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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

By Juro HORIUTI and Yoshihiro KOMOBUCHI**)

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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.

Short Notes

thus produced filtered off, the filtrate sealed in a reaction vessel I (Fig. 1) with 1 g reduced nickel or in that II (Fig. 2) with nickel film evaporated on the wall and then kept at 100°C for a recorded time. Every above process was carried out in vacuum. Both the reaction vessels were of "Halió" glass^{*)} and respectively of 100 c.c. (I) and 60 c.c. (II) capacity. The former was provided with a blind tube B of *ca.* 4 mm inner diameter as shown in Fig. 1, with which the hydrogen pressure P inside was determined, without opening the reaction vessel, by measuring head difference Δh (Fig. 1) held by the gas enclosed in the blind tube of length L , according to the formula,

$$P = \frac{\Delta h (L-h) \rho'}{h \cdot \rho}$$

where h is the height of the solution in B and ρ or ρ' is the density respectively of mercury or solution. The amount of hydrogen evolved was determined in the case of the reaction vessel II simply by extracting the gas from a breakable joint after the reaction.

Nickel in I was prepared *in situ* by reducing nickel oxide. Nickel film in II was evaporated on the wall from nickel wire (99.99%) of JOHNSON MATHEY & Co., U. S. A. by heating it in 10^{-7} mm Hg vacuum with an induction furnace; wire used was left inside II during the reaction.

It was thus found that there occurs actually the corrosion of nickel as indicated by the formation of hydrogen and nickel hydroxide or oxide, when nickel is treated as in the experimental condition described above, whereas the hydrogen evolution is altogether suppressed, when effectively contaminated with carbon monoxide, as seen from results of runs described below.

Run 1. Reduced nickel in I was found to evolve gas noncondensable at liquid nitrogen temperature, at constant rate after a certain induction period as shown by crosses in Fig. 3.

The noncondensable gas was identified with hydrogen by burning it with copper oxide and observing the melting point and the vapour pressure of the product. White precipitate was observed to be formed simultaneously. The solid mass inclusive of the catalyst was subjected to electron and X-ray diffraction investigations by Dr. MATSUI, formation of Ni, NiO and $\text{Ni}_3\text{O}_2(\text{OH})_4$ being thus confirmed.

Run 2. Experiment of Run 1 was repeated besides that 90 mmHg carbon monoxide was introduced into the reaction vessel before reaction, when the catalyst was covered with alkaline solution, and then the reaction was conducted in its presence. Hydrogen was evolved nearly at the same rate as in the case

*) A sort of Pyrex glass supplied by SIBATA & Co., Tokio.

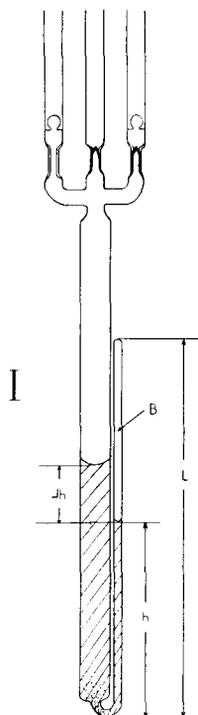


Fig. 1 Reaction vessel I.

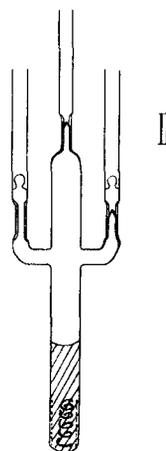


Fig. 2 Reaction vessel II.

of Run I.

The blind tube was now sealed off, water inside distilled off, 115 mmHg carbon monoxide admitted over the catalyst thus dried, the gas evacuated after 30 minutes to 10^{-6} mmHg, the water previously removed distilled back into the reaction vessel, and the reaction conducted as before for 25 hours, every step of the above procedure being carried out in vacuum without exposing the content to atmosphere.

No evolution of noncondensable gas was observed, as examined by the pressure of the gaseous content extracted after the reaction from a breakable joint, as shown by circles in Fig. 3.

Run 3. Similar run was conducted with evaporated film in II for 160 hours. It was found 0.14 mmHg hydrogen evolved in the reaction vessel. The appropriate rate of evolution was approximately proportional to the estimated surface area of nickel film and of wire present, as compared with the result of Run 1 on the base of $32 \text{ m}^2/\text{g}$ surface area³⁾ of reduced nickel in the latter case. Considerable amount of white precipitate was formed.

Short Notes

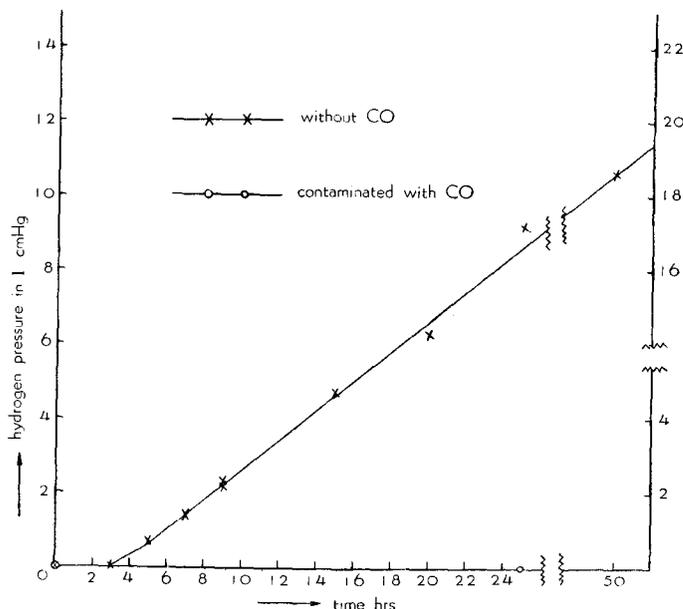


Fig. 3 Hydrogen evolution.
Reaction vessel I; Reduced nickel.

Run 4. Normal potassium hydroxide solution was sealed in II similarly but without nickel and kept at 100°C for 16 days for control. White precipitate was formed to the same extent as in Run 3 but no hydrogen evolved.

Hydrogen evolution accompanying the corrosion, thus provides the possibility of accounting for the discrepancy raised above of hydrogen exchange rates but not quantitatively at the moment, the hydrogen quantity used in the exchange experiment, which is required for the quantitative control, being not given in LEWINA'S paper²⁾.

It is suggested on the basis of the above results that the well-known persistence of nickel against alkali corrosion⁴⁾ might possibly be due to the protection by carbon monoxide, which is known to be evolved to a considerable extent from ordinary nickel material, when heated in vacuum⁵⁾.

The authors wish to express their gratitude to Dr. T. MATSUI, who has kindly conducted the electron and X-ray diffraction investigations of the precipitates. Their best thanks are also due to Professor T. KWAN, Dr. A. MATSUDA and Dr. K. TANAKA for their kind helps and to the Grant in Aid for Fundamental Scientific Research of the Ministry of Education.

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