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Abstract

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ISOTOPE EFFECT IN THE CRITICAL TEMPERATURE

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Literature data on the influence of isotopic substitution on critical quantities are very limited (Table 1), and the regularities of this influence are still not clear. It was shown (⁹) that in the series H_2—HD—D_2, as the molecular weight (M) increases, the critical temperature (T_k) increases, and it depends approximately linearly on $1/\sqrt{M}$. However, the replacement of hydrogen by deuterium in H_2O (⁷), PH_3, or HBr (⁸) produces the opposite effect—a decrease in T_k.

Table 1

Critical parameters of isotopic compounds

Substance	T_k, °K	P_k, atm	V_k, cm^3/mol	Substance	T_k, °K (⁸)	Substance	T_k, °K	P_k, atm (⁷)	V_k, cm^3/mol (⁷)	Substance	T_k, °K (⁸)
He^3	3.34 (¹)	1.15 (¹)	73.0 (²⁴)	HCl	324.2	H_2S	373.3			H_3P	325.1
He^4	5.26 (³)	2.26 (³)	57.8 (¹⁰)	DCl	323.5	D_2S	372.2 (⁸)			D_3P	323.6
H_2	33.24 (¹¹)	12.80 (¹¹)	66.9 (¹²)	HBr	363.1	H_2Se	414.4			H_3As	373.1
HD	35.91 (⁴)	14.64 (⁴)	62.8 (⁴)	DBr	362.0	D_2Se	412.4 (⁸)			D_3As	372.1
D_2	38.35 (⁵)	16.43 (⁵)	60.3 (⁴)*	HJ	423.9	H_2O	647.4	218.5	55.6	H_3N	405.7
				DJ	421.8	D_2O	644.7 (⁷)	218.6	55.2	D_3N	405.5

* This value refers to deuterium containing 0.022 n-D_2 and 0.978 o-D_2.

In the present work, T_k values of eleven deuterated compounds (Table 2) and their hydrogen analogues were compared. The synthesis of deuterochloroform is described in (^{14}), and that of deuterated alcohols in (^{16}). To obtain deuteronitromethane, ordinary nitromethane was repeatedly exchanged with a 0.02 M solution of NaOD in D_2O at 110°C in sealed ampoules. Deuterobenzene C_6D_6 and methyldeuterobenzene $C_6D_5CH_3$ were obtained as a result of prolonged repeated exchange with a 52 mol.% solution of D_2SO_4 in D_2O. The substances were carefully purified and dehydrated. The density (ρ_4^{20}), refractive index (n_D^{20}), and boiling temperature of the hydrogen compounds agreed with reliable literature data (^{17}) with accuracies, respectively, of $1 \cdot 10^{-4}$ g/cm^3; $1 \cdot 10^{-4}$; and 0.1-0.2°.

T_k was determined from the disappearance and appearance of the meniscus. The procedure and apparatus were similar to those described in (^{7}). Three capillary ampoules were filled with each substance. The capillaries with isotopic analogues were kept in the thermostat under identical conditions. For each pair of such capillaries, 20 measurements were made. Along with measurements of the differences $\Delta T_\text{k} = T_\text{k,H} - T_\text{k,D}$, determinations of the absolute values of T_k were carried out in

Table 2

Isotope effect in the critical temperature

Substance	D**, %	ΔT_k, deg.	T_k, °K	V, cm^3/mol at 293°K	Substance	D**, %	ΔT_k, deg.	T_k, K°	V, cm^3/mol at 293°K
C_6H_6	0		562.1	88.87	C_2H_5OH	0		515.8	58.36
C_6D_6*	91	1.4	560.7	88.69	C_2H_5OD	98	0.9	514.9	58.45
		***							
$C_6H_5CH_3$	0		594.0	106.29	$CH_3(CH_2)_2OH$	0		537.1	74.79
$C_6D_5CH_3$*	65	1.0	593.0	106.20	$CH_3(CH_2)_2OD$	99	1.0	536.1	74.89
		****							
CH_3NO_2	0		588.0	53.65	$(CH_3)_2CHOH$	0		508.7	76.55
CD_3NO_2*	96	1.0	587.0	53.66	$(CH_3)_2CHOD$	99	0.3	508.4	76.67
$CHCl_3$	0		536.8	80.17	$CH_3(CH_2)_3OH$	0		560.9	91.56
$CDCl_3$	98	0.9	535.9	80.19	$CH_3(CH_2)_3OD$	98	0.5	560.4	91.73
CH_3COOH	0		594.8	57.24	$(CH_3)_2CHCH_2OH$	0		549.7	92.41
CH_3COOD	99	0.7	594.1	57.27	$(CH_3)_2CHCH_2OD$	97	0.3	549.4	92.67
					$CH_3CH_2CHOHCH_3$	0		538.1	91.90
					$CH_3CH_2CHODCH_3$	96	0.4	537.7	92.13

* The product studied did not exactly correspond to the formula, and also contained isotopic analogues with a smaller number of deuterium atoms.

** In the group or ring in which it was substituted.

*** With linear extrapolation to 100% D, $\Delta T_k = 1.6°$.
**** At 100% D, $\Delta T_k = 1.5°$.

in cases where it did not exceed 300°C. The results (Table 2) for hydrogen-containing compounds agree, to within 0.1-0.2°, with the values of T_k given in the review (15), as the most reliable among the data of a number of authors. Above 300°C only ΔT_k was measured, while the values of $T_{k,\mathrm{H}}$ were taken from (15). For all substances the root-mean-square error in determining ΔT_k is about 0.1°, which for the butanols and isopropanol corresponds to 20-30%, and for the remaining substances to about 10% of the value of ΔT_k.

In all cases we found that replacement of a light isotope by a heavy one lowers T_k. From the data of Table 1 it is evident that, with the exception of helium and hydrogen, an isotope effect in T_k of the same sign is also observed for the substances studied earlier. Thus, for substances of various classes of inorganic and organic compounds in the region of moderate temperatures, the relation

$$T_{k,\mathrm{D}} < T_{k,\mathrm{H}}, \tag{1}$$

apparently is a general regularity. Applying the known equalities $a = 27R^2T_k^2/64P_k$ and $a = 9RT_{kV}k/8$, where a is the van der Waals constant, we have:

$$\frac{a_\mathrm{D}}{a_\mathrm{H}} = \frac{T_{k,\mathrm{D}}^2 P_{k,\mathrm{H}}}{T_{k,\mathrm{H}}^2 P_{k,\mathrm{D}}}, \tag{2}$$

$$\frac{a_\mathrm{D}}{a_\mathrm{H}} = \frac{(T_k V_k)_\mathrm{D}}{(T_k V_k)_\mathrm{H}}. \tag{3}$$

For the isotopic analogues of water, according to (3), $a_\mathrm{D}/a_\mathrm{H} = 0.989$. For the deuterium compounds listed in Table 2, V_k or P_k were not studied. An approximate idea of the difference between V_D and V_H in the region of T_k can be obtained

according to the values of the volumes and the mean coefficients of thermal expansion $\bar{\alpha}_D$ and $\bar{\alpha}_H$ at lower T. We measured the density of the indicated substances in the interval 293–343°K, at intervals of 5°, and calculated V and α.

As is seen from Table 2, at 293° for chloroform, nitromethane, and acetic acid, within the limits of the determination error (0.05%), $V_D = V_H$. For C_6D_6 and $C_6D_5CH_3$, V_D is less than V_H by 0.1–0.2%. This is explained by the fact that, at room temperature, in these compounds the molar volume is still appreciably affected by the decrease in the amplitude of zero-point molecular vibrations when H is replaced by D ([21]). In alcohols, on the contrary, V_D exceeds V_H by 0.1–0.2%, which is probably a consequence of an increase in the degree of association by means of hydrogen bonding when hydroxyl hydrogen is replaced by deuterium (^{13}). However, at T close to T_k of the substances listed, when the quantities $h\nu^*$ are small in comparison with kT, and there is almost no association, the influence of both indicated factors should be insignificant. In the region studied (293–343°K), in all cases $\bar{\alpha}_D > \bar{\alpha}_H$, but their difference is so small that it can give a difference in the isothermal values V_D and V_H of the order of $1 \cdot 10^{-4}\%$ per degree. Moreover, with increasing T up to T_k, the values $\bar{\alpha}_D$ and $\bar{\alpha}_H$, owing to the weakening of intermolecular interaction, will become much closer. Consequently, there are grounds to suppose that for substances liquid at intermediate temperatures, in the region of their T_k, and with an accuracy up to 0.1%,

$$V_D = V_H. \tag{4}$$

The condition $T_{\mathrm{k,D}} < T_{\mathrm{k,H}}$ can only give a decrease of $V_{\mathrm{k,D}}$ relative to $V_{\mathrm{k,H}}$, but not the opposite result. Thus, in view of (4), probably,

$$V_{\mathrm{k,D}} \ll V_{\mathrm{k,H}}. \tag{4'}$$

Then, for compounds in which ΔT_k is about 1°, from (3), (1), and (4) we find:

$$a_D < a_H, \tag{5}$$

whence, in view of (4), it follows that

$$\pi_D < \pi_H, \tag{6}$$

where $\pi = a/V^2$ is the internal pressure. Thus, at intermediate T, substitution of hydrogen by deuterium apparently leads to a decrease in the van der Waals interaction.

From the standpoint of the nature of dispersion forces this follows from the Slater and Kirkwood equation (^{18}). Applying the latter to isotopic analogs and replacing, in the first approximation, $(r_D/r_H)^3$, where r is the distance between molecules, by V_D/V_H, we obtain:

$$\frac{\varepsilon_D}{\varepsilon_H} = \left(\frac{V_H}{V_D}\right)^2 \left(\frac{\alpha_{0,\mathrm{D}}}{\alpha_{0,\mathrm{H}}}\right)^{3/2}, \tag{7}$$

where ε is the intermolecular dispersion energy, and α_0 the static polarizability. The lowering of the zero-point energy of the corresponding atomic bonds upon replacement of hydrogen by deuterium causes an increase in the frequencies of electronic transitions. As follows from the dispersion equation (^{19}), this leads to a decrease in polarizability, since, owing to the identity of the electron shells, the probabilities of electronic transitions in isotopic analogs should differ only insignificantly. A decrease in polarizability upon replacement of hydrogen by deuterium has also been established experimentally for water (^{13,20}), hydrogen peroxide (^{20}), benzene and cyclohexane (^{21}), and deuteroethanes (^{22}). Along with this, at intermediate temperatures in all the substances studied, except C_6D_{12}, C_6D_6, and $C_6D_5CH_3$, $V_D > V_H$. In the latter, at room T, V_H exceeds V_D by 0.1–0.2%, but this difference in percentage rela-

* ν is the frequency of intermolecular vibrations (tens of cm^{-1}).

is several times smaller than the isotope effect in a_0 $^{(21)}$. Hence, in view of (7), it follows that

$$|\varepsilon_D| < |\varepsilon_H|. \tag{8}$$

The decrease in the van der Waals interaction upon replacing hydrogen by deuterium is also indicated by the fact that the compressibility then increases $^{(16)}$. The lower strength of the van der Waals forces in deutero-compounds, as compared with their hydrogen analogues, can also explain the larger values of $\bar{\alpha}$ in the former.

However, the isotope effects described in a, π, and ε, and hence the conclusion that the van der Waals interaction decreases when a light isotope is replaced by a heavy one, cannot be extended to the region of low temperatures. In view of the fact that, at such temperatures, the amplitude of the zero molecular vibrations has a strong influence on the molar volume, the latter in liquid tritium, deuterium, and He^4 is considerably smaller than in their light analogues at the same temperature. For example, for D_2 and H_2 at 19.5°K the corresponding difference is about 17% $^{(23)}$. In these cases the difference in molar volumes prevails over the decrease in polarizability, and then it follows from (7) that, in liquid D_2 and He^4, the dispersion interaction is stronger than, respectively, in H_2 and He^3. The isotope effect in the critical parameters of D_2 and He^3 shows that this is indeed so. Substituting the values of P_k and T_k into (2), we obtain for D_2 and H_2: $a_D/a_H = 1.037$, and for He^4 and He^3: $a_4/a_3 = 1.26$; whereas the percentage difference in the molecular weights of the isotopes is three times greater for hydrogen than for helium, the percentage difference in T_k, P_k, and a, on the contrary, is 3-7 times greater for the helium isotopes. This depends on the especially low T_k of the latter. Since, in the low-temperature region, the heavy isotope has a smaller molar volume than its light analogue, then, according to the relation $\pi_D/\pi_H = (a_D/a_H)(V_H/V_D)^2$, for hydrogen and helium we have: $\pi_D > \pi_H$ and $\pi_4 > \pi_3$.

Thus, at temperatures in the region where liquid helium and hydrogen exist, replacement of a light isotope by a heavy one leads to an enhancement of the van der Waals interaction, i.e., to an inverse effect, opposite to the effect at intermediate temperatures.

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