The Relative Adsorbabilities of Hydrogen and Deuterium

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The unexpected results of Beebe, Klar and others on the relative adsorbabilities of H_2 and D_2 on metal surfaces are explained by a statistical-mechanical treatment. By constructing simple partition functions for the adsorbed molecules and atoms, equal adsorption at low temperatures and an inversion temperature at higher temperatures are predicted. Both predictions are fulfilled by the experimental results.

THE experiments of Beebe *et al.*[1] and Klar[2] on the relative adsorbabilities of hydrogen and deuterium have brought forward the interesting fact that there exists an inversion temperature below which hydrogen is more strongly absorbed and above which deuterium is more strongly absorbed. The catalysts employed were copper (Beebe) and nickel (Klar). Considerably below the inversion temperature in the region $-80°C$, Beebe finds both isotopes equally absorbed. (Here more "strongly absorbed," "equally absorbed," etc., apply to the equilibrium amount taken up by the metal surface.) In the following it will be shown that these experimental results are in strict conformity with the theoretical predictions of statistical mechanics. Using a form of the Langmuir isotherm due to Fowler,[3] simple partition functions will be constructed for the adsorbed molecules, and from this the relative adsorbability of the two hydrogen isotopes will be deduced.

In terms of statistical mechanics, the Langmuir isotherm is:

$$p = \frac{\theta}{1-\theta}(kT)\frac{F_g}{F_a}\exp -\frac{E_0}{kT},\qquad(1)$$

where p is the equilibrium pressure in the gas phase, θ is the fraction of the surface covered, F_g is the partition function for a gas molecule, and F_a is the partition function for an adsorbed molecule. T is the absolute temperature and k the Boltzmann constant. E_0 is the difference in

energy at the absolute zero between a gas molecule in its lowest state and an adsorbed molecule in its lowest state. If adsorption results in the dissociation of the adsorbed molecule into two atoms, the isotherm is:

$$p = \left(\frac{\theta}{1-\theta}\right)^2 (kT)\frac{F_g}{F_a^2}\exp -\frac{E_0}{kT}.\qquad(2)$$

For molecular adsorption we then have for the ratio of pressures of D_2 and H_2 in the gas phase necessary to produce an amount of adsorption θ:

$$\frac{p}{p'} = \frac{F_g}{F_g'}\frac{F_a'}{F_a}\exp -\left(\frac{E_g-E_a}{kT}\right),\qquad(3)$$

where a primed quantity refers to H_2 and an unprimed quantity to D_2. E_g is the difference in zero-point energy between gaseous D_2 and H_2 and E_a is the same quantity for adsorbed H_2 and D_2. For atomic adsorption we have:

$$\frac{p}{p'} = \frac{F_g}{F_g'}\frac{F_a'^2}{F_a^2}\exp -\frac{E_g-2E_a}{kT}.\qquad(4)$$

The quantities F_g and F_g' are well known, and since the vibrational partition functions in each are contributing a factor very nearly unity, we may write for the ratio:

$$\frac{F_g}{F_g'} = \left(\frac{m(D_2)}{m(H_2)}\right)^{3/2}\frac{I(D_2)}{I(H_2)} = (2)^{5/2}.\qquad(5)$$

Here the I's are moments of inertia, and the m's are masses of H_2 and D_2. Eq. (5) will be an excellent approximation at ordinary temperatures (0–500°C) and at lower temperatures where the rotations cannot be treated classically, the deviations will tend to cancel each other.

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[1] Beebe, Low, Wildner, and Goldwasser, J. Am. Chem. Soc. **57**, 12 (1935).

[2] Klar, Naturwiss. **22**, 822 (1934).

[3] R. H. Fowler, Proc. Camb. Phil. Soc. **31**, 260 (1935).

For temperatures at which a loose molecular adsorption predominates, we may evaluate F_a and F_a' as follows. It is logical to assume that the molecule is held to the metallic surface by five loose vibrations, these having replaced the three translational and two rotational degrees of freedom in the gas phase. The sixth degree of freedom, namely the internal vibration of the two hydrogen atoms, will remain virtually un-perturbed. (The fact that liquefaction scarcely changes the fundamental frequencies of a molecule insures the truth of the last sentence.) The five loose vibrations may be treated classically so that:

$$\frac{F_a'}{F_a} = \frac{\Pi^5_{i=1} kT/h\nu_i'}{\Pi^5_{i=1} kT/h\nu_i} = \frac{\Pi^5_{i=1} \nu_i}{\Pi^5_{i=1} \nu_i'}. \tag{6}$$

The ν_i and ν_i' are the five loose vibrational frequencies for the adsorbed deuterium and hydrogen molecules, respectively. The Π's are symbols for continued products. Since identical forces are involved in the vibrations of the two isotopic molecules, we have

$$\nu_i = \frac{1}{2\pi}\left[\frac{f_i}{m(D_2)}\right]^{\frac{1}{2}} \quad \text{and} \quad \nu_i' = \frac{1}{2\pi}\left[\frac{f_i}{m(H_2)}\right]^{\frac{1}{2}}, \tag{7}$$

where f_i is the force constant for ith normal mode of vibration. Substituting in Eq. (5) we have:

$$\frac{F_a'}{F_a} = \frac{\Pi^5_{i=1} \frac{1}{2\pi}\left[\frac{f_i}{m(D_2)}\right]^{\frac{1}{2}}}{\Pi^5_{i=1} \frac{1}{2\pi}\left[\frac{f_i}{m(H_2)}\right]^{\frac{1}{2}}} = (\tfrac{1}{2})^{5/2}. \tag{8}$$

Further, since the internal mode of vibration of the hydrogen molecule is practically unchanged, $E_g - E_a$ (of Eq. (3)) is to a first approximation zero. Substituting this result, along with (5) and (8), in Eq. (3) we obtain:

$$p/p' = 1 \tag{9}$$

or namely that hydrogen and deuterium are equally absorbed at temperatures for which molecular adsorption predominates. This result is confirmed experimentally by Beebe and his co-workers.

At higher temperatures where atomic adsorption is important, we must use Eq. (4). For the case in which each atom is held to the absorbing surface by three loose vibrations which may be treated classically, we find:

$$\frac{F_a'^2}{F_a^2} = \frac{\Pi^3_{i=1}\left(\frac{1}{2\pi}\right)^2 \frac{f_i}{m_D}}{\Pi^3_{i=1}\left(\frac{1}{2\pi}\right)^2 \frac{f_i}{m_H}} = (\tfrac{1}{2})^3. \tag{10}$$

Substituting (10) and (5) in (4), there results

$$\frac{p}{p'} = (\tfrac{1}{2})^{\frac{1}{2}} \exp -\left[\frac{E_g - 2E_a}{kT}\right]. \tag{11}$$

This result predicts that at low temperatures H_2 will be more strongly absorbed, but that at a temperature:

$$T = \frac{2E_a - E_g}{k} \frac{2}{\log 2} \tag{12}$$

an inversion will occur, with D_2 being more strongly absorbed.

For the general case where the three vibrations cannot be treated classically we still have the result that the inversion will take place at a temperature

$$T = \frac{2(E_a' - E_a) - 1800}{\left[\frac{5}{2}\log 2 + 2\log\frac{F_a'}{F_a}\right]R}, \tag{13}$$

where E_a' and E_a are, respectively, the zero-point energies in calories of an absorbed H or D atom, and 1800 is $-E_g$ (the difference in zero-point energy between gaseous D_2 and H_2). Eq. (13) shows the inversion should take place at ordinary temperatures providing the three vibration frequencies for the absorbed H atom are around 1000 cm^{-1}, and $(\tfrac{1}{2})^{\frac{1}{2}}$ times this for D. The approximations (uniform surface etc.) involved in the derivation of Eq. (4) make any quantitative predictions of Eq. (13) of doubtful value, but the prediction of an experimentally observed inversion temperature show that the approach is essentially correct. Eq. (13) also shows that not every absorbing surface will exhibit an inversion

temperature, as certain sets of vibrational frequencies will make T negative or experimentally out of reach.

The parallelism between the absorbability of the hydrogen isotopes and the rate with which they hydrogenate ethylene has been pointed out by Beebe and Klar.[1, 2] On nickel the ratio α of the rate of the light hydrogen reaction to the heavy hydrogen reaction actually "turns over" in the region of the inversion temperature, while on copper[4] between 0°C and 300°C α falls from 2.07 to approximately unity.

[4] Wheeler and Pease, J. Am. Chem. Soc. 58, 1665 (1936); 57, 1144 (1935).

LETTERS TO THE EDITOR

Raman Spectrum of Thiophosgene

In an analysis of the ultraviolet absorption spectrum of thiophosgene it became desirable to know the vibration frequencies of the molecule. Each of the six normal vibrations should be excited in the Raman spectrum, which was accordingly measured, using the liquid substance. The exciting frequency was the 5876A line of a specially constructed helium discharge lamp, though a few lines scattered from the 6678A helium line gave corroborative data. The spectrograph was a large aperture glass prism instrument giving a dispersion of about 100A/mm in the region involved. The Hα and neon lines were used as standards. The following frequencies, (cm^{-1}) with rough relative intensities, were found: 200 (1), 287 (3), 363 (1), 496 (5), 660 (0), 1121 (10), 1388 (2). Using the same nomenclature as has been given for the case of phosgene,* the three relatively intense symmetric vibrations are assigned as follows: $\nu_1 = 1121$, $\nu_2 = 496$, $\nu_3 = 287$. The two antisymmetric planar vibrations will probably be $\nu_4 = 660$, $\nu_5 = 363$, and the nonplanar oscillation $\nu_6 = 200$. It seems probable that the Raman interval 1388 is to be interpreted as due to the excitation of the combination $(\nu_1 + \nu_3)$. A preliminary survey of the infra-red spectrum of thiophosgene vapor confirms the above values both as regards magnitude and assignment. The analysis of the ultraviolet absorption band system reveals that the most prominently excited vibrations are the symmetrical ones. The details of the ultraviolet and infra-red data will shortly be published, as well as a comparison with the corresponding data for formaldehyde and phosgene, and a discussion of the force constants in these molecules.

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* Bailey and Hale, Phil. Mag. 25, 98 (1938).

Statistical Mechanics of Mobile Monolayers

Following a suggestion to the writer by Professor R. H. Fowler, the methods of Mayer and Ackermann[1, 2] giving the saturated vapor pressure curves for condensing systems have been adapted to the problem of mobile monolayers. The problem is simplified as an example in the theory of dissociating (clustering) assemblies,[3] and the equation giving the saturated vapor tension F_c and the critical area A_c for a monolayer of X molecules is easily found to be of the form

$$F_c A_c / XkT = (1+\nu)/(1+\sigma),$$

where ν and σ are sums which can be evaluated in terms of the molecular fields. For the latter, point functions of the radius alone are useless, but it is found sufficient to specify only the number of bonds with nearest neighbors and the mean energy per bond. Good agreement is obtained with the data of Adam and Jessop on the fatty acids[4] by assuming six bonds with mean energy 3.8×10^{-14} erg per bond, for the vapor-duplex change at large molecular areas. And in myristic acid for the duplex-liquid change at small molecular areas good agreement is found with the modified duplex equation

$$(F_c - F_0)(A_c - A_0)/XkT = (1+\nu)/(1+\sigma)$$

with six bonds of mean energy 5.6×10^{-14} erg per bond, provided the spreading effect of the liquid surface is

$$F_0 = -11.2 \text{ dynes/cm}$$

and the area occupied by the clustered molecules is

$$A_0 = (14 + 0.2t)X,$$

where t is the temperature in degrees Centigrade. This last agreement is supporting evidence for Langmuir's duplex theory of the expanded film.[6]

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August 8, 1938.

[1] Joseph E. Mayer, J. Chem. Phys. 5, 67 (1937).
[2] Mayer and Ackermann, J. Chem. Phys. 5, 74 (1937).
[3] W. Band, J. Chem. Phys. 6, 654 (1938).
[4] Adam and Jessop, Proc. Roy. Soc. A110, 423 (1926).
[5] Adam and Jessop, Proc. Roy. Soc. A112, 362 (1926).
[6] Langmuir, J. Chem. Phys. 1, 769 (1933).