The Kinetics of Deuterium Ions Discharge and Ionization of Adsorbed Deuterium Atoms on a Pt-Electrode

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The mechanism of separation of the hydrogen isotopes in electrolysis is closely related to the mechanism of overvoltage, so that, in general, a study of the former process can shed light on the latter. This relation has been widely utilized and on the basis of the data thus obtained most investigators [1-4] are inclined to favour the mechanism of slow recombination for a large number of metals, platinum among others. However, the assumption of a recombination mechanism is of necessity based on indirect considerations, inasmuch as no experimental data are to be had on the rates of the individual stages of the separation process. In this connection considerable theoretical interest attaches to the derivation of such data for the process of the electrolytic evolution of deuterium.

A straightforward method of determining the rate of discharge of the hydrogen ion on a Pt-electrode with formation of an adsorbed atom[5] has recently been developed and applied. In the present paper this method is applied to a comparative determination of the rates of discharge of hydrogen and deuterium ions and their dependence on the composition of the solution.

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[3] H. Walton and G. Wolfenden, J. Chem. Soc., **1937**, 1677; Trans. Farad. Soc., **34**, 436 (1938).

[4] Horiuti and Okamoto, Sci. Pap. Inst. Phys. and Chem. Res. (Tokyo), **28**, 231 (1936).

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Method

The method used was based on a measurement of the complex conductance per unit surface [6] of a platinum electrode in a current of variable frequency[7]. To determine the rate of discharge of deuterium the conductance was measured first in heavy water and then for comparison in ordinary water. In addition, polarization capacity curves (charging curves) were obtained in heavy and in ordinary water.

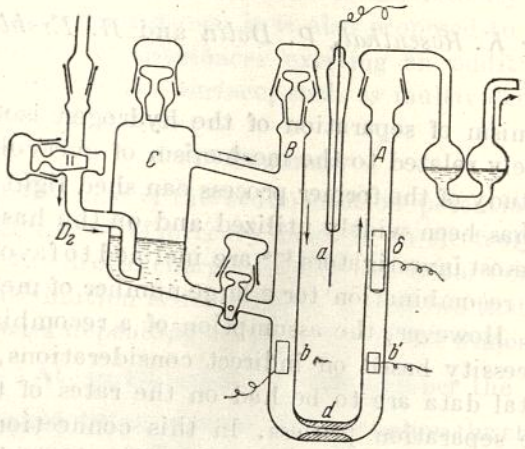

Fig. 1. Measuring cell.

The measuring cell (Fig. 1) consisted of three compartments A, B, and C. Part A contained an auxiliary platinized Pt-electrode δ in the form of a cylinder, the measuring electrode a being mounted along its axis (a was introduced after the cell was filled with solution). Part B contained the reversible hydrogen electrode b; A and B were separated by a capillary tube d. The volume of solution in the cell was about 2 cm³. The electrode under investigation was a platinum wire 0.03 mm in diameter, 12.5 mm long and of surface area 0.0118 cm². The electrolyte was saturated with hydrogen in vessel C, the electrodes δ, b and b' being saturated simultaneously; the latter served

[6] Throughout this paper the conductance will refer to unit surface of the electrode.

[7] For a description of the method see footnote [5].

as reference electrode when measuring the polarization capacity of electrode δ with direct current.

Preparation of solutions and experimental procedure

The measurements were made in the following solutions: 0.16 N H_2SO_4 + 2 N Na_2SO_4 in H_2O; 0.14 N D_2SO_4 + 2 N Na_2SO_4 in D_2O; 0.016 N NaOH + 2 N Na_2SO_4 in H_2O; 0.14 N NaOD + 2 N Na_2SO_4 in D_2O. In addition, measurements were carried out in the following solutions in ordinary water: 1 N HCl + 2 N NaCl; 0.1 N HCl + 2 N NaCl; 0.01 HCl + 2 N NaCl. The D_2SO_4 and NaOD solutions in D_2O, and H_2SO_4 and NaOH in H_2O were obtained by electrolysis of a 2 N Na_2SO_4 solution (salt recrystallized and calcinated at 900°) in H_2O and D_2O respectively. The polarization was effected with large platinized Pt-electrodes saturated with hydrogen and deuterium, the stop cock separating the anodic and cathodic spaces being closed. The deuterium used to saturate the solutions in D_2O was obtained by electrolysis of a concentrated solution of NaOD, which in turn was obtained by the slow interaction between D_2O vapour and metallic soduim.

All the solutions were prepared from c. p. reagents and purified immediately before the experiment by adsorption of possible contaminations on a freshly platinized electrode in an atmosphere of hydrogen or deuterium respectively. It was necessary to verify that this treatment was sufficient for our purposes and that the data obtained in the D_2SO_4 and NaOD solutions could really be attributed solely to the properties of heavy hydrogen and not to the influence of chance impurities. The experiment was, therefore, carried out as follows. We first obtained the capacity and ohmic conductance curves[8] of the electrode under investigation (preliminarily treated in aqua regia, washed and heated to red heat in air) in a H_2SO_4 or NaOH solution in H_2O; the measurements were then carried out under exactly the same conditions in a solution of D_2SO_4 or, respectively NaOD; the procedure was finally repeated (without pretreatment in aqua regia or heating) in the original H_2SO_4 or NaOH solutions. Coincidence

[8] The curves representing the dependence of the components (capacitive and ohmic) of the complex conductance of the electrode on the polarization at a given frequency are called here capacity and ohmic conductance curves respectively.

of the curves obtained in H_2SO_4 or NaOH before and after the experiment with heavy water showed that our electrode underwent no changes in the D_2O solutions.

The actual measurements were carried out as follows. We measured the capacitive and ohmic components of the conductance of the electrode at a given frequency as a function of the anodic polarization in the interval 0.0—1.0 V, always starting from 0.0 V and gradually increasing the potential towards anodic values—the runs were then repeated at different frequencies. The measurements were made at room temperature 18—20°C.

Experimental results

1. Capacity and ohmic conductance curves in 0.16 *N* H_2SO_4 + 2 *N* Na_2SO_4 and 0.14 *N* D_2SO_4 + 2 *N* Na_2SO_4.

The measurements were made over a frequency range of 10 to 6000 cycles and a potential range of 0 to 1 V. The results are shown in Figs. 2 and 3 [9]. As appears from the figures [10], the curves taken down in both 0.16 *N* H_2SO_4 and 0.14 *N* D_2SO_4 are similar to the ones previously obtained [5] in solutions of H_2SO_4.

It should be observed that the absolute values of the capacitive and ohmic components of the conductance in the polarization range 0—0.2 V and in the frequency range 200—6000 cycles are considerably less in D_2O than in H_2O. This is due to slower discharge of the D-ion as compared with the H-ions. At the lower frequencies the

[9] It should be borne in mind that the impedance measured experimentally consists of the impedance of the electrode under investigation (which is to be determined) and the series connected resistances of the auxiliary electrode the resistance of the intervening solution, and the resistances of all the connecting wires, including the metallic electrodes themselves. In view of the large surface area of the auxiliary electrode its resistance can be neglected. The remaining resistances are purely active and according to calculations comprise 0.08Ω for our system in H_2O (the acid and alkaline solutions have practically the same conductance inasmuch as they contain both 2 *N* Na_2SO_4). The vector difference was taken between the experimentally measured impedance and the correction for this active resistance. Up to 3000 cycles the correction does not exceed 20% of the measured magnitude. The data given in Figs. 2 and 3 have been corrected in this manner.

[10] On these figures the positive direction of the axis of potentials has been chosen from left to right for the solutions in D_2O and *vice versa* for those in H_2O.

capacitive components in D_2O and H_2O are practically equal and correspond to the capacities found from the charging curves. Under these conditions the distribution of hydrogen and deuterium on platinum almost attains equilibrium, and the difference between their rates of discharge cannot be manifested. At high frequencies the capacitive components decrease in both solutions (curves *f* and *f'*, Fig. 2) and approach in magnitude the capacity of the double

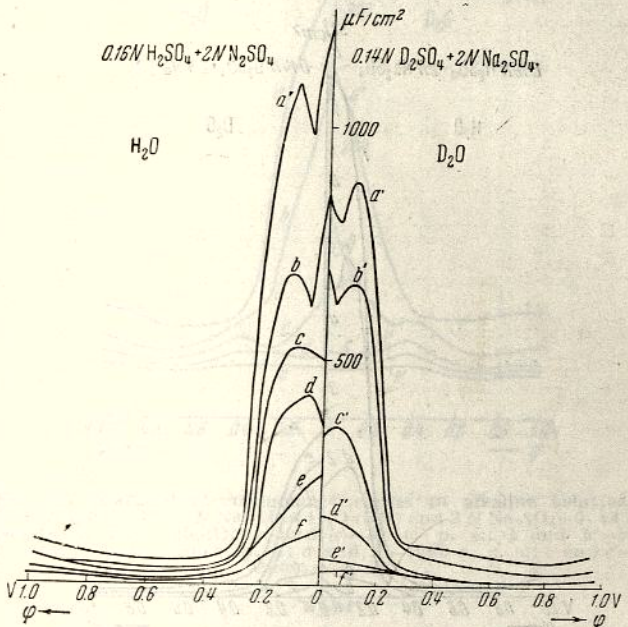

Fig. 2. Capacity curves in acid solutions: 2 *N* Na_2SO_4+0.16 *N* H_2SO_4 in H_2O (left) and 2 *N* Na_2SO_4+0.14 *N* D_2SO_4 in D_2O (right); *a* and *a'*—10 c. p. s., *b* and *b'* – 50 c. p. s., *c* and *c'*—200 c. p. s.; *d* and *d'*—1000 c. p. s., *e* and *e'*—3000 c. p. s.; *f* and *f'*—6000 c. p. s.

layer, being less, however, in D_2O than in H_2O. This can be explained by the slowness of the discharge process, as a result of which at these frequencies the filling of the atomic layer remains practically unchanged on passing of alternating current. The capacitive component of the conductance is thus to be attributed in the main to the double layer which is probably the same in both solutions. As for the ohmic component, at low frequencies it is the same in H_2O and D_2O (Fig. 3, curves *a* and *a'*, *b* and *b'*, *c* and *c'*, *d* and *d'*), but with increasing frequency grows more rapidly in H_2O than in D_2O and at 3000 cycles

(curves e and e', Fig. 3) is approximately 2.2—2.3 times as great in H_2O as in D_2O. (Curves f and f' taken at 6000 c. p. s. are unreliable, s. footnote [1] on p. 216). As has been shown elsewhere [5], the magnitude of the ohmic component found at high frequencies characterizes the rate of discharge. We thus see that under these conditions the rate of discharge of H is 2.2—2.3 times as large as that of D (in the ratio of the conductances at 3000 cycles).

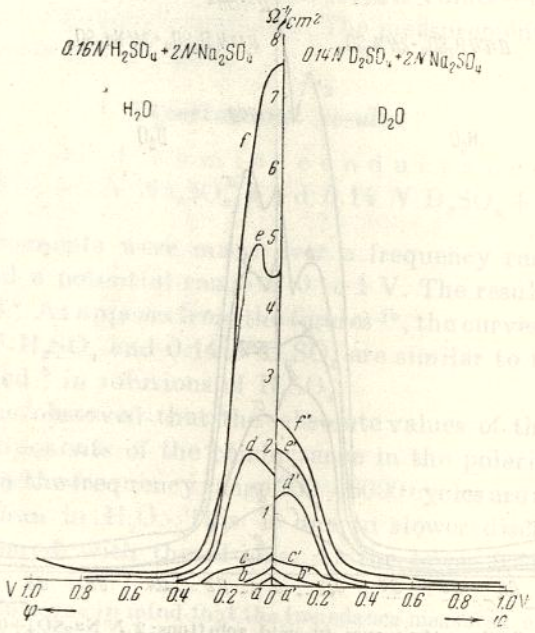

Fig. 3. Ohmic conductance curves in acid solutions (see legend under Fig. 2).

2. Solutions of 0.16 N NaOH + 2 N Na_2SO_4 in H_2O and 0.14 N D_2SO_4 + 2 N Na_2SO_4 in D_2O

The capacitive and ohmic conductance curves in these solutions are plotted in Figs. 4 and 5. It will be seen that the curves obtained in D_2O do not differ in form from those in H_2O. A comparison of the two families of curves leads to the same conclusions as in the case of acid solutions. It should be observed that according to Fig. 5 (curves e and e') the ratio of discharge rates of H and D is equal to 2.1—2.4 in alkaline solution.

3. Influence of HCl concentration on the capacitive and ohmic conductance components of the electrode in H_2O.

It follows from the Volmer—Frumkin theory of slow discharge that in acid solutions with an excess of neutral salt the rate of dis-

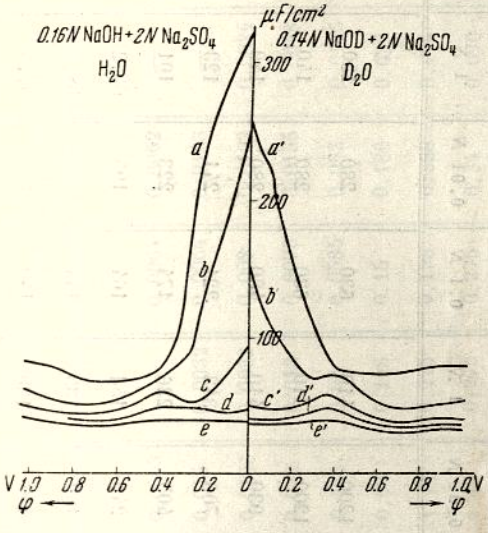

Fig. 4. Capacitive conductance curves in alkaline solutions 2 N Na_2SO_4+0.16 N NaOH in H_2O (left) and 2 N Na_2SO_4+0.14 N NaOD in D_2O (right); a and a'—10 c. p. s.; b and b'—50 c. p. s.; c and c'—200 c. p. s.; d and d'—1000 c. p. s.: e and e'—3000 c. p. s.

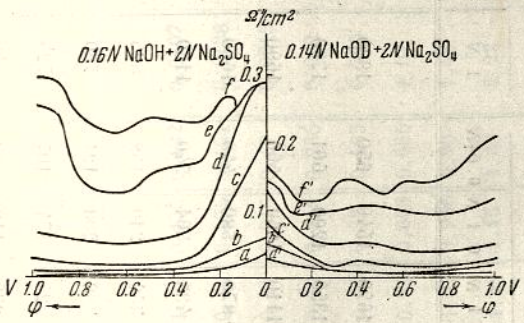

Fig. 5. Ohmic conductance curves in alkaline solutions (see legend under Fig. 4).

charge of hydrogen ions (at a constant potential referred to the reversible hydrogen electrode in the same solution) should vary as the

Table 1

Dependence of the capacity component of the conductance μF/cm² on the frequency at different polarization in HCl 2 *N* NaCl solutions

Polarization 0.0 V				0.10 V			0.20 V			0.25 V		
HCl / C.p.s.	1 *N*	0.1 *N*	0.01 *N*	1 *N*	0.1 *N*	0.01 *N*	1 *N*	0.1 *N*	0.01 *N*	1 *N*	0.1 *N*	0.01 *N*
10	1690	1540	650	1880	1200	1200	410	630	280	150	240	185
20	1350	1200	601	1790	966	1200	410	630	280	140	194	185
30	1110	1060	560	1690	870	930	410	480	280	140	184	149
50	870	580	440	1600	870	700	343	221	241	123	106	112
200	435	304	240	1160	725	405	236	174	223	101	83	112
500	366	240	158	825	500	240	154	164	195	63.2	81.5	112
750	338	203	121	760	455	182	135	144	185	58.5	76	112
1000	324	174	107	725	405	168	130	140	158	57.5	70	102
2000	230	112	63	540	255	96	118	125	130	57.5	70	92
4000	128	52.5	44	340	148	70.5	95	91	99	49	53	74
6000	91	42	38	217	106	59.5	72	84.5	76	38	50	62.5

Table 2

Dependence of ohmic component (Ω^{-1}/cm^2) of the conductance on the frequency at different polarizations in HCl+2 *N* NaCl solutions

Polarization 0.0. V				0.10 V			0.20. V			0.25 V		
HCl / C.p.s	1 *N*	0.1 *N*	0.01 *N*	1 *N*	0.1 *N*	0.01 *N*	1 *N*	0.1 *N*	0.01 *N*	1 *N*	0.1 *N*	0.01 *N*
10	1.12	0.175	0.132	0.0107	0.012	0.0093	—	0.0064	0.0062	—	0.0032	—
20	0.15	0.175	0.154	0.0138	0.0138	0.015	0.0032	0.0064	0.0103	—	0.0032	0.0093
30	0.21	0.215	0.17	0.0215	0.0138	0.0186	0.0032	0.008	0.0103	0.0024	0.0048	0.0093
50	0.32	0.215	0.235	0.032	0.0175	0.023	0.012	0.0096	0.0155	0.0048	0.0048	0.0103
200	0.58	0.32	0.465	0.276	0.385	0.465	0.06	0.0585	0.062	0.0175	0.015	0.023
500	0.87	0.665	0.665	1.07	1.12	0.98	0.148	0.15	0.186	0.032	0.043	0.055
750	1.07	0.966	0.93	1.48	1.62	1.18	0.215	0.193	0.338	0.074	0.072	0.093
1000	1.38	1.15	1.03	2.23	2.3	1.48	0.275	0.275	0.34	0.096	0.096	0.116
2000	2.7	2.1	1.33	5.65	4.1	1.84	0.64	0.64	0.85	0.26	0.26	0.31
4000	4.44	2.76	1.5	10.8	6.2	2.0	1.18	1.1	1.55	0.53	0.48	0.62
6000	5.6	3.0	1.65	12.0	6.75	2.1	1.49	1.58	1.69	0.58	0.87	0.85

square root of the concentration of $H^{\bullet}$; in alkaline solutions under the same conditions the rate of discharge of the hydrogen ions should vary as the square root of the concentration of hydroxyl ions [11]. With the aim of verifying these relationships we investigated the

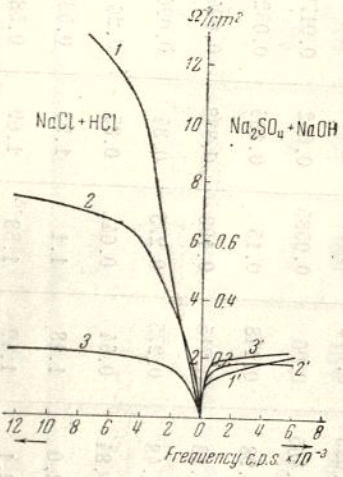

Fig. 6. Dependance of the ohmic component of the conductance on the frequency at 0.1 V in acid and alkaline solutions. *1*—2 *N* Na Cl+1 *N* HCl; *2*—2 *N* NaCl+0.1 *N* HCl; *3*—2 *N* NaCl+0.01 *N* HCl; *1'*—2 *N* Na_2SO_4+1*N* N OH; *2'*—2 *N* Na_2SO_4+ +0.1 *N* NaOH; *3'*—2 *N* Na_2SO_4+ +0.01 *N* NaOH.

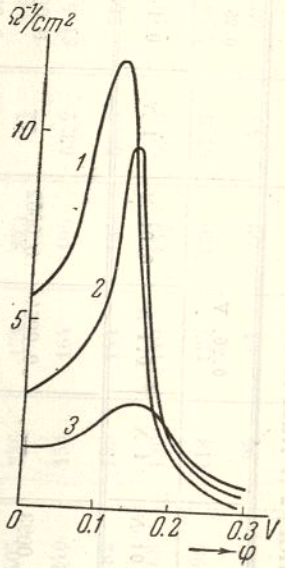

Fig. 7. Dependance of the ohmic component of the conductance at 6000 c. p. s. on the potential. *1*—1 *N* HCl+2 *N* NaCl; *2*—0.01 *N* NaCl+2 *N* NaCl; *3*—0.01 *N* HCl+2 *N* NaCl

influence of the concentration of HCl and NaOH on the complex conductance of a Pt electrode in 2 *N* solutions of NaCl in H_2O. The capacitive and ohmic components of the conductance were measured in solutions of 1 *N* HCl + 2*N* NaCl, 0.1 *N* HCl + 2 *N* NaCl and 0.01 *N* HCl + 2 *N* NaCl over a range of polarization from 0 to 1 V.

All the data are listed in Tables 1 and 2. The dependence of the ohmic conductance on the frequency at a constant potential equalling 0.1 V is depicted in Fig. 6, curves *1*, *2*, *3*. With a tenfold change

[11] These conclusions are valid provided the composition of the solution does not affect the properties of the adsorbed hydrogen atoms. This condition is probably satisfied only approximately for Pt.

in the concentration of HCl the limiting conductance changes by a factor of 2—3 (Table 2). Hence, in this case our data are in approximate agreement with the theory.

The trend of the ohmic conductance measured at high frequencies as a function of the potential of the electrode in the chloride solutions displays several peculiarities. As may be seen from Fig. 7, the limiting conductance increases at all concentrations when the potential is shifted in anodic direction, passes through a rather sharp maximum, and then falls off. It is interesting that with growing dilution of the solution this maximum becomes slightly displaced towards more positive potentials. These phenomena are much less marked in the sulphate solutions.

4. Influence of NaOH concentration on the capacitive and ohmic components of the conductance of a Pt-electrode in H_2O.

The capacitive and ohmic components of the conductance were measured in 1 N NaOH + 2 N Na_2SO_4, 0.1 N NaOH + 2 N Na_2SO_4 and 0.01 N NaOH + 2 N Na_2SO_4 solutions in the frequency range 10—6000 cycles and in the same range of potentials as for the acid solutions. The dependance of the ohmic component on the frequency of 0.1 V is represented in Fig. 6 (curves *1'*, *2'*, and *3'*). All the data are summarized in Tables 3 and 4. It is evident from the tables and the figure that the capacity and the ohmic conductance depend but slightly on the concentration of the alkali, as it was also observed by Dolin and Ershler[5].

5. Direct current charging curves in 0.16 N H_2SO_4 + 2 N Na_2SO_4 and 0.14 N D_2SO_4 + 2 N Na_2SO_4 solutions

Fig. 8, *II* depicts the curves (dotted lines—in H_2O, full lines—in D_2O) obtained on charging a platinized Pt-electrode of 3 cm^2 apparent surface area with a current of density 0.313×10^{-4} A/cm^2. The electric charge in coulombs per apparent unit area is plotted as abscissae against the potential of the electrode referred to the reversible hydrogen electrode in the same solution as ordinate. It may be seen from the figure that heavy hydrogen is bound more firmly to the Pt-electrode than light hydrogen, since the potential of

Table 3

Dependence of the capacity component of the conductance μF/cm² on the frequency at different polarization in NaOH+2 *N* Na_2SO_4 solutions

Polarization 0.0 V				0.1 V			0.20 V			0.25 V		
NaOH / C.p.s.	1 *N*	0.1 *N*	0.01 *N*	1 *N*	0.1 *N*	0.01 *N*	1 *N*	0.1 *N*	0.01 *N*	1*N*	0.1 *N*	0.01 *N*
10	365	320	385	330	275	365	313	215	298	278	128	164
20	336	308	360	300	257	335	250	193	280	211	128	164
30	288	260	335	240	225	312	220	183	270	206	101	130
50	220	243	270	134	178	260	134	119	164	106	87	96
200	52.6	49.5	53	46.5	41.2	46.5	45	46.5	42	46.5	48	39.5
500	49.6	43.5	48	42.6	39.8	45	44	43.5	39.5	46,5	44	32.8
1000	42	38.5	37.5	39.4	37.5	35.5	44	42	33.5	45	43	30.8
3000	35.5	35	31.5	36.5	34.5	31.5	44	39.5	31.8	45	41	30
6000	34.2	33.5	31.5	36,3	34	31.5	44	39.8	31	45	39.5	29.5

Table 4

Dependence of ohmic component (Ω^{-1}/cm^2) of the conductance on the frequency at different polarizations in NaOH+2 *N* Na_2SO_4 solutions

Polarization 0.0 V				0.10 V			0.20 V			0.25 V		
C. p. s.	1 *N*	0.1 *N*	0.01 *N*	1 *N*	0.1 *N*	0.01 *N*	1 *N*	0.1 *N*	0.01 *N*	1 *N*	0.1 *N*	0.01 *N*
10	0.019	0.027	0.024	0.0107	0.0164	0.016	0.0096	0.00817	0.0077	0.0064	0.0065	0.0077
20	0.021	0.036	0.032	0.016	0.027	0.024	0.0107	0.0164	0.0106	0.0096	0.0096	0.0106
30	0.048	0.042	0.048	0.032	0.1365	0.024	0.016	0.025	0.0138	0.0137	0.0183	0.012
50	0.074	0.054	0.058	0.06	0.0435	0.046	0.048	0.0315	0.033	0.0275	0.021	0.019
200	0.174	0.183	0.24	0.12	0.137	0.174	0.048	0.074	0.087	0.0275	0.0355	0.048
500	0.192	0.24	0.256	0.128	0.154	0.185	0.0565	0.077	0.113	0.0385	0.0418	0.06
1000	0.253	0.27	0.276	0.157	0.17	0.197	0.093	0.093	0.11	0.068	0.057	0.071
3000	0.275	0.28	0.285	0.178	0.178	0.21	0.137	0.144	0.15	0.103	0.123	0.115
6000	0.39	0.3	0.3	0.228	0.215	0.225	0.177	0.215	0.19	0.16	0.2	0.173

complete removal of the former is more anodic by 15 mV than that of the latter. The similarity of the charging curves in H_2O and D_2O testifies to the similarity in the properties of the atomic layers of

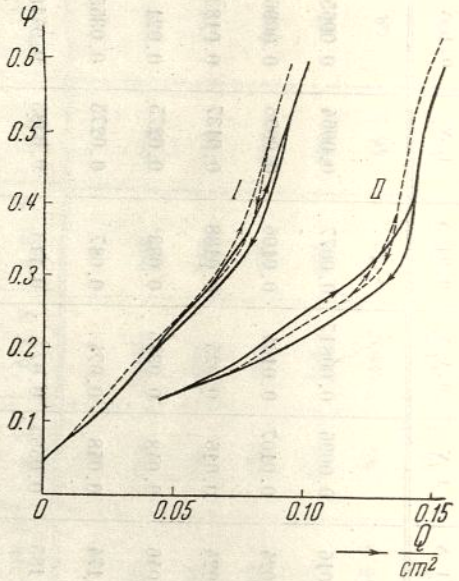

Fig. 8. Charging curves in alkaline and acid solutions. *I*—2 *N* Na_2SO_4+0.16 *N* NaOH in H_2O (dotted line) and 2 *N* Na_2SO_4+0.14 *N* NaOD in D_2O (full line); *II*—2 *N* Na_2SO_4+0.16 *N* HSO_4 (dotted line) and 2 *N* Na_2SO_4+0.14 *N* D_2SO_4 (full line).

H and D. It should be observed that the curves we obtained in D_2O correspond to somewhat less stable conditions than in H_2O as judged by the loop between the direct and inverse runs.

6. Direct current charging curves in 0.16 *N* NaOH + 2 *N* Na_2SO_4 and 0.14 *N* NaOD + 2 *N* Na_2SO_4 solutions

The charging curves were obtained under the same conditions; the current density was equal to 0.32×10^{-4} A/cm². In alkaline as in acid solutions heavy hydrogen is more firmly bound to the Pt-electrode than light hydrogen (Fig. 8, *I*). These curves correspond to even less stable conditions.

Discussion of the results

Let us first consider the results relating to the character of the inhomogeneity of the platinum electrode surface and to the discharge process of the hydrogen ion. According to the theory of slow discharge, the rate of the discharge process should depend on the potential. Previous measurements [5] have shown, however, that the rate of discharge is independent of the potential over a considerable range. A similar independence was observed in the present investigation; the curves of Fig. 3 show that the resistance component at 3000 cycles practically does not depend on the potential throughout the range 0—0.15 V (curves *e* and *e'*).

According to a theory developed by T e m k i n [12], this should be so for a surface with a certain type of inhomogeneity for which the heat of adsorption is a linear function of the extent of surface covered [13].

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[12] M. T e m k i n and V. P y z h o v, Acta Phys. Chim., **12**, 327 (1940); J. Phys. Chem. (Russ.), **13**, 851 (1939).

[13] Such surfaces are sometimes called surfaces with a logarithmic adsorption isotherm.

Physically the fact that the rate of discharge is independent of the potential is due to the variation of the potential entailing a variation not only of the electric field govering the discharge but also of the extent of surface covered by hydrogen (which is determined by the equilibrium conditions). The latter affects the rate of discharge inasmuch as the discharge occurs only on the part of the surface which is free of adsorbed hydrogen. With a change of potential both these factors exert opposing influences. Thus, *e. g.* if the potential increases in the positive direction, the electric field varies in such a manner that the discharge is retarded, whereas the free surface increases and hence the discharge is accelerated. The rate of discharge can be independent of the potential when these two factors cancel one another. As shown by Temkin, this can be the case for a surface with a logarithmic adsorption isotherm. It follows from these considerations that such an independence can be observed only when a considerable extent of surface is covered, *i. e.* when the change in the free surface with the potential can still be sufficiently great. For a small extent of surface covered the free surface can evidently increase but slightly with a positive shift of the potential, and under these conditions the influence of the potential on the discharge may become apparent. These considerations are confirmed by the curves of Fig. 3, according to which at high frequencies the ohmic conductance is independent of the potential only in the range 0—0.15 V and falls off by a factor of 20 as the potential shifts to 0.3V. Hence in this range the influence of the electric field on the discharge rate of the H-ion postulated by the theory of slow discharge can be detected by experiment.

It should be observed that according to the theory, the opposing influence of the field and the adsorption should neutralize one another for a surface with a logarithmic adsorption isotherm in the region where the charging curve has a linear form. This theory predicts that the influence of the potential on the discharge should become evident as the steep rise of the charging curve is approached. However, in considering Fig. 8, *II*, we see that in the solution in which curves *e*, *e'* of Fig. 3 were obtained, the steep rise of the charging curve only starts at 0.3 V. Hence the mutual neutralization of the field and the surface covering disappears considerably earlier than the theory demands. This result shows that the inhomogeneity of the surface is of a more complicated character than assumed by the above theory [14].

The influence of the hydrogen ions concentration on the discharge in acid solutions observed in these measurements is in approximate agreement with the Volmer-Frumkin theory, inasmuch as the rate increases roughly as the square root of the concentration. (It may be seen from Table 2 that the conductance at 4000 cycles and 0.010 V increases approximately as the square root of the concentration). In alkaline solutions the rate of discharge is independent of the concentration; this conforms with earlier measurements [5] and is apparently to be explained by the peculiarities in the behaviour of the hydride film on platinum in alkaline solutions as already stated before [5].

In the present experiments we were interested primarily in comparing the results of measurements in H_2O and D_2O. Attention should be drawn here, first of all, to the element of ambiguity connected with our choice of the conditions for such a comparison. The method used actually allows of comparing the rates of discharge in H_2O and D_2O measured at equal potentials referred to the corresponding

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[14] It was pointed out earlier [5] by one of us (Ershler) that the dependence of the capacity and the conductance on the frequency found in Dolin and Ershler's paper leads us to assume the presence of different types of areas on Pt, between which the surface diffusion of adsorbed hydrogen occurs with difficulty. A similar analysis of the results of the present paper (which will be more fully discussed elsewhere) also showed in conformance with the conclusions of the text, that these areas do not fit into the scheme of a surface with logarithmic adsorption isotherm (for more detail see K. Rosenthal, «The Kinetics of Ionization and Discharge of Heavy Hydrogen on Pt», Thesis, Karpov Institute of Physical Chemistry, Moscow, 1944).

reversible gas electrodes (hydrogen electrode in H_2O and deuterium electrode in D_2O), or, in other words, at equal overvoltages. However, the conditions on the surface of the Pt-electrode in H_2O and D_2O may differ widely. Here appears the fundamental difference between these experiments and the experiments on separation of the isotopes, where the two isotopes react under strictly identical conditions and where it may be assumed, for example, that the difference in the discharge rates of H and D is due (besides the difference in the concentrations) only to the difference in the activation energies of discharge of the two ions. Under the conditions of comparison chosen in the present experiment, however, the observed difference in the discharge rates may be due, besides, to unequal adsorption of hydrogen and deuterium; to the difference in the potentials of Pt in H_2O and D_2O, (inasmuch as the potentials are «equal» only by convention, since we compare potentials referred to the corresponding reversible gas electrodes); and finally, to the different heats of wetting of Pt by water and deuterium oxide [15].

Therefore, the ratio of the discharge rates of H and D observed here cannot be considered directly in the usual process of electrolytic separation, in which all these factors are undoubtedly identical for both isotopes.

Despite all these difficulties, a comparison of the data for H_2O and D_2O permits us to ascertain the following important circumstance. In acid solutions at potentials corresponding to the reversible gas electrodes the ratio of the discharge rates of H in H_2O and D in D_2O is 2.3 (Fig. 9, curve *1*). A close value is observed for this ratio at the same potentials in alkaline solutions (Fig. 9, curve *2*).

In the light of these data the important argument against the possibility of a discharge mechanism of separation advanced by Halpern and Gross [1] is invalidated; this argument was based on the experimentally established fact that the separation factor is independent of the reaction of the solution. In accepting the mechanism of slow discharge for separation we are forced to explain the absence of a dependence of the separation factor on the reaction of the solu-

[15] The last factor should play a part since the adsorption of an atom in solution is probably accompanied by the displacement of an adsorbed solvent molecule from the corresponding surface area. This circumstance was pointed out to us by M. Temkin.

tion by assuming that the ratio of the discharge rates of hydrogen and deuterium ions (in acid solutions) equals the same ratio for the H_2O and D_2O molecules (in alkaline solutions). Such an assumption, necessitated by the discharge mechanism appears extremely forced;

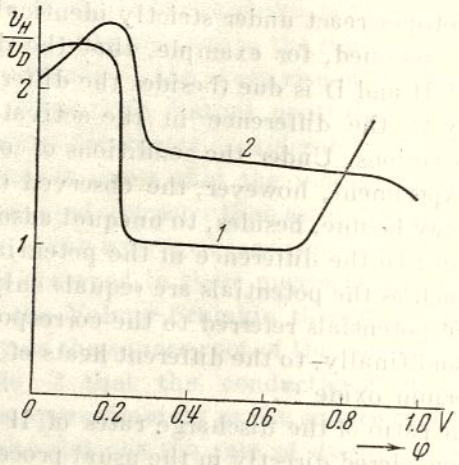

Fig. 9. Dependence of the ratio of discharge rates of hydrogen and deuterium v_H/v_D in acid (curve 1) and alkaline (curve 2) solutions on the potential.

in the recombination mechanism, on the other hand, the separation factor is naturally independent of the nature of the discharging particles. It was for this reason that we found the recombination mechanism preferable. Our measurements have directly established that for Pt the substitution of alkaline solutions for acid solutions does not cause, all other conditions remaining the same, any great change in the ratio of the discharge rates of H and D. Hence, one of the most substantial arguments against the mechanism of slow discharge loses its force for platinum.

The following results are also worthy of attention. It may be seen from Fig. 9 that for acid solutions the ratio of the discharge rates of H and D remains close to 2.5 throughout the range of potentials 0—0.2 V. At higher anodic potentials it approaches unity. The same relation, though less sharply expressed, is also observed in alkaline solutions. It can be explained qualitatively if we assume that the difference in the measured rates of discharge on H and D is due in

part to a greater extent of surface covered by deuterium as compared to hydrogen. In this case, on going over to a lesser surface covering (*i. e.* to more positive potentials) we should expect the ratio of the discharge rates to decrease. Such an assumption is also supported by the results of direct measurements of the extent of surface covered. Thus, a comparison of the charging curves of Pt in H_2O and D_2O immediately reveals a greater extent of surface covered by deuterium. If on the basis of these curves we plot the characteristic curves (dependence of the number of adsorbed H atoms on the potential, Fig. 10) by the method used in the paper of F r u m k i n and Š l y g i n [16] we see that at equal potentials deuterium is adsorbed to a greater extent than hydrogen [17].

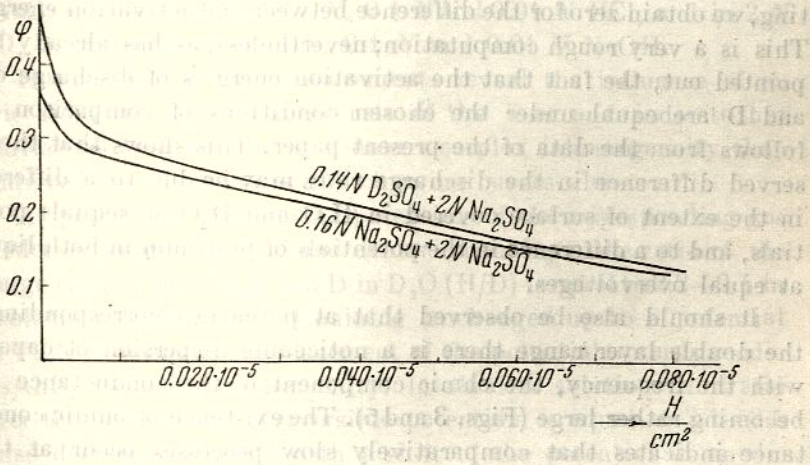

Fig. 10. Dependence of the amount of adsorbed H and D atoms on the potential.

[16] A. F r u m k i n and A. Š l y g i n, Acta Phys. Chim., 5, 819 (1936).

[17] In order to plot the curves of Fig. 10, it is necessary to have a charging curve, obtained under conditions sufficiently close to equilibrium. This condition is approximately satisfied in acid solutions in H_2O (the dotted curves *II* in Fig. 8, corresponding to anodic and at cathodic polarization, almost coincide) whereas in acid solutions in D_2O (Fig. 8, full curves *II*) the anodic and cathodic polarization curves form a loop. The equilibrium charging curve was plotted in this case by drawing a number of vertical straight lines and connecting the midpoints of the segments intercepted on these lines by the anodic and cathodic curves.

It should be observed that the characteristic curves allow of computing the difference between the binding energies of deuterium and hydrogen with platinum. Without giving the details of the computation we can point out that this difference is equal to 1.7 kg.-cal. per mole.

This value can be used to compute the difference between the activation energies of discharge of H and D under the conditions of comparison [18]. It is sufficient for this purpose to know the difference between the initial and final binding energies of the discharge process. The latter, as we already know, is 1.7 kg.-cal. For the former we shall consider as a first approximation the bonds of D in D—O and H in H—O. According to the calculations of E y r i n g the difference between the energies of these bonds is also 1.7 kg.-cal. on subtracting, we obtain zero for the difference between the activation energies. This is a very rough computation; nevertheless, as has already been pointed out, the fact that the activation energies of discharge of H and D are equal under the chosen conditions of comparison also follows from the data of the present paper. This shows that the observed difference in the discharge rates may be due to a difference in the extent of surface covered in H_2O and D_2O at «equal» potentials, and to a difference in the potentials of platinum in both liquids at equal overvoltages.

It should also be observed that at potentials corresponding to the double layer range there is a noticeable dispersion of capacity with the frequency, the ohmic component of the conductance also becoming rather large (Figs. 3 and 5). The existence of ohmic conductance indicates that comparatively slow processes occur at these potentials, *viz.*: 1) the formation of double layer; 2) deposition and removal of particularly firmly bound hydrogen atoms (a certain amount of which may remain on the surface even at such potentials); 3) deposition and removal of oxygen atoms. It is so far difficult to choose between these assumptions.

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[18] This computation is based upon the application of Brönsted's relation to the transition from hydrogen to deuterium when the reaction is analogous for both. According to this relation, the change in the activation energy upon this transition should equal a fraction of the result obtained by subtracting from the difference of the initial bond energies the difference of the final bond energies of both particles in the given reaction (for details see Rosenthal [14], *l. c.*)

We wish to express our gratitude to Prof. A. Frumkin for suggesting this investigation and for his constant interest and participation in the discussion of its results.

Summary

1. The complex conductance of a platinum electrode was measured in acid and alkaline solutions of 2 *N* Na_2SO_4 in H_2O and in D_2O as a function of the potential and current frequency. Charging curves of platinum were obtained in the same solutions.

2. The complex conductance of a platinum electrode as a function of the potential and current frequency was measured in aqueous 2 *N* NaCl in the presence of 1 *N*, 0.1 *N* and 0.01 *N* HCl, and in 2 *N* Na_2SO_4 in the presence of 1 *N*, 0.1 *N* and 0.01 *N* NaOH.

3. The results of the measurements reveal the influence of an electric field on the discharge rate of the ions and indicate that the surface of platinum is of a more complex inhomogeneity than was inferred on the basis of the charging curves alone.

4. At potentials close to the potentials of the corresponding gas electrodes (hydrogen in H_2O and deuterium in D_2O) the ratio of the discharge rates of H in H_2O and D in D_2O (H/D) is equal to 2.2—2.4 in acid solutions, this value remaining unchanged up to a potential of 0.2 V; with a further displacement of the potential towards anodic values this ratio approaches unity. In alkaline solutions the ratio H/D for the corresponding reversible potentials is equal to 2.1—2.5 and also decreases slightly with a shift of the potential in anodic direction.

5. The close values of H/D for the alkaline and acid solutions at potentials approaching the reversible ones discards the most substantial argument against the mechanism of slow discharg for the process of the separation of isotopes on platinum.

6. The difference between the binding energies of H and D with platinum was computed from the charging curves and found equal to 1.7 kg.-cal. This, as well as other considerations, allows us to assume that the difference between the activation enegies of the discharge of H and D under the conditions of comparison chosen in the present investigation is not great.

7. It is pointed out that the difference in the discharge rates of

H and D here observed may be due to an unequal extent of surface covered by adsorbed atoms in the two cases, as well as to different potentials of platinum in H_2O and D_2O at equal overvoltages.

8. It is concluded that slow processes proceed during the charging of the electrode at potentials corresponding to the double layer range and the nature of these processes is suggested.

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