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Solubility of Hydrogen in Small Particles of Palladium

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The solubility of hydrogen in palladium, m, defined as the number of dissolved hydrogen atoms divided by the total number of metal atoms has been measured between 273 and 343 K from 13.3 to 53.3 kPa. At a given temperature and pressure, m was found to decrease linearly as the percentage dispersion D of the metal increased, m being zero at $D = 100\%$. Measurements of m were carried out under conditions such that the surface of the metal particles was covered with almost a monolayer of hydrogen. This chemisorbed hydrogen seems to affect solubility of hydrogen in bulk palladium in a way similar to that of silver in palladium–silver alloys. Values of m are potentially helpful in the characterization of used palladium catalysts.

INTRODUCTION

A recurrent theme in heterogeneous catalysis is the interaction between surface and bulk states. This can be particularly important in the case of very small particles as found in supported metal catalysts with metal dispersion between 10 and 100%.

A particularly well-suited system for such an investigation is the palladium–hydrogen system. As a matter of fact, the absorption of hydrogen in bulk palladium and in relatively poorly dispersed palladium black has been extensively investigated since Thomas Graham reported the absorption of hydrogen into palladium in 1866.

However, both the absorption and adsorption of hydrogen into and on very small palladium crystallites have not been systematically investigated as yet. In 1968, Aben (*1*) reported hydrogen sorption isotherms at 343 and 195 K for supported palladium samples. He found that the total amount of hydrogen uptake in the β-phase decreases as the dispersion of the metal increases, and he attributed his observation to the decrease of hydrogen solubility with increasing dispersion of the metal.

This finding can now be reexamined as we have shown recently (*2*) that absorbed hydrogen in the β-phase hydride can be removed readily by outgassing a supported palladium sample for 720 s at room temperature (RT). Thus, by outgassing the sample for 1200–1800 s at RT and by assuming that the adsorbed hydrogen was not significantly removed but all absorbed hydrogen was removed, we were able to separate absorbed hydrogen from adsorbed hydrogen. This finding provides a useful tool to study the adsorption of hydrogen on a palladium surface and the absorption of hydrogen into palladium crystallites. In fact, we have shown previously (*2*) that the amount of adsorbed hydrogen can be determined by taking the difference between the total hydrogen measured on a clean Pd surface (i.e., by the *sorption method*), and that measured on a surface covered with adsorbed hydrogen (i.e., by the *back-sorption method*). The dispersion of Pd determined in this way agrees with

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dispersion determined by hydrogen titration at 373 K, oxygen titration at RT, CO chemisorption at RT, oxygen chemisorption at RT and X-ray line broadening (*2*).

The difference in the removal of absorbed and adsorbed hydrogen is very clearly shown also for bulk palladium samples. Thus, Aldag and Schmidt (*3*) have studied the interaction of hydrogen with palladium wires by flash filament desorption. The sorption of hydrogen rapidly reached equilibrium in about 2200 s, even at 200 K and approximately 7×10^{-7} Pa. The peak maximum of the desorption spectra corresponding to absorbed hydrogen was at about 250 K, but the peaks corresponding to adsorbed hydrogen were at 370, 450 and 600–800 K.

Similar observations have been reported by Yamabe *et al.* (4) who investigated the desorption of hydrogen sorbed by Pd supported on silica–alumina between 273 and 308 K. Yamabe *et al.* concluded that hydrogen is sorbed by palladium in three states, i.e., weakly adsorbed H_2, absorbed H and strongly adsorbed H. Their results show that the absorbed hydrogen and the weakly chemisorbed hydrogen can be completely removed by outgassing for 1 hr at 293 K, after which only the strongly chemisorbed hydrogen remained on the surface.

Lynch and Flanagan (*5*) have also investigated the effect of pumping on the equilibrated Pd–H_2 system. After reducing their palladium black sample at 298 K, they outgassed it for 12 hr at 298 K; hydrogen was then admitted to the sample and an isotherm was measured. The isotherms measured by this hydrogen back-sorption method were very reproducible even if the sample had been outgassed for 18 hr. Therefore, they concluded that there is a sharp division between strongly held and weakly held hydrogen and that strongly chemisorbed hydrogen cannot be removed by simple evacuation at 298 K.

In our present study, we have used the hydrogen back-sorption method to study the solubility of hydrogen into small palladium crystallites between 273 and 343 K, from 13.3 to 53.3 kPa. The dispersion of palladium varied between 12 and 73%. In the course of this work, the amount of hydrogen chemisorbed on palladium at various temperatures and pressures was also investigated.

EXPERIMENTAL METHODS

Samples

A 2.40% Pd/SiO_2 sample was prepared by cation exchange. The preparation has been described (*6*). The support was silica gel obtained from Davison Chemical Co. (grade 62). After the ion exchange, the final slurry was filtered, the filtrate was washed with 25 cm^3 of distilled water/g of support, and then dried in a vacuum oven overnight at room temperature. The product will be designated as precursor.

A portion, called sample A (1.050 g), of the precursor was outgassed for 2 hr at RT and the Pd $(NH_3)_4^{2+}$ ions were decomposed in flowing oxygen by gradually increasing the temperature to 673 K at a rate of 90 K hr^{-1} (*7*). The catalyst was reduced for 1 hr at 653 K in flowing hydrogen (space velocity 1.0 s^{-1}).

A second portion, called sample B of the precursor was first reduced for about 0.5 hr at R T in static hydrogen at approximately 70.7 kPa. The temperature was increased to 663 K and subsequently reduced at this temperature in flowing hydrogen for 12 hr (space velocity 1.0 s^{-1}).

Sample C, 2.84% Pd/SiO_2, was prepared by impregnation (*8*). A measured amount of $PdCl_2$ was dissolved in a small quantity of concentrated HCl (12.0 *M*). The solution was evaporated at 343 K to almost dryness to boil off excess acid, and distilled water was added to obtain the required amount of salt solution, which was just enough to wet the pore of the sup-

port. This salt solution was mixed with the support (Davison grade 62) and was stirred vigorously. The sample was calcined overnight in air at 773 K and reduced at 653 K for 1 hr.

Sample D, 4.88% Pd/Al_2O_3, was obtained from Engelhard Industries. A fresh sample was oxidized for 300 s in oxygen at approximately 573 K and was subsequently reduced at 653 K for 2 hr in flowing hydrogen. For all samples, the metal content was determined by analysis and the dispersion of the metal was obtained by titration with hydrogen at 373 K (*2*).

Measurement of Solubility of Hydrogen in Palladium

The solubility of hydrogen in palladium was measured by the hydrogen back-sorption method (*2*). Except for sample C, the work was carried out in a conventional volumetric adsorption apparatus (*9*). To carry out the hydrogen back-sorption method employed for samples A, B, and D, the standard procedure was as follows. After the proper pretreatments of a sample as described earlier, the sample was outgassed at RT, then hydrogen was admitted, and the system was allowed to reach equilibrium (at least 3 hr at 298 K). *The sample was then outgassed for 1200 s at 298 K, followed by exposure to a measured amount of hydrogen.* This system was allowed to reach equilibrium for at least 3 hr at 303 K and about 53.3 kPa. The isotherm at 303 K was then taken and the waiting period between subsequent data points of the isotherm was 0.5 hr. While keeping the originally dosed amount of hydrogen in the system after measuring the 303 K isotherm, the isotherms at 273, 323 and 343 K were then taken in the manner similar to that of 303 K isotherm.

For sample C, experiments were carried out in a new volumetric apparatus which has been described elsewhere (*10*). The pressure in the system was monitored by a precision pressure gauge built by Texas Instruments Inc. For each individual isotherm at a given temperature, namely 273, 303 and 323 K, a standard procedure for carrying out the hydrogen back-sorption method is described by the following: the sample was first brought to equilibrium with hydrogen at RT for at least 3 hr and at approximately 39.9 kPa and was subsequently *outgassed for 1200 s at RT* (about 298 K). A measured amount of hydrogen was admitted to the system to attain a pressure of about 60.0 kPa. After 0.5 hr equilibration, the first data point of the isotherm was then taken. Before measuring each subsequent data point, a small portion of hydrogen was removed from the system. Then the system was allowed to reach equilibrium at the new pressure for about 0.5 hr before data were taken. It is clear that the condition of the surface at 298 K and zero pressure will play the role of a reference state as discussed below.

Hydrogen (Liquid Carbonic) was purified by diffusion through palladium. Except for sample C the apparent dead volumes at various temperatures were determined by helium (Liquid Carbonic Grade A, passed over Cu wire and through a liquid nitrogen trap) as described elsewhere (*2*). For sample C, the apparent dead volumes were determined with neon (Matheson, Research Grade, used without further purification) by the same method.

RESULTS

Values of palladium dispersion for samples A, B, C, and D were 73, 51, 12 and 21%, respectively.

Typical isotherms at various temperatures are shown in Fig. 1. From the uptake at a given temperature and at 26.7 kPa, the apparent solubility m', $H_t(T,P)/Pd_t$, for various samples can be calculated, where Pd_t is the total amount of palladium atoms present in the sample,

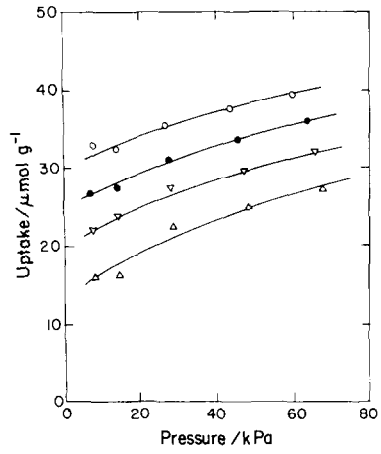

FIG. 1. Hydrogen back sorption isotherms (sample B). (○) 273 K; (●) 303 K; (▽) 323 K; (△) 343 K.

and $H_t(T,P)$ is the total uptake of dissociated hydrogen H as measured experimentally at temperature T and pressure P. These values of m' are plotted against dispersion in Fig. 2. In Fig. 2, the solubility m at 273, 303 and 323 K for bulk palladium is also shown as given by Wicke and Nernst (*11*). Also shown in Fig. 2 are values of solubility obtained from data of Aben (*1*). These values, at 26.7 kPa and 343 K, are equal to the difference between the total uptake taken from Aben's sorption isotherms and the uptake due to the adsorption calculated from the dispersion of the metal.

As seen in Fig. 2, values of m' at a given temperature T and 26.7 kPa may be extrapolated linearly to 100% dispersion to yield an intercept, called $\Delta\theta(T,26.7)$. Similarly, by repeating the same procedure as described above, we obtain other values of $\Delta\theta(T,P)$, namely the intercepts at 100% dispersion at any given temperature T and pressure P. As discussed below, $\Delta\theta(T,P)$ is actually the difference in the fraction of surface covered with H atoms on a sample with 100% dispersion at a given temperature T and pressure P, and that at 298 K and zero pressure, the reference state mentioned above in the description of procedure.

Since $\Delta\theta(T,P)$ is a function of temperature and pressure, we may plot $\Delta\theta(T,P)$ against pressure at a given temperature as shown in Fig. 3. By extrapolating the straight-line plots at a given temperature in Fig. 3 to zero pressure, we obtain the intercept, called $\Delta\theta(T,0)$. If we assume that hydrogen is chemisorbed in a monolayer at 273 K and zero pressure, we can call $\Delta\theta(T,0)$ more simply $\theta(T,0)$, and plot it against temperature (Fig. 4). The validity of the assumption that $\theta(273,0) = 1$ is discussed below.

The total hydrogen uptake as measured by hydrogen back-sorption includes the

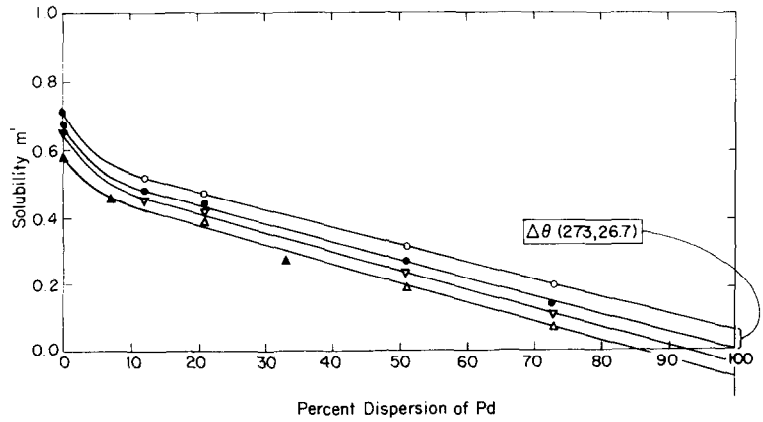

FIG. 2. Solubility of hydrogen in Pd at 26.7 kPa H_2. Apparent solubility m': This work: (○) 273 K; (⊗) 303 K; (▽) 323 K; (△) 343 K; Aben (*1*): (▲) 343 K. Solubility m: Wicke and Nernst (*11*): (●) 273 K; (■) 303 K; (▼) 323 K.

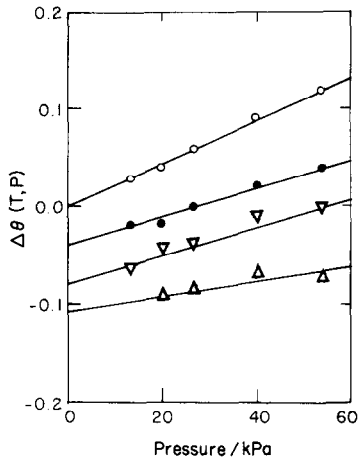

FIG. 3. $\Delta\theta(T,P)$ vs pressure for the Pd–H_2 system. (○) 273 K; (⊗) 303 K; (▽) 323 K; (△) 343 K.

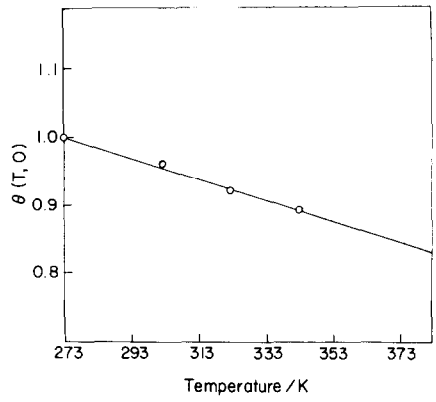

FIG. 4. Surface coverage $\theta(T,0)$ vs temperature for the Pd–H_2 system, extrapolated to zero pressure.

amount of hydrogen due to both chemisorption and solubility at various temperatures and pressures. For a sample with percentage dispersion D, the correction due to chemisorption is: $\Delta\theta'(T,P) = \Delta\theta(T,P) \times (D/100)$. Therefore, the true amount of the absorbed hydrogen at a given temperature and pressure, $H_b(T,P)$, is equal to the difference between the total hydrogen uptake determined by the hydrogen back-sorption method under the same conditions, and the amount of hydrogen $\Delta\theta'(T,P)$ due to chemisorption.

Correcting for chemisorption in this manner gives the true solubility m, $H_b(T,P)/Pd_t$, which is plotted against pressure in Fig. 5. At a given pressure, the solubility is also plotted against percentage dispersion D of palladium, and a typical

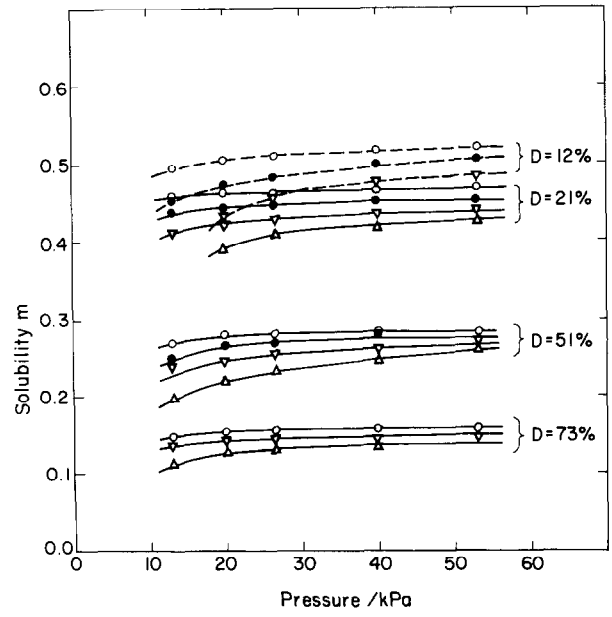

FIG. 5. Solubility m of hydrogen in palladium of dispersion D vs pressure. (○) 273 K; (⊗) 303 K; (▽) 323 K; (△) 343 K.

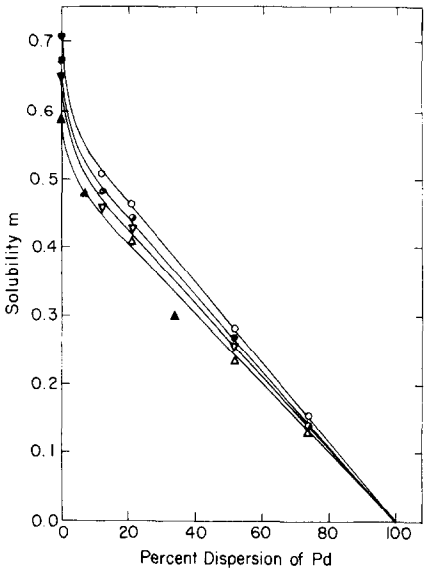

FIG. 6. Solubility m of hydrogen in Pd at 26.7 kPa. This work: (○) 273 K; (⊗) 303 K; (▽) 323 K; (△) 343 K; Wicke and Nernst (*11*): (●) 273 K; (■) 303 K; (▼) 323 K; Aben (*1*): (▲) 343 K.

plot is shown in Fig. 6. Here again the solubility is a linear function of dispersion but is now zero at 100%,

$$m = \frac{H_b(T,P)}{Pd_t} = c\left(1 - \frac{D}{100}\right), \qquad (1)$$

where c is a constant equal to the intercept obtained by extrapolating the straight line to zero dispersion. Since the number of bulk palladium atoms (Pd_b) is equal to the difference in the number of total palladium (Pd_t) and surface palladium atoms (Pd_s) and since $D = (Pd_s/Pd_t) \times 100$ Eq. (1) may be rearranged to give:

$$\frac{H_b(T,P)}{Pd_b} = c. \qquad (2)$$

DISCUSSION

Chemisorption

If solubility of hydrogen in small palladium particles is defined as $m = H_b/Pd_t$ where H_b is the number of bulk hydrogen atoms and Pd_t is the total number of palladium atoms in the particle, then clearly, m must be zero when the dispersion of the metal reaches 100%. Thus, the nonzero intercepts on the right ordinate axis of Fig. 2 gives prima facie evidence that the solubility data must be corrected for changes in chemisorption when the system is taken from its original reference state at 298 K and zero pressure to the state at T and P corresponding to a data point of the backsorption isotherm. Admittedly, such an interpretation of the intercepts is highly intuitive, as it rests in the first place on the simple minded assumption that the straight lines of Fig. 2 can be extrapolated as straight lines to 100% dispersion. It is not surprising that after the corrections based on this interpretation and described in the previous section, corrected values of solubility as shown on Fig. 6, are well behaved in the sense that they now all extrapolate to zero at 100% dispersion.

But were the corrections justifiable in the first place? They seem to be physically meaningful for the following reasons. First of all, these corrections ascribed to changes in surface coverage increase with pressure and decrease with temperature, as is excepted from a weak chemisorption in the vicinity of a complete monolayer. This can be seen from Fig. 3 and from values of isosteric heats and standard entropies of adsorption calculated from the data of Fig. 4 and listed in Table 1. Both heats and entropies have correct signs and reasonable values. The values are uncertain although they are not inconsistent with those of others (5). Indeed, if it is granted that a monolayer is maintained on palladium at 273 K and at extrapolated zero pressure, the values of heat and entropy listed in Table 1 and (5) clearly fall into two groups: below monolayer (larger heats and entropies) and above monolayer (smaller heats and entropies). Third, the assumption of monolayer coverage at 273 K and zero pressure, leads to Fig. 4 which

TABLE 1
CALCULATED ISOSTERIC HEATS q_{st} AND STANDARD ENTROPIES $\Delta\bar{S}$ OF CHEMISORPTION OF HYDROGEN ON PALLADIUM IN THE MONOLAYER REGION

$\Delta\theta(T,P)$	$\theta(T,P)^a$	Temp (K)	Pressure (kPa)	q_{st} (kJ mol^{-1})	$-\Delta\bar{S}^b$ (J K^{-1} mol^{-1})
0.04	1.04	273	18.0	25.1	77.4
		303	53.3		
0.03	1.03	273	13.3	28.9	88.7
		303	46.7		
0.01	1.01	273	4.7	35.6	107.9
		303	33.3		
		323	60.7		
0.00	1.00	303	26.7	27.6	79.9
		323	53.3		
−0.02	0.98	303	13.3	41.8	121.3
		323	38.7		
−0.03	0.97	303	7.3	57.3	167.4
		323	31.3		
−0.06	0.94	323	13.3	69.0	197.1
		343	59.3		

[a] $\theta(T,P)$ is the fraction of surface covered, with the assumption that hydrogen chemisorption reaches a monolayer coverage at 273 K and zero pressure.
[b] $\Delta\bar{S} = -(q_{st}/T) - R \ln P(\text{atm})$.

indicates a value of fraction of surface coverage of about 0.84 at 373 K and zero pressure. But this is the same value reported by Sermon (*12*) for the same conditions, following a detailed study of hydrogen chemisorption on palladium. The agreement between our "correction" and the work of Sermon provides evidence in support of the interpretation we have given to our corrections.

With respect to the value of 84% obtained by Sermon and ourselves, let us note that the hydrogen titration at 373 K used in this work to determine the dispersion of the metal, as developed in Ref. (*2*), will slightly underestimate the palladium surface area, but not by 16% as would be the case with hydrogen chemisorption at 373 K, extrapolated to zero pressure but only by 6% if it is assumed, as was shown to be reasonable in Ref. (*2*), that a complete monolayer of oxygen is kept at the surface of palladium under the selected conditions of hydrogen titration. The lack of sensitivity of the hydrogen titration to minor changes in hydrogen chemisorption is a straightforward consequence of the stoichiometry of the titration:

$$PdO + {}^3/_2H_2 \rightarrow PdH + H_2O.$$

At any rate, corrections due to changes in hydrogen chemisorption in the region of a monolayer, interesting as they may be, do not affect significantly reported values of palladium dispersion. Nor do they affect the main conclusions of the present study which will not be discussed.

Solubility

As seen in Fig. 6, the true or corrected solubility m of hydrogen in palladium falls linearly with dispersion of the metal in the range covered by this investigation and that of Aben (*1*). This is a striking result and its meaning deserves further scrutiny. It is an unexpected result. Only coincidence could then produce a remarkably linear relation between average values of m and dispersion.

In fact, it seems that the definition of m

as the ratio of number of dissolved H atoms to *total* number of palladium atoms may be misleading. Indeed if solubility is defined as the ratio of number of dissolved H atoms to the number of *bulk* (i.e., nonsurface) palladium atoms, then this solubility is a constant c, at a given temperature and pressure, irrespective of dispersion or average particle size, as shown in Eq. (2). This result then appears very simple, namely, solubility c is independent of particle size, except that the experimental value of c is less than the value corresponding to a bulk sample of dispersion effectively equal to zero, as shown on Fig. 6 by the upturn of the straight lines toward the left ordinate axis. For instance, at 373 K and 26.7 kPa, c is equal to 0.59; whereas the solubility in bulk palladium is 0.70 (*11*). Thus whether we use m or c as a measure of solubility, dispersed palladium dissolves less hydrogen in the β-phase region than bulk palladium.

The nature of that difference is best understood at this stage by a comparison between isosteric heats of hydrogen absorption in palladium–silver alloys obtained from the work of Brodowsky and Poeschel (*13*) on the one hand and in small palladium crystallites obtained from the data of Fig. 5 on the other hand. This comparison, shown on Fig. 7, reveals that in first rough approximation, the isosteric heat of solution at a given value of solubility m is approximately equal for a bulk palladium alloy containing an atomic percentage of silver equal to x and for a collection of small palladium particles with a percentage dispersion also equal to x.

The meaning of this comparison becomes apparent if it is remembered that the solubility of hydrogen in supported palladium samples is measured under conditions such that the palladium surface is covered with a monolayer of hydrogen. But it is well known that with respect to magnetic susceptibility, palladium is affected both by dissolved hydrogen or alloyed silver, as if the rigid band approximation were valid, i.e., as if each solute atom would contribute its s electron to the unfilled d band of the metal (*14*). While the true picture of this electronic interaction is believed today to be more complex (*13*), the empirical observations concerning a similar change in the electronic properties of palladium due to either hydrogen or silver remain correct and are confirmed by the present work which suggests that *surface* hydrogen decreases the heat of solution and therefore the solubility of hydrogen in palladium particles like bulk silver does it in bulk palladium–silver alloys, as shown in Fig. 7.

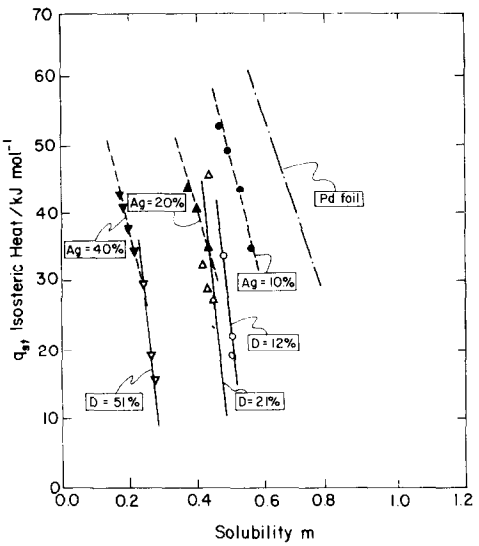

FIG. 7. Isosteric heat vs solubility. Pd particles: (—) this work (T = 273–343 K); Pd–Ag foils: (---) Brodowsky and Poeschel (1965) (T = 303–373 K); Pd foil: (—·) Wicke and Nernst (1964) (T = 273–323 K).

A more detailed explanation of the effect of dispersion of palladium on solubility of hydrogen requires a more subtle distinction between surface atoms and possibly several kinds of subsurface (or bulk) atoms, as well as a clearer understanding of the electronic structure of palladium hydride.

In the meantime, the empirical results collected in Figs. 5 and 6 can be used in the characterization of supported palladium catalysts. As an example consider a palladium catalyst with $D = 60\%$. After use, a new measurement of dispersion yields $D' = 30\%$. This could mean either a doubling of the average crystal size or a poisoning of half of the palladium particles with the same original size, the poisoning being such that the entire palladium surface of 50% of the particles is entirely blocked to hydrogen adsorption or absorption. A measure of hydrogen solubility m, say at 323 K and 26.7 kPa, could decide between the two alternatives. If the value of m for the used catalyst is 0.36, sintering has indeed taken place. But if m turns out to be 0.11, poisoning must have taken place. Another alternative, brought to our attention by a reviewer, is that 50% of the surface of each particle has been blocked by the poison. In this case, the value of m should be the same as before, namely 0.26.

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