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Abstract

Full Text

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Equilibrium Distribution of Tritium in the Isotopic Exchange of Hydrogen

(Presented by Academician A. N. Frumkin on 23 V 1961)

In recent years tritium has found wide application as a tracer atom, since it is the only radioactive isotope of hydrogen. It is known that the tracer-atom method presupposes identity of the properties of the isotopes used. At the same time, the considerable difference between the masses of tritium and protium may lead to a noticeable difference in the chemical properties of these two hydrogen isotopes and, in particular, to a sharply nonuniform distribution of tritium among hydrogen-containing substances during tritium-protium exchange. Thus, whenever tritium-protium exchange is present, it is always necessary to know and take into account the equilibrium (thermodynamic) isotope effect characteristic of the system under study. As is known, the quantitative measure of such an effect is the distribution coefficient

$\alpha = ([\mathrm{T}]/[\mathrm{H}])_1 : ([\mathrm{T}]/[\mathrm{H}])_2$,

where the subscripts 1 and 2 denote the reacting components for which the ratios of the equilibrium concentrations of tritium and protium are taken.

Information on the distribution coefficients of tritium in systems of hydrogen-containing substances is extremely scant. Unfortunately, the lack of corresponding experimental data cannot at present be remedied by calculating the equilibrium constants of tritium-protium exchange by the method of Urey (ˆ1), Bigeleisen–Mayer (ˆ2), and Tatevskii (ˆ3), with subsequent conversion to distribution coefficients (4-7). This is due to the absence of the basic-frequency data of the vibrational-rotational spectra of tritium-containing substances that are needed for the calculations, with the exception of tritium-containing hydrogen and water (ˆ1, ˆ8). However, it is possible to obtain approximate values of the tritium distribution coefficients for any systems of hydrogen-containing substances by using the regularity of isotope distribution for any monovalent element that we have discovered (ˆ5, ˆ6). According to this regularity, the distribution coefficient of an isotope in a pair of substances is equal to the ratio of the β-factors* of these substances; the value of the β-factor, in the first approximation, is determined exclusively by the number of outer electrons and the number of completed electron shells of the atom of the element bonded in the molecule of the given substance to the isotope under study (including the

Figure 1. Dependence of the β-factor on the atomic number of the element bonded to hydrogen

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outer electrons shared with any other atoms in the molecule). On the basis of this regularity, the β-factor of any hydrogen-containing substance with respect to tritium-protium exchange may be equated to the corresponding β-factor of the diatomic hydride of that element whose atom in the hydride molecule is isoelectronic with the atom of the element bonded to the exchanging hydrogen atom in the molecule of the substance.

hydrogen in the molecule of the substance. For example, the β-factors of CH_4, NH_3, and H_2O, as well as of other compounds with C–H, N–H, and O–H bonds (but not free radicals or individual ions), may be equated to the β-factor of HF, since in the molecules of all these compounds the number of outer electrons (including shared ones) at the C, N, O, and F atoms is the same and equal to 8, and the numbers of completed electron shells also coincide. For BH_3 and other borohydrides the β-factor may be equated to the β-factor of the NH radical (6 outer electrons). For SiH_4, PH_3, and H_2S the β-factors are close to the β-factor of HCl, etc. In this case the β-factors for tritium-protium exchange of diatomic hydrides (including free radicals) are easily calculated from the known observed vibrational frequencies of these hydrides (ν_{H}) [9] and the vibrational frequencies of the corresponding tritides (ν_{T}), found from the ratio of the reduced masses of the tritide (μ_{T}) and hydride (μ_{H}):

Fig. 1. Dependence of the β-factor on the atomic number of the element bonded to hydrogen

$$\nu_{\mathrm{T}} = \nu_{\mathrm{H}}\sqrt{\mu_{\mathrm{T}}/\mu_{\mathrm{H}}}; \qquad \beta = \frac{\nu_{\mathrm{T}}}{\nu_{\mathrm{H}}}\frac{1-e^{hc\nu_{\mathrm{H}}/kT}}{1-e^{-hc\nu_{\mathrm{T}}/kT}}e^{-\frac{hc}{2kT}(\nu_{\mathrm{H}}-\nu_{\mathrm{T}})}.$$

Table 1 gives the values of the corresponding β-factors for 20°. The dependence of the β-factor on the atomic number of the element bonded to hydrogen, analogous to the corresponding dependence in the case of deuterium exchange [5-7], is shown in Fig. 1. Table 2 gives the values of the tritium distribution coefficient ($\alpha = \beta_1/\beta_2$) in various paired systems of hydrogen-containing substances for 20°. As we have shown [5-7], the regularity that makes it possible to find an

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* β-Factors ($^{5-}$7) serve as a quantitative measure of the thermodynamic nonequivalence of two isotopes of some element in a given substance; they are calculated from the fundamental vibrational frequencies of the two isotopic forms of the substance and, unlike ratios of sums over states, do not contain symmetry numbers of these forms.

approximate value of the distribution coefficient of a hydrogen isotope in any system of hydrogen-containing substances is in complete agreement with the available numerous data on deuterium exchange [7]. The validity of this same regularity

Table 1

Atomic number	Element	Hydride vibrational frequency, cm^{-1}	Tritide vibrational frequency, cm^{-1}	β_{20°	Atomic number	Element	Hydride vibrational frequency, cm^{-1}	Tritide vibrational frequency, cm^{-1}	β_{20°
1	H	4154.65	878.0	4.8	20	Ca	1260	745.0	2.1
3	Li	1359.2	878.0	2.7	25	Mn	1580	928.7	2.9
5	B	2268	1417	5.0	27	Co	1890	1109	4.0
6	C	2732	1694	7.8	28	Ni	1926.6	1130.9	4.1
7	N	3300	2029	13.7	29	Cu	1866.0	1094.2	3.9
8	O	3571.6	2180	18.3	30	Zn	1497.3	877.5	2.7
9	F	3958.4	2397	27.4	35	Br	2559.3	1495.9	7.9
11	Na	1132.9	680.6	1.9	37	Rb	908.5	530.6	1.6
12	Mg	1432.9	859.6	2.5	38	Sr	1172.2	684.4	2.0
13	Al	1624.3	970.7	3.0	47	Ag	1691.9	985.8	3.3
14	Si	2080	1242	4.6	48	Cd	1338.1	779.4	2.3
15	P	2380	1417	6.3	53	I	2230.1	1297.6	5.7
17	Cl	2885.7	1711	10.5	55	Cs	875.5	509.3	1.5
19	K	964.5	570.7	1.7					

Table 2

Substance	$\beta^*_{20^\circ}$	H_2	CH_4	NH_3	H_2O	HF	PH_3	H_2S	HCl	HBr	HJ	LiH	NaH	KH	RbH	CsH
H_2	4,8	1	0,17	0,17	0,15	0,18	0,46	0,46	0,46	0,61	0,84	1,8	2,5	2,8	3,0	3,2
CH_4	(27,6)	5,7	1	1	0,87	1,0	2,64	2,64	2,64	3,50	4,85	10,2	14,6	16,15	17,15	18,4
NH_3	(27,6)	5,7	1	1	0,87	1,0	2,64	2,64	2,64	3,50	4,85	10,2	14,6	16,15	17,15	18,4
H_2O	31,6	6,6	1,14	1,14	1	1,2	3,0	3,0	3,0	4,0	5,6	11,8	16,7	18,6	19,7	21,0
HF	27,4	5,7	1	1	0,87	1	2,6	2,6	2,6	3,46	4,8	10,2	14,4	16,0	17,1	18,3
PH_3	(10,5)	2,2	0,38	0,38	0,33	0,39	1	1	1	1,33	1,84	3,9	5,5	6,2	6,6	7,0
H_2S	(10,5)	2,2	0,38	0,38	0,33	0,39	1	1	1	1,33	1,84	3,9	5,5	6,2	6,6	7,0
HCl	10,5	2,2	0,38	0,38	0,33	0,39	1	1	1	1,33	1,84	3,9	5,5	6,2	6,6	7,0
HBr	7,9	1,7	0,28	0,28	0,25	0,29	0,75	0,75	0,75	1	1,39	2,90	4,20	4,70	5,0	5,3
HJ	5,7	1,2	0,21	0,21	0,2	0,21	0,54	0,54	0,54	0,72	1	2,10	3,0	3,35	3,56	3,8
LiH	2,7	0,6	0,10	0,10	0,09	0,10	0,26	0,26	0,26	0,34	0,48	1	1,42	1,60	1,70	1,80
NaH	1,9	0,4	0,07	0,07	0,06	0,07	0,18	0,18	0,18	0,24	0,33	0,70	1	1,1	1,2	1,3

Substance	β^*_{20}	H_2	CH_4	NH_3	H_2O	HF	PH_3	H_2S	HCl	HBr	HJ	LiH	NaH	KH	RbH	CsH
KH	1,7	0,36	0,06	0,06	0,05	0,06	0,15	0,15	0,15	0,22	0,30	0,63	0,90	1	1,1	1,1
RbH	1,6	0,33	0,06	0,06	0,05	0,06	0,15	0,15	0,15	0,21	0,28	0,60	0,85	0,94	1	1,1
CsH	1,5	0,30	0,05	0,05	0,05	0,05	0,14	0,14	0,14	0,20	0,26	0,56	0,80	0,88	0,94	1

* The values of the β-factor in parentheses are conventionally taken to be equal to the β-factors of the corresponding halogen hydrides.

The agreement in the case of tritium confirms the fact that the β-factor of water, calculated from the known observed* vibration frequencies in the molecules H_2O and T_2O and equal to 31.6 (for 20°), is close to the corresponding β-factor of hydrogen fluoride (27.4). These numerical values also characterize the degree of approximation with which the regularity determines the magnitudes of the β-factors and distribution coefficients.

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REFERENCES

[1] H. C. Urey, *J. Chem. Soc.*, **1947**, 562.
[2] J. Bigeleisen, M. Mayer, *J. Chem. Phys.*, **15**, 261 (1947).
[3] V. M. Tatevskii, *ZhFKh*, **25**, 261 (1951).
[4] A. I. Brodskii, *ZhFKh*, **9**, 755 (1937).
[5] Ya. M. Varshavskii, S. E. Vaisberg, *DAN*, **100**, 97 (1955).
[6] Ya. M. Varshavskii, S. E. Vaisberg, *ZhFKh*, **29**, 523 (1955).
[7] Ya. M. Varshavskii, S. E. Vaisberg, *Usp. khim.*, **29**, 1434 (1957).
[8] R. Stats, H. Morgan, J. Goldstein, *J. Chem. Phys.*, **24**, 916 (1956).
[9] G. Herzberg, *Spectra and Structure of Diatomic Molecules*, IL, 1949.

* Although corrected values of the frequencies and all corrections for anharmonicity of vibrations are well known for the H_2O and T_2O molecules, we used the observed (i.e., uncorrected) values, so as not to introduce an additional error in comparison with the results of calculations for other hydrides, where the corrections are unknown.

Note: Figure translations are in progress. See original paper for figures.

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