

The Vapor Pressures of o and p-H₂ and D₂

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The Vapor Pressures of *o*- and *p*-H₂ and D₂*

In a recent article on the vapor pressures of *o*- and *p*-hydrogen and *o*- and *p*-deuterium,¹ the derivation of the differences in sublimation-heats² (ΔE) was stopped at the differences in attractive potentials (ΔE_A). It was remarked that the step from ΔE_A to ΔE could not be made without a knowledge of the relation between E , E_0 (the zero-point energy), r , E_A and E_R (the repulsive energy). The timely publication of such a relationship by Hobbs³ enables us to complete our argument. We have

$$E = -E_A + E_R + E_0, \quad (1)$$

where E_0 is given by³

$$E_0 = \frac{Cd}{(r-d)^2(r+0.800d)} \quad (2)$$

with r the intermolecular distance; d , a molecular radius determined from the repulsive forces ($=2.70\text{\AA}$); C , a constant. The equilibrium condition is

$$E'(r) = 0. \quad (3)$$

From (1) and (3) we find

$$\Delta E = -\Delta E_A(r) + \Delta E_0(r), \quad (4)$$

$$\Delta E \equiv E_{o-H_2} - E_{p-H_2} \quad (4a)$$

or

$$\Delta E \equiv E_{p-D_2} - E_{o-D_2}, \quad (4b)$$

the value of r in (4) being determined by (3). In calculating the terms on the right-hand side of (4) it is understood that r is held constant.⁴ E_0 depends only on the volume and the repulsive forces (through d). Since we are considering the repulsive forces to be held constant, $\Delta E_0(r) = 0$ and $\Delta E = -\Delta E_A(r)$.

Taking $r = 3.752$ and 3.573 (corresponding to $V = 22.65$ cc and 19.56 cc of cubic close-packing) for H₂ and D₂, respectively, and recalculating from Eqs. (14) and (15) of our paper,¹ we find

$$\text{for H}_2: \Delta E = -\Delta E_A(r) = -1.68 \text{ cal./mole} \quad (5)$$

$$\text{for D}_2: \Delta E = -\Delta E_A(r) = -1.16 \text{ cal./mole.}$$

We find experimentally that $\Delta E = -1.78$ cal./mole for both hydrogen and deuterium.

The volume change in passing from *o*-H₂ to *p*-H₂ can be shown to be

$$\frac{V_o - V_p}{V} = -\frac{18}{r^2} \Delta E_A(r) \frac{1}{E''(r)}$$

with r , as before, the root of $E'(r) = 0$.

The volume change of the motionless solid ($E_0 = 0$) is likewise

$$\frac{V_o^0 - V_p^0}{V^0} = -\frac{18}{R^2} \Delta E_A(R) \frac{1}{\phi''(R)},$$

where

$$\phi'(R) = -E_A'(R) + E_R'(R) = 0.$$

It is evident that the much smaller value of $E''(r)$, compared to $\phi''(R)$, will give $V_o - V_p$ a much greater value than $V_o^0 - V_p^0$. This accounts for the difference between ΔV (observed) and ΔV^0 (calculated).⁵

Finally, we should like to take this occasion to correct two trivial errors in our paper.¹ On page 157, the upper limit of the last integral in Eq. (2) should be " ∞ " and not " T ;" and in the last line of the same page, read "0.2 percent" instead of "0.1 percent."

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¹ K. Cohen and H. C. Urey, *J. Chem. Phys.* **7**, 157 (1939).

² $-\Delta\epsilon$ in our previous notation.

³ M. E. Hobbs, *J. Chem. Phys.* **7**, 318 (1939).

⁴ Cf. K. Cohen and H. C. Urey, reference 1, p. 161.

⁵ §§4 and 5, reference 1.

The Separation of Gases by Thermal Diffusion*

A simple approximate treatment of the case in which there are no complications due to convection will be presented later. It has the advantage that it can be easily worked out for mixtures containing any number of species. A result for the separation of two gases in the presence of others is as follows:

$$\frac{d \ln (x_1/x_2)}{d \ln T} = \frac{m_2 - m_1}{2 \sum m_i x_i}.$$

Here T denotes absolute temperature, x mole fraction, i any gaseous species (the summation is over all species), and m denotes the *square root* of the molecular weight.

The only data published are for binary mixtures. Comparison shows that the calculated separations agree well with the experimental in a few cases, fairly well in others (the calculated being higher) and are about double the experimental in the worst cases. The cases in which the lower temperature is extremely low are among the worst.

Interpretation of the equation suggests practical importance, since the separation of two heavier gases ought, according to it, to be improved by addition of a light gas such as hydrogen or helium. In the case of the separation of the isotopes 35 and 37 of chlorine by diffusion of hydrogen chloride, the maximum effect, as measured by the left-hand side of the equation, would correspond to a multiplication by four in the case of added hydrogen, three in the case of helium. The addition of helium might however be the more advantageous, since the agreement of the equation with data is poorest on the average for binary mixtures containing hydrogen and nearly the best for those containing helium.

The devices of Clusius and Dickel¹ and Brewer and Bramley² seem to act as ensembles of units in cascade, in which units ordinary thermal diffusion is taking place, and we may perhaps expect their operation to be susceptible of improvement by addition of light gas.

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May 8, 1939.

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¹ Clusius and Dickel, *Naturwiss.* **26**, 546 (1938); **27**, 148 (1939).

² A. K. Brewer and A. Bramley, *Phys. Rev.* [2] **55**, 590(A) (1939).