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Author(s)	MIYAHARA, Koshiro; TSUMURA, Akiko
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EQUILIBRATION OF HYDROGEN CATALYZED BY GLASS AND QUARTZ SURFACES

By

Koshiro MIYAHARA and Akiko TSUMURA^{*)}

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Abstract

The catalytic activities of vessels of quartz, soda glass, Pyrex, Terex and Hario for the equilibration of hydrogen was examined by means of a mass spectrometer. It was found that the catalytic activity of these vessels, preliminarily cleansed with bichromic acid mixture and evacuated at 300°C for an hour, increased, passed a maximum and decreased slowly along with the repetition of reactions at 300°C each for 30 min. followed by 10 min. evacuation at the same temperature, and was variously affected by different contaminations of wall or impurities in gas. The activation energy of the equilibration was *ca.* 14 Kcal/mole.

Introduction

It has been pointed out by one of the present authors¹⁾ that an important knowledge of the reaction mechanism is imparted by the observation of initial rates of formation of P₂ and PD accompanying catalyzed deuteration of protium compound, where P denotes protium. These rates could however be masked by the equilibration reaction between P₂ and D₂, *i.e.*



catalyzed *e.g.* by wall of the reaction vessel.

ROGINSKY²⁾ observed parahydrogen conversion catalyzed by glass, and FARKAS³⁾ and recently ELEY⁴⁾ reported an exchange of deuterium gas with protium held by the well-outgassed wall of quartz or glass vessel. The present authors found now that the reaction (1) was actively catalyzed at 300°C under certain condition by quartz, soda glass, Pyrex as well as sorts of Pyrex made in Japan, *i.e.* Terex^{**)} and Hario^{***)} and the catalytic activity was variously affected by different contaminations of wall or impurities in gas.

Experimental

§1. Hydrogen Mixture

Deuterium gas of 99.5 D%^{****)} was purified by passing it through a

*) Research Institute for Catalysis, Hokkaido University.

) TOKYO SHIBAURA Electric Co. *) SHIBATA Chemical MFG., TOKYO.

****) STUART Oxygen Co., San Francisco, U.S.A.

heated palladium thimble and a trap packed with glass wool and cooled by liquid nitrogen. Protium gas electrolytically prepared was passed successively through silica gel, P_2O_5 and heated platinized asbestos and finally a liquid nitrogen trap. The hydrogen mixture was prepared by mixing protium gas with *ca.* 4% deuterium gas both purified as above and stored in a flask of soda glass evacuated at 10^{-6} mmHg at room temperature.

§ 2. Reaction Procedure

Cylindrical vessel V of a definite form and *ca.* 100 cc. capacity was fused, after being preliminarily cleansed with bichromic acid mixture or intentionally contaminated or just washed, to a capillary trap T as shown in Fig. 1 and outgassed at $300^\circ C$. The trap T was dipped in liquid nitrogen, when wash water in the vessel was exhausted and the vacuum-gauge G indicated 10^{-4} mmHg, to protect the vessel from contamination. After further evacuation for an hour at 10^{-6} mmHg at $300^\circ C$, the hydrogen mixture was introduced from the reservoir R into the vessel at 15–20 cmHg and the cock C_2 closed.

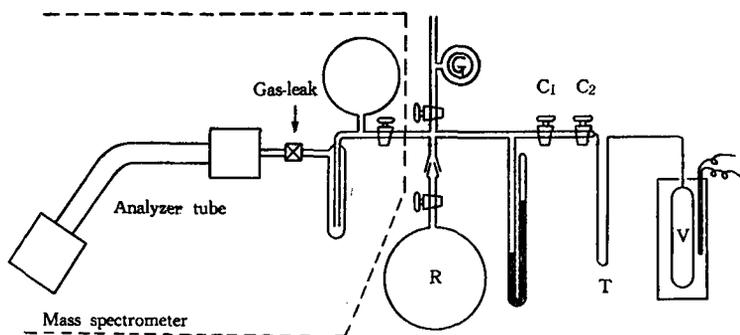


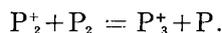
Fig. 1. Reaction apparatus.

The reaction was followed by sampling the reacted gas in the gas-pipette C_1 - C_2 of *ca.* 1 cc. volume at a recorded time, preliminarily pipetting out about the same amount of gas and discarding it by evacuation for a short time to wash out unreacted gas in the trap T; the sample was then passed into the mass spectrometer for analysis. A run of reaction was usually continued for 30 min. and followed by evacuation of the vessel for 10 min. and then by the next run of the same duration. The reaction temperature was maintained usually at $300^\circ C \pm 1^\circ C$ in an electric furnace by means of a potentiometer type regulator.

§ 3. Measurements

Sample gas was analyzed by means of the HITACHI RMD-3 type mass

spectrometer particularly designed for analysis of the relative abundances of P_2 , PD and D_2 in hydrogen gas by determining potentiometrically the ratios of any two of the three ion-currents of mass-number 2, 3 and 4; the result was corrected for an appreciable amount of P_3^+ ion produced by the secondary reaction in the ionization chamber of the mass spectrometer, *i. e.*



The inner surface of the ionization chamber was coated with gold to minimize the reaction (1) catalyzed by the surface; to make the memory effect uniform, the hydrogen mixture mentioned above was previously passed from the reservoir R into the analyzer tube of the mass spectrometer and its composition determined before every measurement. The concentration ratio $[PD]/[P_2]$ of PD and P_2 in the hydrogen mixture was thus found constantly at $([PD]/[P_2])_0 = (20 \pm 1) \times 10^{-4*}$.

The effect of hydrogen possibly held by the wall of the evacuated vessel was investigated by preliminary experiments with cleansed fresh vessels of enhanced catalytic activity**⁾ with the result that the value of $[PD]/[P_2]$ of hydrogen asymptotically approached to the equilibrium value relevant to the initial composition of the hydrogen mixture and the equilibrium constant 4 of reaction (1). This fact assured a negligible effect of hydrogen held by the evacuated vessel hence that the reaction could be effectively followed by the ratio $[PD]/[P_2]$.

Results

§ 4. Reaction with Cleansed Vessel

Vessels of soda glass, Hario, Terex, Pyrex and quartz were cleansed by heating it in bichromic acid mixture at 100°C for six hours and washing for ten or more times with hot and then cold distilled water.

It was preliminarily observed that the catalytic activity of thus cleansed vessels was enhanced by the repetition of runs of reaction (1) at 300°C, each followed by 10 min. evacuation, to a remarkably high value as compared with that of the vessel heated at 300°C for the same period of time constantly either in vacuum or in the hydrogen mixture and evacuated for 10 min. as illustrated in Table 1 for Hario vessel, where the activity was given in terms of the

*) The content of PD in D_2 gas increased from the original value 1% to 2% by passing it through palladium thimble. The PD content in the hydrogen mixture should then be 0.08%. The increase of the PD content to the observed value, *i. e.* 0.2%, is presumably due the equilibration (1) caused by the ionization chamber or the electron gun.

**⁾ The catalytic activity of the vessel was enhanced by conduction of the first several runs. Cf. § 4.

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increase $([PD]/[P_2])_{30}$ of the ratio $[PD]/[P_2]$ by the reaction for 30 min.

TABLE 1. Effects of different treatments at 300°C for 4 hr. on the catalytic activity of Hario vessels.

Treatment	300°C constantly in vacuum	300°C constantly in hydrogen mixture	Repetition of six runs
$(\frac{[PD]}{[P_2]})_{30}$	0.0000	0.0010	0.0250

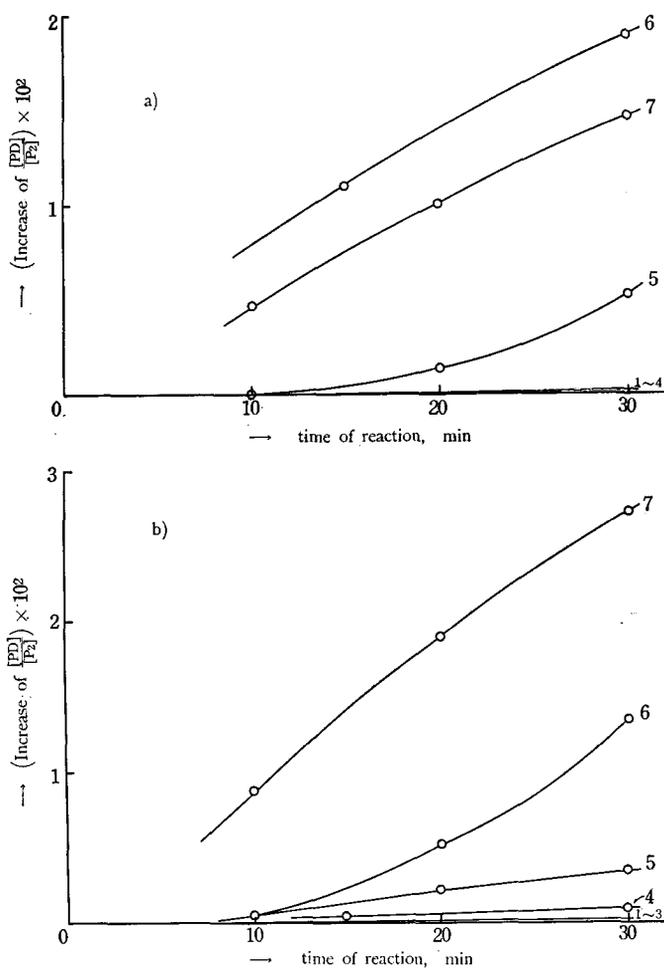


Fig. 2. Activities of cleansed vessels at 300°C by repetition of runs. a) Soda glass. b) Hario.

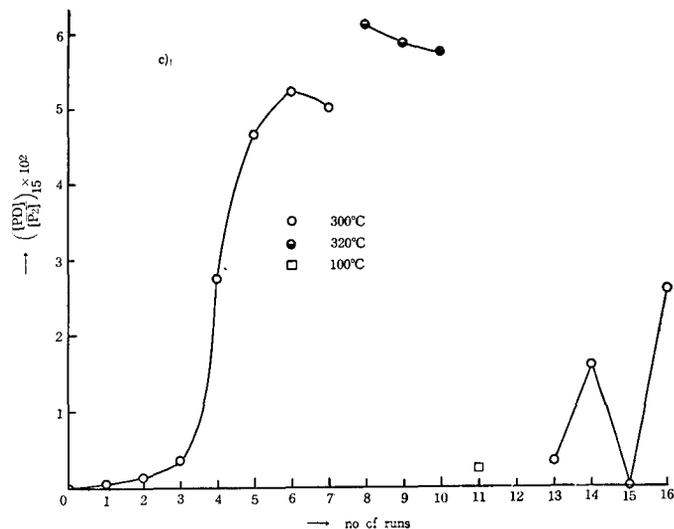


Fig. 2. c) Activity of cleansed quartz vessel at 300°C by repetition of runs.

Fig. 2a and 2b show respectively typical results obtained by the repetition of runs at 300°C with cleansed vessels of soda glass and Hario. Runs are numbered, as indicated with figures annexed respectively to appropriate curves, for each series of them conducted with one and the same vessel. Qualitatively similar results were obtained with quartz, Pyrex and Terex vessels as shown respectively in Fig. 2c and by the curves (a) in Fig. 6. These results show that any vessel cleansed as above was rendered catalytically active by several runs of reaction (1) conducted in it in succession at 300°C each for 30 min. followed by 10 min. evacuation. The activity passed then a maximum and decreased slowly along with further repetition of the runs as illustrated by the first ten runs of Fig. 2c or the first six runs of Table 3.

§ 5. Effect of Contamination of Wall

a) *Bichromic acid mixture.* The vessel of soda glass used in the experiment of Fig. 2a and fresh vessels of Hario and quartz were cleansed as above and then intentionally contaminated with bichromic acid mixture used for cleansing, and evacuated at 300°C for an hour. This treatment practically inhibited the reaction as observed for successive six or seven runs at 300°C each for 30 min. followed by 10 min. evacuation.

b) *Uncleansed soda glass vessel.* Soda glass vessel, washed just twice with cold water but not cleansed particularly, catalyzed the reaction fairly actively from the first run and the activity increased more rapidly than in the case of

cleansed vessels, as shown by curves of run 1, 2 and 3 in Fig. 3. Runs 4 and 5 in this figure were conducted as described in §6, c).

The vessel was now cleansed as described in §4 resulting in the catalytic activity varying very similar to that in cleansed fresh vessels along with repetition of runs.

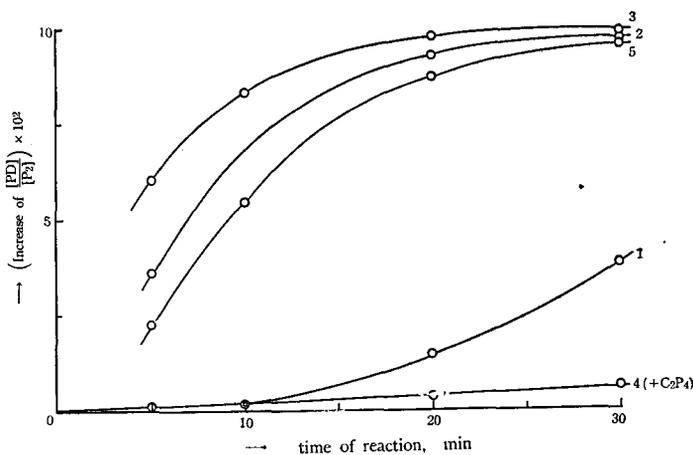


Fig. 3. Activity of uncleaned soda glass vessel at 300°C.

c) *Sodium hydroxide.* The fresh vessels of Hario and soda glass cleansed as described in §4 were now intentionally contaminated with an aqueous sodium hydroxide and evacuated for an hour at 300°C. The reaction was actively catalyzed by these vessels thus contaminated from the first run

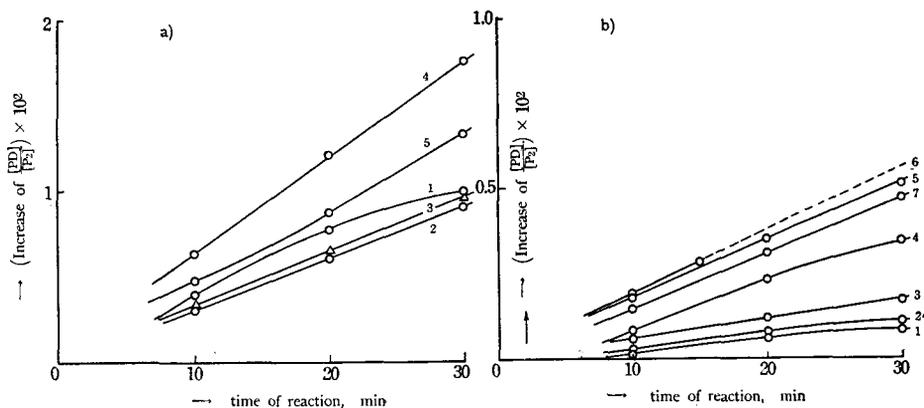


Fig. 4. Activity at 300°C of soda glass vessel contaminated with dilute aqueous sodium hydroxide.
a) Contaminated. b) After cleansing.

and the catalytic activity increased rapidly along with the repetition runs as shown in Fig. 4a and 5. Further cleansing with bichromic acid mixture extinguished the catalytic activity of Hario vessels but not of soda glass one^{*)}, which was active, as shown in Fig. 4 b, from the first run after the cleansing.

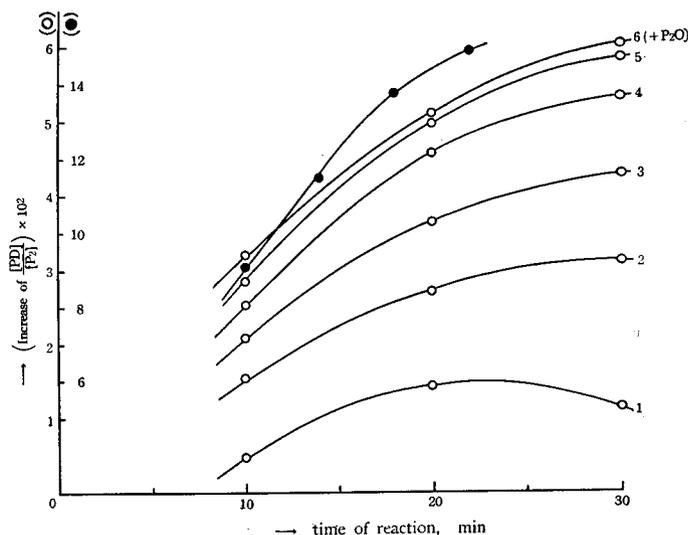


Fig. 5. Activity at 300°C of Hario vessel contaminated with conc. aq. sodium hydroxide.

Solid circles—exchange rate between 18 mmHg D₂O vapour and 203 mmHg P₂ in the same vessel.

Fresh Pyrex or Terex vessel was now treated with hot concentrated aqueous sodium hydroxide and washed many times with hot and then with cold distilled water. Its catalytic activity increased much more rapidly along with the repetition of runs than that of the fresh vessel of the same glass cleansed with bichromic acid mixture, as shown in Fig. 6.

d) *Phosphoric acid.* A fresh Terex vessel cleansed and catalytically activated by the repetition of runs was contaminated with phosphoric acid and evacuated at 300°C for an hour. The reaction was completely inhibited in this vessel for the successive ten runs.

§6. Effects of Impurities in Hydrogen Mixture

a) *Water vapour.* Water was preliminarily distilled several times in

^{*)} Soda glass vessel once contaminated with NaOH aq. and evacuated at 300°C as above differs from a cleansed fresh vessel of the same glass in this respect. Cf. §4.

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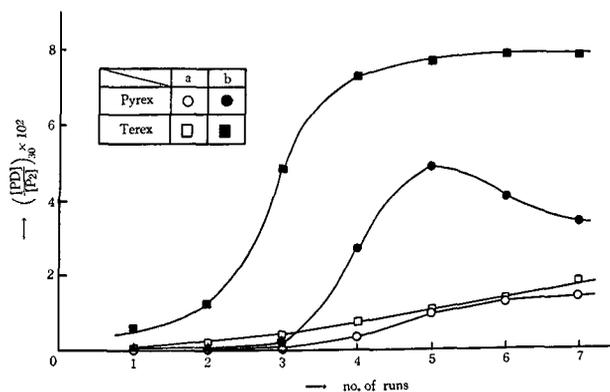


Fig. 6. Activity of Pyrex and Terex vessels at 300°C.

Curves a—vessel cleansed with bichromic acid mixture.

Curvss b—vessel treated with hot aqueous sodium hydroxide.

vacuum and its vapour was mixed with the hydrogen mixture directly before the experiment. A quartz vessel was preliminarily cleansed as described in § 4 and catalytically activated by succession of ten runs at 300°C as shown in Fig. 2c. After subsequent two runs, each conducted at 100°C for 30 min. and at room temperature for 20 hr. respectively followed by 10 min. evacuation, the trap T was heated by torch-flame for a few minutes under evacuation, the evacuation was continued for further 10 min., two runs (runs 13 and 14 in Fig. 2c) were conducted with the hydrogen mixture alone, then another (run 15) with the hydrogen mixture mixed with 1.0 mmHg water vapour and finally the run 16 with the hydrogen mixture alone again each followed by 10 min. evacuation. The trap T was maintained at room temperature in runs 13, 14 and 15 but kept in liquid nitrogen during run 16 and the evacuation subsequent to run 15*).

Table 2 shows the results obtained similarly with cleansed Terex vessel side by side with the above results of Fig. 2c. The rates are given in terms of the increase $([PD]/[P_2])_{15}$ or $([PD]/[P_2])_{20}$ of the ratio $[PD]/[P_2]$ for the first 15 min. or 20 min.

These results of Table 2 show, on the one hand, that the reaction in these vessels is completely inhibited by a small amount of water vapour mixed with hydrogen mixture but restored by short evacuation and, on the other hand, that the effects both of catalytic poisoning of water vapour and its elimination

*) Cf. § 2.

TABLE 2. Effect of 1.4 mmHg water vapour added on the catalytic activity of cleansed quartz and Terex vessels; 300°C, 160 mmHg hydrogen mixture.

Quartz	No. of runs	10	13	14	15 (P ₂ O added)	16
	$\left(\frac{[PD]}{[P_2]}\right)_{15}$	0.556	0.034	0.166	0	0.260
Terex	No. of runs	8	9	10	11 (P ₂ O added)	12
	$\left(\frac{[PD]}{[P_2]}\right)_{20}$	0.140	0.048	0.100	0	0.123

by evacuation is conspicuous as compared with that of vapours of grease and mercury etc. which should be operative, if any, in the absence of liquid nitrogen trap.

b) *Ammonia*. Ammonia was obtained from its concentrated aqueous solution by fractional distillation repeated in vacuum from -30°C to -195°C. Table 3 shows the effect of ammonia on the catalytic activity of a fresh cleansed soda glass vessel at 300°C; after the first eight successive runs the bath of the trap T was changed from the beginning of 10 min. evacuation subsequent to run 8 from liquid nitrogen to alcohol cooled at -30°C till the end of run 9 of the Table and then replaced. The catalytic activity of the vessel decreases, as shown by the Table, in run 9, but does not completely disappear. It is recovered, moreover, only partly by evacuation in distinction from in the case of water vapour as seen from the result of runs 10 and 11 conducted in the absence of ammonia. These effects may possibly be due to some condensation in the trap T at liquid nitrogen temperature, but not necessarily to admixed ammonia alone.

TABLE 3. Effect of 1.5 mmHg ammonia added and temperature on the catalytic activity of soda glass vessel; 160 mmHg hydrogen mixture.

No. of runs	1	2	3	4	5	6	7	8	9 (NP ₃ added)	10	11
React. temp. °C	350	350	350	350	350	350	300	300	300	300	300
$\left(\frac{[PD]}{[P_2]}\right)_{30}$	0	0	0.330	0.560	0.507	0.475	0.319	0.316	0.054	0.118	0.123

c) *Ethylene*. Ethylene was prepared by dropping chemically pure ethanol in hot phosphoric acid and fractionally distilled in vacuum many a time from

—80°C to —195°C. The curves 4 and 5 in Fig. 3 show the results of two runs of the same numbers, which were conducted in succession to runs 1, 2 and 3 described in §5, b) in the same uncleaned soda glass vessel, respectively in the presence and absence of *ca.* 0.6% ethylene mixed with the hydrogen mixture keeping the trap immersed in liquid nitrogen. The catalytic activity of the vessel was markedly reduced by the presence of ethylene but restored almost completely in run 5 by evacuation subsequent to run 4.

d) *Air.* The catalytic activity of the quartz, Hario and soda glass vessels, either cleansed or contaminated, was completely suppressed by exposing them to air of few mmHg pressure. The vessels thus poisoned recovered its catalytic activity gradually by the repetition of runs with the hydrogen mixture alone, just as the cleansed fresh vessels.

§7. Temperature Effect

The activation energy of the reaction is calculated to be 14 Kcal/mole from the results of runs 6 and 7 in Table 3. This value of the activation energy is remarkably smaller than 21–24 kcal/mole, observed by ELEY⁹⁾ for the exchange reaction between deuterium gas and protium held by glass wall well-outgassed at 400°C, but of the magnitude near that of reaction (1) on metallic catalysts⁹⁾.

Discussion

§8. Effect of Repetition of Runs

It is seen from the experimental results that vessels of soda glass, quartz, Pyrex, Terex and Hario are imparted with marked catalytic activity for reaction (1) by repetition of the runs, *i. e.* by heating at 300°C alternately in hydrogen and in vacuum as compared with by heating the vessel at the same temperature for the same period of time constantly either in vacuum or in the hydrogen mixture. Since the reaction is nearly inhibited by contamination with bichromic acid mixture as described in §5, a), the catalytic activity of the cleansed vessel described in §4 could not be due to the cleansing agent itself, *i. e.* bichromic acid mixture, which might escaped being washed out.

The catalytic activity of vessels was, on the other hand, completely suppressed, as described in §6, d), by a small amount of air and is recovered only slowly by repetition of runs in distinction from the cases of water vapour, ammonia or ethylene, where the activity was readily recovered by short evacuation. It may be concluded from these facts that the catalytic activity of vessels is effected chiefly by slow reduction of adsorbed oxygen or some oxides by hydrogen and the rapid desorption of water formed by evacuation at 300°C or

above. This is in accord with the decisive inhibition of the reaction by cleansing or contaminating a vessel with a strong oxidant, *i. e.* bichromic acid mixture, and the subsequent slow recovery by repetitions of runs as described in §4 and §6.

It might be suggested further that the present reaction is caused by the dissociation and recombination of hydrogen from the fact that the equilibration reaction was completely hindered by phosphoric acid, which is a well-known poison to the catalytic recombination of hydrogen atoms⁶⁾.

§9. Participation of Wall in the Catalysis observed

Metallic catalysts for deuteration of protium compounds are usually catalytically activated by heating them in air at 600°C, and then in hydrogen at 300°C, followed by outgassing at 300°C. This procedure, which is very similar to that of activation of vessels in the present experiments, might probably give rise to the catalytic activity of the vessel wall itself as well as of the metallic catalysts. In fact it was recently found by ENYO⁷⁾ that the equilibration reaction between protium and deuterium was half completed during two month at room temperature in a Hario vessel, treated just as the above activation of metallic catalysts, *i. e.* heated at 400°C in hydrogen for 12 hr. and outgassed at the same temperature. This is semiquantitatively in agreement with the present experimental result of run 12 in Fig. 2c that the value of $[PD]/[P_2]$ changed by 5×10^{-4} for twenty hours at room temperature with a sufficiently activated quartz vessel, which amounts to *ca.* 40% equilibration for two months.

It is warned that the vessel wall may possibly share the catalytic action with metallic catalyst on the equilibration of hydrogen, *e. g.* in case of it accompanying the catalyzed deuterations of light ethylene, noting that ethylene does not completely inhibit the equilibration as described in §6, c).

§10. Catalytic Action of Sodium

Uncleansed soda glass vessel is extraordinarily activated by heating in vacuum at or above 300°C, which catalyzed the reaction appreciably in course of few days at room temperature or from the first run at 300°C^{*)}, although the hydrogen mixture stored in the same vessel R in (Fig. 1), preliminarily evacuated at 10^{-6} mmHg without heating, did not perceptively reacted for several months as evidenced by the experimental results described in §3. The predominant catalytic activities of the uncleaned soda glass vessel as well as of the vessel contaminated with sodium hydroxide described in §5, b) or §5, c),

Cf. §5, b).

suggest that sodium is one of the principal agents of the catalytic activity of soda glass.

The descent of the curve 1 in Fig. 5 in its later part, observed in a vessel thickly contaminated with sodium hydroxide, shows, besides, that sodium actively catalyzed the hydrogen exchange between hydrogen and water remaining in the vessel; water was actually trapped in T on evacuation after the reaction, while the exchange reaction was confirmed between 203 mmHg protium gas and 18 mmHg heavy water vapour of 99.7 D% in the same vessel, subsequent to run 6, as shown by the solid circles in Fig. 5. The catalytic activity of a vessel contaminated with aqueous solution of NaOH was apparently unchanged by mixing the hydrogen mixture with water vapour as shown by curves of runs 5 and 6 in Fig. 5, which is understood by its much smaller amount than that trapped in T during the first five runs of the series hence than that remaining in the vessel.

It has been reported that the hydrogen exchange took place between hydrogen gas and aqueous solution of NaOH in glass vessels⁹⁾. The bearing of the present experimental results to the latter one will be investigated further.

Finally the authors wish to express their sincere thanks to Professor Juro HORIUTI, Director of the Institute, for his kind advices.

Summary

1. It was found by means of a mass spectrometer that soda glass, quartz, Pyrex, Terex and Hario, preliminarily cleansed with bichromic acid mixture and outgassed at 300°C for an hour, catalyzed the equilibration $P_2 + D_2 = 2PD$ (P: protium); the catalytic activity increased, passed a maximum and decreased slowly along with the repetition of runs at 300°C each for 30 min. followed by 10 min. evacuation at the same temperature. The activation energy of the reaction was *ca.* 14 Kcal/mole.

2. Contamination of vessel wall by sodium hydroxide accerelated the equilibration as well as the hydrogen exchange between hydrogen gas and water, whereas phosphoric acid completely inhibited the equilibration; from the latter result it was suggested that the equilibration occurred through the dissociation and the recombination of hydrogen on vessel wall.

3. The catalytic activity of vessel wall was reduced by water vapour, ammonia and ethylene mixed with hydrogen but recovered by short evacuation, whereas air as well as the cleansing agent, bichromic acid mixture, extinguished the catalytic activity, which was only slowly recovered by runs and subsequent evacuations repeated many a time. It was concluded from the above results

that the catalytic activity was imparted to vessel wall by slow reduction of adsorbed oxygen or some oxides by hydrogen followed by rapid desorption of water formed.

4. It was warned on the basis of the present experimental results that the heating of a vessel followed by outgassing might cause the vessel wall to participate in catalyzing the equilibration under investigation.

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