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DEPENDENCY ON pH OF NICKEL CORROSION IN AQUEOUS SOLUTIONS

By

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Introduction

It has been shown in the foregoing paper¹⁾ that nickel is corroded by 1N-KOH solution in the absence of air to evolve hydrogen at 100°C. while the corrosion is altogether inhibited by carbon monoxide.

Nickel is, as well-known, lively attacked by acidic solution, but not at all by neutral water in the absence of air as reported by a number of authors²⁾. HIROTA and HORIUTI³⁾ thus observed in the absence of air as well as of carbon monoxide that nickel did not perceptibly react with neutral water at 100°C but the accuracy of the determination is not sufficient to decide in conjunction with the result of the above experiment¹⁾ whether the rate of hydrogen evolution should actually decrease from alkaline toward neutral solution.

The present paper is concerned with the observation of the rate of hydrogen evolution by corrosion over the contiguous pH-range to that of the foregoing experiment¹⁾ for deciding the above question.

Experimental

The solution used was a sort of SÖRENSEN'S buffer solutions, i.e. mixture of 0.1 M-glycine +

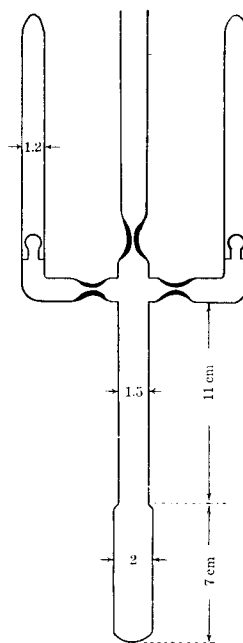


Fig. 1.
Reaction Vessel and
Solution Reservoir.

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0.1 M-KCl solution and 0.1 N-KOH solution, whose pH has been extensively investigated⁴⁾ up to 70°C. The pH of the solution was extrapolated at 100°C by virtue of a linear relation observed⁴⁾ between pH and temperature from 10°C to 70°C, as shown in the fourth column of Table 1 against the mixing ratio of the solutions given in the foregoing two columns; pH of the solution without glycine (Run 6) was however indirectly evaluated on the basis of the ionization constant 48×10^{-14} of water⁵⁾ at 100°C. KOH solution was prepared from 5.610 g "Guaranteed Grade" KOH from Kanto Chemical Co. Tokio (Cica Brand) and 1000 cc water deionized by ion-exchange resin and distilled before use. Glycine-KCl solution was mixed from 0.751 g "Guaranteed Grade" glycine of Kanto Chemical Co. Tokio, 0.746 g "Guaranteed Grade" KCl of Kokusan Chemical Laboratory, Tokio and 100 cc of the same water as above.

Ten cc of the above buffer solution was put in a Hialo glass^{*)} vessel shown in Fig. 1 with two breakable joints, and sealed off after being alternately frozen under evacuation to 10^{-6} mmHg and molten in closed space 4 to 5 times for exhausting dissolved air.

Fig. 2a shows seven reaction vessels each charged with 1.6 g Ni(OH)₂ and attached, as shown in Fig. 2b, with a solution reservoir prepared as above. The reaction vessels were put in an electric furnace as shown in the Figures, evacuated, heated at $300 \pm 20^\circ\text{C}$ and the contents simultaneously reduced for 8 days with hydrogen purified as before¹⁾, repeatedly evacuating water formed and recharging hydrogen, until no stain of condensed water was perceptible at the wall of the trap T, cooled by liquid nitrogen. Above process of simultaneous reduction has been adopted for the sake of homogeneity of nickel preparations^{**)}. Reaction vessels were then evacuated at $350 \pm 20^\circ\text{C}$ for 7 days, each being sealed off at constriction S₁ attached as it was with a solution reservoir. Each run was initiated by opening the breakable joint J₁ to transfer the content of the reservoir into the reaction vessel and by sealing off constriction S₂ to finish the latter.

The reaction vessels were now kept at 100°C for 20 hours in a water bath, then cooled by water for 2 minutes, left standing for 1.5 hours at room temperature, attached to a vacuum line by a breakable joint, which was opened to allow the gaseous content to expand into a definite space and the pressure of noncondensable gas in the space

*) A sort of pyrexglass supplied by Sibata Glass Co., Tokio.

***) Run 1 has been conducted separately prior to these seven simultaneous runs.

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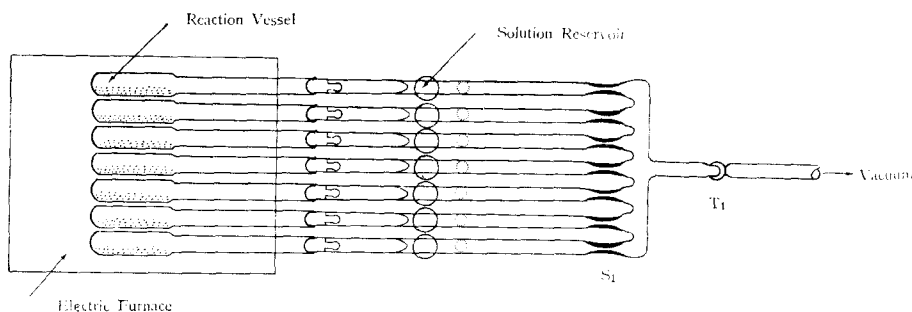


Fig. 2 a.

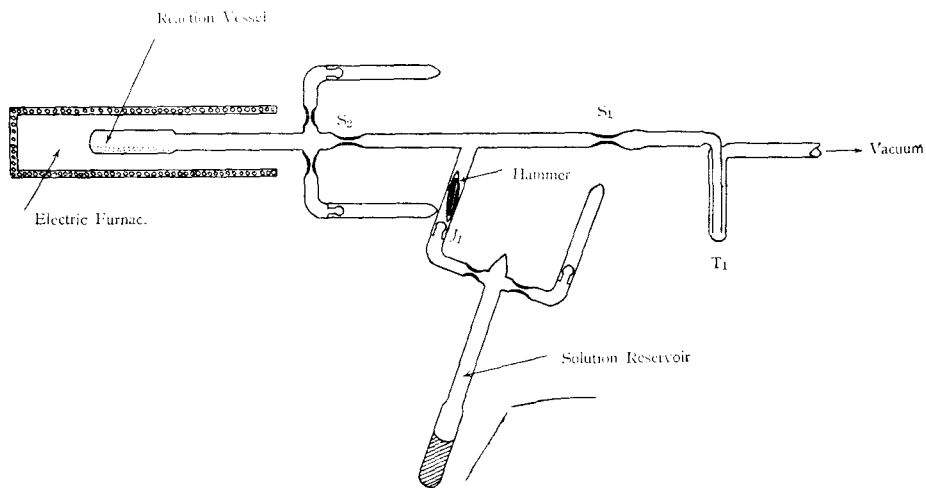


Fig. 2 b.

read off by a manometer. The latter pressure reading was reduced to that P_{H_2} of the same amount of hydrogen in 25 cc volume of the gas phase in the reaction vessel at 25°C with proper corrections as shown in the second last column of Table 1.

Results

Number of runs in Table 1 gives the order of them being carried out. Fifth and sixth columns show the pH of solution before and after the reaction measured at room temperature under atmosphere by BECKMAN pH meter Model G.

Table 1 shows that pH of solution is not appreciably varied by the reaction except in Run 2 which was disturbed by an accident as foot-

TABLE 1. Amount of Hydrogen Evolved by Corrosion of 1 g Reduced Nickel in 10 cc Aqueous Solution for 20 hours at 100°C.

No. of Runs	Solution *)				Pressure of hydrogen evolved P_{H_2} mm Hg	Time of finished reaction vessel left standing at room temperature before the reaction at 100°C	
	Mixing Ratio		pH				
	0.1 N-KOH cc	0.1 M-glycine + 0.1M-KCl cc	Extra-polated at 100°C	Observed at 22°C			
				Before Reaction	After Reaction		
1 a)				8.6	8.6	8.8	30 min
2 b)	7	3	10.1	12.4	10.5	7.0	30 hrs
3	4	6	8.0	9.8	10.2	6.3	30 "
4	1	9	7.1	8.0	8.2	7.6	30 "
5 c)	0	10	6.6	7.4	8.0	9.8	55 "
6	10	0	11.3	12.7	12.0	9.4	6 "
7	5	5	9.0	10.5	10.5	7.5	20 min
8	5.3	4.7	9.4	10.8	10.6	9.9	45 "

*) It was observed in the case of Runs 4 and 5 that microbubbles were evolved immediately after the solution contacted in vacuum with the reduced nickel and after several minutes the solution acquired faintly blue tint, which grew with time while left at room temperature but not during the reaction at 100°C. The smaller the fraction of glycine-KCl solution, the weaker the blue tint of the solution at a definite time after its contact with nickel.

- a) This run was conducted prior to the simultaneous runs (from No. 2 to 8) quite similarly as latters but using 20 cc pure water in place of buffer solutions.
- b) One of breakable joints was accidentally broken during the reaction at 100°C. By this breakable joint the reaction vessel was fused to the vacuum line, the air inside exhausted as in the case of preparation of the solution, the reaction vessel sealed off at the latter breakable joint and the reaction conducted normally besides. Greenish white precipitate was observed in the solution after the reaction.
- c) Hydrogen was evolved by 6.2 mmHg in the reaction vessel, while it was left standing for 55 hours at room temperature before the reaction at 100°C as determined by drawing hydrogen inside from one of the breakable joints. The latter breakable joint was sealed off and the reaction at 100°C was started leaving 3.0 mmHg hydrogen inside. The P_{H_2} -value given in the Table is the sum of 3.6 mmHg hydrogen evolved at 100°C and the above amount formed at room temperature.

noted to the Table and that hydrogen is evolved under such condition by 6-10 mmHg in the reaction vessel for 20 hours throughout the pH-range of observations. Since however hydrogen is evolved even at room temperature before the reaction at 100°C, the above data gives the upper bound to the rate of hydrogen evolution at 100°C. Glycine might however be evolving or consuming hydrogen by some side reaction resulting perhaps in the blue tint observed. The possibility of this disturbing the above conclusion is excluded by the comparison of

Runs 1 and 4 or 5, which show that much the same amount of hydrogen is evolved at approximately the same pH irrespective of the presence or absence of glycine. The upper bound thus established is now compared with the result of the foregoing experiment¹⁾, that hydrogen was evolved as much as 160 mmHg*²⁾ in 20 hours from 1N-KOH solution at the same temperature in the presence of the same quantity (1g) of reduced nickel.

It is hence concluded that the rate of hydrogen evolution is diminished by a factor of more than 16 with decrease of pH from that of 1N-KOH to that ranging between 6.6 and 11.3, where the minimum rate probably lies.

The above conclusion is in accord with the former interpretation of the discrepancy¹⁾ between the experimental result of HORIUTI and OKAMOTO⁶⁾, and that of LEWINA⁷⁾, inasmuch as hydrogen is evolved with increase of pH possibly to dilute the deuterium shifted hydrogen thus resulting in the apparent increase of its exchange rate in the latter case.

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*²⁾ It was found in the foregoing work¹⁾ that *ca.* 60 mmHg hydrogen was evolved in 65 cc volume of the gas phase in 20 hours. This hydrogen pressure is reduced as given in the text, to 25 cc volume of the gas phase in the present reaction vessel.