molecules. This interaction can be allowed for approximately if it is remembered (as was done above) that every charged adsorbed molecule is in a field of potential φ_s, which can be found from the Poisson equation with corresponding boundary conditions. It is essential to stress that φ_s takes into account only the interaction of the charged adsorbed molecules among themselves. It can be regarded as the potential of dipoles with a great distance between the charges, of the order of the Debye length ($\sim 10^{-4}$ - 10^{-5} cm). Hence it is evident that this interaction will be far stronger than the slight dipole–dipole interaction between the adsorbed particles.

The above calculations are based on the simplest model for the surface of a semiconducting adsorbent. Its merit lies in the fact that on its basis it is possible to obtain a clear picture of the chemisorption isotherms and to establish in a very simple way the physical causes of deviations from the Langmuir law. Further, such a model of the surface was examined in the theory of the surface layer (see Kauffe[4]), in which the derivation of the isotherms was based on a number of unjustified additional assumptions and the conclusion was reached that in the adsorption of an acceptor gas the isotherm is logarithmic for an n type and of the Freundlich type for a p type semiconductor. In fact, as our calculations show, no such correspondence exists.

The characteristics of chemisorption on a real semiconducting surface will be examined in another paper.

SUMMARY

1. A consistent method has been developed for calculating adsorption isotherms in the electronic theory of chemisorption.
2. For the case of a non-uniform surface with no non-adsorption levels a general expression has been obtained for the isotherm in terms of p and N/p for a non-degenerate semiconductor having an arbitrary distribution of energy levels in its bulk.
3. Expressions for a number of typical distributions of energy levels in a semiconductor have been obtained from the general form of the isotherm, and shown to correspond to those of the Henry, Freundlich, and logarithmic types. There is no direct relation between the type of semiconductor and the form of the isotherm which is obtained.
4. In calculating isotherms in the electronic theory of chemisorption the long range Coulombic interaction between the adsorbed particles is automatically taken into account.

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Institute of Physical Chemistry, the USSR Academy of Sciences
M. V. Lomonosov State University, Moscow

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RATES OF INDIVIDUAL STAGES IN THE CATHODIC EVOLUTION OF HYDROGEN. I.

L. I. Krishtalik

The mechanism of the electrolytic evolution of hydrogen is determined by the relation between the rates of the individual stages in the conversion of hydrogen ions into adsorbed atomic and molecular hydrogen and the corresponding reverse processes. The purpose of the present work was to evaluate the various possible ways in which hydrogen can be evolved, starting from a theoretical calculation of the steady-state values of the above rates by the activated-complex method. Our calculations were based on the assumption of simple adsorption, i.e. adsorption of non-interacting atoms on a uniform surface. Although this assumption is true only at low saturations of the surface, it is adequate for determining the order of magnitude of the corresponding quantities.

The following expression was deduced previously[1] for the discharge current:

$$\vec{i}_{dis} = \varepsilon \frac{kT}{h} \kappa \frac{\gamma^{\beta}_{H_3O^+}}{\gamma^{+}} \cdot 10^{15} \cdot 56^{-\beta} c^{\beta}_{H_3O^+} p^{\alpha/2}_{H_2} a^{\alpha}_{H_2O} \times$$
$$\times \exp\left\{-\frac{1}{RT}\left[\alpha \Delta H_{a_{H_2O}} + \beta \Delta H_{a_{H_3O^+}} + \alpha \Delta H_{a_H} + \Delta H^{*}_{0O} + \alpha T\left(S^{0}_{H_2O} + \frac{1}{2} S^{0}_{H_2}\right)\right]\right\} \times$$
$$\times (1-\theta) \exp \frac{\alpha \eta F - \beta \psi_1 F}{RT}. \qquad (1)$$

Here ϵ is the charge on the electron, κ the transmission coefficient, γ the activity coefficient, a the activity, ΔH_a the energy of adsorption, and ΔH^{*}_{0O} the overall activation energy of discharge, which does not depend on the heat of discharge and is determined from the activation energy at the equilibrium potential ΔH^{*}_{0e}, the energy of adsorption, and the entropy of the reactants by means of the equation

$$\Delta H^{*}_{0O} = \Delta H^{*}_{0e} - \alpha\left[\Delta H_{a_H} + \Delta H_{a_{H_2O}} - \Delta H_{a_{H_3O^+}} + T\left(S^{0}_{H_2O} + \frac{1}{2} S^{0}_{H_2} - S^{0}_{H_3O^+} - S_e\right)\right]. \qquad (2)$$

ΔH^{*}_{0O} can be found by constructing a potential energy diagram, in which the potential energy curves for the M–H and O–H bonds are arranged so that their zero-point energy levels are at the same height. The degree of saturation of the surface is indicated by θ and the overvoltage by η; the remaining symbols have their usual significance.

The derivation of the equation for the electrochemical desorption current is essentially similar to that of equation (1), and therefore will not be given here:

$$\vec{i}_{des} = \varepsilon \frac{kT}{h} \kappa \frac{\gamma^{\beta'}_{H_3O^+}}{\gamma^{+'}} \cdot 10^{15} \cdot 56^{-\beta'} c^{\beta'}_{H_3O^+} p^{\alpha'/2}_{H_2} a^{\alpha'}_{H_2O} \times$$
$$\times \exp\left\{-\frac{1}{RT}\left[\alpha' \Delta H_{a_{H_2O}} + \beta' \Delta H_{a_{H_3O^+}} + \alpha' \Delta H_{a_{H_2}} - \alpha' \Delta H_{a_H} + \Delta H^{*'}_{0O} + \alpha' T\left(S^{0}_{H_2O} + \frac{1}{2} S^{0}_{H_2}\right)\right]\right\} \exp \frac{\alpha' \eta F - \beta' \psi_1 F}{RT} \theta. \qquad (3)$$

The overall activation energy of electrochemical desorption $\Delta H^{*'}_{0O}$ is determined similarly to ΔH^{*}_{0O} from the following equation:

$$\Delta H^{*'}_{0O} = \Delta H^{*}_{0e} - \alpha'\left[\Delta H_{a_{H_2}} + \Delta H_{a_{H_2O}} - \Delta H_{a_{H_3O^+}} - \Delta H_{a_H} + T\left(S^{0}_{H_2O} + S^{0}_{H_2} - S^{0}_{H_3O^+} - S^{0}_{H_2} - S_e\right)\right], \qquad (4)$$

where $S^{0}_{H_2}$ is the standard entropy of adsorbed hydrogen, which with the given choice of standard conditions is equal to zero. As in the derivation of equation (1), the entropy of activation of the complex is taken as a fraction β of the

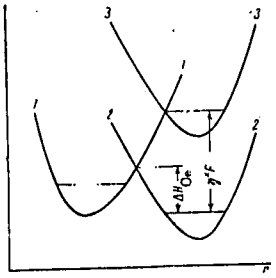

Fig. 1. Potential energy curves: 1) adsorbed hydrogen; 2) H_3O^+ ion at equilibrium potential; 3) H_3O^+ ion at overvoltage η^*, starting from which the activation energy becomes zero.

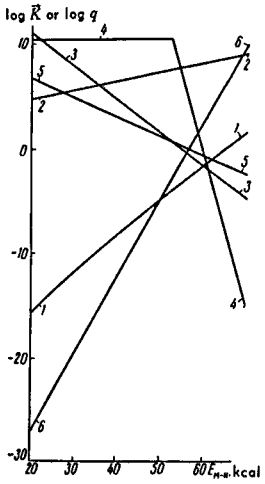

Fig. 2. Calculated values of the rate constants and q: 1) $\vec{K}_{dis}$; 2) $\vec{K}^*_{dis}$; 3) $\vec{K}_{des}$; 4) $\vec{K}_{cat}^*$; 5) $\vec{K}'_{cat}{}^*$; 6) q.

entropy of the H_3O^+ ion[2] (concentrations expressed in mole fractions). The entropy of an electron in the metal $S_e \cong 0$.

The sign of ΔH_{a_H} in equations (3) and (4) differs from that in equations (1) and (2) because, although adsorbed hydrogen represents the final state of the discharge process, it is the initial state in electrochemical desorption.

From the usual potential energy curves it necessarily follows that when the potential is raised to a given value there must be a substantial change in the character of both the discharge and electrochemical desorption processes. As can be seen from Fig. 1, starting from a certain overvoltage, at which the zero-point energy level of the O–H bond is raised until it intersects the potential energy curve of adsorbed hydrogen, the activation energy becomes zero and the rate of the electrode reaction becomes independent of the potential†. Expressions for the rates of such non-activated discharge and electrochemical desorption can be obtained from equations (1) and (3) if it is assumed that

$$\Delta H^*_{00} = 0, \quad \Delta H^{*'}_{00} = 0, \quad \alpha = \alpha' = 0, \quad \beta = \beta' = 1,$$

$$\vec{i}_{dis} = \varepsilon \frac{kT}{h} \kappa \frac{\gamma_{H_2O^+}}{\gamma^*} \cdot 10^{15} \cdot 56^{-1} c_{H_2O} \exp\left(-\frac{\Delta H_{a_{H_2O^+}} + \psi_1 F}{RT}\right) (1-0); \quad (5)$$

$$\vec{i}_{des} = \varepsilon \frac{kT}{h} \kappa \frac{\gamma_{H_2O^+}}{\gamma^{*'}} \cdot 10^{15} \cdot 56^{-1} c_{H_2O} \exp\left(-\frac{\Delta H_{a_{H_2O^+}} + \psi_1 F}{RT}\right) 0. \quad (6)$$

Equations (5) and (6) differ only in the relation between current and θ. This was to be expected, since there is no difference in activation energy here. In equations (5) and (6) the term in $\Delta H_{a_{H_2O^+}}$ and ψ_1 is retained, taking account of their effect on the surface concentration of hydrogen ions but not on the activation energy. The concentrations of the final products of electrolysis (H_2, H_2O) occur in equations (1) and (3) only as a result of their effect on the equilibrium potential, and are therefore absent from equations (5) and (6). Also there is no entropy term, since, on the one hand, the effect of the latent heat of the electrode reaction on the activation energy has vanished and, on the other, $\Delta S^* = 0$, because in the non-activated process the activated complex coincides with the initial state.

† The rate of reaction is not directly dependent on the potential, but can depend on it indirectly if the change in potential leads to a change in the degree of saturation of the surface (see below).

The rate of catalytic recombination of hydrogen atoms, expressed in electrical units, is

$$\vec{i}_{cat} = \varepsilon \frac{kT}{h} \kappa \cdot 6 \cdot 10^{15} g e^{-\Delta H^*_{cat}/RT} \theta^2. \quad (7)$$

Here g is the coordination number of the adsorption centres (we shall take this as $g = 4$) and 6×10^{15} is the greatest number of H atoms which can be adsorbed on 1 cm² of surface. Equation (7) is derived from that given by Temkin[3] for the rate of reaction on a surface, remembering that the wave functions for the distribution of adsorbed particles are practically equal to unity, that the symmetry factor for the activated complex is 2, and that in each individual occurrence of the reaction 2 atoms of hydrogen are removed from the surface.

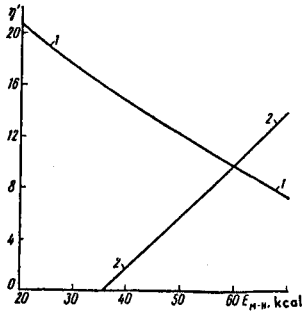

Fig. 3. Overvoltages corresponding to start of (1) non-activated discharge and (2) electrochemical desorption.

We may write the above equations in the following form:

$$\vec{i}_{dis} = \vec{K}_{dis}(1-\theta)\cdot 10^{\eta'}, \quad \vec{i}^{*}_{dis} = \vec{K}^{*}_{dis}(1-\theta), \quad \vec{i}_{cat} = \vec{K}_{cat}\theta^2, \tag{8}$$

$$\vec{i}_{des} = \vec{K}_{des}\theta\cdot 10^{\eta'}, \quad \vec{i}^{*}_{des} = \vec{K}^{*}_{dis}\theta.$$

Here

$$\eta' = \frac{\alpha\eta F}{2.3RT} = \frac{\eta}{0.118}, \quad \alpha = \alpha' = \frac{1}{2}.$$

For the reverse reactions we may write†

$$\overleftarrow{i}_{dis} = \overleftarrow{K}_{dis}\theta\cdot 10^{-\eta'}, \quad \overleftarrow{i}^{*}_{dis} = \overleftarrow{K}^{*}_{dis}\theta\cdot 10^{-2\eta'}, \quad \overleftarrow{i}_{cat} = \overleftarrow{K}_{cat}(1-\theta)^2, \tag{9}$$

$$\overleftarrow{i}_{des} = \overleftarrow{K}_{des}(1-\theta)\cdot 10^{-\eta'}, \quad \overleftarrow{i}^{*}_{des} = \overleftarrow{K}^{*}_{des}(1-\theta)\cdot 10^{-2\eta'}.$$

From the conditions of equilibrium we find that

$$\overleftarrow{K}_{dis} = \vec{K}_{dis}/q, \quad \overleftarrow{K}^{*}_{dis} = \vec{K}^{*}_{dis}/q, \quad \overleftarrow{K}_{cat} = \vec{K}_{cat}q^2, \quad q = \frac{\theta_0}{1-\theta_0}, \tag{10}$$

$$\overleftarrow{K}_{des} = \vec{K}_{des}q, \quad \overleftarrow{K}^{*}_{des} = \vec{K}^{*}_{dis}q.$$

Here θ_0 is the equilibrium degree of saturation of the surface.

In the general case the condition for constant saturation of the surface with hydrogen is written in the form

$$\vec{i}_{dis} - \overleftarrow{i}_{dis} - \vec{i}_{des} + \overleftarrow{i}_{des} - \vec{i}_{cat} + \overleftarrow{i}_{cat} = 0. \tag{11}$$

The steady-state value of θ, all the individual currents††, and the total current can be determined from equations (8)–(11):

$$\vec{I} = \vec{i}_{dis} - \overleftarrow{i}_{dis} + \vec{i}_{des} - \overleftarrow{i}_{des}.$$

The quantities necessary to calculate the value of K_{dis} have been estimated previously. [1] The complicated configuration of the activated complex makes it difficult to estimate an approximate value of ΔH^{*}_{00} for electrochemical desorption by replacing the potential energy surface by potential energy curves for the bonds. There is no doubt, however, that the distance between the potential energy minima corresponding to the initial and final situations of a hydrogen atom is considerably less for electrochemical desorption than for discharge†††. Hence ΔU^{*}_{00} should be considerably smaller than ΔU^{*}_{00} (which is ~10 kcal). We shall subsequently take ΔU^{*}_{00} to be 1.5 kcal, i.e. $\Delta H^{*}_{00} \cong$ ≅ 1 kcal. $\Delta H_{a_{H_2}}$ is composed of the energy of adsorption in the absence of solvent (for physical adsorption it can be estimated at 1–2 kcal) and the energy of repulsion of H_2 and H_2O molecules, hardly exceeding 10 kcal. This estimate of the values of the factors associated with electrochemical desorption is extremely rough, but it should be remembered that the errors do not exceed a few kilocalories, the calculated value of $\vec{K}_{des}$ being very probably slightly too low.

We take the activation energy of catalytic recombination as zero for the exothermic process and equal to ΔH for the endothermic one. In the latter case

$$\Delta H^{*}_{cat} = -104.2 - 2R_{H-H_2O} + 2E_{M-H} + \Delta H'_{a_{H_2}},$$

where 104.2 is the ΔH for the dissociation of H_2, E_{M-H} is the bonding energy of an adsorbed hydrogen atom with the metal (in the absence of solvent), and R_{H-H_2O} (2.1 kcal) is the energy of repulsion between it and the nearest water molecule. [1] $\Delta H'_{a_{H_2}}$ differs from the value estimated above, since on account of the distribution of H_2 molecules in a plane on the electrode surface, the van der Waals energy of attraction is increased (about twice), while the energy of repulsion is decreased owing to the increased intermolecular distances (it is taken as 7 kcal).

The value of θ_0 was calculated from Temkin's equation, [3] the energy of the M–H link being decreased by the value of R_{H-H_2O}.

The calculated values of the constants in equations (8) and q are shown in Fig. 2†. The values of η' at which discharge or electrochemical desorption become non-activated are plotted in Fig. 3. It is of interest that for metals of low E_{M-H} electrochemical desorption is non-activated at any cathodic polarisation (a similar idea was put forward by Frumkin and his coworkers [5]).

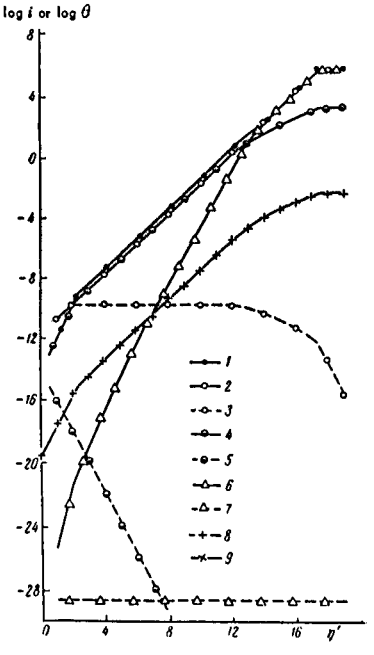

Fig. 4. Current density and degree of saturation of surface for E_{M-H} = 30 kcal:
1) $\vec{I}$; 2) $\vec{i}_{dis}$; 3) $\overleftarrow{i}_{dis}$; 4) $\vec{i}_{des}$; 5) $\overleftarrow{i}_{des}$; 6) $\vec{i}_{cat}$; 7) $\overleftarrow{i}_{cat}$; 8) θ; 9) $(1-\theta)$; (only for Figs. 7 and 8).

† The doubling of the exponent in the equations for $\overleftarrow{i}^{*}_{dis}$ and $\overleftarrow{i}^{*}_{des}$ is due to the fact that for these processes $\beta = 1$, while η' contains the quantity $\alpha = \frac{1}{2}$.

†† We disregard the emission mechanism for the removal of hydrogen put forward by Kobozev, [4] since calculation by the activated-complex method leads to the conclusion, in agreement with those of Frumkin and coworkers, [5] that this mechanism cannot be responsible for conducting away any appreciable fraction of the current. At the same time, with metals of high voltage the emission current should be great enough to be observed experimentally. We propose to examine this question in greater detail later.

††† This fact is ignored in the calculations of Gerischer. [6]

* The calculation was carried out for $\psi_1 = 0$, $c_{H_3O^+} = 1$ M, $p_{H_2} =$ = 1 atm, and $a_{H_2O} = 1$.

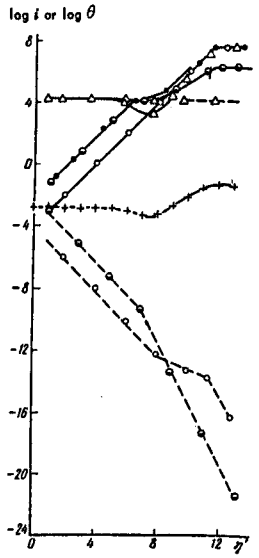

Fig. 5. Current density and degree of saturation of surface for E_{M-H} = 52.5 kcal. The key to the curves is the same as in Fig. 4.

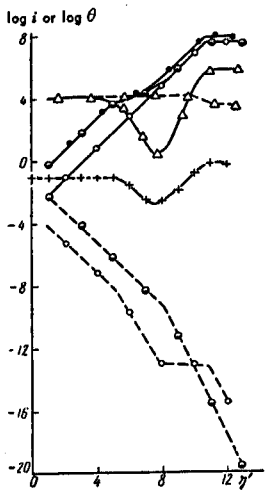

Fig. 6. Current density and degree of saturation of surface for E_{M-H} = 55 kcal. For key to curves see Fig. 4.

Typical log i - η' curves are illustrated in Figs. 4–8. Figs. 9 and 10 show, in η' - E_{M-H} and log $\vec{i}$ - E_{M-H} coordinates, the boundaries of the regions in which the various mechanisms for the electrolytic evolution of hydrogen operate†.

For metals with low bonding energy (Fig. 4, E_{M-H} = = 30 kcal) at low polarisations $\vec{i}_{dis} = \vec{i}_{dis}$, and the total current is equal to that for non-activated electrochemical desorption (Figs. 9 and 10, region I). The relation between current and potential is determined by the dependence on it of θ, which under these conditions has the form $\theta = q \times$ $\times 10^{2\eta'}$. The Tafel constant in region I is therefore 0.059 V, $\partial\eta/\partial$pH = 0.059 V. Region I relates to extremely low current densities, so that its quantitative experimental investigation is very difficult.

With further increase in the polarisation (Fig. 4) the current density is determined by the discharge stage and the removal of hydrogen atoms from the surface by electrochemical desorption (region II) or, at higher overvoltage, by catalytic recombination (region III). The relationships here are completely described by the usual equations of the slow discharge theory. A slight increase in the constant b is possible on passing from one way of removing hydrogen to another.

Finally, as the polarisation is increased, the limiting discharge current is approached, i.e. a non-activated discharge process with a constant degree of saturation of the surface. A limiting discharge current is a necessary consequence of the fact that the activation energy of discharge is finite and decreases with increase in the potential. Our calculation makes it clear why this phenomenon has never been observed up to the present, for it implies immense current densities, of the order of 10^5 A/cm² and above (up to 10^9 A/cm²), the investigation of which is associated with exceptional experimental difficulties†.

Fig. 5 illustrates the curve for E_{M-H} = 52.5 kcal. Here the rate of electrochemical desorption far exceeds the rate of discharge right up to extremely high current densities. Adsorbed hydrogen is replaced not by discharge of hydrogen ions but by adsorption from the gas phase. Similar relationships are observed also in other cases (Figs. 6 and 7).

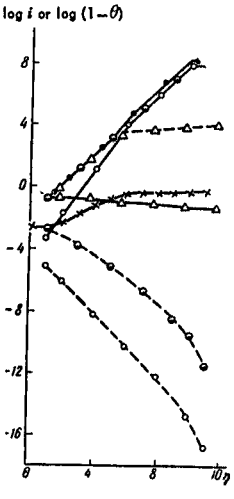

Fig. 7. Current density and degree of saturation of surface for E_{M-H} = 60 kcal. For key to curves see Fig. 4.

† These boundaries are somewhat arbitrary in character. In actual fact the transition from one mechanism to another occurs gradually. The same applies to the sharp breaks in the curves in Figs. 4-8. A continuous transition from $\alpha = \frac{1}{2}$ to $\alpha = 0$ (non-activated processes) is more probable.

† A similar conclusion can be reached in another way. The actual activation energy of discharge for $\eta = 0$ at a mercury cathode amounts to 21.7 kcal. [2] With $\alpha = \frac{1}{2}$ it becomes zero at η = = 1.88 V, which corresponds to a current density of 10^4 A/cm².

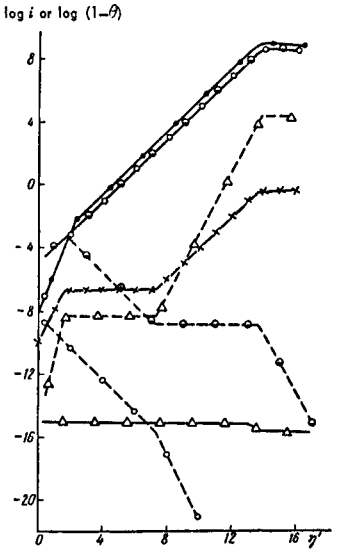

Fig. 8. Current density and degree of saturation of surface for E_{M-H} = 70 kcal. For key to curves see Fig. 4.

Thus for cathodes with a quite wide range of E_{M-H} values it is probable that the mechanism of hydrogen evolution up to definite polarisations and current densities (region IV in Figs. 9 and 10) is essentially a slow electrochemical desorption of atomic hydrogen previously adsorbed from the gas phase. This mechanism, which we will call for brevity the "adsorption-electrochemical" mechanism, has, as far as we are aware, never previously been discussed in detail, which is probably connected with the widely held view that adsorption from the gas phase is slow at high cathodic polarisations. [7] As is clear from the above, this rate is quite high and can increase substantially with increase in polarisation owing to the decrease in the degree of saturation of the surface (Fig. 7).

Usually discharge is followed by removal of adsorbed hydrogen. A peculiar feature of the mechanism discussed above is the fact that here the process of discharge plays no appreciable part.

The dependence of the current on polarisation, hydrogen-ion concentration, and other factors in the adsorption-electrochemical evolution of hydrogen is described by equation (3) and is completely analogous to that for the slow-discharge mechanism. As in the latter case, each individual change at the slowest stage is associated with the transfer of one electron ($\vec{I} = \vec{i}_{des}$), whereas when electrochemical desorption is the slow process, following after discharge, two electrons are transferred ($\vec{I} = \vec{i}_{des} + \vec{i}_{dis} = 2\vec{i}_{des}$). The difference between the adsorption-electrochemical and slow-discharge mechanisms should become apparent in experiments with labelled atoms, leading to a difference in the isotopic composition of the hydrogen evolved.

The region of the adsorption-electrochemical mechanism includes electrodes having different degrees of saturation of the surface, from very low ($\theta \cong 10^{-8}$) to very high ($1 - \theta \cong 10^{-6}$). Hence the assumptions made in the calculations cannot be true for the whole of this region and its boundaries and the corresponding kinetic laws should later be made more precise by taking into account the interaction between the adsorbed atoms.

Returning to Fig. 5, we note that region IV is terminated by the limiting current. The maximum adsorption current $\vec{i}_{cat}$ then coincides with the current at which the transition to non-activated electrochemical desorption is observed. With other values this coincidence does not occur and instead of sharply defined plateaus inflections appear in the curves (Fig. 6). The values of η' and $\log \vec{I}$ corresponding to these inflections are plotted in Figs. 9 and 10 as broken curves. The areas under them are characterised by surface saturations which are extremely close to the equilibrium values.

At high E_{M-H} (very large θ_0) i_{cat} at equilibrium is much lower than its maximum possible value and there is no limiting adsorption current (Fig. 7).

When the potential is raised further, there is a new growth in the current, the magnitude of which is determined by slow discharge with electrochemical (and in part catalytic, see Fig. 5) removal of hydrogen, followed by the limiting discharge current (Fig. 5) or discharge and electrochemical desorption current ($\theta = \frac{1}{2}$, $\vec{i}^{*}_{dis} = \vec{i}^{*}_{des}$, see Figs. 6 and 7†). With E_{M-H} = 60 kcal (Fig. 7), after the adsorption-electrochemical mechanism the slow electrochemical desorption of hydrogen atoms formed by the discharge of hydrogen ions becomes predominant (region V).

With the metals which adsorb hydrogen most strongly the mechanism of slow electrochemical adsorption predominates (Figs. 9 and 10). At low polarisations, however, the current is determined by the rate of discharge and electrochemical desorption and the reverse process occur at practically the same rate, which determines the degree of saturation of the surface (Fig. 8). As is clear from equations (8)–(10), under these conditions $1 - \theta = 10^{2\eta'}/q$ and $\vec{i}_{dis} = K_{dis}10^{3\eta'}/q$. Thus we have for slow discharge on an almost completely saturated surface (region VI) a constant b equal to 0.04 V and $\partial\eta/\partial pH = 0.02$ V, although the relation between η and ψ_1 potential has the normal character for slow discharge ††.

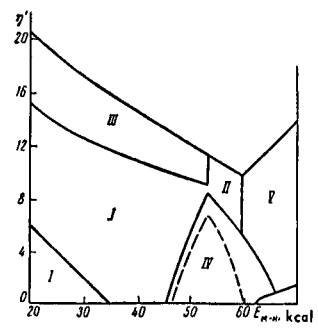

Fig. 9. Regions with different mechanisms of hydrogen evolution. For key see text.

† The point at which the limiting current appears is determined by the start of non-activated discharge (Fig. 6) or non-activated electrochemical desorption (Fig. 7). The start of another non-activated process is sometimes shown by a change in the character of the θ–η' relationship (Fig. 8).

†† Values close to those indicated for b and $\partial\eta/\partial pH$ have been observed experimentally at certain cathodes [8,9]. Our calculation did not take into account the dependence of E_{M-H} on the saturation of the surface. It may be supposed, however, that at such high saturations ($1 - \theta \leqslant 10^{-6}$) this dependence could be neglected. We do not examine here the possible changes in b associated with a change in the ψ_1 potential (e.g. see Conway and Bockris [10]).

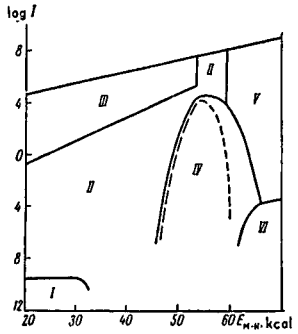

Fig. 10. Regions with different mechanisms of hydrogen evolution. For key see text.

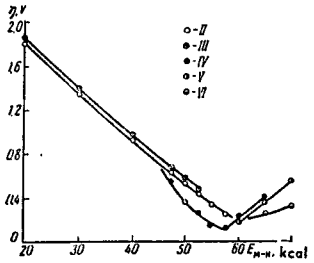

Fig. 11. Values of the constant a for various mechanisms of hydrogen evolution. For key see text.

It is of interest that, on the basis of our calculations, we have been unable to discover a region in which the mechanism of hydrogen evolution could be related to a slow catalytic recombination. On metals which have a weak adsorptive capacity for hydrogen $\Delta H^{*}_{cat} = 0$, and $\vec{i}_{cat}$ could, with appropriate values of θ, account for enormous current densities ($> 10^{10}$ A/cm^2); but on metals of high E_{M-H}, the large activation energy prevents recombination from playing a part in the conduction of the current. For the intermediate group of metals the recombination current has an intermediate value, but then conditions are created which are favourable to adsorption currents (region IV).

Calculated values for the constant a in the Tafel equation are plotted in Fig. 11. It is characteristic that, for the different variants both of slow discharge (II, III, VI) and of slow electrochemical desorption (IV and V), the fall in a with increase in E_{M-H} is finally replaced by a rise. The rate of discharge increases with increase in E_{M-H} as a result of a fall in the activation energy, but at high E_{M-H} it falls because of the sharp drop in the fraction of the metal surface which remains free. The activation energy of electrochemical desorption increases with increase in the bond energy, but for not too high bond energies (with θ of the order of 10^{-1} or less) the simultaneous increase in the extent of saturation of the surface with hydrogen has a greater effect on the rate of the process†.

The calculations given above were of an exploratory character in view of the rough estimates for a number of the quantities in equations (1)–(7). Many of these approximations, however, relate more to the absolute values of the current densities than to their ratio. A more detailed examination shows that changing within reasonable limits the values of any of the thermal quantities used in the calculation has no fundamental effect on the qualitative picture described above.

We have calculated the rate of catalytic recombination from equation (7), which is correct for conditions of perfectly random distribution of adsorbed atoms on the metal surface. This distribution is established as a result of surface migration of the atoms or reaction with the solution.

The recombination current, determined by the rate of surface migration, is expressed by the following equation:

$$\vec{i}_{cat} = \xi \frac{kT'}{h} \kappa \cdot 6 \cdot 10^{15} g e^{-\lambda E_{M-H}/RT} \theta^2. \quad \dagger \qquad (12)$$

Values of $\vec{K}'_{cat}$, the rate constant for recombination, calculated from equation (12) (λ taken as $\sim \frac{1}{4}$, [5]) are plotted in Fig. 2. For $E_{M-H} > 60$ kcal, $\vec{K}'_{cat} > \vec{K}_{cat}$, i.e. surface migration occurs more rapidly than recombination, and equation (7) is completely applicable (regions V, VI, and partly IV). It is strictly applicable also at lower values of E_{M-H}, when $\vec{i}_{dis}$ and $\vec{i}_{des} > \vec{i}_{cat}$ (regions I and II). Calculation of the rate of recombination from equation (12) leads to a contraction of regions III and IV, but the qualitative picture remains unchanged. It should be emphasised that equation (12) gives a lower limit to the rate of recombination, since some effective migration of atoms on the surface†† is due to discharge and electrochemical desorption.

As was noted earlier, the model of the so-called simple adsorption used in this work is approximate and is obviously inappropriate to a number of cathodes. We therefore intend to compare calculated and experimental results in a later communication, in which a more realistic model will be taken for the adsorbed layer†††. It is also proposed to discuss in greater detail the peculiarities of the processes of discharge and electrochemical desorption at not very high cathodic (or even anodic) potentials.

† In a number of papers [6,11] only effects associated with activation were taken into account and the influence of the degree of surface saturation was not examined.

† The derivation of equation (12) is similar to that given by Frumkin et al. [5]

†† If the value of $\vec{i}_{cat}$ (or $\vec{i}_{cat}$) calculated from equation (12) comes out less than $\vec{i}_{dis}$ or $\vec{i}_{des}$, then ipso facto the condition of applicability of this equation is not fulfilled; in such a case $\vec{i}_{cat}$ should obviously have a value intermediate between those calculated from equations (7) and (12) (regions III and partly IV).

††† A comparison of calculation with experiment for metals of high hydrogen overvoltage was given previously. [1]

SUMMARY

On the hypothesis of simple adsorption, the activated-complex method has been applied to calculate, as functions of the potential, the steady-state values of the degree of saturation of the surface and the densities of the polarising current and the currents corresponding to the forward and reverse reactions of discharge, electrochemical desorption, and catalytic recombination. Calculations for metals with differing adsorption energies indicate the following six probable mechanisms of electrolytic hydrogen evolution: Slow non-activated electrochemical desorption (I), slow discharge with electrochemical (II) or catalytic (III) removal of hydrogen atoms from the metal surface, slow electrochemical desorption of hydrogen atoms previously adsorbed from the gas phase (adsorption-electrochemical mechanism IV), slow electrochemical desorption following discharge (V). and slow discharge with a very small fraction, determined by electrochemical desorption, of free surface (VI). With some cathodes it is probable that the polarisation curve consists of two branches, which may be parallel to one another (mechanisms IV and III) or may intersect (I and II, VI and V).

With change in the M–H bonding energy the overvoltage passes through a minimum, owing to the fact that the value of E_{M-H} affects both the activation energy and the saturation of the surface.

The existence of limiting discharge currents (and electrochemical desorption currents) is probable, the absolute magnitudes of which are extremely high (of the order of 10^5 A/cm^2 and above).

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CHANGES IN THE ELECTRICAL CONDUCTIVITY OF GLASSES ACCOMPANYING CRYSTALLISATION

A. Ya. Kuznetsov

The study of the changes in properties accompanying the transition of a substance from the vitreous to the solid state can give valuable information on the relationships between the structures of these phases. However, the amount of work in this field is insignificant in comparison with the immense amount of experimental data on the vitreous state. The properties of greatest interest in this connection are those which change most sharply during phase transitions, one of them being the electrical conductivity. It has been shown experimentally that during the crystallisation of a glass the conductivity can change by several powers of ten, [1-5] but the causes of such changes have not yet been finally clarified. In most cases investigators have used multicomponent glasses, which it was not possible to convert completely into the solid phase, so that the electrical conductivity of a heterogeneous system was in fact measured.

Obviously, changes in electrical conductivity accompanying crystallisation can in principle be due to two factors: change in structure of the substance accompanying the phase transition and change in grain-size and degree of dispersion, which determine the magnitude of the contact resistances at the grain boundaries.

In order to ascertain the role of these factors, measurements of electrical conductivity were made on glasses corresponding in composition to the compounds $Na_2O \cdot SiO_2$, $Na_2O \cdot 2SiO_2$, and $PbO \cdot SiO_2$, and also on the products resulting from their complete crystallisation. Since the first factor remained basically invariable, an attempt was made to change the character of the crystallisation and the size of the crystals. For these purposes the glasses were crystallised at different temperatures, with simultaneous determination of the optical properties of the solid phases. By keeping the glasses for a long period at each temperature, complete crystallisation was achieved for each composition. In every case the separation of only one solid phase was observed, namely the corresponding silicate (Table 1). The above method allowed considerable variation in the dimensions of the crystals separating from the glass and consequently also in the contact resistances at the boundaries between the crystals.

The crystallisation of a glass is accompanied by a considerable fall in electrical conductivity, at temperatures of about 100° by a factor of 10^{-2} - 10^{-3} with soda glasses, and 10^{-3} - 10^{-5} with lead glasses (see Figure). It is remarkable that the character of the crystallisation has little influence on the conductivity; in spite of the considerable

TABLE 1.

Comp. of glass	Temperature of crystallisation, °C	Solid phase	Linear dimensions* of majority of crystals, mm
$Na_2O \cdot SiO_2$	1050	$Na_2O \cdot SiO_2$	0.8 —1
$Na_2O \cdot SiO_2$	1000	$Na_2O \cdot SiO_2$	0.2 —0.1
$Na_2O \cdot SiO_2$	940	$Na_2O \cdot SiO_2$	0.07—0.04
$Na_2O \cdot 2SiO_2$	850	$Na_2O \cdot 2SiO_2$	0.5 —0.2
$Na_2O \cdot 2SiO_2$	800	$Na_2O \cdot 2SiO_2$	0.1 —0.08
$Na_2O \cdot 2SiO_2$	760	$Na_2O \cdot 2SiO_2$	0.01—0.005
$PbO \cdot SiO_2$	740	$PbO \cdot SiO_2$	0.6 —1
$PbO \cdot SiO_2$	690	$PbO \cdot SiO_2$	0.07—0.1
$PbO \cdot SiO_2$	640	$PbO \cdot SiO_2$	0.01—0.005

* Measurements were made on partly crystallised samples.