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Activation Process and the Nature of Active Centres in Electrocatalytic Hydrogenation

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The present investigation is the outgrowth of our work on the activating action of poisons upon electrodiffusion and electrocatalysis[1].

Electrocatalytic hydrogenation of the double bond in cinnamic acid[2] has proved a fairly convenient procedure, first, for tracing how the activating action of the poison changes with its concentration in the solution as well as on the surface of the electrode, and, secondly, for determining the effect produced by the poison on the activation energy of electrocatalysis. The data thus obtained and interpreted on the basis of the theory of "active ensembles" developed by N. I. Kobosev[3] have thrown considerable light on the principal problems of electrocatalysis: (1) how the activation process is bound up with the electrical and chemical properties of the metal (the value of hydrogen overvoltage) and (2) what are the active centres in electrocatalysis.

In addition we have obtained data essential for the general theory of overvoltage and refuting the one-sided electrostatic inter-

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[1] N. I. Kobosev a. Monblanova, (a) Acta Physicochimica URSS, **1**, 611 (1934); J. Phys. Chem. (Russ.), **6**, 308 (1935); (b) Acta Physicochimica URSS, **4**, 395 (1936); **7**, 645 (1936).

[2] In the article by Kobosev a. Klachko-Gurvich (Acta Physicochimica URSS, **10**, 1, 1939) in which the data of the present work have been partly made use of, there was made a misprint in the formula of cinnamic acid: for $C_2H_5CH = CHCOOH$ read $C_6H_5CH = CHCOOH$.

[3] N. I. Kobosev, Acta Physicochimica URSS, **9**, 1 (1938).

pretation of electrode processes in terms of the concepts put forward by Erdey Gruz, Volmer[4] and others.

The experimental procedure and the calculations have been described in our previous work[1].

Since cinnamic acid is sparingly soluble in other acids, the experiment was run chiefly with a 2% alkaline solution of sodium cinnamate and only single tests were made with a 2% alcoholic solution of cinnamic acid in sulphuric acid.

The operating capacity of the electrolytic cell was 130 cm.^{3}; the surface of the electrode, 8 cm.^{2} (both sides comprised); the temperature (20° C) and current density (0.04 A/cm.^{2}) were kept constant; the electrolyte was continuously stirred.

Effect of sublimate

The action of sublimate upon hydrogenation has been studied both in acidic and alkaline solutions on platinum electrodes. The results are summarized in Tables 1 and 2 and in Fig. 1.

Table 1

Alcoholic solution of cinnamic acid in sulphuric acid. Concentration of cinnamic acid, 2%. Cathode, Pt

No. of measurements	Concentration of $HgCl_2$ (mols/litre) $\times 10^4$	Total activity (current efficiency, per cent)	*n* from total activity
10	0	0	—
10	1	0	—
10	2	0	—
10	4	19.6	1.4
10	6	21.8	—
10	8	19	3.0
10	10	16	1.9
		Average	2.1

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[4] Erdey-Gruz a. Volmer, Z. physik. Chem., 150, 203 (1930).

From the data quoted it is obvious that reduction does not take place on a clean platinum electrode. If corrosive sublimate is applied in an alkaline solution, its activating influence becomes apparent at a concentration of 5×10^{-7} mols/litre. With the concentration increased to 5×10^{-6} mols/litre the current efficiency becomes 12% (against 0% in the absence of sublimate); it attains its maximum of 27% at a concentration of 1×10^{-5} mols/litre and then falls down as the concentration increases to 1×10^{-4} mols/l.

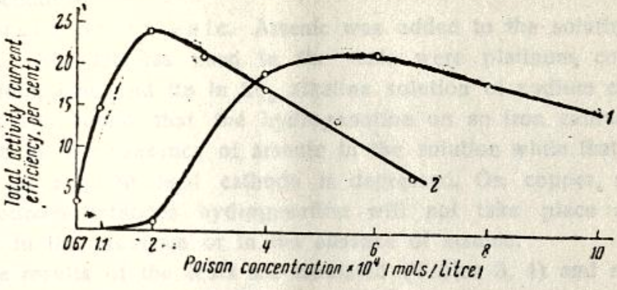


Fig. 1.

Percentage yield as a function of poison concentration. *1* — cathode Pt, poison $HgCl_2$; *2* — cathode iron, poison As_2O_3. (Scale on the graph relates to curve *1*).

Table 2

2% alkaline solution of sodium cinnamate.
Cathode, Pt

No. of measurements	Concentration of $HgCl_2$ (mols/litre) $\times 10^6$	Current efficiency per cent
5	0	0
5	0.5	12
7	1	20.8
7	5	26.5
7	10	27.2
5	50	26
5	100	24

In an acid solution the activating influence begins at a concentration of 4×10^{-4} mols/litre, attains its maximum at a concentration of 6×10^{-4} mols/litre, and falls down with further increase of concentration.

Effect of arsenic. Arsenic was added to the solution as K_3AsO_4. The cathodes used in the tests were platinum, copper, silver, iron, lead and tin in 2% alkaline solution of sodium cinnamate. It was found that the hydrogenation on an iron cathode is activated by the presence of arsenic in the solution while that proceeding on a tin or lead cathode is depressed. On copper, silver and platinum cathodes hydrogenation will not take place at all whether in the presence or in the absence of arsenic.

The results of the tests are tabulated (Tables 3, 4) and represented graphically (Figs. 2, 3).

Table 3

Iron cathode

No. of measurements	Concentration of As_2O_3 in (mols/litre) $\times 10^4$	Total activity (current efficiency, per cent)	Specific activity* $\times 10^4$	n	
				From total activity	From specific activity
7	0	0	0	—	—
5	0.67	3.0	4.5	5.2	—
5	1.0	15.0	15.0	2.54	—
9	2.0	24.3	12.1	—	1.7
9	2.7	21.1	8.0	3.0	1.9
7	4.0	18.0	4.5	1.0	—
5	5.4	14.2	2.6	0.74	1.6
5	6.7	10.4	1.55	0.84	1.7
			Average	2.2	1.7

* The value for the specific activity is the ratio of the total activity to the concentration of the poison.

The curves in Fig. 4 show the relation between the sodium cinnamate reduction and the duration of electrolysis on pure and on poisoned lead.

From the data presented it may be seen that an iron cathode is very greatly activated by arsenic; the current efficiency increases from 0 to 24% as the concentration of arsenic (As_2O_3) rises from 0 to 2.01×10^{-4} mols/litre and falls down with further increase of concentration.

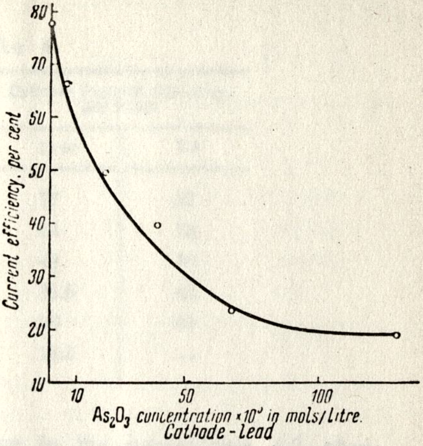


Fig. 2.

In the case of tin and lead cathodes, however, the addition of arsenic to the solution causes the reduction ratio to drop steadily for all concentrations of arsenic in the solution.

As shown by the curves in Fig. 4, the decrease in the yield cannot be explained by the natural decrease in the concentration of sodium cinnamate due to hydrogenation. Thus, on the non-poisoned cathode the yield has dropped from 72% to 60% within 2 hours after the outset of electrolysis, while on the poisoned cathode it has decreased from 75 to 15% during the same time.

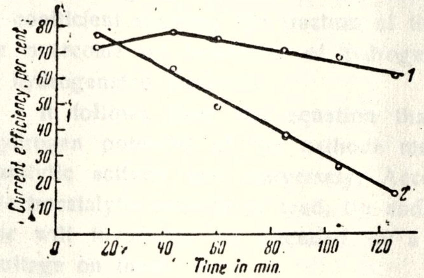


Fig. 3. Percentage yield as a function of time. Cathodes: 1 — pure lead; 2 — poisoned lead.

A similar sharp decrease is observed with the mercury cathode when arsenic is added to the solution. If no arseniate is available in the latter the reduction shows a yield of 99%. But the yield drops to 29% when the concentration of As_2O_3 attains a value of 4×10^{-4} mols/litre.

According to the generally adopted concept (1a) the overvoltage of hydrogen on a cathode and its electrocatalytic activity are increased as the adsorption potential of the hydrogen atom on this cathode decreases. This relationship has been treated extensively in an article on electrodiffusion of hydrogen, where it was demonstrated that the acceleration in the process of electrodiffusion or electrocatalysis β and the increase in the overvoltage ΔE obey a logarithmic relation of the type

Table 4

Concentration of poison As_2O_3 (mols/litre) $\times 10^4$	Cathode (current efficiency, per cent)	
	Lead	Tin
0	77	87
0.67	64	78
2.02	49	70
4.04	39.5	65
6.74	23	60
20.7	18.5	—

$$\lg \beta = \frac{\Delta E}{RT/p},$$

where β is the velocity ratio of electrodiffusion or electrocatalysis corresponding to change of the cathode potential by ΔE; p is a coefficient showing the fraction of the adsorption potential which is overcome on transition of hydrogen atom from the cathode to a hydrogenated molecule.

It follows from the equation that every agent increasing the hydrogen potential of the cathode must also increase its electrocatalytic activity and conversely. Accordingly, a decrease in the electrocatalytic activity of lead, tin and mercury due to added arsenic will invariably be attended by a decrease of hydrogen overvoltage on them.

Reference may be made here to some preliminary results obtained in testing the influence of arsenic on the potential of a lead cathode both in the presence and in the absence of cinnamic acid. They furnish unmistakable evidence that the effect of As_2O_3 is to reduce the potential on lead. (Table 5.)

Table 5

Current density $= 0.02$ A/cm.². Electrolyte, 1% KOH + 2% cinnamic acid

Concentration of $As_2O_3 \times 10^4$ (mols/litre)	Decrease in cathode potential ΔE	$-\lg\beta$	$\frac{RT}{P} = -\frac{\Delta E}{\lg\beta}$
0	0	—	—
2.0	0.010	0.08	0.120
4.0	0.010	0.20	0.050
6.0	0.015	0.29	0.052
2.0	0.035	0.53	0.066
4.0	0.050	—	—
		Average	0.072

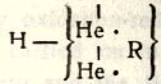
The addition of cinnamic acid is in itself apt to depolarize the cathode markedly by reducing its potential from 2.08 to 1.85 V, *i. e.* by 0.23 V. In the absence of cinnamic acid the decrease in the potential of a lead cathode is much more pronounced (see Table 6).

Table 6

Current density $= 0.02$ A/cm.². Electrolyte, 1% KOH

Concentration of $As_2O_3 \times 10^4$ (mols/litre)	Potential of Pb cathode referred to standard electrode	Decrease in potential of Pb-cathode ΔE
0	2.13	0
2	1.985	0.145
4	1.950	0.180
6	1.925	0.205
8	1.920	0.210
10	1.895	0.235

p is easily determinable from the average value of $\frac{RT}{p}$ in the last column, since RT is known to be equal to 0.054. We find p near to unity (about 0.78), which must be taken to mean that in the case of lead nearly the entire energy of the union between the

H-atom and the cathode is overcome when the former is passing to the double bond. This implies that the potential curves of the complexes MeH and  $H-\left\{\begin{matrix}\overset{|}{He}\cdot\\ \overset{|}{He}\cdot\end{matrix}\;R\right\}$ intersect in some point lying near the dissociation level Me — H. In other words, it is at a considerable distance from the cathode that the molecule subject to hydrogenation may possibly enter into reaction with the H-atoms already liberated by evaporation.

The determination of p still lacks precision which further investigation will probably furnish.

Unfortunately, our former experiments on the hydrogenation of pyridine on nickel[1b] have proved unfit for this purpose, since considerable amounts of film are forming on the cathode during this reaction, and the potential of purely ohmic origin is therefore greatly enhanced. If pyridine is acting upon the electrodiffusion[1a] of hydrogen through palladium the value of p for the polarization side has an obviously improbable order of 1/19 whilst for the diffusion side it is close to unity[5].

Effect of thin electrolytic layers of metal

There are two ways to follow in studying the influence of extraneous metals on reduction: either the dissolved salt of a given metal may be added to the solution under test and the change in the yield judged by the current as recorded after a definite interval has elapsed, or else the extraneous metal may be preliminarily deposited on the cathode electrolytically from the solution of its salt[6]. The advantage of the second method lies in the possibility to estimate the amount of the metal deposited on the electrode concerned.

It was this method that we used in studying the effect of mercury deposited on smooth or platinized platinum as well as the effect of lead deposited on an iron cathode.

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[5] An erratum is to be noted in Acta Physicochimica URSS, **1**, 611 (1934); Figs. 12 and 14 should change places.

[6] Drosdov, J. Phys. Chem. (Russ.), **3**, 351 (1933); Tafel, Z. physik. Chem., **50**, 713 (1905); Z. Elektrochem., **27**, 394 (1921).

Mercury and lead were deposited from a 0.1% solution of mercurous nitrate and a normal plumbite solution respectively. In order to obviate any oxidation-reduction processes near the electrodes, deposition was carried on in an atmosphere of hydrogen. The strength of the current and the time of polarization of the cathode in the solution of the salt of the metal tested were determined by the amount of metal which one desired to deposit on the cathode (the separation of the metal at the cathode was assumed to be the only possible electrochemical reaction).

The density of current was 0.012 mA/cm.^{2}; the amount of metal was expressed in terms of the number of monatomic layers capable of coating the apparent cathode surface.

The results of the measurements are summarized in Tables 7, 8, 9 and in Figs. 5 and 6 (curve *I*).

Table 7

Cathode — smooth platinum

No. of measurements	Number of atomic Hg layers on cathode surface	Total activity (current efficiency, per cent)	Specific activity	*n* from specific activity
5	0	0	0	—
6	1.5	11.2	7.6	1.5
7	3.0	25.1	8.4	—
5	4.5	30.0	6.7	3.8
6	6.0	21.0	5.0	2.6
5	12	29.3	2.4	1.8
			Average	2.4

The data quoted show (1) that no reduction takes place on ean cathodes of smooth or platinized platinum; (2) that very small mounts of Hg, such as are able to coat a smooth platinum surface with 1.5 atomic layers, calculated for the geometric surface of the electrode, suffice to increase the reduction from 0 to 11%.

Maximum activating influence is observed within the range of 4—6 atomic layers; the yield falls down as the coating grows thicker.

Table 8

Cathode — platinized platinum

No. of measurements	Number of atomic Hg layers on cathode surface	Total activity (current efficiency, per cent)	Specific activity	n	
				From total activity	From specific activity
4	0	0	0	—	—
5	1.0	0	0	—	—
7	2.0	4	2	4.0	(6.0)
8	3.0	17	5.6	3.0	(6.7)
5	4.5	37.5	8.33	1.1	—
5	6.0	40	6.7	2.1	1.8
7	7.5	42	5.6	—	3.6
5	9.0	34.6	3.8	—	—
5	10.5	33	3.1	3.4	1.1
5	12	26.1	2.2	3.4	2.[illegible]
			Average	2.8	2.

Table 9

Cathode — iron

No. of measurements	Number of atomic Pb layers on cathode surface	Total activity (current efficiency, per cent)	Specific actity
9	0	0	—
7	0.5	15.5	31
5	1.0	21.2	27.2
5	1.5	30.5	20
7	2.25	36.4	16
5	3.0	40.4	13.5
5	6.0	44	7.3
5	15	53.4	3.6
5	apparent surface of Pb	60.14	—

After such electrode is glowed, the yield drops to 0%. In th case of platinum-plated cathode the activating influence of mercur is observable when its coating on the cathode is 2 atomic layer thick. Maximum activating influence is observed with a coating ranging in thickness between 5 and 7 atomic layers; further deposition of mercury tends to reduce the yield.

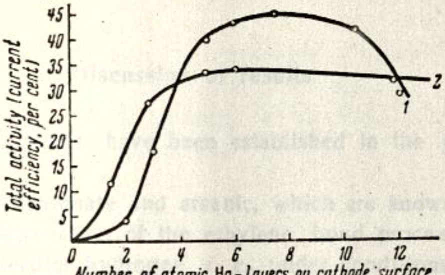

Fig. 4. *1* — platinized platinum; *2* — smooth platinum.

It is very remarkable that the amount of mercury corresponding to the beginning and maximum of activating influence is of

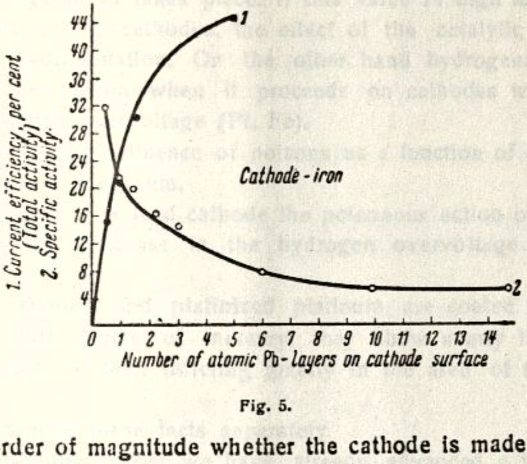

Fig. 5.

the same order of magnitude whether the cathode is made of smooth or platinized platinum in spite of the fact that the area of the true surface of one of the electrodes is several hundred or even thousand times that of the other.

No reduction will take place on pure iron (see Table 8). But an amount of deposited lead as large as to cover half a surface of the iron cathode with a monatomic layer is sufficient for increasing the reduction from 0 to 15%. The percentage of reduction grows when more and more lead is deposited from the solution, and no maximum can be noticed either in total or specific activity.

Discussion of results

The following facts have been established in the present investigation.

1. Corrosive sublimate and arsenic, which are known to poison the catalytic hydrogenation of the ethylene bond proceeding under the action of molecular hydrogen, *i. e.*, under conditions of natural catalysis, both exert an activating influence when electrolytic hydrogenation of cinnamic acid is being conducted on cathodes of iron and platinum, *i. e.*, under conditions of forced catalysis.

2. The character of the action exerted by these poisons is dependent upon how great is the value of overvoltage on the metal on which hydrogenation takes place. If this value is high as in the case of Sn, Pb or Hg cathodes, the effect of the catalytic poison is to inhibit hydrogenation. On the other hand hydrogenation is activated by the poison when it proceeds on cathodes with low values of hydrogen overvoltage (Pt, Fe).

3. The activating influence of poisons as a function of concentration possesses a maximum.

4. In the case of a lead cathode the poisonous action of As_2O_3 is related to the decrease in the hydrogen overvoltage of the cathode.

5. When smooth and platinized platinum are coated electrolytically with thin layers of mercury, they show nearly identical behaviour in spite of their differing greatly in the area of the true surface.

Let us examine these facts separately.

1. In a previous paper we have already advanced a theoretical interpretation of the main fact, *viz.*, that catalytic poisons act oppositely upon the rate of ordinary catalysis and electrocatalysis.

The most simple reaction of electrolytic hydrogenation, *i. e.*, the process in which an H-atom adsorbed by the metal is transferred to a non-saturated molecule A, is to be represented as follows:

$$A + H|Me| = |Me| + A_H - \varphi_H + \varphi_{AH},$$

where φ_H and φ_{AH} are energies of the union of an H-atom with the metal and hydrogenated molecule respectively.

The activation barrier (energy of activation) of such process may be expressed by the function:

$$q_r = p\varphi_H - q\varphi_{AH}, \tag{1}$$

where p and q are coefficients (generally below unity) characterizing the shape of the potential curves of molecules MeH and AH.

As is seen from this equation, the activation energy on electrocatalytic hydrogenation of a non-saturated molecule grows with the increase in the energy of the union between the H-atom and the metal of the cathode:

$$\frac{\partial q_r}{\partial \varphi_H} = p > 0. \tag{2}$$

In the actual cases of hydrogenation it is always the closed linkage and not the free one which is saturated.

Accordingly the value of φ_H will express the energy of a more complicated process than the isothermal rupture of elementary linkage A—H. This will not, however, affect the type of the functional dependence of q_r upon φ_H, as has been shown in our previous work[1]:

$$q_r = p\varphi_H - q'\varphi'_{AH}. \tag{1a}$$

However, φ'_{AH} in that case expresses a more complex energy equivalent than the mere energy of the linkage A—H. But so far as the character of the molecule under hydrogenation (whose properties determine the value of φ'_{AH}) is not altered, we are not interested in the aspect of the term $q'\varphi'_{AH}$.

Equation (1) holds therefore true; this implies that the activation energy of the "forced" electrolytic hydrogenation decreases and hence the rate of reaction grows as the energy of the linkage between hydrogen and metal is reduced:

$$v_r = \left(v_0 \, e^{\frac{q\varphi_{AH}}{RT}} \right) e^{-\frac{p\varphi_H}{RT}} = v_0' \, e^{-\frac{p\varphi_H}{RT}}. \qquad (3)$$

Consequently the electrolytic hydrogenation is sharply accelerated by a decrease in the energy of the linkage of the H-atom with the metal and attains its maximum velocity when acted upon by free atoms of hydrogen.

It is very likely that on metals with a high overvoltage of hydrogen (Hg, Pb, Sn) hydrogenation is largely determined by the action of such free atoms; this fact is substantiated by the observations of Kobosev and Nekrassov[7] on the reduction of a suspension of WO_3.

It may be mentioned here that, according to Gurney's[8] quantum-mechanical theory of discharge, where the electron is supposed to effect its transition to the H_3O^+-ion by means of the "tunnel-effect", considerable quantities of H-atoms can as a matter of fact be observed to form in that manner near the electrodes.

According to Kobosev and Nekrassov[7], the increase of the hydrogen overvoltage with the decrease in the linkage energy of the H-atom (φ_H) follows the equation:

$$\Delta E = \Delta E_0 - \varphi_H + nRT \ln C. \qquad (4)$$

Thus the metals with a low overvoltage of hydrogen (Pt, Ni, Fe) have a high linkage energy φ_H, while the reverse is the case with the metals of high hydrogen overvoltages (Sn, Pb, Hg), whose linkage energy φ_H is low.

The experimental data on the linkage energy of metallic hydrides, scanty as they are, are still sufficient to bear out this general statement.

Kobosev and Anochin[9], for instance, have found the energy of the linkage Pt—H to be equal on the average to about

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[7] Kobosev u. Nekrassov, Z. Elektrochem., **36**, 538 (1930).

[8] Gurney, Proc. Roy. Soc., (A), **134**, 137 (1931); (A), **136**, 378 (1932).

[9] N. Kobosev a. Anochin, J. Phys. Chem., (B), **13**, 18 (1931).

50 cals., in the case of electronic desorption of hydrogen from platinum. Kondratjew[10] reports a value of 8.5 cals. for the linkage energy of the H-atom in the hydride of mercury Hg—H, which is very near to the figure obtained by Kobosev and Nekrassov[7] from the value of hydrogen overvoltage (about 10 cals.). We thus see that the linkage energy φ_H at the two opposite ends of the overvoltage scale Pt—Hg is about 50 and 10 cals. respectively.

Hence, according to equation (3), the ratio of the rate of electrocatalytic hydrogenation on Pt, Fr, Ni to that on Hg, Pb, Sn is

$$\frac{v_{Pt}}{v_{Hg}} = e^{-\frac{40\,000\,p}{RT}},$$

this ratio being equal to 10^{-30p} at ordinary temperature.

Even if we were to take p as great as 1/10, the electrocatalytic activity of platinum would be 1/1000 that of mercury.

We should not, therefore, be surprised by the fact that hydrogenation of cinnamic acid will not proceed at all on platinum and iron though it gives a yield of 99% (from current measurements) on mercury and 87—78% on tin and lead.

It is also easy to understand that the coating of metallic surfaces of low hydrogen overvoltage (high value of φ_H), with poisons, particularly with metals of high overvoltage (and hence of small value of φ_H), should increase their electrocatalytic activity because it reduces the mean adsorption potential of the hydrogen atom. That the properties of the surface are here actually reduced to a mean between those of the underlying metal and the poison, say platinum and mercury, rather than there occurs a mere replacement of the atom of the former by those of the latter, is proved by the fact that platinum coated with several mercury layers, is still far from having attained the activity of pure mercury.

In the case of metals with high overvoltage, however, the linkage energy of Me—H is so small that adsorption of any other atom, say As, is only apt to increase the value of φ_H and conse-

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[10] Kondratjew a. Eliashevich, The elementary Processes in Gases, (1933).

quently to inactivate the surface. In other words, as the linkage energy of As — H is less than in the case of platinum (iron) but greater than in that of mercury (lead), the natural effect of arsenic is to activate platinum (iron) and to poison mercury (lead).

From this point of view it seems hardly probable that there should exist chemical methods of activation with regard to such cathodes as lead and mercury.

Let us endeavour to estimate the change in the energy of the union between the H-atom and metal due to the poisoning of the electrode.

The hydrogen atoms separating under the action of the current are on the one hand used up in the reduction of cinnamic acid and on the other react with each other to leave the surface of the cathode in the form of molecular hydrogen. The strength of the current is proportional to the rate of these two processes:

$$i = K_r C_{\mathrm{H}}^{x} + K_m C_{\mathrm{H}}^{m},$$

where K_r and K_m are the reaction rate constants of reduction and formation of the molecules respectively; x and m are the exponents of the respective reaction.

The current efficiency for the substance obtained by reduction may be written as follows:

$$\gamma = \frac{K_r C_{\mathrm{H}}^{x}}{i}.$$

Experiments show that the effect of poisoning is to increase the current efficiency. According to our concept the increase in reduction rate responsible for the increase in yield must not be explained on the basis of increased concentration of hydrogen atoms on the surface of the cathode due to their slowed down recombination. We believe the reason to lie in the reduced energy (φ_{H}) of the linkage of H-atoms with the surface of the electrode. With small amounts of poison one may therefore take it for granted that the concentration of hydrogen atoms remains constant. Then the ratio between the yields of reduced substance for two concentrations of the poison will be

$$\frac{\gamma_{\mathrm{I}}}{\gamma_{\mathrm{II}}} = \frac{K_r^{\mathrm{I}}}{K_r^{\mathrm{II}}}. \qquad (5)$$

Expressing K_r by means of the Arrhenius equation we get:

$$\frac{\gamma_{I}}{\gamma_{II}} = e^{\frac{q_r^{II} - q_r^{I}}{RT}},$$

or, after replacement of q_r by its expression in terms of φ_H according to equation 1 (a)

$$\frac{\gamma_{I}}{\gamma_{II}} = e^{\frac{p\varphi_H^{II} - p\varphi_H^{I}}{RT}} = e^{p\frac{\Delta\varphi_H}{RT}}. \qquad (6)$$

Equation (6) permits, after measuring the current efficiency for two concentrations of the poison, to find the value of the change in the linkage energy of the hydrogen atom due to the poisoning of the electrode ($p\Delta\varphi_H$).

The values obtained by applying equation (8) to the case of iron and platinum cathodes are given in Tables 10 and 11, it being assumed that no other factors besides the decrease of φ_H are responsible for the accelerated rate of hydrogenation. As reduction on these cathodes failed to take place in the absence of poison, the values of $p\Delta\varphi_H$ were calculated with reference to that value of energy linkage at which reduction was observed to set in.

Should we succeed in detecting a decrease in the activation energy on poisoning the cathode, we would furnish direct experimental evidence that the activating effect of poison in electrocatalysis is just due to a lowering of the activation barrier rather than to stopping of recombination processes or similar factors. The experiments started along this line have shown that the decrease in question is a matter of fact.

These experiments were run at three temperatures differing from one another no less than by 15°.

In order to make the gas evolving from the cathode region soon enough assume the temperature at which records were performed, there was placed between the cell and the gas burette a red-copper coil-pipe immersed in water of respective temperature.

Table 10

Cathode — Fe

Poison (As_2O_3) concentration (mols/litre)	$p\Delta\varphi_H$ in cals.	Poison: lead. Number of atomic layers of Pb	$p\Delta\varphi_H$ in cals.
6.7×10^{-5}	0		
1.14×10^{-4}	950.8	0	0
2.02×10^{-4}	1230	1.5	183.5
		3.0	395.5
		6.0	610.8
		15.0	724.1
			793

The varying degrees in poisoning the cathode were attained by performing the first set of experiments with a solution containing $HgCl_2$ in a concentration of 1×10^{-4} mols per litre, the second, with a cathode on which mercury was deposited prelimi-

Table 11

Cathode	Poison: mercury. Number of atomic layers of Hg	$p\Delta\varphi_H$ in cals.	Poison: mercury. Number of atomic layers of Hg	$p\Delta\varphi_H$ in cals.
Smooth platinum.	1.5	0	2	0
	3.0	472	3	317
	4.5	575	4	547
	6.0	597	5	599
			7	605
			11	749
Platinized planum	2	0		
	3.0	999		
	4.5	1345		
	6.0	1354		
	7.5	1330		

narily in such an amount as to coat the surface with 1.5 atomic layers and, finally, the third, with an amalgamated platinum cathode.

The results are summarized in Table 12.

The activation energy was calculated by the formula:

$$q_r = \frac{2.3\, RT_1\, T_2 \lg \gamma_1}{\Delta T \gamma_2}.$$

Table 12

Electrode	Concentration of poison	Temperature	Current efficiency (per cent)	Activation energy in Kg. cals.
Platinum	$HgCl_2$ 1×10^{-4} mols/litre	0	6.5	5.952
		18	13	
		51	36	
Platinum	Coated with 1.5 atomic layers of mercury	0	18	2.317
		15	23.5	
		30	27	
Amalgamated platinum		0	47.6	1.208
		30 6	52	
		50.5	60	

It is evident from the Table that the more the surface of the cathode is poisoned the less activated is the reaction; *i. e.*, the activation energy, or the mean adsorption potential of the cathode surface falls as the amount of mercury deposited on the latter increases.

We have also conducted experiments with zink and lead used as cathodes. However, the yield obtained with these metals was greatly dependent upon the preliminary treatment of their surface and the result were therefore variable. Experiments along this line are being continued.

The fact that we have found the activation energy to be reduced by enhanced poisoning seems to furnish incontrovertible evidence in favour of our concept of the inverse dependence of the electrolytic activity of metals and their overvoltage upon the adsorption potential of the H-atom. And whatever view may be held concerning the mechanism of overvoltage no doubt can arise about the truth of the statement put forward by Kobosev and Nekrassov, *viz.*, that the energy of the union between the H-atom and the surface of the metal is the principal characteristic of the latter, determining the value of its hydrogen overvoltage when it is used as cathode.

From this standpoint, the theory of Gruz and Volmer[3] must not be accepted without qualification, since it pays no attention to the above factor (the nature of the metal). Its experimental basis becomes objectionable owing to the results obtained in our experiments with the poisoning of smooth and platinized platinum which have shown that a great difference in the true surface is not attended by only such pronounced difference in the "polarization" surface of the metal. Otherwise how should we explain the fact that we observed both smooth and platinized platinum to be equally activated by electrolytically equal amounts of deposited mercury. It will be apparent that the "polarization surface" of a metal, *i. e.*, such as is accessible to the lines of force, does not extend over the entire true surface but only embraces the tangent plane whose area cannot possibly vary too much with the degree of roughness of the metal.

Physically, the picture is fairly clear, since it is hardly probable indeed that the lines of force might "crawl" into the depth of the complicated relief of a metallic surface.

On the ground of the results obtained by us we must call in question the usual interpretation of the experiments of Bowden and Rideal[11] on the saturation of different surfaces to an equal potential value. It is claimed that the varying electrochemical behaviour of these surfaces is due to nothing but a great difference in the area of polarization surface. Assuming close values for polarization surfaces of different metals, as it folows from our results, we can no longer subscribe to the view of Gruz and Volmer

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[11] Bowden a. Rideal, Proc. Roy. Soc., (A) **120**, 595 (1938).

who consider the polarization of different metals as a mere charging of condensers of varying capacity.

The implication of what has been stated above is that the active centres, or definite atomic ensembles of amorphous phase (is denoted in terms of Kobosev's[3] theory of formation of active ensembles), may present spots with increased or decreased adsorption potential which goes parallel with their being formed on normal or electrolytic catalysis.

Spots with low adsorption potential may possibly occur among the elements of a normal metallic lattice, say the faces of the crystals. A certain combination of atoms within such normal lattice may perform the functions of an "active ensemble" in electrocatalysis. Any destruction of the crystalline surface which would form an adsorption layer of amorphous phase with a large store of free energy on the metal should effect its electrocatalytic activity unfavourably. Consequently, in that respect too, the electrocatalysis is the reverse of the normal catalysis. And indeed it is known from the experiments of Tafel[6] that roughness of the surface can make the metal fully indifferent to electrocatalysis. We meet here with a curious poisoning of the metal by its own amorphous phase.

If, however, sufficiently stable linkages have to undergo the process of convertion, say in the case of saturation of ethylene bond the adsorption potential of the atoms within the normal lattice of such metals as platinum, iron or nickel turn out to be too great to call forth the reaction of hydrogenation at ordinary temperature.

In creating active ensembles on such metals one is compelled to resort to the adsorption of the poison molecules which reduce the adsorption potential of the metal.

Here too, the active ensembles are created at the expense of the adsorbed amorphous phase, yet the adsorption potential drops instead of increasing. As has already been pointed out, the action of the poison cannot be considered to be a mere substitution of one metal, say Hg, for another, say Pt, at the surface. We should rather speak of a formation of a two-dimensional alloy with intermediate properties. But irrespective of the details of this picture, the case of formation of active ensembles with a reduced adsorption potential can be analyzed after the principles and equations suggested by Kobosev in his "Theory of formation of active ensembles on surfaces".

Thus, in the case of electrocatalysis on poisoned electrodes the active ensembles are those composed of a definite number of atoms of the poison which activate a definite number of atoms of the metal.

Thus number of atoms n can be found from the dependence of the specific and total activity of the poison upon its concentration according to the equations:
(specific activity)

$$n = 1 + \frac{\lg \frac{a_{\max}}{a}}{\lg \frac{\alpha_{\max}}{\alpha} - \frac{\alpha_{\max} - \alpha}{2.3\,\alpha_{\max}}},$$

(total activity)

$$n = \frac{\lg \frac{A_{\max}}{A}}{\lg \frac{\alpha'_{\max}}{\alpha} - \frac{\alpha'_{\max} - \alpha}{2.3\,\alpha'_{\max}}},$$

where a — specific activity; α — the amount of poison on the surface; A — total activity; $\alpha_{\max}$ — position of the maximum of specific activity, *i. e.*, current efficiency per unit amount of poison. $\alpha'_{\max}$ — the position of the maximum of total activity, *i. e.*, current efficiency without reference to the amount of poison.

In the case of mercury we may safely use the above equations which are derived for a non-crystallizing layer.

In the case of lead the maxima of specific and total activity fail to occur at all (see Fig. 6). According to Kobosev this must be ascribed to a strong crystallization of the layer (high coefficient of crystallization), and indeed, the crystallization should be most sharply expressed in such fusible metals as lead, tin, etc.

The results of calculations (n) performed by making use of these two equations are brought together in Tables 11 and 12. It may be seen that the calculation based on specific activities gives more stable values of n, but on the average the two methods yield fairly consistent data:

$$n \begin{cases} \text{from specific activity} = 1.7;\ 2.4;\ 2.4;\ \text{average } 2.1. \\ \text{from total activity} = 2.0;\ 2.1;\ 2.8;\ \text{average } 2.3. \end{cases}$$

Thus, on electrolytic hydrogenation of the ethylene bond in cinnamic acid the average number of active atoms of Pt and Fe in an active ensemble is 2.

It may be noted here that the same number of atoms in the active ensemble has been obtained by analyzing the data on normal hydrogenation of ethylene bond in fumaric acid on palladium [12].

The result obtained is quite natural. It shows that an addition of two H-atoms to the double bond invariably requires an ensemble of 2 activated atoms of the metal, whether this addition is to be effected in the case of normal or electrolytic catalysis. The difference lies in the fact that in normal hydrogenation the active ensemble is a combination of atoms of amorphous phase with increased chemical potential, while in the case of electrolytic hydrogenation it is composed of atoms depressed by the adsorption of the poison.

A comparative study of specific activity curves for smooth and platinized platinum (Fig. 7) from the viewpoint of the theory of ensembles affords further evidence in support of the conclusion that the polarization area is independent of the roughness of the cathode surface. In fact, according to the equation of Kobosev [3]

$$\frac{a_{\mathrm{I\,max}}}{a_{\mathrm{II\,max}}} = \frac{s_1}{s_2}.$$

The ratio between the maxima of specific activities for a given reaction on two different catalyst samples is equal to the ratio between the surfaces of these samples. From Fig. 6 it is apparent that the maximum values of specific activities for smooth and platinized platinum are practically equal, and this implies that the surfaces of the metals are equal too. The sole difference between the samples is in the position of the maxima which in the case

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[12] N. Kobosev a. Klachko-Gurvich, Acta Physicochimica URSS, 10, 1 (1939).

of platinized platinum are located at large degrees of covering of the surface. According to Kobosev's theory this should be interpreted to mean that the regions of migration are smaller in the case of platinized platinum, which is quite consistent with its greater dispersity.

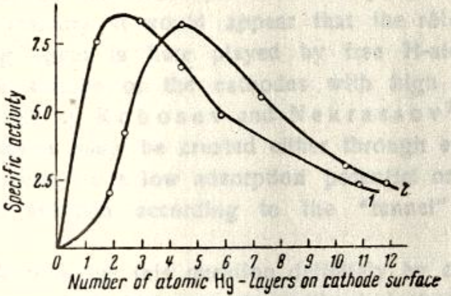

Fig. 6. *1* — smooth platinum; *2* — platinized platinum.

Considerable interest is due to the fact that we have found the active ensemble to consist of a definite number of atoms in the case of electrocatalysis.

In the case of normal catalysis the limited number of atoms in our active ensemble is due not only to the structure but also to the energy inactivity of large atomic groupings. Yet in the case of electrocatalysis no other factors besides that of the structure would seem to come into play. And it appears surprising enough that the structural factor should be so sharply expressed. On the other hand, even taking the extreme values of *n* and not the mean ones, we shall find the ensembles consisting of more than 5—6 atoms to be inactive. A probable explanation of such a high selective power in the case of electrocatalysis is that if a molecule is attacked by 2 slightly adsorbed H-atoms, this may possibly result in the dehydrogenation of the saturated linkage:

$$R -- CH_2 — CH_2 — R + 2H \rightarrow RCH = CHR + H_2,$$

i. e., in recombination of hydrogen through successive hydrogenation and dehydrogenation of the double linkage. An indication toward the possibility for such processes actually to take place is furnished by the behaviour of H-atoms in relation to ethylene hydrocarbons.

In the light of the theory of active ensembles the problems come to the fore as to what are the details in the structural mechanics of an electrocatalytic reaction proceeding on liquid metals, say mercury. It would appear that the rôle of a principal hydrogenating agent is here played by free H-atoms whose presence at the surface of the cathodes with high overvoltage has been established by Kobosev and Nekrassov[7].

These atoms may be created either through evaporation from the cathode owing to a low adsorption potential or else they may form in the solution according to the "tunnel" mechanism of Gurney[8].

We hope to solve this question definitely by carrying on the process of electrolytic hydrogenation without electrodes (with a spark gap) in order to be sure that the H-atoms formed will be in free and not in adsorbed condition.

This method, along with the poisoning of the electrodes, should also prove to be useful for studying the influence which the physico-chemical nature of the cathode exerts not only upon the rate but also upon the trend of hydrogenation.

Conclusions

1. The influence of catalytic poisons (arsenic, mercury) upon electrolytic hydrogenation of cinnamic acid has been studied with cathodes of high (Hg, Pb, Sn) as well as low (Pt, Fe) hydrogen overvoltage.

2. Poisoning was effected either by introducing the poisons into the solution or depositing thin layers of mercury and lead on platinum and iron cathodes.

3. It has been found that while the poisons exert their depressing action on metals with high hydrogen overvoltage, they activate the metals with low overvoltage. According to previously developed concepts this result should be interpreted in terms of the energy change in the adsorption union of the H-atom with the cathode due to poisoning. It has been shown that both the electro-

catalytic activity and hydrogen overvoltage are reduced in a lead cathode by the action of As_2O_3.

4. It has been established that the activating influence of poisons attains its maximum at a certain concentration and this has served — on the basis of Kobosev's theory — for estimating the number of atoms in an active ensemble in the case of hydrogenation of cinnamic acid. This average number of atoms is 2. Contrary to what is observed with normal catalysis, the active centres are spots with reduced adsorption potential.

5. It has been proved — consistently with the developed views on the mechanism of electrocatalysis and overvoltage that the process of electrolytic reduction is activated with less energy if the poison is adsorbed by the cathode.

6. Comparative poisoning of smooth and platinized platinum has shown that the "polarization surface" of both of them is practically equal. This evidence refutes the conceptions of Bowden-Rideal. Erdey-Gruz, Volmer and others, and the experimental basis of the purely electrostatic theories of overvoltage becomes objectionable.

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