

297. *The Interpretation of the Dissociation Pressures of the Palladium-Hydrogen System.*

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THE author (*Min. Mag.*, 1935, **24**, 99) has recently considered the interpretation of the water-vapour pressures of the zeolites, a group of hydrated aluminosilicates which are capable of losing part or all of their water without breakdown of their crystal structure; since no new solid phase is formed, the system zeolite-water vapour is bivariant.

It was shown that if a compound of a volatile and a non-volatile component can undergo partial or complete dissociation without the appearance of a new solid phase, then the following equation holds, provided (i) that the lattice positions occupied by the volatile component are all of the same kind, and (ii) that the molecular complexity of the volatile component is the same in the solid and the gaseous phase; the equation was derived by equating the number of molecules calculated to be escaping from and condensing on unit surface of the crystal in unit time:

$$\log p = 4.50 + \frac{1}{2} \log T - \log x/(1-x) - E_0\{1+f(x)\}/RT \ln 10 - 2 \log \{1+\phi(x)\} + \log 4\sqrt{RE/\chi a_0 DN} \sqrt{\pi}$$

N and R have their usual significance, χ is a constant introduced to correct for certain assumptions (in practice, for the zeolites, it proved negligible within the experimental error), p is the dissociation pressure in mm. of mercury, T the absolute temperature, x the unoccupied fraction of the lattice positions available for the volatile component, E the difference between the activation energies of dissociation and recombination, in cal. per g.-mol. of volatile component, D the mean distance between lattice positions for the volatile component, and a the "condensation area," *i.e.*, the difference between the cross-section of a molecule of the volatile component and of the channels along which these molecules migrate. Both E and a often vary considerably with x , owing to lattice shrinkage, and the unknown functions $f(x)$ and $\phi(x)$ express this variation, E_0 and a_0 being the values of E and a when $x = 0$.

It was found for the zeolites that E is often a linear function of x , and that if the lattice-shrinkage is a linear function of x (as is often the case), $\{1+\phi(x)\}$ is adequately expressed by $\{1-x(r_0-r_1)/(r_0-\rho)\}$, where r is the effective radius of the channels along which the volatile component has to pass in its migration, and becomes r_0 and r_1 at complete hydration and complete dehydration respectively; ρ is the effective radius of the molecule of the volatile component. In the above formula, a_0 and D must refer to the same crystallographic direction; both will vary with direction in the crystal, but their product does not.

The above equation adequately explained the vapour-pressure phenomena shown by the zeolites, and it seemed desirable to test it with other systems. It was found to apply to the absorption by dehydrated zeolites of other vapours (*loc. cit.*), to the equilibrium of calcium sulphate hemihydrate, and to the compounds of potassium benzenesulphonate with several vapours; and its application to the palladium-hydrogen system is now described.

This system has been the subject of numerous studies, but the results are discordant, probably owing, at least in part, to the autocatalytic nature of the reaction in any one metal grain, which renders the attainment of true equilibrium difficult, especially in a series of experiments with increasing hydrogen content (Ubbelohde, *Trans. Faraday Soc.*, 1932, **18**, 275). The several sets of experimental data are in general agreement as to the approximate character of the equilibrium curves, but they differ widely as to the actual values of the dissociation pressures. The probable relative accuracy of the several sets of data cannot be discussed here, but probably none of them strictly represents true equilibria, and slight impurities in the palladium used might account, in part, for the discrepancies. For comparison with the proposed equation, each worker's data have been considered separately, and only a few series of experiments with increasing hydrogen content have been rejected.

There is adequate evidence that the hydrogen is present in the atomic state (*idem, ibid.*) and is accommodated in the interstices of the metal lattice. It is still uncertain whether there is one solid phase or two, but, as Ubbelohde points out (*loc. cit.*, p. 291, footnote), the only evidence in favour of two phases (Linde and Borelius, *Ann. Physik*, 1927, **84**, 747) must be discounted in view of the autocatalytic nature of the absorption in any one metal grain and the slow attainment of the final equilibrium, and the same considerations apply to the work of Mundt (*ibid.*, 1934, **19**, 721) on palladium-gold-hydrogen alloys. Since it is agreed that the metal atoms remain on a face-centred cubic lattice throughout, it appears reasonable to attempt the interpretation of the dissociation pressures, in the first place, on the assumption that no second phase is formed.

In the close-packed palladium lattice, the cell-side of which is 3.888 Å. for the pure metal, the cavities between the metal atoms form a second face-centred lattice, and have a radius of 0.57 Å., but the channels connecting one cavity with another are very narrow, and it is clear that hydrogen atoms (radius 0.55 Å.; Bohr, *Phil Mag.*, 1913, **26**, 476) cannot migrate as such within the structure. There is evidence, however, that the hydrogen is partly ionised (Coehn and Specht, *Z. Physik*, 1930, **62**, 1), and protons could migrate readily. The mechanism of migration within the crystal is not, however, of importance for the calculation of the dissociation pressure, and it is highly probable that the radius of the cavities (which increases with the marked lattice-expansion consequent on the absorption of hydrogen) will, in conjunction with the radius of the hydrogen atom, control the "condensation area," *a*.

It has usually been supposed that the composition Pd₂H has a special significance; indeed, it is often regarded as the true limiting composition of the alloys, any hydrogen in excess of this amount being regarded as adsorbed, or, still more vaguely, as "loosely held." It has been repeatedly shown, however, that the composition above which extra hydrogen is "loosely held" is actually nearer PdH_{0.55}. Further, unless evidence can be brought that the true unit cell of palladium-hydrogen alloys is a multiple of that of palladium, the limiting composition must be PdH, for the minimum number of lattice positions in any one set in a close-packed cubic structure is 4. There is no evidence of a multiple cell, and it appears legitimate to make a first attempt at interpretation by assuming this limiting composition. If Duhm's estimate (*Z. Physik*, 1935, **94**, 435) of the degree of ionisation of the hydrogen is correct, the hydrogen must be lodged in the large cavities, and the structure will be a sodium chloride type; but if the hydrogen is almost or quite completely ionised, as has been suggested, other structures are possible.

Now, in true equilibrium, the above equation must hold for the minute partial pressure of atomic hydrogen in the gas; assuming for the dissociation equation of hydrogen

$$\log [H_2] = 2\log [H] + q/RT \ln 10 - 1.50 \log T - 3.66$$

[H₂] and [H] being in mm. Hg, we have for the palladium-hydrogen system

$$\log p = 8.27 + 2\log 4\sqrt{RE}/\chi a_0 DN \sqrt{\pi} - \frac{1}{2} \log T - 2\log x/(1-x) - 4\log \{1 + \phi(x)\} - \frac{(2E_0 - q)\{1 + f(x)\}}{RT \ln 10}$$

Here *p*, the partial pressure of hydrogen molecules, is practically equal to the total pressure; and *q* is the molecular heat of dissociation of hydrogen. The proportion of hydrogen lattice positions occupied is taken as (1 - *x*), to conform to the convention used for the zeolites.

If the lattice expansion on absorption of hydrogen is assumed to be proportional to the hydrogen absorbed (as appears probable from the data of Linde and Borelius, *loc. cit.*, on electrolytically prepared alloys), *a*₀{1 + $\phi(x)$ }² may be replaced by

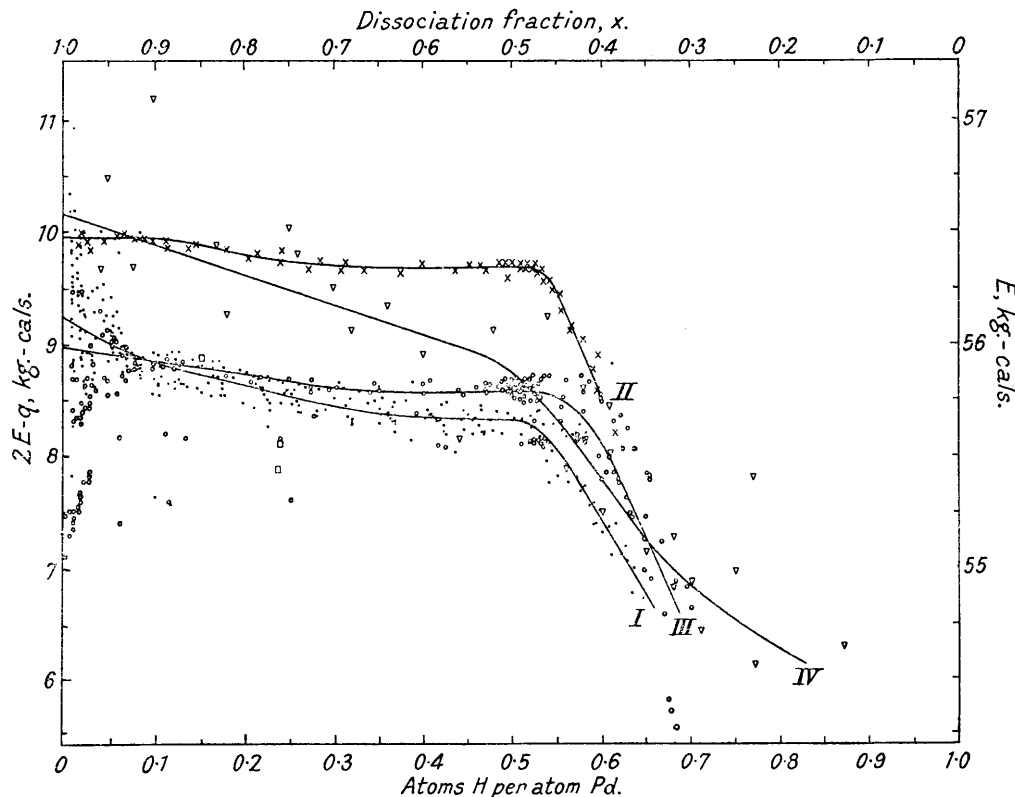
$$a_1 \{1 + (1-x)(r_0 - r_1)/(r_1 - \rho)\}^2,$$

where *a*₁ is the value of *a* for pure palladium (*x* = 1), and *r* and ρ are defined as above; the experimental data are not adequate definitely to confirm or disprove this assumption.

Hoitsema's data (*Z. physikal. Chem.*, 1895, **17**, 1) were considered first because they are the most numerous. From them the values of the constants were deduced

as $(r_0 - r_1)/(r_1 - \rho) = 12$ approx. and $C' (= \log 4\sqrt{RE_1}/\chi a_1 DN\sqrt{\pi}) = 1.89$, while $(2E - q)$ varies with x in a non-linear manner, as shown in curve I in the figure. In order to show the agreement of the calculated and the observed results in the minimum of space, values of $(2E - q)$ were calculated from each observed pressure and the other two constants, and these are plotted as dots in the figure.

The descending isotherms of Lambert and Gates (*Proc. Roy. Soc.*, 1925, **108**, A, 456) are not suitable for accurate computation, since there is only one complete and two partial isotherms, so that, however accurate the data may be in themselves, it is not possible to derive accurate constants from them. If it is assumed that the variation of $2E - q$ with x is negligible for hydrogen contents below $\text{PdH}_{0.1}$, $(r_0 - r_1)/(r_1 - \rho)$ is again approximately 12. This value being accepted, $C' = 2.16$, and $2E - q$ varies with x as shown



in curve II in the figure; again, values of $2E - q$ calculated from each observed pressure and the other two constants are plotted for comparison, as crosses.

Gillespie and Hall's data (*J. Amer. Chem. Soc.*, 1926, **48**, 1207) proved too erratic to fix $(r_0 - r_1)/(r_1 - \rho)$ unambiguously; if this is assumed to be 12, however, $C' = 1.95$, and the $2E - q$ values plotted as circles in the figure are obtained; through these, the smooth curve III is drawn. Ipatieff and Tronow's high-pressure data (*J. Physical Chem.*, 1934, **38**, 623) are still more erratic; assuming $(r_0 - r_1)/(r_1 - \rho) = 12$ and $C' = 2.16$, $2E - q$ can be computed for each observation, and these results are plotted as triangles, erratically distributed about the smooth curve IV.

By assuming $(r_0 - r_1)/(r_1 - \rho) = 12$ and $C' = 1.89$, reasonable values of $2E - q$ (squares in fig.) are calculated from Dewar's three observations (*P.*, 1897, **13**, 192). On the other hand, Sieverts's data (*Z. physikal. Chem.*, 1914, **88**, 103, 451) lead to completely different constants. The probable explanation is that, at the very low hydrogen contents

and high temperatures of these experiments, an appreciable part, if not most, of the hydrogen is adsorbed on the surface of the metal, but further study is necessary in this field before any definite conclusion can be reached.

Hence, the proposed equation is capable of explaining all the sets of experimental data if appropriate constants are used; which data (and constants) are correct can only be shown by further experiment. Moreover, all the values of $2E - q$ found are in fair agreement with the calorimetric value of the heat of combination (Mond, Ramsay, and Shields, *Proc. Roy. Soc.*, 1893, **62**, 290), *viz.*, 8740 cal. per g.-mol. of hydrogen at 0° for the range Pd to PdH_{0.5}, as will be seen from the table.

It was seen above that $(r_0 - r_1)/(r_1 - \rho)$ is best taken as 12, while r_1 is 0.57 Å.; if $(r_0 - r_1)$ is known, ρ can be calculated approximately. Unfortunately, most of the lattice-expansions given in the literature are useless, since the authors have assumed the composition of the alloy examined (Thoma, *Z. physikal. Chem.*, 1889, **3**, 69; Yamada, *Phil. Mag.*, 1923, **45**, 241; McKeehan, *Physical Rev.*, 1923, **21**, 334; Hanawalt, *ibid.*, 1929, **33**, 444). Only Linde and Borelius (*loc. cit.*) worked with material of known composition, and their results for electrolytically prepared alloys may probably be accepted as accurate; an expansion proportional to the hydrogen content was observed, and leads on extrapolation to 4.093 Å. for the cell side of PdH, or $(r_0 - r_1) = 0.102$ Å. Hence $r_1 - \rho = 0.008$ Å., giving 0.562 Å. for the radius of the hydrogen atom.

For the zeolites it proved possible to compute a by assuming for χ the probable value of unity. For the palladium-hydrogen system, it is by no means so certain that χ approximates closely to 1, so that a cannot be calculated with any accuracy; some of the other assumptions involved in the derivation of the equation and in its application to the experimental data are also likely to vitiate the calculation of a . It has, however, been made for each value of $\log 4\sqrt{RE_1}/\chi a_1 DN\sqrt{\pi}(= C')$, on the assumption that $\chi = 1$, and the results are included in the table. All are certainly much too high; if $r_1 - \rho = 0.008$ Å., as deduced above, a should be 0.0002 sq. Å. How far this discrepancy arises from the imperfections of the equation itself, and how far from inaccuracies in the experimental data or approximations made in the application of the equation to the data remains uncertain. The calculations of a were made by taking the heat of dissociation of hydrogen, q , as 10.3×10^4 cal. per g.-mol. (Bodenstein and Jung, *Z. physikal. Chem.*, 1926, **121**, 127), which leads to the several values of E_1 , the net activation energy of the hydrogen absorption process for pure palladium and atomic hydrogen, shown in the table.

It is not at all clear what significance is to be attached to the sudden fall in E at hydrogen contents greater than about PdH_{0.52}, shown in curves I, II, and III; it may possibly indicate that, contrary to the assumption made above, a second phase is formed, the transition line falling at compositions slightly richer in hydrogen than PdH_{0.5} for all temperatures, at least up to about 200°; or it may indicate that the hydrogen really occupies more than one set of equivalent lattice positions, which would involve a larger unit cell in the alloys than in pure palladium; or, again, it may be that the assumption of a linear relation between the lattice expansion and the hydrogen content is not correct, and that with a proper choice of the function $\phi(x)$, a smoother curve for E would result; or the fall may be a real physical phenomenon. The experimental data are not adequate to decide which of these possibilities is correct, but several unsuccessful attempts were made to reach interpretations on the first three assumptions.

Dissociation constants for the palladium-hydrogen system, calculated from the available data.

	$(r_0 - r_1)/(r_1 - \rho)$	C'	E_1 , kg.-cals.	a , sq. Å.	Q, \dagger kg.-cals.
Hoitsema	12	1.89	56.1	4.1	8.32
Lambert & Gates	12	2.16	56.5	2.2	9.52
Gillespie & Hall	12*	1.95	56.0	3.6	8.43
Ipatieff & Tronow	12*	2.16*	56.6	2.2	9.20
Dewar	12*	1.89*	—	—	8.0†

* Assumed.

† Heat of reaction per g.-mol. H₂ at 0°, over the range Pd to PdH_{0.5}.

‡ Heat of reaction at a composition about PdH_{0.2}.

SUMMARY.

An equation developed from simple kinetic theory is shown to give a reasonably satisfactory account of the dissociation pressures of the palladium–hydrogen system, on the assumption that there is only one phase present throughout. The limiting composition of the system is PdH, which possibly has sodium chloride type structure. The equation is probably a first approximation to the truth.

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