

SUMMARY

1. Two methods for symmetrising an original eigenfunction have been examined and a strict derivation has been given of the principal expressions.
2. The use of group theory in quantum chemistry can be simplified on the basis of the following postulates:
 - I. The complete eigenfunction of the total system in the ground state is invariant with respect to transformations by operations of the symmetry group of the molecule.
 - II. The quantum-mechanical electron density distribution in the closed electron shells of the molecule has the same symmetry as the residual nuclear field.
 - III. The best molecular orbital, which is a linear combination of atomic orbitals, can only be real.
 - IV. The square of the molecular orbital is invariant with respect to transformations by operations of the symmetry group of the molecule.
3. After carrying out the operations of the symmetry group of the molecule, we can use the above postulates to find all the possible identity expressions of the original variation function, from which we can determine all possible equalities of the coefficients of the variation function, c_i ; in all cases this leads to a reduction of the secular determinant. In many cases the results of the simplified secular equation are the same as when the ordinary group method is used.

1. E. Wigner, "Gruppentheorie und ihre Anwendung auf die Quantenmechanik der Atomspektren", Braunschweig, 1931.
2. H. Eyring, J. Walter, and G. Kimball, "Quantum Chemistry" (Translated into Russian), Inostr. Lit., Moscow, 1948.
3. E. Bauer, "Vvedenie v Teoriyu Grupp i ee Prilozhenie v Kvantovoi Fizike" (Introduction to Group Theory and its Use in Quantum Physics), ONTI, NITP SSSR, 1937.
4. C. C. I. Roothaan, Rev. Mod. Phys., **23**, 69 (1951).

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Received 17th April 1958

RATES OF INDIVIDUAL STAGES AND MECHANISM OF CATHODIC HYDROGEN EVOLUTION. II

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In a preceding paper¹ some possible mechanisms for the cathodic evolution of hydrogen were examined. Account was taken of the fact that at sufficiently high cathodic polarisations the activation energy of discharge, owing to its finite value, should become zero, and consequently the rate of discharge will cease to depend on the potential ($\alpha = 0$). It must also be remembered, however, that the activation energy of the reverse process, ionisation, is finite too; consequently, at a sufficiently positive potential the rate of ionisation will be independent of it ($\beta = 0$). The activation energy of discharge then coincides with the heat of reaction of the process, and the quantitative relationship between the rate

of discharge and the potential changes ($\alpha = 1$). We shall describe such a process as "barrierless".

Thus the normal discharge process ($\alpha = \frac{1}{2}$) can occur only within a certain range of potentials; at more negative potentials non-activated discharge (and barrierless ionisation, $\alpha = 0, \beta = 1$) should take place, and at more positive potentials barrierless discharge (and non-activated ionisation, $\alpha = 1, \beta = 0$). Similar considerations apply also to electrochemical desorption and adsorption processes. The above conclusions can also be deduced directly from the usual form of potential curves (Fig. 1).

The initial equation for the rate of discharge can be written, independently of any assumptions as to the values of α , ΔH , and ΔS of activation, in the following form:

$$\vec{i}_{dis} = s \frac{kT}{h} \kappa \frac{\gamma_{H_3O^+}}{\gamma^+} \cdot 10^{15} \cdot 56^{-\beta} c_{H_3O^+}^{\beta} a_{H_2O}^{\alpha} p_{H_2}^{\alpha/2} (1 - \theta) \times \exp \left\{ -\frac{1}{RT} [G^{*0} - \beta G_1^{00} - \alpha G_2^{00} - \alpha \eta F + \beta \phi_1 F] \right\}. \quad (1)$$

This follows from Eqns. (5), (11), (14), (20), and (21) in a previous paper². The symbols here and in the rest of this paper have similar meanings to those used previously^{1,2}.

By expressing G^{*0} in terms of the energy and entropy of activation, and accepting the relationship $S = \beta S_{H_3O^+}^{00}$ for the entropy of the activated state³, we can obtain an expression for the rate of normal discharge².

For non-activated discharge $\alpha = 0$, and the activated state coincides with the initial state for the individual stage in the reaction, i.e. with the ion H_3O^+ adsorbed and the electron in the metal ($G^{*0} = G_1^{00} = G_1^{00} + \Delta G_{H_3O^+}^{00}$). Hence

$$\vec{i}_{dis} = s \frac{kT}{h} \kappa \frac{\gamma_{H_3O^+}}{\gamma^+} \cdot 10^{15} \cdot 56^{-1} c_{H_3O^+} (1 - \theta) \exp \left[-\frac{\Delta G_{H_3O^+}^{00} + \phi_1 F}{RT} \right]. \quad (2)$$

For barrierless discharge ($\alpha = 1$) the activated state coincides with the final state: i.e. $G^{*0} = G_2^{00} = G_2^{00} + \Delta G_{H_2O}^{00} + \Delta G_{eH}^{00}$.

Remembering that $S_{H_2}^{00} \approx 0$ we obtain

$$\vec{i}_{dis} = s \frac{kT}{h} \kappa \frac{\gamma_{H_3O^+}}{\gamma^+} \cdot 10^{15} a_{H_2O} p_{H_2}^{1/2} (1 - \theta) \times \exp \left\{ -\frac{1}{RT} [\Delta H_{eH_2O} + \Delta H_{eH} + T \left(\frac{1}{2} S_{H_2}^{00} - \Delta S_{eH_2O}^{00} \right) - \eta F] \right\}. \quad (3)$$

Similarly, for electrochemical desorption

$$\vec{i}_{des} = s \frac{kT}{h} \kappa \frac{\gamma_{H_3O^+}}{\gamma^+} \cdot 10^{15} \cdot 56^{-\beta} c_{H_3O^+}^{\beta} a_{H_2O}^{\alpha} p_{H_2}^{\alpha/2} \theta \times \exp \left\{ -\frac{1}{RT} [G^{*0} - \beta G_1^{00} - \Delta G_{H_2O}^{00} - \alpha G_2^{00} - \alpha \eta F + \beta \phi_1 F] \right\}; \quad (4)$$

$$\vec{i}_{des} = s \frac{kT}{h} \kappa \frac{\gamma_{H_3O^+}}{\gamma^+} \cdot 10^{15} \cdot 56^{-1} c_{H_3O^+} \theta \exp \left[-\frac{\Delta G_{H_3O^+}^{00} + \phi_1 F}{RT} \right]; \quad (5)$$

$$\vec{i}_{des} = s \frac{kT}{h} \kappa \frac{\gamma_{H_3O^+}}{\gamma^+} \cdot 10^{15} a_{H_2O} p_{H_2}^{1/2} \theta \times \exp \left\{ -\frac{1}{RT} [\Delta H_{eH_2O} + \Delta H_{eH} - \Delta H_{eH} + T \left(\frac{1}{2} S_{H_2}^{00} - \Delta S_{eH_2O}^{00} - S_{H_2}^{00} \right) - \eta F] \right\}. \quad (6)$$

Eqns. (2) and (5) have already been discussed¹. †

† In the corresponding equations in the previous paper¹ $\Delta G_{H_3O^+}^{00}$ occurs instead of $\Delta H_{eH_3O^+}$, since it was assumed in the deduction that $S^{*0} = \beta S_{H_3O^+}^{00} = S_{H_3O^+}^{00}$ (since $\beta = 1$) instead of the correct $S^{*0} = S_{H_3O^+}^{00}$. The correct values of κ_{dis}^{β} are higher than those given previously¹ by a factor of about 10. The relationship $S^{*0} = \beta S_{H_3O^+}^{00}$ is valid for normal discharge³, but its application to non-activated, and especially barrierless processes is not justified.

A peculiarity of barrierless processes is the fact that their velocities are independent of the activity of the species undergoing discharge, namely, the H_3O^+ ion, because the normal increase in rate with increase in $a_{\text{H}_3\text{O}^+}$ is completely balanced by the shift in the equilibrium potential to more positive values. Also, Eqns. (3) and (6) contain neither $\Delta G_{\text{H}_3\text{O}^+}^{\text{ad}}$ nor the ψ_1 potential because their effects on the surface concentration of H_3O^+ and on the activation energy (heat effect) of the individual stage of discharge cancel one another out.

The boundaries of the regions of different types of discharge and electrochemical desorption processes are represented in Fig. 2. The overvoltage values (η) shown are those at which the corresponding rate constants become equal*. The latter have been taken from a previous paper¹, and have also been calculated from Eqns. (2), (3), (5), and (6), it being assumed that the entropy of the adsorbed H_2 molecules, determined mainly by intermolecular vibrations, is ~ 3 e.u. The remaining quantities have been evaluated earlier^{1,2}.

Starting from the equations for the rates of discharge, electrochemical desorption, catalytic desorption, and the corresponding reverse processes, it is possible to calculate the steady-state surface coverage and the polarising current density, as well as the current densities of the individual electrode reactions. In the previous paper¹ this calculation was carried out on the hypothesis of a simple adsorption of hydrogen atoms. In the present paper account will be taken of the interaction between the adsorbed atoms, using Temkin's model⁴ of a surface electron gas. The kinetic equations for this model⁵ are similar to those for a non-uniform surface or for other types of interaction between adsorbed atoms⁶, and have the following form:

$$\left. \begin{aligned} \bar{i}_{\text{dis}}^* &= K_{\text{dis}0}^* \cdot 10^{2\eta'} (1-\theta) e^{-f\theta}, \\ \bar{i}_{\text{dis}}^* &= (K_{\text{dis}0}^* / q_0) \theta; \\ \bar{i}_{\text{dis}} &= K_{\text{dis}0} \cdot 10^{\eta'} (1-\theta) e^{-\alpha f\theta}, \\ \bar{i}_{\text{dis}} &= (K_{\text{dis}0} / q_0) \cdot 10^{-\eta'} \theta e^{+\beta f\theta}, \\ \bar{i}_{\text{dis}}^* &= K_{\text{dis}}^* (1-\theta), \\ \bar{i}_{\text{dis}} &= (K_{\text{dis}0}^* / q_0) \cdot 10^{-2\eta'} \theta e^{+f\theta}, \end{aligned} \right\} (7) \dagger$$

* It is more accurate to define the boundary values of η as those at which a certain distribution of the potential curves is reached (Fig. 1). The values calculated in this way do not coincide with the data in Fig. 2, owing to the different value of the non-exponential factor for barrierless, normal, and non-activated processes. It is probable that the transition from one value of α to another occurs gradually, and the curves for $\log i$ (with $\theta = \text{const.}$) against η do not consist of two intersecting straight lines, but have a more complex form. For our approximate calculation we adhered to the simplified linear relationship, since it gives most simply acceptable values for the current densities corresponding to the transition from one process to another.

† In the calculations a small correction was introduced into Eqns. (7) and (8) to allow for the change in $\Delta H_{\text{H}_3\text{O}^+}$ with change in the energy of the M-H link³.

$$\left. \begin{aligned} \bar{i}_{\text{des}}^* &= K_{\text{des}0}^* \cdot 10^{2\eta'} \theta e^{-f\theta}, \\ \bar{i}_{\text{des}}^* &= K_{\text{des}0}^* q_0 (1-\theta); \\ \bar{i}_{\text{des}} &= K_{\text{des}0} \cdot 10^{\eta'} \theta e^{+\alpha f\theta}, \\ \bar{i}_{\text{des}} &= K_{\text{des}0} q_0 \cdot 10^{-\eta'} (1-\theta) e^{-\beta f\theta}, \\ \bar{i}_{\text{des}}^* &= K_{\text{des}}^* \theta, \\ \bar{i}_{\text{des}}^* &= K_{\text{des}0}^* q_0 \cdot 10^{-2\eta'} (1-\theta) e^{-f\theta}, \\ \bar{i}_{\text{cat}} &= K_{\text{cat}0} \theta^2 e^{2f\theta}, \\ \bar{i}_{\text{cat}} &= K_{\text{cat}0} q_0^2 (1-\theta)^2; \\ \bar{i}_{\text{cat}} &= K_{\text{cat}}' \theta^2 e^{\frac{1}{4}f\theta}, \\ \bar{i}_{\text{cat}} &= K_{\text{cat}0}' q_0^2 (1-\theta)^2 e^{-\frac{1}{4}f\theta}. \end{aligned} \right\} \begin{array}{l} (a) \\ (b) \\ (c) \\ (a) \\ (b) \end{array} \quad (8) \quad (9)$$

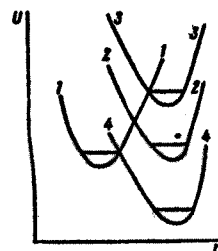


Fig. 1. Potential curves: 1) adsorbed H atom; 2) H_3O^+ ion in region of normal discharge; 3) H_3O^+ ion (at a more negative potential non-activated discharge occurs); 4) H_3O^+ ion (at a more positive potential barrierless discharge occurs).

Here the zero subscript indicates that the corresponding quantities relate to zero surface coverage; $q_0 = \theta_0 / (1 - \theta_0)$, where θ_0 is the equilibrium surface coverage disregarding any interaction of the adsorbed atoms; and $f = C/RT$, where C is a quantity defining the drop in bonding energy as the surface becomes saturated ($E_{\text{M-H}} = E_{\text{M-H}}^0 - C\theta$). According to Temkin's hypothesis⁴ the value of C should be practically the same for all metals. In subsequent calculations C is taken as 10 kcal (experimental values vary between 7 and 16 kcal^{4,7}).

Two types of calculation were undertaken. In the first $\bar{i}_{\text{cat}}$ was found from equations deduced on the hypothesis of a perfectly random distribution of H atoms over the metal surface [Eqns. (7) in the previous paper¹ and (9a) in the present paper]. In the second type of calculation this hypothesis was retained for metals with fairly high heat of adsorption for hydrogen (see Krishtalik¹), but for low $E_{\text{M-H}}$ it was assumed that the rate of recombination is governed by the rate of surface migration of hydrogen atoms [Eqns. (12)¹ and (9b) in this paper; activation energy of migration $\approx \frac{1}{4}E_{\text{M-H}}$].

Since processes of discharge and electrochemical desorption disturb the regular distribution of atoms on a surface, the first type of calculation can give correct results even with low values of $E_{\text{M-H}}$. In certain cases, especially in the region of transition from one mechanism to another, relationships are to be expected which are intermediate between the results obtained by the two methods of calculation. With the surface-electron-gas model, the probability of

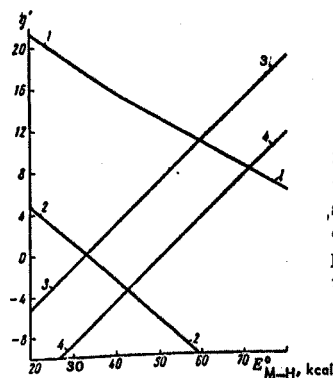


Fig. 2. Boundaries of regions: 1) non-activated discharge; 2) barrierless discharge; 3) non-activated electrochemical desorption; 4) barrierless electrochemical desorption. Cathodic polarisation regarded as positive. $\eta' = \eta F/2RT = \eta/0.118$.

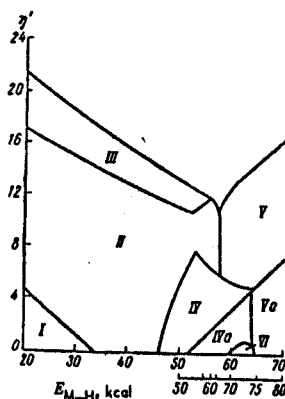


Fig. 3. Regions with different mechanisms of hydrogen evolution. First method of calculation. Along the abscissae the upper scale corresponds to values of the bonding energy at equilibrium, and the lower scale to the values at zero coverage of the surface with hydrogen. For key see text.

occurrence of the process of discharge (or electrochemical desorption) for a given point on the surface depends mainly on the overall degree of surface coverage, and not on the distribution of neighbouring adsorbed atoms.

Figs. 3 and 4 show the boundaries of regions with different mechanisms of hydrogen evolution obtained by the first method of calculation, and Figs. 5 and 6 the corresponding boundaries obtained by the second method. Values of equilibrium exchange currents for discharge and electrochemical and catalytic desorption are plotted in Fig. 7.

For low bonding energies the rate of hydrogen evolution at low polarisations is governed by non-activated discharge ($b = 0.06$ V, $\partial\eta/\partial pH = \partial\eta/\partial\psi_1 = 0$) — region I in Figs. 3–6. The very low current densities corresponding to this region have not yet been studied experimentally.

Normal slow discharge with electrochemical desorption (II) (non-activated or normal) occurs over a wide range of current densities. At high overvoltages removal of hydrogen by catalytic recombination (III) is appreciable. The upper curves in Figs. 3–6 indicate the appearance of a limiting current for discharge (over regions II and III) or electrochemical desorption (over IV).

For medium values of the bonding energy an adsorption–electrochemical mechanism becomes probable, i.e. slow electrochemical desorption of a hydrogen atom which has appeared on the electrode surface not as a result of discharge of an H_3O^+ ion but by adsorption from the gas phase¹. Depending on the values of E_{M-H} and η , the electrochemical desorption is either barrierless (IVa) or normal (IV) (see also Fig. 8). An adsorption–electrochemical mechanism is characterised by the appearance in some cases of a limiting current for catalytic adsorption, which at high values of E_{M-H} is represented by an inflection in the curve. Regions of low limiting adsorption current correspond to surface coverage close to the equilibrium value. With increase in polarisation the adsorption–electrochemical mechanism is replaced by slow discharge (II) or slow electrochemical desorption (IV).

For high values of E_{M-H} slow discharge with catalytic removal (VI) is probable, with $i_{dis} = i_{cat} - i_{cat}$ for $i_{cat} \approx i_{cat} \gg i_{dis}$ and a practically equilibrium coverage close to unity ($1 - \theta < 10^{-2}$). This region (VI) is distinguished from III, for which $i_{cat} \gg i_{cat}$ and $\theta \gg \theta_0$. The upper limit of region VI is established by the fact that the current for non-activated electrochemical desorption, increasing with potential considerably more rapidly than the discharge current, becomes equal in magnitude to the latter.

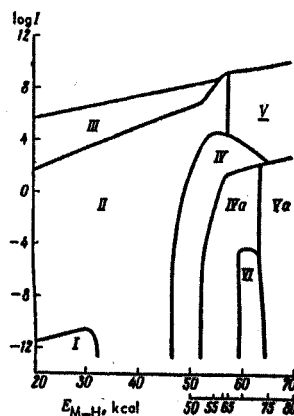


Fig. 4. Regions with different mechanisms of hydrogen evolution. First method of calculation.

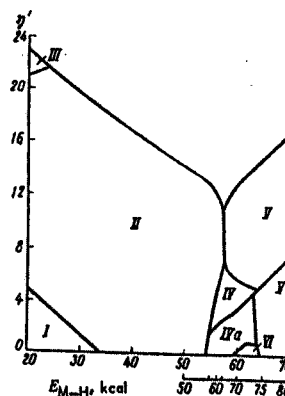


Fig. 5. Regions with different mechanisms of hydrogen evolution. Second method of calculation.

The similar values of the currents for discharge, electrochemical desorption, and the reverse processes, and their different variation with potential may yield a complicated relationship between the total current and the potential (Fig. 9), in which the value of the coefficient b for the linear portion of the $\log I - \eta$ curves can vary within region VI from 0.02–0.03 V to 0.11–0.12 V. For the highest values of E_{M-H} calculation indicates a mechanism of slow electrochemical desorption, either barrierless (Va) or normal (V).

Any reasonable change in the values of constants assumed in the calculations does not fundamentally affect

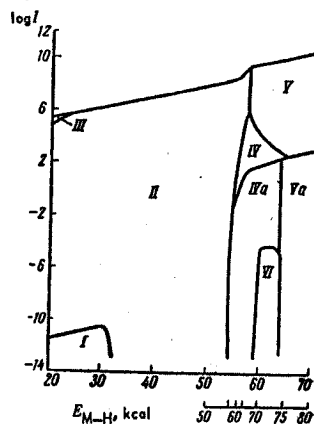


Fig. 6. Regions with different mechanisms of hydrogen evolution. Second method of calculation.

the qualitative picture described above (for exceptions see below). A similar order of magnitude is also obtained without taking into account the interaction between the atoms if the figures which are compared refer to the same values of E_{M-H} at equilibrium instead of zero surface coverage. Therefore a slight inaccuracy in estimating the value of C can hardly have any appreciable effect.

Both the present and previous¹ calculations have shown no region in which the rate of hydrogen evolution is governed by the rate of catalytic recombination. On the basis of the assumptions made in the previous paper¹ such a mechanism cannot be realized, because over the whole region of medium and high bonding energies the exchange current for electrochemical desorption would considerably exceed the exchange current for discharge. Taking into account the possibility of barrierless electrochemical desorption makes the corresponding exchange currents equal (Fig. 7). The discharge current may be greater than the calculated value both because of inexactness in the calcu-

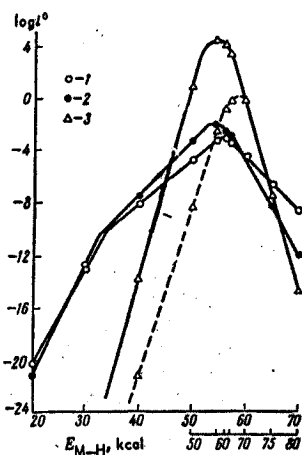


Fig. 7. Equilibrium values of exchange currents: 1) i_{dis}^0 ; 2) i_{des}^0 ; 3) i_{cat}^0 . The broken line shows i_{cat}^0 for the second method of calculation.

lation and also because of a shift in the ψ_1 potential to more negative values, which generally takes place in pure acid solutions. If $i_{dis}^0 > i_{des}^0$, the removal of hydrogen occurs by a catalytic mechanism.

The rate of catalytic desorption in a given E_{M-H} range is calculated on the assumption that the activation energy is equal to the heat of recombination. This will evidently overestimate the value of i_{cat} , and the error may be particularly marked for E_{M-H} of the order of 50–60 kcal, for which the heat effect is small. If this is taken into account, it is possible to have $i_{dis}^0 > i_{cat}^0 > i_{des}^0$, i.e. slow catalytic desorption becomes possible. We then have $b = 0.03$ V for random distribution of atoms on the surface, and b approximates to 0.12 V if the rate of recombination is governed by surface migration⁵.

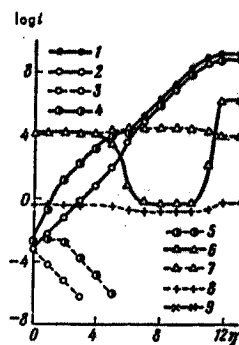


Fig. 8. Current densities and degrees of surface coverage for $E_{M-H} = 60$ kcal: 1) i_1 ; 2) i_{dis} ; 3) i_{des} ; 4) i_{cat} ; 5) i_{des} ; 6) i_{cat} ; 7) i_{cat} ; 8) θ [scale for θ (degree of coverage) or $1-\theta$ not given in the diagram (Ed. of Translation)]; 9) $(1-\theta)$.

These relationships can be observed only at quite high exchange currents, i.e. at values of the constant a of the order of several 0.01 V. At high current densities there may be a tendency for a limiting current of catalytic desorption to appear, with subsequent transition to electrochemical removal of hydrogen. It follows from these considerations that, by varying the composition of the solution, it should be possible, having lowered the rate of discharge, to pass from slow recombination to an adsorption-electrochemical mechanism. Estimation of the possible values of the partial exchange currents shows that slow recombination is possible only for cathodes having bonding energies with hydrogen close to 60 kcal. With very high surface coverage ($E_{M-H} > 70$ kcal) the rate of catalytic recombination is practically constant, and hence it cannot determine the variation of current with potential.

Adsorption of various impurities on the electrode has differing effects on the closely similar rate of discharge, barrierless electrochemical desorption, and catalytic recombination (Fig. 7), as a result of which the mechanism of hydrogen evolution on these electrodes can vary depending on the method of preparation of the electrode and the solution. This applies not only to $E_{M-H} \approx 60$ kcal but also to

Cathode material	Experimental values of constants		Reference	E_{M-H}^0 calc.	Suggested mechanism of hydrogen evolution	E_{M-H}^0 expt. and reference
	a	b				
Pb	1.56	0.11	[8]	25.5	Slow discharge with electrochemical desorption (II)	—
Tl	1.55	0.14	[8]	26	ditto	—
Hg	1.415	0.113	[8]	28.5	" "	—
Cd	1.40	0.12	[8]	29	" "	—
Sn	1.24	0.12	[9]	32.5	" "	—
Zn	1.24	0.12	[8]	32.5	" "	—
Ag	0.48—0.95	0.11—0.13	[10—12]	37.5—51	" "	—
Au	0.77—0.81	0.11—0.12	[8,13,14]	43	" "	—
Cu	0.55	0.10	[14]	49	" "	—
Fe	0.70—0.77	0.12	[14,15]	45	" "	68 [7,16,17]
Co	0.8—0.7	0.14—0.15	[18]	45—48	" "	64 [17]
Ni	0.51—0.63	0.09—0.14	[12,19]	47—50	" "	67 [7,16,17]
Mo	0.25	0.04	[9]	~70 or ~75	Barrierless adsorption—electrochemical (IVa). Slow discharge at $\theta \approx 1$ and electrochemical desorption.	72 [17]
W	0.67	0.10	[14]	73.5	Slow discharge with catalytic removal (VI). Barrierless adsorption—electrochemical (IVa). Slow discharge at $\theta \approx 1$ and electrochemical desorption.	74
	0.55—0.62	0.10—0.11	[12,25]	73 or 80—83	Slow discharge with catalytic removal (VI). Slow electrochemical desorption (V).	[7,16,17]
	0.43—0.44	0.06	[25]	73.5	Barrierless adsorption—electrochemical (IVa) or barrierless electrochemical desorption (Va)	
	0.25—0.30	0.1—0.14	[12,20]	55—60	Slow discharge with electrochemical desorption (II). Slow catalytic recombination.	65
Pt	0.07—0.1	0.03	[20]	~80	Barrierless adsorption—electrochemical (IVa).	[16,17]
	0.34	0.05	[25]	71.5	Slow discharge with electrochemical desorption (II).	65
	0.39	0.10	[14]	53	Barrierless adsorption—electrochemical (IVa).	[7,17]
Pd	0.16—0.28	0.12	[21]	55—65	Barrierless adsorption—electrochemical (IVa).	65
Rh	0.21	0.055	[14]	67	Barrierless adsorption—electrochemical (IVa).	[7,16,17]

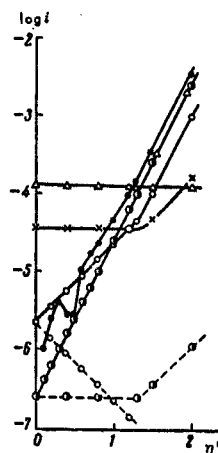


Fig. 9. Current densities and degree of surface coverage for $E_{M-H} = 72.5$ kcal. For key see Fig. 8.

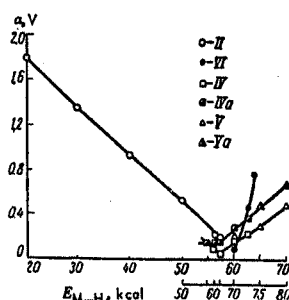


Fig. 10. Values of the constant a for various mechanisms of hydrogen evolution. For key see text.

higher bonding energies. In contrast to the results in the previous paper which indicated the possibility of slow discharge at very high degrees of surface coverage ($b = 0.04$ V, $\partial\eta/\partial pH = 0.02$ V, $\partial\eta/\partial\psi_1 = 1$), no such slow-discharge region has appeared in the present calculation. However, the possibility of its appearing as a result of appropriate change in the surface is not excluded.

Fig. 10 shows calculated values of the constant a for various mechanisms of hydrogen evolution. The Table sets out experimental values of the constants a and b . In a number of cases they refer to solutions of different composition, and the conditions assumed in our calculation are not strictly observed. Data relating to polarisation curves of incorrect shape, probably associated with variations in the ψ_1 potential, are omitted from the Table.

In a number of cases the current densities corresponding to the transition from one branch of the polarisation curve to another differ greatly from the calculated values, which are extremely sensitive to all inaccuracies in the calculation. The proposed mechanism of hydrogen evolution, experimental values of E_{M-H} , and the values of E_{M-H} which according to our calculation correspond to the values of a and b , are indicated in the Table.

For metals of low bonding energy there is no reliable evidence of the adsorption of hydrogen; E_{M-H} for them is very probably less than 50 kcal¹⁶. From indirect data their

adsorption capacity would seem to decrease in the order $Cu > Au > Ag > Zn, Sn, Cd, Pb$,¹⁶ in conformity with our calculation. Slow discharge^{8,11,14} is the most probable mechanism for these cathodes.

For metals of the iron group the most probable mechanism is again slow discharge with electrochemical desorption²². Here the calculated values of E_{M-H} are substantially lower than the experimental. This is probably because the experimental values for adsorption energies relate to the rapid adsorption of hydrogen by a freshly sublimed film of metal, which has not already absorbed any hydrogen⁷. In electrolysis, however, the surface layer of iron contains dissolved hydrogen⁸, which may lead to a diminution in the bonding energy.

Similar phenomena are observed on a palladium electrode. The polarisation of an active Pd electrode in acid solutions is due to the slowness of diffusion of H_2 molecules^{23,24}. With an electrode which has first been saturated with hydrogen, slow discharge occurs¹⁴, the calculated value of E_{M-H} being lower than the experimental. In absence of prior saturation of the metal with hydrogen, values of $b \approx 0.12$ V²¹ are obtained at high current densities, and the calculated values of E_{M-H} corresponding to the experimental results cover a wide range (possibly because of different degrees of saturation of the cathode with hydrogen).

For other metals the agreement between calculated and experimental values of E_{M-H} is perfectly satisfactory, especially if the approximate character of the calculation and the possible effect of the experimental conditions on the mechanism of the process, discussed above, are remembered.

SUMMARY

The finite value of the activation energies of discharge and ionisation should lead to the existence, together with the normal processes ($\alpha = \frac{1}{2}$), of non-activated ($\alpha = 0$) and barrierless ($\alpha = 1$) processes of discharge and electrochemical desorption. On the basis of this fact and also of the interaction between the adsorbed atoms, the rates of formation and removal of hydrogen atoms have been calculated by the activated-complex method. The relationship between these velocities, depending on the experimental conditions, determines the overall mechanism of hydrogen evolution. Certain probable mechanisms have been examined. The results of the calculations are in satisfactory agreement with experiment.

24. L. Kandler, C. A. Knorr and C. Schwitzer, *Z. phys. Chem.* **A180**, 281 (1937).
25. B. E. Conway and J. O'M. Bockris, *J. Chem. Phys.*, **26**, 532 (1957).

Received 16th April 1958

THERMODYNAMIC PROPERTIES OF ELECTROLYTES IN NON-AQUEOUS SOLUTIONS VII. INVESTIGATION OF THE SOLUBILITY OF SILVER CHLORIDE AND CAESIUM CHLORIDE IN ALCOHOLS, KETONES, AND MIXED SOLVENTS BY MEANS OF RADIO-ACTIVE TRACERS

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One of us has shown¹ that the change in the properties (solubility, dissociation constant, and e.m.f.) of electrolytes on passing from one solvent to another is determined by the change in the free energy of solvation of the ions and molecules. Owing to the low accuracy of the values for the energy of solvation and the absence of systematic data on these quantities for non-aqueous solutions, it is necessary to determine these energy changes directly from experimental results. To evaluate the change in free energy of solvation of ions ΔA_{sol} it is convenient to use dimensionless quantities — the mean activity coefficients γ_0 , based on the state of the ions in dilute aqueous solution as standard².

The magnitude of $\log \gamma_0$ for ions is defined as the difference in free energy of solvation of the ions in water and in the non-aqueous solvent:

$$\log \gamma_0 = \frac{\Delta A_{\text{sol}}(H_2O) - \Delta A_{\text{sol}}(M)}{2.3 \Sigma \nu RT} = \frac{\Delta \Sigma A_{\text{sol}}}{2.3 \Sigma \nu RT} \quad (1)$$

The value of ΔA_{sol} or $\log \gamma_0$ may be determined from measurements of any thermodynamic property of dissolved electrolytes — vapour pressure, solubility, e.m.f., etc. In previous work^{3,4} values of $\log \gamma_0$ were obtained from e.m.f. measurements on cells without transport for certain salts of the alkali metals and HCl in alcohols.

In the present work the change in energy of the ions or the value of $\log \gamma_0$ has been obtained from solubility data:

$$\log \gamma_0 = \log \frac{S_{H_2O} \gamma_{H_2O}^*}{S_M \gamma_M^*},$$

where S_{H_2O} and S_M are the solubilities in water and in the non-aqueous solvent respectively, and $\gamma_{H_2O}^*$ and γ_M^* are the corresponding concentration activity coefficients.

For sparingly soluble salts the values of γ^* are close to unity, and their ratio even more so. Consequently

$$\log \gamma_0 = \log \frac{S_{H_2O}}{S_M} \quad (2)$$

The determination of $\log \gamma_0$ from solubility has a number of advantages over its determination from e.m.f. measurements, since it does not require electrodes reversible with respect to the ions of the salt, nor the complex electro-metric apparatus made necessary in the e.m.f. method by

1. L. I. Krishtalik, *Zhur. Fiz. Khim.*, **33**, 1715 (1959) [Rus. J. Phys. Chem., 125 (1959)].
2. L. I. Krishtalik, *ibid.*, **31**, 2403 (1957).
3. M. I. Temkin, "Trudy Soveshchaniya po Elektrokhemii, 1950" (Transactions of the Conference on Electrochemistry 1950), Izd. Akad. Nauk SSSR, Moscow, 1953, p. 181.
4. M. I. Temkin, "Voprosy Khimicheskoi Kinetiki, Kataliza i Reaktsionnoi Sposobnosti" (Problems of Chemical Kinetics, Catalysis, and Reactivity), Izd. Akad. Nauk SSSR Moscow, 1955, p. 484.
5. L. I. Krishtalik, *Zhur. Fiz. Khim.*, **33**, 2729 (1959) [Rus. J. Phys. Chem. 572 (1959)].
6. M. I. Temkin, *ibid.*, **15**, 296 (1941).
7. O. Beeck, *Advances in Catalysis*, **2**, 151 (1950); Russian translation: "Kataliz. Voprosy Teorii i Metody Issledovaniya", Moscow, 1955, p. 198; *Discuss Faraday Soc.*, **8**, 118 (1950).
8. A. N. Frumkin, V. S. Bagotskii, Z. A. Iofa, and B. N. Kabanov, "Kinetika Elektrodnykh Protseessov" (Kinetics of Electrode Processes), Izd. Moskov. Univ., Moscow, 1952.
9. J. O'M. Bockris, and R. Parsons, *Trans. Faraday Soc.*, **44**, 860 (1948).
10. B. N. Kabanov, *Zhur. Fiz. Khim.*, **8**, 486 (1936).
11. J. O'M. Bockris and B. Conway, *Trans. Faraday Soc.*, **48**, 724 (1952).
12. J. O'M. Bockris and A. Azzam, *Trans. Faraday Soc.*, **48**, 145 (1952).
13. J. O'M. Bockris and N. Pentland, *Trans. Faraday Soc.*, **48**, 833 (1952).
14. N. Pentland, J. O'M. Bockris, and E. Sheldon, *J. Electrochem. Soc.*, **104**, 182 (1957).
15. V. A. Kuznetsov and Z. A. Iofa, *Zhur. Fiz. Khim.*, **21**, 201 (1947).
16. B. M. W. Trapnell, "Chemisorption", London, 1955.
17. D. P. Stevenson, *J. Chem. Phys.*, **23**, 203 (1955).
18. A. Murtazaev, *Zhur. Fiz. Khim.*, **23**, 1247 (1949).
19. A. Legran and S. Levina, *ibid.*, **14**, 211 (1940).
20. S. Schuldiner, *J. Electrochem. Soc.*, **101**, 426, 1954.
21. S. Schuldiner and J. P. Hoare, *J. Electrochem. Soc.*, **102**, 485 (1955).
22. A. N. Frumkin, *Zhur. Fiz. Khim.*, **31**, 1875 (1957).
23. A. N. Frumkin and N. A. Aladzhanova, *ibid.*, **18**, 493 (1944).