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Short Notes

FAST AND SLOW SORPTIONS OF HYDROGEN ON EVAPORATED PALLADIUM FILMS

By Akiya MATSUDA and Toshio NAKATA^{*)}

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It is well-known that the initial rapid hydrogen chemisorption is followed by the slow sorption on evaporated films of transition metals¹⁻⁶⁾. The two sorts of hydrogen sorption, however, have not been distinctly separately observed, mainly because of the situation that the former is too rapid to be followed.

The present authors have observed now both the rapid chemisorption and the slow sorption on palladium films separately by means of an arrangement similar to that used by one of the present authors⁷⁾ but that the diameter of tungsten filament of the PIRANI gauge was diminished from 20 to 13 μ and the diameter of the combining tubes was increased from 10 to 18 mm, which has reduced the time lag of the PIRANI gauge 40 times as small as the previous one.

The palladium film was deposited on the wall of the reaction vessel from a "spectroscopically pure" palladium wire of 1 mm diameter from TANAKA Noble Metal Co. Ltd. Tokyo, heated with an induction furnace. The palladium film obtained was of 10 mg weight and of 60 cm² apparent area, which was sintered at 400°C in high vacuum for 5 hours before sorption measurements.

A definite dose *ca.* $5 \cdot 10^{-8}$ moles of hydrogen was admitted step by step to the evacuated reaction vessel accumulating one dose after another, the pressure *P* indicated by the PIRANI gauge being followed with time *t* by an oscillograph in each run after an admission. The dose of hydrogen was the same throughout for each series of runs thus carried out. Earlier runs in a series were conducted every five minutes, while the later ones every 10 minutes to allow a sufficient time for the pressure change to be completed. A typical example of the series of runs is shown in Plate 1 (oscillogram). Hydrogen was sorbed within half a second in earlier runs leaving a small but sharply constant residual pressure, which was stepped up, as shown in the oscillogram, with successive runs. After several first runs the slow sorption appeared as seen from the oscillogram, when the time interval between the runs was lengthened to ten minutes as for

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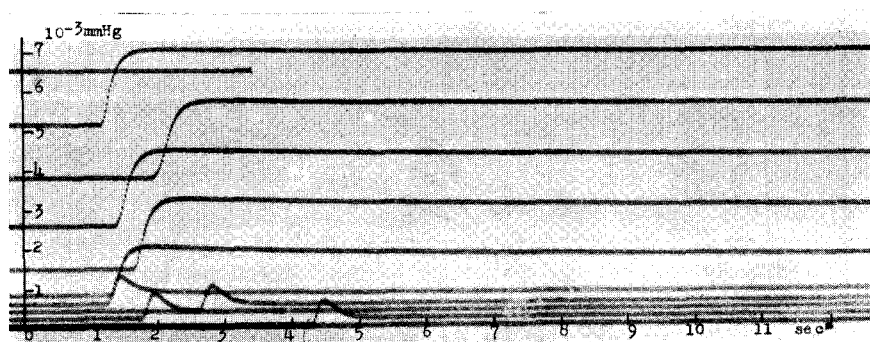


Plate 1 The pressure change with time t for a series of hydrogen admission.

all later runs throughout. In these runs, however, the maximum pressure observed within the first half a second is lower than the pressure which would be revealed by hydrogen admitted without sorption. It is concluded from this fact that the rapid sorption takes place side by side with the slow sorption at this stage, the amount of the slow sorption being, however, negligibly small during this short period of the rapid sorption as extrapolated from the observed rate of the slow sorption. Later runs, subsequent to these intermediate runs, indicate the slow sorption alone but not the rapid one in the above sense. The slow sorption observed in the intermediate and the later runs continued for a few minutes, the pressure remaining constant for the rest of 10 minutes time interval allowed.

The amount of rapid sorption in earlier runs was given by the excess of the amount of hydrogen admitted over that of the constant residual amount of hydrogen. The amount of rapid sorption in the intermediate runs was determined at the difference between admitted amount of hydrogen and the residual hydrogen at the maximum of the oscillogramm mentioned above, while that of slow sorption as the amount of hydrogen decrease in gas from the above maximum to the final constant pressure. The amount of sorption in later runs is given simply by the difference of hydrogen amount admitted and the constant residual amount of hydrogen finally attained. We see from the above results that the rapid and slow sorptions are so distinctly observed separate from each other, that the amount of hydrogen uptake in each sorption could readily be severally evaluated as above.

Fig. 1 shows the logarithm of the total sum n_r of the successive amounts of rapid sorption, evaluated as above, plotted against the logarithm of the residual pressure for earlier runs or the maximum pressure attained after admission for

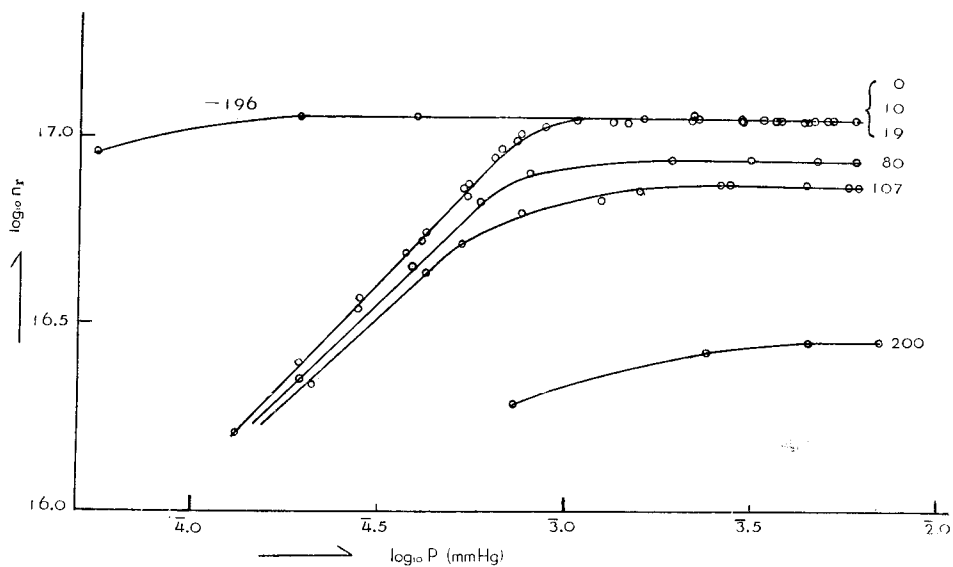


Fig. 1 The isotherms of the fast chemisorption of hydrogen on an evaporated palladium film.

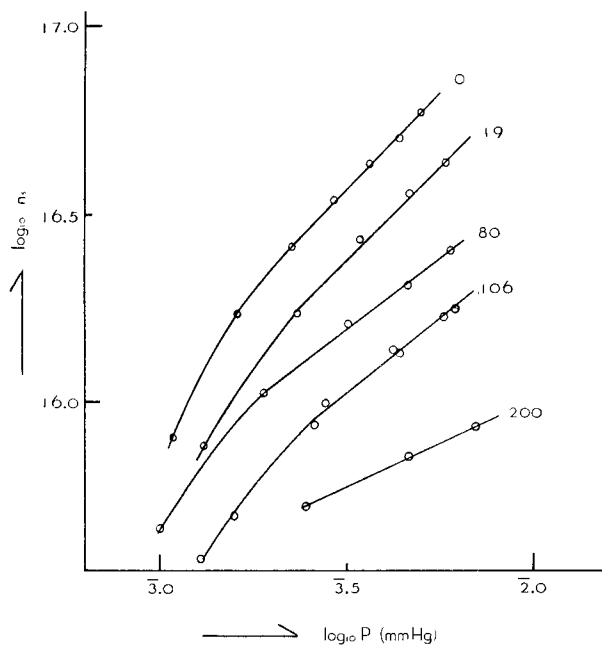


Fig. 2 The isotherms of the slow sorption of hydrogen on an evaporated palladium film.

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intermediate and later runs, and Fig. 2 the similar plot of the total sum n_s of the successive amounts of slow sorption versus the residual pressure finally attained. The n_s approaches a saturation value $n_{r,s}$ with increasing pressure as seen from Fig. 1. The plot of $n_{r,s}$ against the temperature in Fig. 3 shows that it increases linearly with decreasing temperature up to $n_{r,\infty}$ at room temperature, remaining there constant throughout the lower temperatures.

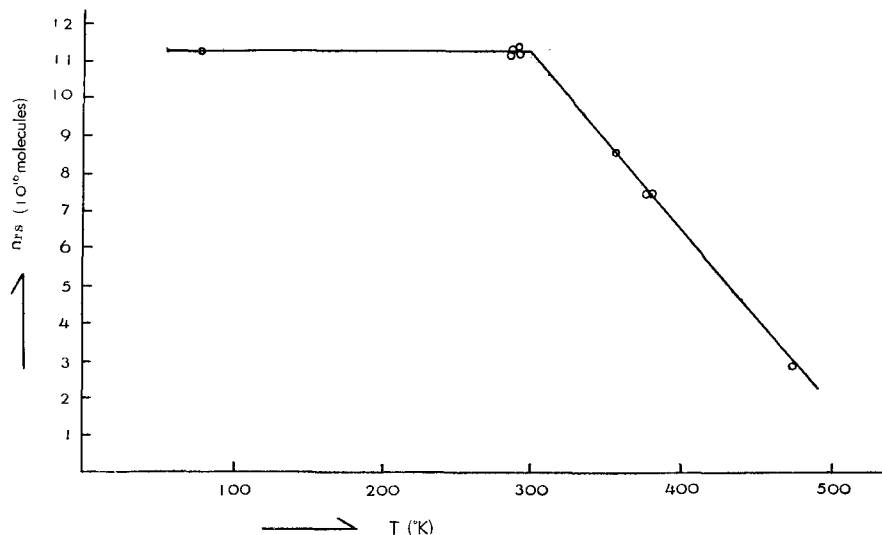


Fig. 3 The saturation value $n_{r,s}$ of the fast chemisorption plotted against the absolute temperature T .

The amount of adsorption sites is evaluated to be $2.3 \cdot 10^{17}$ from $n_{r,\infty}$, which is assumed with BEECK^{2,3)} to correspond to the full coverage of the surface; the number of sites per apparent unit area is thus calculated at $4 \cdot 10^{15}$ and hence the roughness factor of the palladium film is 3.0, on the base of $1.3 \cdot 10^{15}$ palladium atoms exposed per unit true area each to adsorb one hydrogen atom, as calculated under the assumption that three principal planes are exposed by equal areas.

The rate of rapid sorption is estimated at $2.5 \cdot 10^{14}$ atoms/sec cm² at 0°C from $P-t$ diagrams, which is in agreement with the value of $1.3 \cdot 10^{14}$ atoms/sec cm² calculated by the absolute rate equation⁸⁾ with the activation energy zero as deduced from the observed temperature independence of the initial rate of the rapid sorption.

It was found, on the other hand, that the rate of the slow sorption obeys the ROGINSKY-ZELDOVICH's equation and that the amount of the slow sorption increases proportional to the weight of the palladium film as has already been observed by BEECK *et al*⁹⁾, while that of the rapid sorption increases with the

weight only slowly.

Details will be published in later publications. The authors are much indebted to Prof. J. HORIUTI for his valuable advice and discussions during the course of this work.

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CORROSION OF NICKEL BY AQUEOUS ALKALI

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HORIUTI and OKAMOTO¹⁾ have previously observed that the rate of catalyzed exchange of deuterium between hydrogen and water at 100°C in the presence of nickel wire was almost unchanged by varying pH of water from that of pure water to 10⁻³N-KOH solution. LEWINA²⁾ has reported later that the exchange rate was about fivefolded from pure water to 0.53 N-NaOH solution at 80°C in the presence of the same catalyst.

This discrepancy has stimulated the present authors to investigate, if hydrogen be evolved along with the corrosion of nickel by concentrated alkali, in the exchange experiment, to dilute deuterium in gas giving rise to an apparent increase of the exchange rate.

Normal solution of "First Grade Reagent" of potassium hydroxide from Wako Pure Chemicals Co., Osaka, was digested at 100°C for 8 days, the precipitate***)

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) It was previously shown by ABE [Sc. Papers. Inst. Phys. Chem. Research, Tokio, **38, 287 (1941)] that even reagent grade alkali is contaminated with colloidal iron, which catalyses the hydrogen exchange between hydrogen gas and aqueous alkali, and the colloidal iron is converted into faintly bluish flakes of FeO·H₂O by digesting aqueous alkali in vacuum at 100°C.