

The Calculation of the Adsorptive Separation Factors of Hydrogen Isomers

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Static and gas chromatographic studies of hydrogen mass isomers and spin isomers have been carried out by many authors.¹⁻⁸⁾ Recently the gas chromatographic separation of radioactive isomers has been carried out at the temperature of liquid nitrogen in separate experiments by Carter and Smith,⁹⁾ King,¹⁰⁾ and West and Marston¹¹⁾; an apparent separation factor between each pair among the nine isomers has thus been determined. On the other hand, a quantum mechanical explanation of the separation between para- and ortho-hydrogen has been given by several other investigators, and a qualitative agreement with experiments has been obtained.¹²⁻¹⁶⁾

There are still, however, several problems left to be resolved. (i) Why is the elution of tritium hydride, which is composed of two atoms of different weights (a hetero-isomer) faster than that of deuterium, which is composed of two like atoms (a homo-isomer), although they have the same mass? (ii) Ortho-hydrogen and hydrogen deuteride can hardly be separated at all by gas chromatography, except for a single experiment of one

of the present authors using an interconverting double-column method. Why does the mass effect play an insignificant role in this case? (iii) Para- and ortho-tritium have not yet been separated. Is it not possible to separate them experimentally?

This paper will deal with a quantum mechanical treatment of the separation factors of hydrogen isomers at the temperature of liquid nitrogen using Evett's model,^{12a)} with particular emphasis on the explanation of the trend for hetero-isomers to be adsorbed strongly on an adsorbent surface than homo-isomers.

Theory

It is assumed that each atom of a molecule to be adsorbed on an adsorbent surface is subjected to a potential of the Lennard-Jones type along an axis perpendicular to the adsorbent surface. The potential is expanded in powers of the distance in the vicinity of the equilibrium position, and the higher terms are disregarded.

$$V = -U + \frac{1}{2}K(Z_a - Z_0)^2 - U + \frac{1}{2}K(Z_b - Z_0)^2 \quad (1)$$

Here Z_a and Z_b are, respectively, the distances from the adsorbent surface to the atoms a and b; Z_0 is the equilibrium distance and K and U are constants. Z_a and Z_b can be replaced by $Z + m_b d \cos \theta / (m_a + m_b)$ and $Z - m_a d \cos \theta / (m_a + m_b)$ respectively, where Z is the distance from the center of the gravity of the molecule to the adsorbent surface; m_a and m_b are the atomic weights and θ is the angle between the molecular axis and the axis normal to the adsorbent surface. We then have:

$$V = -2U + K(Z - Z_0)^2 + |m_a - m_b| K d (Z - Z_0) \cos \theta / (m_a + m_b) + (m_a^2 + m_b^2) K d^2 \cos^2 \theta / 2 (m_a + m_b)^2 \quad (2)$$

where d is the distance between the centers of the atoms in the molecule. The second term leads to vibrational wave functions for a harmonic oscillator:

$$G_n(\xi) = (2MK/\pi^2 \hbar^2)^{1/8} (2^n n!)^{-1/2} H_n(\xi) e^{-\xi^2/2} \\ \xi = (2MK/\hbar^2)^{1/4} (Z - Z_0)$$

1) Y. L. Sandler, *J. Phys. Chem.*, **58**, 58 (1954); *J. Chem. Phys.*, **29**, 97 (1958).

2) C. M. Cunningham and H. L. Johnston, *J. Am. Chem. Soc.*, **80**, 2377 (1958); Cunningham, Chapin and Johnston, *ibid.*, **80**, 2382 (1958).

3) S. Ohkoshi, Y. Fujita and T. Kwan, *This Bulletin*, **31**, 770 (1958); S. Ohkoshi, S. Tenma, Y. Fujita and T. Kwan, *ibid.*, **31**, 772, 773 (1958); T. Kwan, *J. Res. Ins. Catalysis, Japan*, **8**, 18 (1960); I. Fujita and T. Kwan, *Japan Analyst*, **12**, 15 (1963).

4) W. R. Moore and H. R. Ward, *J. Am. Chem. Soc.*, **80**, 2909 (1958); *J. Phys. Chem.*, **64**, 832 (1960).

5) C. O. Thomas and H. A. Smith, *ibid.*, **63**, 427 (1959).

6) W. A. Van Hook and P. H. Emmett, *ibid.*, **64**, 673 (1960).

7) H. A. Smith and P. P. Hunt, *ibid.*, **64**, 384 (1960);

P. P. Hunt and H. A. Smith, *ibid.*, **65**, 87 (1961).

8) S. Furuyama and T. Kwan, *ibid.*, **65**, 190 (1961).

9) E. H. Carter, Jr., and H. A. Smith, *ibid.*, **67**, 1512 (1963).

10) J. King, *ibid.*, **67**, 1397 (1963).

11) D. L. West and A. L. Marston, *J. Am. Chem. Soc.*, **86**, 4731 (1964).

12) a) A. A. Evett, *J. Chem. Phys.*, **31**, 565 (1959); b) A. A. Evett, *ibid.*, **33**, 789 (1960).

13) D. White and E. N. Lassettre, *ibid.*, **32**, 72 (1960).

14) E. M. Mortensen and H. Eyring, *J. Phys. Chem.*, **64**, 433 (1960).

15) T. Takaishi, presented at the 13th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1960.

16) S. Ono and I. Yasumori, presented at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1964.

where M is the total mass. The third term has matrix elements only between vibrational states of different quantum numbers and is regarded as a perturbation. The last term leads to hindered rotational wave functions. Following Wilson, the rotational wave functions are expanded in powers of $\cos \theta (=x)$ and the recursive method is used to calculate the coefficients $a_{l,m,2k}$ and $a_{l,m,2k+1}$ in wave functions¹⁷⁾:

$$F_{l,m}^e(x) = (2\pi)^{-1/2} (1-x^2)^{m/2} e^{im\varphi} \sum_{k=0}^{\infty} a_{l,m,2k} x^{2k}$$

$$F_{l,m}^o(x) = (2\pi)^{-1/2} (1-x^2)^{m/2} e^{im\varphi} \sum_{k=0}^{\infty} a_{l,m,2k+1} x^{2k+1}$$

In carrying out the calculation, the term

$$(2I_{ab}/\hbar^2) (Kd^2/2) (m_a^2 + m_b^2) / (m_a + m_b)^2 = \lambda^2$$

is regarded as a parameter.

If m_a and m_b are equal, the third term of 2 vanishes identically and 2 reduces to Evett's equation.^{12a)} The unperturbed hindered rotational energies μ of hetero-isomers, as well as those of homo-isomers, are obtained in units of $\hbar^2/2I_{ab}$, where I_{ab} is the moment of inertia of the molecule. For a partition function of a hydrogen molecule at a low temperature (the temperature of liquid nitrogen), only a few low-lying energy levels are important. For para-hydrogen, ortho-deuterium and para-tritium, the exclusion principle requires that their rotational states should be associated only with even l values. For ortho-hydrogen, para-deuterium and ortho-tritium, on the other hand, states are associated with odd l values. The symmetry consideration violates the exclusion principle for hetero-molecules. Hence, for the calculation of the partition function, the energy levels to be taken into account are $F_{0,0}^e(x)$ for para-hydrogen, ortho-deuterium and para-tritium; $F_{1,1}^e(x)$ for ortho-hydrogen, para-deuterium and ortho-tritium, and both states for hetero-isomers. These two energy levels are both even states with respect to $\cos \theta$.

The term $K|m_a - m_b|d \cos \theta (Z - Z_0) / (m_a + m_b)$ is treated as a perturbation. As this term is an odd function with respect to both $(Z - Z_0)$ and $\cos \theta$, the first-order perturbation energy and the second-order contribution from even states vanish identically, and it is enough to consider only the first excited state of the vibration combined with odd states of rotation. The second-order perturbation energy is:

$$E'' = \hbar^2/2K(m_a + m_b) \times 4K^2 d^2 (m_a - m_b)^2 / (m_a + m_b)^2 \times \langle 0 | \xi | 1 \rangle^2 \sum_{l'} \langle l, m | x | l', m \rangle^2 / (\Delta E_{\text{vib}} + \Delta E_{\text{rot}}) \quad (3)$$

TABLE I. SECOND ORDER PERTURBATION ENERGIES OF HYDROGEN DEUTERIDE, TRITIUM HYDRIDE AND TRITIUM DEUTERIDE AT SEVERAL POTENTIAL BARRIERS B

Species	States m	Perturbation energy E'' , cal./mol. B/λ		
		4	8	12
HD	0	16.87	24.45	29.23
	1	10.98	19.14	25.16
HT	0	32.59	44.91	54.97
	1	22.10	37.68	50.00
DT	0	5.00	6.74	
	1	3.74	6.11	

It is evaluated for hydrogen deuteride, tritium hydride and tritium deuteride at several potential barriers, B , in Table I, where

$$B = \lambda^2 \Lambda I_{H_2} (m_a + m_b)^2 / 2I_{ab} (m_a^2 + m_b^2) = Kd^2/4$$

and

$$\Lambda = \hbar^2/2I_{H_2}$$

The energies:

$$E = \mu \Lambda I_{H_2} / I_{ab} + E''$$

are plotted against the potential barrier, B , in Figs. 1 and 2.

So far as the separation factor between isomers of the same molecular weight is concerned, only rotational energies need be considered. However, for hydrogen isomers of different molecular weights, A and B, translational and vibrational factors should also be taken into account. The separation factor is defined as:

$$S = ([A]/[B])_{\text{gas}} / ([A]/[B])_{\text{ads}} \quad (4)$$

Here the following arrangement is to be understood:

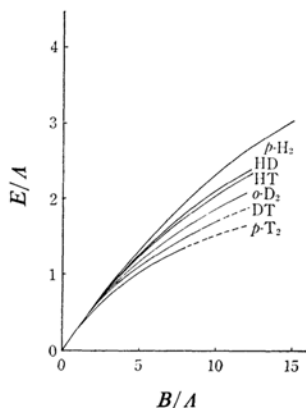
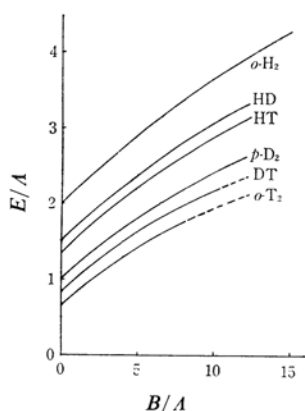


Fig. 1. The rotational energies combined with the second-order perturbation energies against the potential barrier B . State: $l=0, m=0$

17) A. H. Wilson, *Proc. Roy. Soc.*, 118A, 623 (1928).

TABLE II. SEPARATION FACTORS

Species		Experimental			Calculated		
A	B	Carter and Smith ⁹⁾		King ¹⁰⁾ * ₂	B/Λ		
		I* ₁	II* ₂		4	8	12
<i>p</i> -H ₂	<i>o</i> -H ₂	1.37			1.05	1.27	1.48
<i>o</i> -D ₂	<i>p</i> -D ₂	1.09* _{1,4)} 1.10* _{3,3)}			1.02	1.03	1.08
<i>p</i> -T ₂	<i>o</i> -T ₂				0.85	0.92	0.94
HT	D ₂	1.12	1.05	1.13	1.10	1.13	1.27
<i>o</i> -H ₂	HD	(1.00)			1.26	1.44	1.59
<i>p</i> -H ₂	HD	(1.37)			1.33	1.83	2.36
<i>p</i> -H ₂	HT	2.01			1.46	2.42	3.36
<i>p</i> -H ₂	D ₂	2.25			1.64	2.69	4.10
<i>p</i> -H ₂	DT	3.30			1.73	3.37	5.90
<i>p</i> -H ₂	T ₂	3.86			2.00	4.20	8.58
H ₂	HD		1.22		1.31	1.71	2.12
H ₂	HT		1.42	1.23	1.44	2.27	3.02
H ₂	D ₂		1.49	1.38	1.61	2.52	3.68
H ₂	DT		1.85		1.70	3.16	5.29
H ₂	T ₂		2.08	1.68	1.97	3.98	7.69

*₁ Active alumina*₂ Ferric oxide on alumina*₃ Molecular sieves 5AFig. 2. The rotational energies combined with the second-order perturbation energies against the potential barrier B . State; $l=1$, $m=1$

(i) Between spin isomers, A should be the molecule in a state associated with an even l .

(ii) Between molecules of different weights, A should be the lighter molecule.

(iii) Between isobaric molecules, i.e., between tritium hydride and deuterium, A should be the tritium hydride.

Assuming that Langmuir's adsorption equation is obeyed and that the relation $[A]_{\text{ads}} \propto b_A[A]_{\text{gas}}$ holds approximately (because the extent of adsorption is small), 4 can be written in terms of Langmuir's adsorption coefficient, b , as $S = b_B/b_A$. When A and/or B is a mixture of spin isomers, b_A is expressed approximately as $b_{A_1} \times b_{A_2} / (x_{A_1}b_{A_2} + x_{A_2}b_{A_1})$, where the suffix on

A refers to the kind of spin isomer and where x is the mole fraction in the adsorbed phase. As the translational and vibrational parts of b_{A_1} and b_{A_2} are equal, 4 is rewritten as:

$$S = (b_B/b_A)_{\text{trans, vib}} \times \left(\frac{x_{A_1}/b_{A_1} + x_{A_2}/b_{A_2}}{x_{B_1}/b_{B_1} + x_{B_2}/b_{B_2}} \right)_{\text{rot}} \quad (5)$$

In order to simplify the calculation of the separation factor, we assume that, in the adsorbed phase, a translational degree of freedom along the Z axis is replaced by a vibrational degree of freedom along the same axis and that the other modes of translation and vibration are almost the same as in the gas phase. The separation factor, S , is then expressed as:

$$S = \sqrt{\frac{M_A}{M_B}} \exp \left(\frac{(1/2)h(\nu_A - \nu_B)}{kT} \right) \times \frac{x_{A_1}(Q/q)_{A_1} + x_{A_2}(Q/q)_{A_2}}{x_{B_1}(Q/q)_{B_1} + x_{B_2}(Q/q)_{B_2}} \quad (6)$$

where M is the molecular weight; ν the frequencies of vibration along the Z axis ($\sqrt{2K/4\pi^2M}$) and Q and q the partition functions of rotation in the gas phase and in the adsorbed phase respectively.

The calculated values of the separation factor at the temperature of liquid nitrogen are summarized in Table II for potential barriers of 4Λ , 8Λ and 12Λ .

Discussion

The adsorptive separation factor of a pair of isomers can be separated into three parts:

S_{trans} , S_{vib} and S_{rot} . S_{trans} depends solely on the total mass ratio of molecules and decreases with an increase in the mass ratio, running from 1 to 0.577. It is, however, always less than unity. S_{vib} depends on both B and the mass ratio, and it increases either with an increase in the mass or in the mass ratio. It runs from 1 to 3.78 when $B=8A$, and from 1 to 5.11 when $B=12A$. S_{rot} is a complicated function. In general, it increases as B and the total mass ratio increase, but the reverse may be the case at particular values of B and the mass ratio.

White and Lassette have assumed that the molecule is not completely free to move along directions parallel to the adsorbent surface and that it is confined within a definite range of the surface.¹³⁾ In this case, S_{trans} may exceed unity, depending on the area of the cage. However, this situation may conveniently be disregarded, as the contribution of S_{trans} is not very large. The most important contribution comes from S_{vib} , which increases exponentially as B increases. Therefore, the value of B should be carefully estimated when a separation factor between isomers of different molecular weights is going to be considered.

Comparing the calculated values with the experimental results (Table II), it can be seen that the values at $B=8A$ conform well to the experiment I of Carter and Smith using a highly active alumina column, and the values at $B=4A$, to the experiment II of Carter and Smith and to that of King, using ferric oxide on alumina column. At $B=12A$, the calculated values deviate greatly from the experimental results. Therefore, for an alumina column or its modifications, the value of B is most likely to fall within the range from $4A$ to $8A$. The agreement is plausible, except for several cases which we shall discuss later.

In spite of having the same mass, the elution of tritium hydride become faster than deuterium. The calculated values, 1.10 ($B=4A$) and 1.13 ($B=8A$), can be compared with the experimental values, 1.12 (alumina), and 1.05 and 1.13 (ferric oxide on alumina). This surprising agreement may in part be accidental, for the introduction of another potential, V_ϕ , which is to be discussed later, somewhat reduces the values. To anticipate the later discussion, the decrement is small, however. Moreover, we can see from Table II that the

elution of lighter molecules tends to be faster than that of heavier molecules.

There are still several disagreements. For the separation factor between para- and ortho-hydrogen, B should take a value as large as $10A$ in order to obtain the best fit with the experimental value (1.37). Evett, in his first paper,^{12a)} estimated B to be $14A$ in order to account for both the experiment of Sandler at 90°K (1.67)¹⁾ and that of Cunningham and Johnston at 20°K (16).²⁾ In his later work, however, Evett found that the value of B could be reduced to about $6A$, which was thought to account for the heat of adsorption (2000 cal./mol.), if another potential in the direction of ϕ was introduced:^{12b)}

$$V_\phi = D \cos 2\phi$$

This assumption is acceptable, for we may consider the substrate surface to be an array of attractive centers. In the present case, also, the potential favors the separation of para- and ortho-hydrogen and may bring about the agreement of the calculated value with the experimental value at an appropriate B value.

It may also be the case for the separation of ortho-hydrogen and hydrogen deuteride, where the agreement is somewhat poor. We have good reason to assume that the potential V_ϕ may reduce the separation factor considerably, as the level associated with $m=1$ is affected greater than with $m=0$.

The potential V_ϕ may not be very important for separation factors between heavy molecules or between molecules in states of the same m values. Hence, the correction should be small for values which are already in good agreement.

The separation factors between para-tritium and ortho-tritium are very close to unity. Here, the partition among various energy levels is taken into account, as they are closer together for heavier molecules. The result is practically the same as that which is obtained disregarding higher levels. The separation factor is a very insensitive function in this case, running from 1 ($B=0$) to 0.98 ($B=\infty$). Therefore, it is very probable that the experimental separation of para- and ortho-tritium is very difficult, if not impossible.

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