Isotope Effect on Physical Adsorption on a Non-homogeneous Surface

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Non-homogeneity of adsorption sites is shown, by a model calculation, to account for a non-monotonic temperature dependence of the isotope separation factor α in adsorption of a monoatomic gas on a solid adsorbent. Such a non-monotonic dependence was experimentally observed by Purer, Kaplan and Smith.

The model calculation shows that a non-monotonic temperature dependence of α arises when there are two types of adsorption site, one for which the energy of interaction with the adsorbed atom is characterized by a shallow but narrow potential well and the other for which the well is deeper and wider. It is also shown that wide holes or planar sections in the solid adsorbent and narrow holes correspond, respectively, to these two types of adsorption site which exist when the adsorbent is a porous glass.

1. INTRODUCTION

The statistical mechanical theory of isotope effects in condensed phases has successfully explained the process of evaporation from pure liquids [1] and dilute solutions.[2] Use of this theory yields satisfactory calculated isotope separation factors for chemical exchange processes, distillation, exchange distillation and adsorption.[3] The isotopic effect in the methane/wet glass system is well described by the statistical model.[4]

In these cases and many others, the inverse isotopic effect (i.e. the vapour pressure of the heavy isotope in the condensed phase exceeds that of the lighter one) and the non-monotonic temperature dependence of the isotope effect was ascribed to the difference in the internal vibrations of the molecule in the gas and in the condensed phases. However, since there are no internal vibrations in the case of adsorption of atoms one should expect only a monotonically decreasing dependence of the isotope effect on temperature.

For adsorption of an atom that performs three harmonic vibrations, we can write:

$$\alpha = K'/K = \prod_{\text{ext}}^{3}(u/u')\exp[(u'-u)_{\text{ad}}/2]\times[1-\exp(u'_{\text{ad}})]/[1-\exp(-u_{\text{ad}})] \tag{1}$$

where K and K' are the respective equilibrium constants of the heavy and light isotopes: condensed phase $\rightleftharpoons$ gas phase reactions. The value of u is given by: $u \equiv h\nu/kT$. The prime refers to the light isotope.

For low temperatures $h\nu/kT \gg 1$ (as in our case) and the following approximations can be made:

(*a*) that the excitation term in eqn (1) can be omitted since:

$$[1-\exp(-u'_{\text{ad}})]/[1-\exp(-u_{\text{ad}})] \approx 1;$$

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(*b*) that the variations are harmonic. Recalling that for atom/surface interaction the reduced mass μ is equal to the atom mass m, we can write:

$$\nu = \frac{1}{2\pi}\sqrt{f/m}$$

where ν is the frequency and f is the force constant.
Rewriting eqn (1) we obtain:

$$\alpha \equiv K'/K = \prod_i^3 \left(\frac{m}{m'}\right) \exp\left[\frac{h\sqrt{f_i}}{4\pi k}\left(\frac{m'^{-\frac{1}{2}} - m^{-\frac{1}{2}}}{T}\right)\right]. \tag{2}$$

We observe from eqn (2) that α is a *monotonically decreasing function* of the temperature. Inclusion of the excitation term does not affect the nature of α against τ. Consequently, the experimental results of Purer, Kaplan and Smith are quite unexpected. They observed a *non-monotonic* temperature dependence of the isotope separation factor in neon [see fig. 2 of ref. (7); reproduced as " full curve " in fig. 1]. Since the low temperature results shown on the curve are not directly measureable,[7] the maximum must be viewed with reserve, the isotope effect curve in the experimentally accessible high-temperature region is clearly concave downward.

In the next section it is shown that the observed temperature dependence does not contradict Bigeleisen's isotope effect theory, provided more than one type of adsorption site is considered.

In section 3 it is shown that the mathematical properties of the potentials which emerge from the analysis are consistent with the porous surface structure of the glass adsorbent.

2. ISOTOPE EFFECT IN ADSORPTION OF ATOMS ON NON-HOMOGENEOUS ADSORPTION SITES

In gas chromatography, the isotopic separation factor α is experimentally determined from the relation:

$$\alpha = \tau'/\tau = K'/K \tag{3}$$

where τ and τ' are the net retention times of the isotopes in the adsorbed phase. Suppose we have M different types of adsorption sites, type i being characterized by specific retention times t_i and t_i'. Then, if N_i is the number of sites of type i in the column, we can write:

$$\tau = \sum_{i=1}^{M} N_i t_i \quad \text{and} \quad \tau' = \sum_{i=1}^{M} N_i t_i'$$

Substituting into eqn (3):

$$\alpha = \sum_{i=1}^{M} N_i t_i \Big/ \sum_{i=1}^{M} N_i t_i'. \tag{4}$$

α can become a non-monotonic function of the temperature for the simplified case where $M = 2$.
With $M = 2$ we have from eqn (4):

$$\alpha = \frac{N_1 t_1 + N_2 t_2}{N_1 t_1' + N_2 t_2'}. \tag{5}$$

Define

$$S_1 \equiv t_1/t_1' \quad \text{and} \quad S_2 \equiv t_2/t_2' \tag{6}$$

as the isotopic separation factors on sites 1 and 2 respectively. Also define

$$R \equiv N_2/N_1. \tag{7}$$

Substituting into eqn (5) we obtain:

$$\alpha = \frac{S_1(t_1'/t_2')+RS_2}{(t_1'/t_2')+R}. \tag{8}$$

Let T and T^* be two temperatures, so that $T > T^*$ and let us examine the variation of α^* against α.

Substituting into eqn (8) we have:

$$\frac{S_1^*(t_1'/t_2')^*+RS_2^*}{(t_1'/t_2')^*+R} \quad \text{against} \quad \frac{S_1(t_1'/t_2')+RS_2}{(t_1'/t_2')+R}$$

which, upon rearrangement, yields

$$AR^2+BR+C \text{ against } 0 \tag{9}$$

where:

$$A = (S_2^*-S_2)$$
$$B = (t_1'/t_2')^*(S_1^*-S_2)-(t_1'/t_2')(S_1-S_2^*)$$
$$C = (t_1'/t_2')(t_1'/t_2')^*(S_1^*-S_1).$$

S_1, S_1^*, S_2 and S_2^* may be explicitly expressed by use of eqn (2), which involves three modes of vibrations on the adsorption site. However, the complexity of the problem is reduced if we consider only vibration vertical to the surface.

Thus:

$$S_i = \frac{\sqrt{m}}{\sqrt{m'}} \exp\left[\frac{h\sqrt{f_i}}{4\pi k}\left(\frac{m'^{-\frac{1}{2}}-m^{-\frac{1}{2}}}{T}\right)\right] \tag{10}$$

$$S_i^* = \frac{\sqrt{m}}{\sqrt{m'}} \exp\left[\frac{h\sqrt{f_i}}{4\pi k}\left(\frac{m'^{-\frac{1}{2}}-m^{-\frac{1}{2}}}{T^*}\right)\right]. \tag{11}$$

Arbitrarily assuming that $f_1 > f_2$ we can write the inequalities:

$$S_1 > S_2 \quad \text{and} \quad S_1^* > S_2^*.$$

Since S itself is a monotonically decreasing function of the temperature [eqn (10), (11)], we can write:

$$S_1^* > S_1 \quad \text{and} \quad S_2^* > S_2. \tag{12}$$

From these inequalities:

$$S_1^*-S_2 > S_1-S_2^*. \tag{13}$$

Hence, the coefficients A and C in expression (9) are positive. If B is positive too, then $AR^2+BR+C > 0$ and α is a monotonically decreasing function of T. However, if B is negative then AR^2+BR+C may be negative. In this case α increases when the temperature is raised from T^* to T; over a sufficiently wide temperature range, α will exhibit a non-monotonic temperature dependence.

Inequality (13) implies that B may become negative if

$$(t_1'/t_2')^* < (t_1'/t_2').$$

Our efforts will therefore be devoted to examining the conditions under which the function (t_1'/t_2') is an increasing function of the temperature.

ANALYSIS OF THE FUNCTION (t_1'/t_2')

It is assumed that on every type of adsorption site i, there occurs the reaction

$$(\text{ads})_1 \rightleftharpoons (\text{gas})$$

with equilibrium constants K_1 for the heavier isotope, and K_1' for the lighter isotope. Let t_g be the retention time of an inert gas in the column, V_g the volume of cavities in the column, and V_{si} the volume (or area, depending on the units of K_i') of an adsorption site of type i.

$$K_i = \frac{V_g}{V_{si}}\frac{t_g}{t_i} \quad \text{and} \quad K_i' = \frac{V_g}{V_{si}}\frac{t_g}{t_i'}.$$

The functions (t_1'/t_2') and (t_1/t_2) can then be written as follows:

$$\frac{t_1'}{t_2'} = \frac{K_2'}{K_1'}\frac{V_{s2}}{V_{s1}} \quad \text{and} \quad \frac{t_1}{t_2} = \frac{K_2}{K_1}\frac{V_{s2}}{V_{s1}}. \tag{14}$$

The ratio of equilibrium constants for the lighter isotope on the two types of sites [6] is given by:

$$\frac{K_1'}{K_2'} = \exp\left(\frac{U_{01}-U_{02}}{kT}\right)\exp\left(\frac{u_1'-u_2'}{2}\right) \tag{15}$$

where U_{01} and U_{02} are the depths of the potential wells for the adsorption on sites 1 and 2, respectively. An arbitrary choice, $f_1 > f_2$, implies that $u_1'-u_2' > 0$. From eqn (15) we can distinguish between two cases:

$$|U_{01}| > |U_{02}| \quad \text{and} \quad |U_{01}| < |U_{02}|.$$

In the first, since $U_{0i} < 0$, we have:

$$\Delta U_0 \equiv U_{01}-U_{02} < 0.$$

When $|\Delta U_0| > (u_1'-u_2')kT$ then $K_1' > K_2'$ increases with T and (t_1'/t_2') decreases [eqn (14)]. When $\Delta U_0 > 0$, K_1'/K_2' decreases with T, and (t_1'/t_2') increases. We can draw the following conclusions.

(*a*) If the interaction of an atom with a site of type 1 is characterized by a narrow and deep potential energy well, and the interaction with a site of type 2, by a wide and shallow well, α will be a monotonically decreasing function of the temperature.

(*b*) If the interaction on a site of type 1 is characterized by a narrow but shallow potential well and that on site of type 2 by a wide but deep one, α may become a non-monotonic function of T. This conclusion can be substantiated by a calculation of α as a function of T.

By substituting eqn (6), (7), (14), into (8) we write:

$$\alpha = S_1\left[\frac{1+r(K_1/K_2)}{1+r(K_1'/K_2')}\right] \tag{16}$$

where r is a weighted ratio of the site sizes:

$$r = \frac{V_{s1}}{N_1}\Big/\frac{V_{s2}}{N_2}.$$

Eqn (16) expresses α as the isotopic separation factor for type 1 sites corrected for the presence of type 2 sites, i.e., corrected for the effect of non-homogeneity of the adsorption sites. Introducing eqn (10) and (15) into (16) yields α as a function of temperature, and of the parameters f_1, f_2, ΔU_0 and r.

From the resulting function and the experimental observation [7] that

$$\left(\frac{d\alpha}{dT}\right)_{T=19.4\text{K}} = 0$$

we can express r in eqn (16) in terms of ΔU_0, f_1 and f_2. Since S_1 and the ratios of equilibrium constants in eqn (16) can be expressed in terms of the same parameters [eqn (10), (15)], the temperature dependence of α can be obtained in terms of ΔU_0, f_1 and f_2.

An estimated value of ΔU_0, in the range of 0-4 kcal mol^{-1} was obtained from data on physical adsorption of atoms.[8] Estimated values of force constants ($\sim 1.8 \times 10^3$ erg cm^{-2}) were derived from fitting eqn (2) to isotope effect data for the vapour pressure of liquid neon.[7]

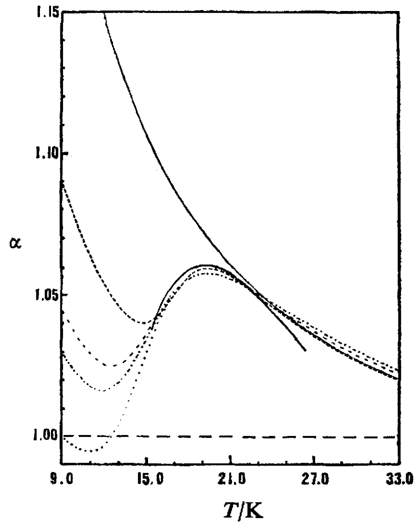

FIG. 1.—Separation factor for neon isotopes plotted against T; non-monotonic full curve, experimental.[7] Monotonic full curve, calculated from eqn (2): $f_1 = 5.38\ 10^3$ erg cm^{-2}. The dashed curves, calculated from eqn (16), with: - - -, $f_1 = 1.534\ 10^3$ erg cm^{-2}, $f_2 = 0.072\ 10^3$ erg cm^{-2}, $\Delta u_0 = 3.74$ kcal mole^{-1}; - -, $f_1 = 0.752\ 10^3$ erg cm^{-2}, $f_2 = 0.023\ 10^3$ erg cm^{-2} $\Delta u_0 = 3.86$ kcal mole^{-1}; - . . . -, $f_1 = 0.507\ 10^3$ erg cm^{-2}, $f_2 = 0.016\ 10^3$ erg cm^{-2} $\Delta u_0 = 3.94$ kcal mole^{-1}; . . . ., $f_1 = 0.195\ 10^3$ erg cm^{-2}, $f_2 = 0.015\ 10^3$ erg cm^{-2}, $\Delta u_0 = 3.93$ kcal mole^{-1}.

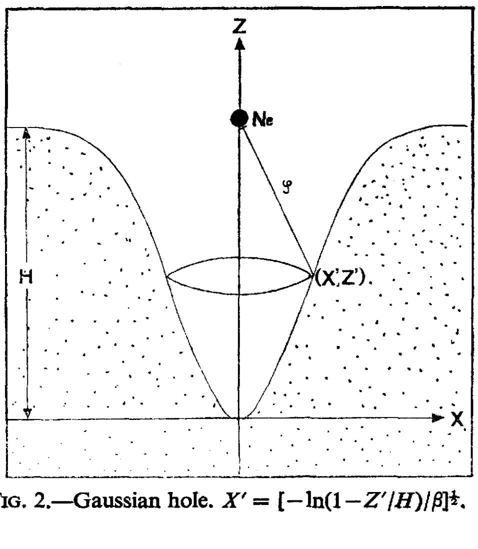

FIG. 2.—Gaussian hole. $X' = [-\ln(1-Z'/H)/\beta]^{\frac{1}{2}}$.

Fig. 1 shows four calculated curves of α against T. α is most sensitive to the values of these parameters at temperatures below 15 K. However, in the temperature range where experiments were carried out,[7] various combinations of f_1, f_2 and ΔU_0 practically converge to the same values of α. In the next section it is shown that holes in the adsorbing solid can furnish the two types of sites required for a non-monotonic dependence of α on T.

3. INFLUENCE OF SURFACE STRUCTURE ON THE INTERACTION BETWEEN THE ADSORBED ATOM AND THE SURFACE

Assume that the adsorbing surface has " gaussian holes " of various dimensions (see fig. 2). The cross-section through the symmetry axis of a hole is described by

$$Z = H(1-e^{-\beta x^2})$$

where H is the depth of the hole and $\sqrt{1/\beta}$ is a measure of its width.

Let $v(\rho)$ be the potential energy of interaction between a neon atom and a molecule in the adsorbing solid, at a distance ρ from each other. The potential energy of interaction between a neon atom on the symmetry axis of the hole, at a height Z from the bottom, and a planar section of the adsorbent, of thickness dZ' and at a height Z' from the bottom of the hole, is then given by:

$$V(Z-Z') = 2\pi n\, dZ' \int_a^\infty Xv(\rho)\, dx = 2\pi n\, dZ' \int_b^\infty v(\rho)\, d\rho \tag{17}$$

where,

$$a = \left[-\frac{1}{\beta}\ln(1-Z'/H)\right]^{\frac{1}{2}}, \qquad b = \left[(Z-Z')^2-\frac{1}{\beta}\ln(1-Z'/H)\right]^{\frac{1}{2}}$$

and n is the density of molecules in the adsorbent.

Let $v(\rho)$ be expressed as a Lennard-Jones potential:

$$v(\rho) = -\frac{2\varepsilon\rho^{*6}}{\rho^6}+\frac{\varepsilon\rho^{*12}}{\rho^{12}}. \tag{18}$$

Substituting eqn (18) into (17) and integrating:

$$V(Z-Z') = -\frac{\varepsilon\rho^{*6}\pi n\, dZ'}{[(Z-Z')^2-(1/\beta)\ln(1-Z'/H)]^2}+\frac{\varepsilon\rho^{*12}\pi n\, dZ'}{5[(Z-Z')^2-(1/\beta)\ln(1-Z'/H)]^5}.$$

The total energy of interaction between the neon atom and the adsorbent is finally given by

$$U(Z) = \int_0^H V(Z-Z')\, dZ' - \frac{\varepsilon\pi n\rho^{*6}}{3}\left[\frac{1}{Z^3}-\frac{\rho^{*6}}{15Z^9}\right] \tag{19}$$

where the second term on the right hand side expresses the energy of interaction with the mass of adsorbent below the bottom of the hole (pore).[9]

Eqn (19) and its second derivative, with respect to Z, were evaluated numerically for parameters ε, n and ρ^* corresponding to a condensed neon adsorbent.[10] Fig. 3 shows the minimum value of $U(Z)$ denoted by U_0, and half the second derivative at the minimum, which is the force constant for a vibration along Z for 10 Å deep holes of varying widths W [defined as the diameter of the hole at half its depth; $W \equiv (4\ln 2/\beta)^{\frac{1}{2}}$].

An infinitely wide pore ($W = \infty$) is, of course, a planar surface. As the pore width is decreased from infinity, the interaction energy increases. For a narrow hole the vertical motion in the hole is associated with small changes in the energy, so that the force constant for such vertical vibration is low in spite of the strong interaction. As the hole becomes comparable in width with the collision diameter of the adsorbed atom the position of minimum energy is shifted upwards. This shift upwards starts at a hole width of ~10 Å, as at this width the radius of curvature at the bottom of the hole ($1/2\beta H = W^2/(8H\ln 2) \simeq 3$ Å) is small enough to appreciably push the atom upwards. As the pore width shrinks to zero the adsorbed atom finds itself on the planar surface of the adsorbent, in an infinitely wide pore. The minimum is located at a distance $H+Z_0$ from the bottom of the reduced pore, where Z_0 is the location of the minimum for the infinitely wide pore, because the planar surface of the bulk adsorbent is located at $Z = H$ in the coordinate system chosen, in which the planar surface of an infinitely wide pore is at $Z = 0$.

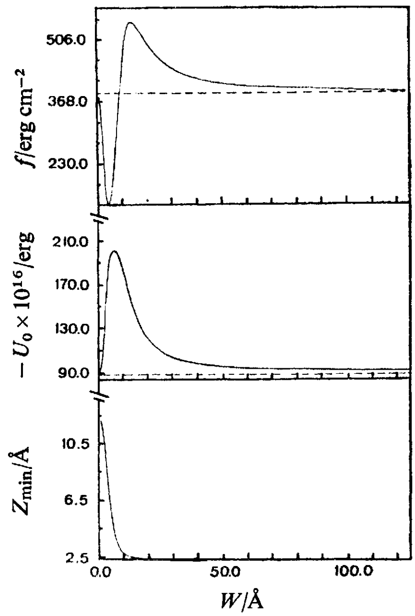

FIG. 3.—Variation of f', u_0 and Z_{min} as functions of hole width W (for a 10 Å deep hole).

This analysis is in agreement with the numerical results presented in fig. 3.

(*a*) Z_{min}, varies from 2.38 Å to H+2.38 Å.

(*b*) For a narrow enough pore

$$f_{hole} < f_{plane} \text{ since } |U_0|_{hole} > |U_0|_{plane}.$$

Consequently, a planar surface of the adsorbent or a wide pore, and a narrow pore (which are consistent with the porous surface structure of the adsorbent[11]) represent respectively, the adsorption sites 1 and 2 that have been shown in the previous section to give rise to a non-monotonic temperature dependence of α (fig. 1).

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