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ON THE ABSORPTION OF HYDROGEN BY SODIUM-
POTASSIUM ELECTRODES.

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MEY¹ has shown that the liquid alloy of sodium and potassium, when used as a cathode for the glow discharge, absorbs all except the inert gases. He found that with hydrogen and nitrogen the hydrides and nitrides of the metals were formed and that the rate of absorption was proportional to the current.

Skinner² and Cunningham³ have experimented on the evolution of gas from various electrodes and have found that most metals liberate gas for a certain period at a rate equal to that defined by Faraday's law for electrolytic decomposition. Chrisler⁴ has observed the electrolytic rate for the absorption of hydrogen by various anodes, among them, anodes composed of sodium-potassium alloy.

This alloy then presents the anomaly that it may absorb hydrogen when operated as cathode or as anode.

The object of the present experiments was to investigate the behavior of sodium-potassium electrodes in glow discharge in hydrogen.

APPARATUS AND EXPERIMENTAL METHOD.

Discharge tubes of the form shown in Fig. 1 were used.

The alloy was introduced into the bulb *B*, which was afterwards sealed off at *F*.

After evacuating the apparatus and washing out with dry hydrogen, the tube was tilted and the alloy allowed to run into the discharge tube. A trap, *D*, prevented specks of oxide from being carried over. A clean

¹ Mey, *Annalen der Physik*, 11, 1903.

² Skinner, *PHYS. REV.*, XXI., p. 1 and p. 169. *Phys. Zeit.*, 6, p. 610. *Phil. Mag.* (6), Vol. 12, p. 481.

³ Cunningham, *Phil. Mag.* (6), IX., 1905, p. 193.

⁴ Chrisler, *PHYS. REV.*, XXIX., Nov., 1909.

surface could thus be obtained. A large glass spiral, later replaced by a mercury-sealed ground joint, provided the necessary flexible connection between the discharge tube and the pump and gauge. The auxiliary electrode, *E*, was used when a preliminary cleansing discharge was sent through the tube to free the upper electrode of gas.

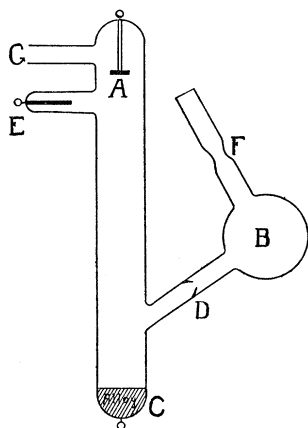


Fig. 1.

The absorption was determined by observing the change in pressure as indicated by a McLeod gauge. The apparatus was calibrated by admitting a known volume of gas and noting the change in gauge reading.

The rates of absorption were determined by plotting curves with pressures as ordinates and total duration of discharge as abscissæ, and determining the slopes of these curves at the required points.

The hydrogen used was produced by electrolysis of barium hydroxide and was carefully dried with sulphuric acid and phosphorus pentoxide.

CATHODE ABSORPTION.

Tables I. and II. give the initial rates of absorption of hydrogen by K-Na cathodes for various current strengths. The results in Table I. are for a cathode 30 mm. in diameter, those in Table II. for one of 16 mm. diameter.

TABLE I.

TABLE II.

Diam. of Tube 30 Mm.		Diam. of Tube 16 Mm.	
Current in milli-amps.	Rate of absorption in mm. ³ per Sec.	Current in milli-amps.	Rate of absorption in mm. ³ per Sec.
0.20	0.141	0.20	0.21
0.40	0.323	0.44	0.33
0.60	0.541	0.48	0.38
0.93	0.885	0.64	0.45
1.00	0.973	0.70	0.68
1.20	1.14	1.10	0.59
1.48	1.44	2.00	0.50
1.60	1.64		
1.91	2.12		
2.20	2.40		
2.30	2.73		
2.50	2.88		
2.80	2.84		
3.20	2.82		
4.20	2.86		
4.70	2.82		

These rates were determined by finding the slope of the pressure-time curve at the point where it meets the pressure axis and therefore represent the initial rates of absorption. When the surface is clean the rate of absorption is a maximum, but decreases rapidly as the film of hydride forms on the surface. The rate of absorption by a clean surface can not be found directly from the observations but must be determined by graphic extrapolation from the curves.

The film of hydride was decomposed and the surface cleaned before each set of observations, by running the alloy as anode at a pressure of about 0.03 mm.

The curves in Fig. 2 show graphically the results given in Tables I. and II.

The curves show that the rate of absorption increases a little more rapidly than the current up to a certain current strength, above which the rate of absorption is constant.

The total areas of the electrodes were in the proportion of about $3\frac{1}{2} : 1$, but the edge of the alloy for about 2 mm. in from the sides of the tube is practically inactive, as shown by the fact the surface shows little or no discoloration in this region. The active electrode areas were in the ratio of about 4.7 : 1. This is very nearly the ratio of the current strengths at which the rates of absorption become constant, which indicates that this takes place at a certain current density,—about 0.5 milliamps. per cm^2

The rate of absorption below this current density is nearly ten times the electrolytic rate.

Two experiments were also tried to determine the effect of the temperature of the cathode on the rate of absorption.

The lower part of the tube containing the alloy was immersed in oil and heated to 140°C . A current of 0.66 milliamps. was used and the rate of absorption was found to be 1.0 mm^3 per sec. This is shown on the curve in Fig. 2 by a point marked with a square, and is much greater than the rate at room temperature for the same current. The cathode was frozen with solid carbon dioxide and probably reached a temperature of at least -20°C . The rate of absorption at 0.8 milliamps. was found to be 0.58 mm^3 per sec. This is also shown on the curve in Fig. 2 and lies considerably below the curve taken at room temperature.

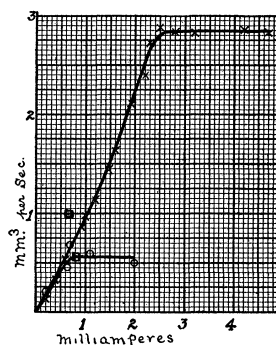


Fig. 2.

ANODE EVOLUTION.

At pressures of one to two millimeters the K-Na anode absorbs hydrogen and at low pressures evolves it. There must be some equilibrium pressure at which it neither evolves nor absorbs. A number of experiments were made to determine this pressure, but while it is sharply defined in any one experiment, it varies from time to time, being dependent on the history of the tube,—primarily on the quantity of hydride available for decomposition: the more hydride present the higher will be the equilibrium pressure. It was found generally to lie below 0.160 mm., this pressure being obtained with a thick coating of hydride. A thin, almost imperceptible coating gave an equilibrium pressure of about 0.06 mm. By continued discharge the supply of hydride may be so far diminished that the equilibrium pressure may be reduced to one or two hundredths of a millimeter. It could probably be reduced still further were it not for the fact that the tube, when operated with an induction coil, tends to reverse at low pressures, becoming in fact, a more efficient rectifier than the "valve" tube with which it was connected.

Until a method was found to account for the quantity of hydride present, measurements of the relative variation of the equilibrium pressure with the current could not be made.

It seemed probable that the decomposition of the hydride was due to the impact of the cathode rays. To test this hypothesis an electromagnet was so placed that a field could be made to pass transversely through the tube a few centimeters above the surface of the alloy. Equilibrium pressure was established at 0.145 mm. with the magnetic field off. On applying the field, the discharge current being kept constant, the pressure in the tube decreased, finally reaching a steady value at 0.053 mm. This could not have been due to any effect arising from the deflection of the rays against the side of the tube, for when the field was reversed, projecting the rays against the opposite wall, the pressure remaining unaltered. On removing the magnetic field the pressure rose to its original value.

That the decomposition of the hydride is due to the impact of the cathode rays, is indicated by the following experiment. A thin film of hydride was formed on the surface of the alloy, which was then insulated. A discharge was then passed from the auxiliary electrode, *E*, as anode, to the electrode *A* as cathode. A strong magnetic field traversed the tube below *E*, preventing the cathode rays from reaching the alloy. The pressure was so low that the tube glowed with a bright green fluorescence. The discharge was passed for five minutes with no change in the appearance of the tube. On removing the field and allowing the cathode rays

to strike the alloy, the pressure rose rapidly, the green fluorescence disappearing in a few seconds. A second application of the field produced no further change in pressure.

The gas liberated by the anode was repeatedly tested spectroscopically; only hydrogen was found.

We have now a means of arriving at some more definite results concerning the equilibrium pressure. By applying the magnetic field during the discharge the pressure may be reduced below the normal equilibrium point without removing hydrogen from the tube, and experiments on the rate of evolution and the equilibrium pressure repeated as often as desired with the assurance that at a given pressure there is always the same quantity of hydride present.

An induction coil was used to supply the current, since at low pressures sufficient potential could not be obtained from the batteries. It was doubtful whether the shunted galvanometer, calibrated on constant current, gave a proper indication of the average current from the coil. A small silver voltmeter was placed in series with the tube and a current of one milliamper, as indicated by the galvanometer, was passed for one hour. The deposit of silver weighed 4 mg., indicating a current of 0.99 millimaps. and showing that the average current was registered with sufficient accuracy by the galvanometer.

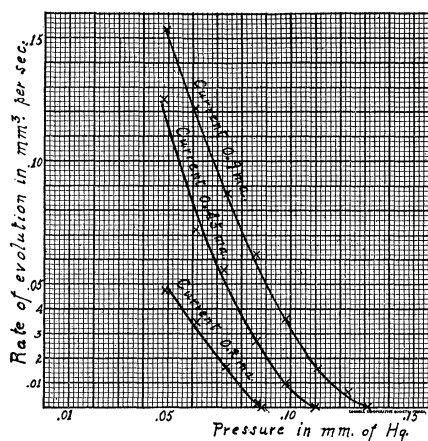


Fig. 3.

TABLE III.
Anode Evolution. Diam. of tube 30 mm.

Current = 0.9 m. amp.		Current = 0.45 m. amp.		Current = 0.20 m. amp.	
Pressure in Mm. of Hg.	Rate of Evolution in Mm. ³ per Sec.	Pressure in Mm. of Hg.	Rate of Evolution in Mm. ³ per Sec.	Pressure in Mm. of Hg.	Rate of Evolution in Mm. ³ per Sec.
0.049	0.153	0.048	0.085	0.049	0.048
0.061	0.121	0.061	0.072	0.062	0.035
0.074	0.087	0.073	0.056	0.074	0.017
0.086	0.062	0.086	0.027	0.087	0.002
0.098	0.036	0.097	0.010	0.088	0.000
0.111	0.016	0.110	0.000		
0.123	0.006				
0.131	0.000				

The rates of evolution at various pressures for given current strengths are given in Table III., and shown graphically in Fig. 3.

The equilibrium pressure and the rate of evolution at any given pressure both increase with the current.

DISCUSSION.

Direct electrical action is insufficient to explain the high rate of cathode absorption observed. We have seen that this rate is considerably affected by the temperature in a sense indicating that the absorption may be largely due to a heating effect.

We have observed that K-Na anodes absorb hydrogen at high pressures, evolve hydrogen at low pressures, if the hydrides are present on the surface, and that, under this condition also, there is an equilibrium pressure at which neither absorption nor evolution takes place. We have also shown that the hydrides are decomposed by the direct impact of the cathode rays.

Apparently these phenomena are due to the rise in temperature produced by the impact of the charged particles.

Sodium and potassium hydrides are both formed at a temperature of about 350° C. and it is probable that in both cases decomposition begins below 400° C.¹ The combination therefore takes place within relatively narrow limits of temperature.

In the foregoing experiments the average temperature of the alloy was rarely above 40° C. and it is therefore unlikely that the average temperature of the surface was sufficient to form the hydrides. The temperature at the point struck by a charged particle of relatively small velocity may, however, be very high and the average temperature of the neighboring molecules might easily be of the order of three or four hundred degrees. Dunoyer² has suggested that this local heating effect may be sufficient to expel electrons from the electrode and even to vaporize the metal. In fact a simple calculation shows that a charged particle falling through ten volts possesses sufficient energy to raise ten atoms of sodium through 400° C. of temperature. We may therefore assume that at the point of impact the temperature is usually above the decomposition temperature and that only in a given zone surrounding this center the conditions exist favorable to the formation of the hydride. Thus at a given instant there is a given fraction of the surface of the electrode active in forming the hydride. When the charged particles fall so close together that the zones of favorable temperature begin to overlap, the active fraction of the surface will not be increased by further increase in the density of the

¹ Moissan, *Compt. Rend.*, 134, p. 18 and p. 71, 1902.

² Dunoyer, "Sur la formation des rayons cathodiques," *Le Radium*, VII., Oct., 1910.

impinging particles. This may be the explanation of the maximum rate of absorption attained at a current density of 0.5 milliamps. per cm.² On this theory we should expect it to be possible to increase the area where dissociation is being produced until it would exceed the area where the hydride is being formed, *i. e.*, with a sufficiently strong discharge, the cathode, if coated with hydride, could be made to liberate hydrogen. This fact has been observed by Chrisler¹ who used a strong discharge in helium as a means of cleansing sodium cathodes, in the same manner that the writer used the anode discharge in hydrogen at low pressure to produce the dissociation of the hydrides. In the case mentioned the decomposition taking place at the hot center is in no way affected by the presence of the helium, while the chances of combination taking place in the zones where the temperature is favorable are greatly diminished, owing to the presence of the inactive gas; a resultant evolution of hydrogen therefore takes place.

The behavior of the K-Na anode is readily explained in the same manner. In fact, from the point of view of heating effects, there is little difference between the two cases, since the energies of the positive and negative particles are comparable in magnitude. It is necessary however to remark on certain differences in the conditions in the two sets of experiments:

1. Much higher potentials were used in the experiments on anode evolution,—due both to the lower pressure and to the valve action of the tube. There was therefore greater heating effect at the surface of the metal.

2. There was much less hydrogen in the neighborhood of the alloy when it was operated as anode,—due to the reduced pressure and to the fact that the hydrogen tends to accumulate near the cathode.

The existence of an equilibrium pressure may be explained as follows; Suppose that at a given pressure and current density, combination and decomposition are taking place at the same rate, due to an effective equality between the portions of the surface that are at a temperature favorable to the formation of the hydride and those that are too hot. If the pressure be raised the velocity of the particles is reduced and the heating effects lessened. There will therefore be a decrease in decomposition and a resultant absorption will take place, reducing the pressure until equilibrium is again established. If the pressure be reduced, the velocity of the particles is increased, the decomposition overbalances the absorption and the pressure is again raised to an equilibrium value.

The equilibrium pressure must also depend on the quantity of hydride

¹ Chrisler, *loc. cit.*

present. The less hydride, the less chance there is for decomposition and the more for combination. To bring about a balance between the two will require an increased area of high temperature, necessitating higher velocity of the impinging particles and consequently, reduced pressure.

The rise of equilibrium pressure with the current may be explained very simply if it be remembered that at equilibrium the areas of formation and decomposition must be effectively equal. If by increasing the current we increase the number of centers of dissociation there will be a resultant liberation of hydrogen which will continue until the increase in pressure diminishes the velocity of the particles sufficiently for equality to be again established.

The curve, Fig. 2, shows that the cathode absorption increases more rapidly than the current. This is what would be expected considering that, under the conditions of the experiment, an increase in current meant an increase both in the number of particles and in their velocity.

SUMMARY.

1. The rate of absorption of hydrogen by K-Na has been measured for various currents. At current densities less than 0.5 milliamps. per cm.² the rate of absorption is approximately ten times that at which hydrogen is liberated by electrolysis with an equal current. With greater current densities the rate of absorption is constant. The rate of absorption increases with the temperature of the cathode.

2. An "equilibrium" pressure has been found at which K-Na anodes neither absorb nor evolve gas. This equilibrium pressure depends on the current and on the quantity of hydride on the surface of the alloy.

3. The rate of evolution by anodes below equilibrium pressure has been measured.

4. It has been shown that sodium and potassium hydrides are decomposed by the cathode rays.

The cathode absorption and anode evolution are regarded as being due to the formation or decomposition of the hydrides by the local heating effects of the impinging charged particles, according as the temperature is favorable to one or the other of these processes.

These experiments were carried on in part at the Cavendish Laboratory and the writer wishes in conclusion to tender his sincere thanks and appreciation to Professor Sir J. J. Thomson for his interest and helpful suggestions during the course of the work, and for his kindness in putting the facilities of the laboratory at the writer's disposal.