and C.L.Wilson, J.Chem.Soc., 941 (1936).
240. L.Gero and R.Schmid, Z.Physik, 118, 210 (1941).
241. J.Franck and R.W.Wood, Phys.Rev., 45, 667 (1934).
242. R.E.Honig, J.Chem.Phys., 16, 105 (1948).
243. H.Neuert, Naturforsch., 7a, 293 (1952).
244. M.V.Vol'kenshtein, "Stroenie i Fizicheskie Svoistva Molekul" (Structure and Physical Properties of Molecules), Izd. Akad.Nauk SSSR, Moscow, 1955; "Molekulyarnaya Optika" (Molecular Optics), Gos.Izd.Tekh.-teor.Lit., Moscow, 1951.
245. H.London, Z.phys.Chem., Neue Folge, 16, 302 (1958).
246. K.Schäfer, Z.Elektrochem., 63, 863 (1959).
247. E.J.Covington and D.J.Montgomery, J.Chem.Phys., 27, 1030 (1957).
248. J.Thewlis, Acta Cryst., 8, 36 (1955). Quoted in ref.254.
249. S.R.Gunn and L.G.Green, J.Amer.Chem.Soc., 80, 4782 (1958).
250. E.C.Kerr, J.Amer.Chem.Soc., 74, 824 (1952); Phys.Rev., 96, 551 (1954).
251. J.A.Dixon and R.W.Schiessler, J.Amer.Chem.Soc., 76, 2197 (1954).
252. C.G.Swain and R.F.W.Bader, Tetrahedron, 10, 182 (1960).
253. O.Ya.Samoilov, Zhur.Fiz.Khim., 20, 1411 (1946).
254. O.Ya.Samoilov, "Struktura Vodnykh Rastvorov Elektrolitov i Gidratatsiya Ionov" (Structures of Aqueous Solutions of Electrolytes and the Hydration of Ions), Izd.Akad.Nauk SSSR, Moscow, 1957.
255. M.K.Phibbs and P.A.Giguère, Canad.J.Chem., 29, 173 (1951).
256. D.W.Davidson, Canad.J.Chem., 34, 1243 (1956).
257. E.F.Gross and V.I.Val'kov, Dokl.Akad.Nauk SSSR, 67, 619 (1949); 68, 1013 (1949).
258. G.Oster and J.G.Kirkwood, J.Chem.Phys., 11, 175 (1943).
259. P.C.Cross, S.Burnham, and P.A.Leighton, J.Amer.Chem. Soc., 59, 1134 (1937).
260. J.H.Hibben, J.Chem.Phys., 5, 166 (1937).
261. L.Pauling, "The Nature of the Chemical Bond" (Translated into Russian), Goskhimizdat, Moscow, 1947.
262. R.Cardinaud, Bull.Soc.chim.France, 629 (1960).
263. I.B.Rabinovich, V.G.Golov, N.A.Efimova, and S.M.Rustamov, Dokl.Akad.Nauk SSSR, 114, 590 (1957).
264. Ya.I.Frenkel', "Kineticheskaya Teoriya Zhidkostei" (The Kinetic Theory of Liquids), Izd.Akad.Nauk SSSR, Moscow–Leningrad, 1945.
265. J.D.Bernal and R.H.Fowler, J.Chem.Phys., 1, 515 (1933); Uspekhi Fiz.Nauk, 14, 586 (1934).
266. G.N.Lewis and R.T.MacDonald, J.Amer.Chem.Soc., 55, 3057 (1933).
267. G.N.Lewis and P.W.Schutz, J.Amer.Chem.Soc., 56, 493 (1934).
268. A.E.Potter, Jnr., P.Bender, and H.L.Ritter, J.Phys. Chem., 59, 250 (1955).

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