The Sorption of Gases on Reduced Nickel. I. Hydrogen, Oxygen, and Hydrogen Bromide.

By Matsuji TAKEBAYASHI.

(Received January 26, 1939.)

Y. Urushibara and the present author have found that reduced nickel and reduced iron reverse the direction of the addition of hydrogen bromide to ethenoid compounds, such as allyl bromide and undecenoic acid, in the same way as oxygen.(1) As for the catalytic activity of reduced nickel

---

(1) This Bulletin, **11** (1936), 692, 754, 798; **12** (1937), 51, 138, 173; **13** (1938), 331, 400, 404, 574.

in these reactions it has been observed that reduced nickel that has never been in contact with air after reduction shows a much greater effect than that that has been exposed to air,⁽²⁾ that the metal reduced at a temperature higher than specified for the hydrogenating catalyst is even more active than that prepared as usually,⁽³⁾ and that nickel filings exhibit an activity comparable to that of reduced nickel.⁽⁴⁾ Further, Urushibara and O. Simamura have found that isostilbene is transformed into stilbene by hydrogen bromide in the presence of either oxygen or reduced nickel.⁽⁵⁾

Thus some reactions other than hydrogenation have been found to be catalyzed by reduced nickel. In all these cases, however, reduced nickel is always with hydrogen bromide, reduced nickel and oxygen can take place of each other, and antioxidants, such as catechol and hydroquinone, eliminate to a greater or smaller extent the effect of reduced nickel as well as of oxygen.⁽⁶⁾

Further, Urushibara and Simamura,⁽⁷⁾ studying the reaction of reduced nickel and hydrogen bromide with and without the addition of oxygen, observed that, while practically no reaction took place in the absence of oxygen, hydrogen and nickel dibromide were produced in the presence of oxygen. A balance experiment revealed that the amount of hydrogen generated was short of the equivalent to that of nickel dibromide produced, thus suggesting the formation of water; and comparative experiments with traces of water but without oxygen led to the very probable assumption that the catalyst accelerating the reaction of reduced nickel and hydrogen bromide to give hydrogen and nickel dibromide was not oxygen but the traces of water produced by the action of hydrogen bromide on nickel oxide formed from reduced nickel and oxygen. In fact, reduced nickel which had been exposed to air reacted with hydrogen bromide without added oxygen in the same way as freshly reduced nickel in the presence of oxygen. However, to exclude the possibility of the catalytic action of molecular oxygen on the reaction of hydrogen bromide and nickel, it seemed desirable to investigate the nature of the sorption of oxygen on reduced nickel.

Thus the present author has been induced to study the sorption of gases, especially hydrogen, oxygen, and hydrogen bromide, on reduced nickel. The experiments described below, however, are by no means intended for an exact investigation of the sorption itself, but have been carried out with a view to knowing the behaviours of reduced nickel toward these gaseous substances.

Apparatus, Materials, and Methods. The main part of the apparatus, as shown in Fig. 1, consists of a burette (B) for measuring the quantity of the gas sorbed, a Töpler pump (T) for pumping out the gas sorbed when

---

(2) Compare Exp. 7 and 8 of this Bulletin, **11** (1936), 693 with Exp. 3 of *ibid.*, **13** (1938), 401.

(3) Compare Exp. 1 and 2 of this Bulletin, **12** (1937), 53 with Exp. 3 of *ibid.*, **13** (1938), 401.

(4) This Bulletin **13** (1938), 400.

(5) *Ibid.*, **12** (1937), 507; **13** (1938), 566.

(6) *Ibid.*, **13** (1938), 400, 404, 566.

(7) *Ibid.*, **13** (1938), 407, 570.

the desorbed amount is to be measured, and a sorption tube (S) made of Terex glass and connected by means of a mercury seal.

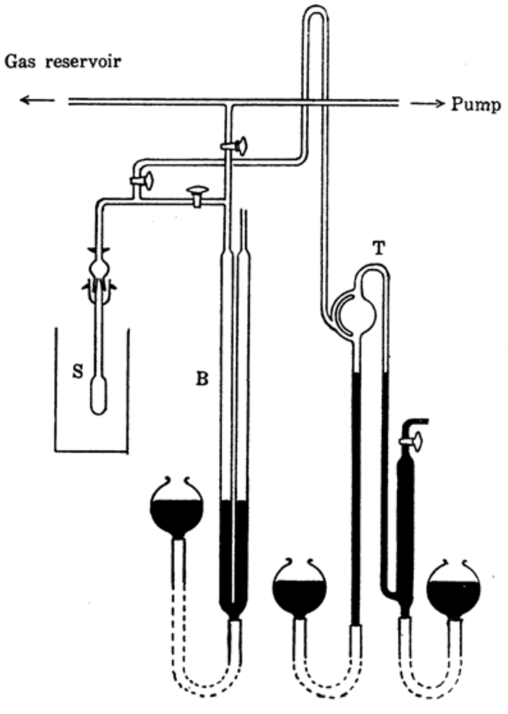

Fig. 1.

Reduced nickel was prepared by reducing nickel oxide (Kahlbaum) with hydrogen at 350–400°C. Hydrogen was generated by the action of dilute sulphuric acid on zinc, and purified according to the directions of A. Klemenc.⁽⁸⁾ Oxygen, a commercial material, was dried by passing over phosphorus pentoxide. Hydrogen bromide was prepared by the action of bromine on hot tetralin and purified according to the directions of A. Klemenc.⁽⁹⁾

In every experiment, 1.00 g. of reduced nickel, prepared as mentioned above, was taken in the sorption tube, heated at 350°C. in the atmosphere of hydrogen for two hours to refresh the surfaces and then in vacuum for an hour to remove hydrogen, and cooled to room temperature in vacuum. Then the sorption tube containing the nickel was immersed in a thermostat; and the gas of 1 atmospheric pressure was introduced into the tube. The volume of the gas sorbed was determined by subtracting the volume of the sorption tube and the connecting tubing from the decrease of the gas in the burette. All the volumes recorded in this paper have been calculated to the normal temperature and pressure. Other particulars of the experiments are given below for respective cases.

Throughout the experiments described in this paper vacuum or evacuation was effected by a rotary pump, and pressures not exceeding 1 mm. Hg were regarded as good for the purpose.

The Sorption of Hydrogen. The sorption of hydrogen on reduced nickel has already been studied by several investigators and the activated adsorption of hydrogen on the metal has been ascertained by them.⁽¹⁰⁾ The present experiments on the sorption of hydrogen were carried out

---

(8) A. Klemenc, "Die Behandlung und Reindarstellung von Gasen", 97, Leipzig (1938).

(9) *Loc. cit.*, (8), 196.

(10) H. Taylor and R. Burns, *J. Am. Chem. Soc.*, **43** (1921), 1273; W. Russel and H. Taylor, *J. Phys. Chem.*, **29** (1925), 1325; N. Nikitin, *Z. anorg. allgem. Chem.*, **154** (1926), 130; A. Benton and T. White, *J. Am. Chem. Soc.*, **52** (1930), 2325; S. Iijima, *Rev. Phys. Chem. Japan*, **7** (1932), 3, 24, 36; **8** (1933), 44; **12** (1938), 1.

for the purpose of comparison with those of oxygen and hydrogen bromide. The relation between time and the amount of hydrogen sorbed on 1.00 g. of reduced nickel at 20°C. was observed as shown in Tables 1 and 2. Curves I and II of Fig. 2 correspond to Tables 1 and 2 respectively.

Table 1.
The Sorption of Hydrogen at 20°C.

Time (min.)	Hydrogen sorbed (c.c.)
3/4	0.93
3	1.12
6	1.21
10	1.26
20	1.32
30	1.36
55	1.38
70	1.39
85	1.42
100	1.42
130	1.44
190	1.45
1225	1.49

Table 2.
The Sorption of Hydrogen at 20°C.

Time (min.)	Hydrogen sorbed (c.c.)
1/2	0.68
2	0.84
4	0.91
9	1.00
14	1.04
24	1.10
45	1.17
75	1.20
105	1.21

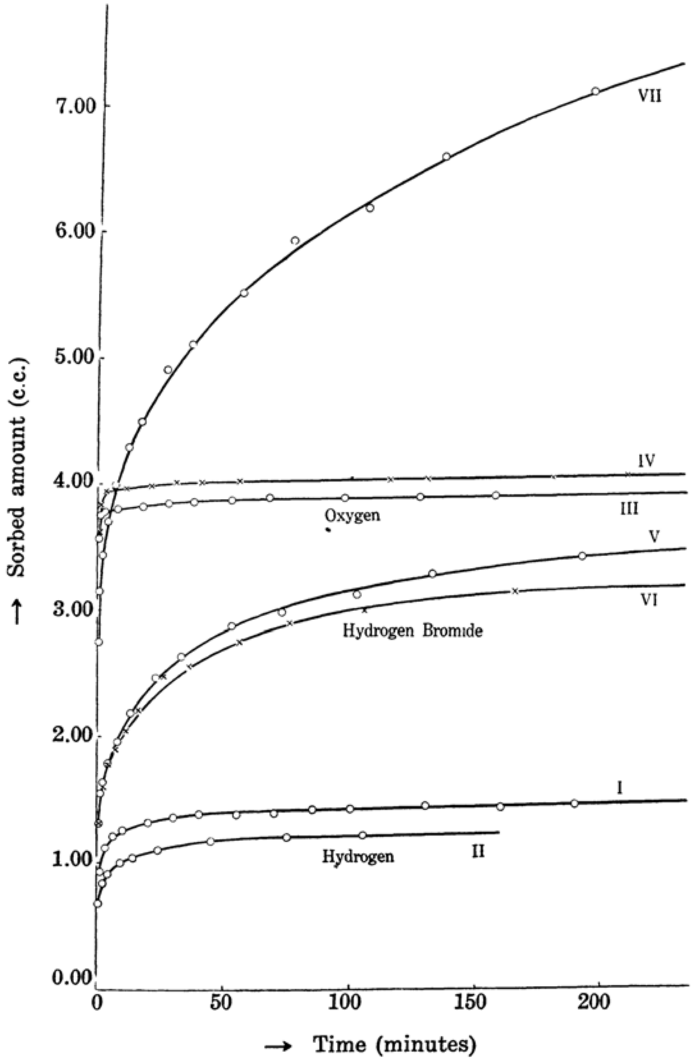

Fig. 2.

In an experiment, reduced nickel (1.00 g.) was nearly saturated with hydrogen at 20°C., when 2.21 c.c. was sorbed in 1220 minutes; then the hydrogen was evacuated for three hours; and hydrogen was again introduced at 20°C., when 0.8 c.c. was sorbed in 1245 minutes. The partial recovery of the capacity for sorption showed that at least a part of hydrogen sorbed on reduced nickel could be desorbed in three hours' evacuation.

The Sorption of Oxygen. It has been observed that reduced nickel is easily oxidized in air, and evolves heat and sometimes takes fire when it comes into contact with air.

The sorption of oxygen on freshly reduced nickel was measured at 20°C. The results are given in Tables 3 and 4 and graphically represented by Curves III and IV in Fig. 2. If compared with hydrogen, oxygen is much more rapidly and abundantly sorbed on reduced nickel. The characteristic shapes of the curves indicate that the sorption is nearly accomplished within one minute or two.

Reduced nickel (1.00 g.) was saturated with oxygen at 20°C., when 3.06 c.c. was sorbed in 1541 minutes, and then stood in vacuum for four hours at the same temperature; oxygen was again introduced at 20°C., when no more oxygen was sorbed in 1406 minutes. Thus it was shown that oxygen, once sorbed on reduced nickel, can never be desorbed in vacuum. It is very probable that the whole oxygen sorbed is bound chemically on nickel. Further the sorption curves (III and IV) indicate that reduced nickel is covered very quickly with a film of the oxide and hereafter oxygen can reach the metal only very slowly through the film. The rapid and abrupt sorption of oxygen on reduced nickel may be attributed partly to a transient rise of the temperature due to the evolution of heat which may favour the very quick formation of the oxide film.

Table 3. The Sorption of Oxygen at 20°C.

Time (min.)	Oxygen sorbed (c c.)
3/4	3.56
1	3.75
3	3.78
8	3.80
18	3.82
28	3.84
38	3.85
58	3.87
68	3.89
98	3.89
128	3.90
158	3.91
1440	3.94

Table 4. The Sorption of Oxygen at 20°C.

Time (min.)	Oxygen sorbed (c.c.)
3/4	3.62
1	3.84
3	3.94
6	3.95
11	3.96
21	3.98
31	4.01
41	4.01
56	4.02
116	4.02
131	4.04
181	4.05
211	4.07
1440	4.08
1566	4.09
1601	4.08
1996	4.09

An approximate calculation from the heat of formation of nickel oxide (58.08 Cal.) indicates that, when 4 c.c. of oxygen is combined with 1 g. of reduced nickel with no loss of heat, the temperature of the metal may be raised from 20°C. to above 200°C. Since it can be supposed that the higher the temperature the more oxygen would be sorbed, the oxidation of reduced nickel and the evolution of heat might be promoted reciprocally under somewhat adiabatic conditions. Thus the phenomenon observed when reduced nickel comes into contact with air is explicable.

It was then examined if the oxygen-stained surface of reduced nickel could be cleaned with hydrogen at comparatively low temperatures. Reduced nickel (1.00 g.), which had sorbed 3.75 c.c. of oxygen to saturation at 20°C. in 1370 minutes and then stood in vacuum for three hours, sorbed 2.48 c.c. of hydrogen at 20°C. in 1187 minutes. After hydrogen was evacuated at 20°C. for three hours, the reduced nickel sorbed 1.14 c.c. of oxygen at 20°C. in 1308 minutes. In a similar way, reduced nickel, which had sorbed 3.43 c.c. of oxygen to saturation at 20°C. in 2570 minutes and stood in vacuum for three hours, sorbed 8.14 c.c. of hydrogen at 96–98°C. in 330 minutes. Then the metal, after evacuation of hydrogen, sorbed 2.52 c.c. of oxygen at 20°C. in 1320 minutes. Thus the oxygen-stained nickel sorbed more hydrogen than freshly reduced nickel, and in view of the amounts of hydrogen sorbed it may be supposed that the reduction of the oxide film with hydrogen of 1 atmospheric pressure can be effected partly even at the ordinary temperature and more profoundly at 100°C. Then the consumption of oxygen by the hydrogen-treated nickel may be attributed to the partial recovery of the capacity for the sorption of oxygen rather than to the oxidation of hydrogen remaining unremoved after three hours' evacuation. In this connection it may be added that reduced nickel, which had sorbed fully hydrogen and stood in vacuum for three hours, sorbed apparently rather a smaller amount (3.10 c.c.) of oxygen than fresh nickel.

The Sorption of Hydrogen Bromide. The sorption of hydrogen bromide on freshly reduced nickel was measured at 20°C. in the dark. The results are given in Tables 5 and 6 and represented by Curves V and VI in Fig. 2. The gradual and extensive sorption suggests an activated adsorption.

Table 5. The Sorption of Hydrogen Bromide at 20°C.

Time (min.)	Hydrogen Bromide sorbed (c.c.)
1/2	1.32
1	1.55
2	1.64
4	1.79
8	1.96
13	2.19
23	2.46
33	2.63
53	2.87
73	2.97
103	3.13
133	3.28
193	3.42
253	3.57
1493	4.99

Table 6. The Sorption of Hydrogen Bromide at 20°C.

Time (min.)	Hydrogen Bromide sorbed (c.c.)
1/2	1.32
1	1.53
2	1.60
4	1.78
7	1.89
11	2.04
16	2.21
26	2.47
36	2.55
56	2.74
76	2.89
106	2.99
166	3.15
1386	4.87

Table 7. The Sorption of Hydrogen Bromide on Oxygen-stained Reduced Nickel at 20°C.

Time (min.)	Hydrogen Bromide sorbed (c.c)
1/2	2.75
1	3.15
2	3.43
4	3.70
7	3.99
12	4.29
17	4.49
27	4.91
37	5.11
57	5.52
77	5.94
107	6.20
137	6.62
197	7.15
257	7.63
317	7.98
1442	12.38
1737	22.39

Reduced nickel (1.00 g.), which had sorbed 3.45 c.c. of oxygen to saturation, consumed much more hydrogen bromide. The results are given in Table 7 and represented by Curve VII in Fig. 2. Here the possibility of the action of molecular oxygen can be readily excluded in view of the clarified nature of the sorption of oxygen on reduced nickel. As already discussed by Urushibara and Simamura⁽⁷⁾ it is supposed that traces of water formed by the action of hydrogen bromide on nickel oxide accelerate the reaction of metallic nickel and hydrogen bromide to give hydrogen and nickel dibromide. Hence, the real amounts of hydrogen bromide withdrawn from the gaseous phase must be far greater than the values of the apparent sorption given in Table 7.

The author expresses his hearty thanks to Prof. Urushibara for his kind guidance and to Dr. I. Sano for valuable advices. Thanks are also due to Nippon Gakujutsu Shinko Kwai (Japan Society for the Promotion of Scientific Research) and to Oji Seishi Co. for grants.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.