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THEORY OF CATALYTIC HYDROGEN WAVES IN ORGANIC POLAROGRAPHY

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I. INTRODUCTION

Catalytic hydrogen waves are an interesting phenomenon, frequently encountered in polarographic practice. They are associated with certain substances whose function is a catalytic one, since they assist the evolution of molecular hydrogen at the cathode without being altered by the electrode process. Catalytic hydrogen waves are observed at potentials less negative than the normal hydrogen waves for the given solution. The catalysts effectively lower the hydrogen overvoltage, thus accelerating (or catalysing) the evolution of hydrogen and justifying the use of the term "catalytic hydrogen waves".

Studies of catalytic waves can yield the rate constants for fast protolytic reactions, they can clarify adsorption phenomena at very low surface coverages, assess the rate of bimolecular free radical interactions, and quantitatively characterise the relationship between the structure of organic catalysts and their catalytic activity.

Catalytic hydrogen waves have also a practical interest. When applied to analytical problems, they enable conventional polarographic apparatus to be operated at the 10^{-7} M level, *i.e.* they raise the sensitivity of classical polarography by 2–3 orders of magnitude. The biological and medical applications of catalytic hydrogen waves are particularly interesting: they have made possible a number of diagnostic procedures such as Brdička's well-known serological polarographic test for cancer.

Herles and Vančura, in 1930, were the first to observe an unusual wave whilst studying the polarograms of blood serum solutions with sodium, potassium, and magnesium salts as supporting electrolytes. A report of these experiments was published, as a short communication[1], in 1932. Heyrovský and Babička repeated the work in 1930, and confirmed the appearance of new waves when proteins were

present in an ammoniacal base solution. The waves were shown to be associated with catalytic evolution of hydrogen, and not with reduction of the proteins[2].

Brdička later discovered[3] that the catalytic effect of proteins and of other sulphur compounds is greatly enhanced by the addition of divalent or trivalent cobalt salts to the ammoniacal buffer solution.

At about the same time Pech observed[4] that catalytic hydrogen waves can also be induced by organic compounds not containing sulphur, such as alkaloids. Since then, a great deal of work has been devoted to the study of catalytic hydrogen waves due to proteins in ammoniacal buffer solutions containing cobalt salts, and waves in solutions of alkaloids and other nitrogen derivatives (see, for example, the literature surveys given in Refs. 5–11). Much experimental information is available in the papers by Kirkpatrick[11], Stromberg *et al.*[12,13], Knobloch[14,15], Kůta and Drabek[16], von Stackelberg *et al.*[17–19], Nürnberg[20], Lamprecht *et al.*[21], and many other workers.

1. Features of Catalytic Hydrogen Waves

Catalytic waves are quite different from the normal, diffusion-limited, polarographic waves. Catalytic limiting currents do not obey the Ilkovič equation; they frequently have very high or very low temperature coefficients; they do not (as a rule) depend on the height of the mercury column above the dropping electrode, but occasionally, and in contrast with diffusion currents, they increase as the height of the mercury column decreases. The shape of catalytic hydrogen waves is always different from that of diffusion-limited waves; the limiting currents and the half-wave potentials of catalytic waves show a complicated dependence on the catalyst concentration and on the composition of the solution.

2. Effect of Catalyst Concentration and Solution Composition on the Catalytic Limiting Current

The effect of catalyst concentration (c_{cat}) and solution composition on the height of catalytic hydrogen waves has been discussed in a large number of papers. It has been shown that the catalytic limiting current increases linearly with c_{cat} at first, but the initial proportionality is not maintained, and at very high values of c_{cat} the limiting current approaches a constant value. This behaviour was first observed by Brdička[22] in his work on the catalytic hydrogen waves of egg albumin in unbuffered solutions of KCl, and on albumin waves in buffered solutions of different compositions and pH. Brdička found that the height of the catalytic wave and its limiting value at high catalyst concentrations are both increased by raising the buffer capacity of the solution and by lowering the pH.

Brdička derived the following empirical relation[22] between limiting current and cobalt ion concentration for catalytic waves in protein solutions containing cobalt salts:

$$i_{lim} = K\,[Co^{2+}]^{0.74}.$$

The concept of catalyst regeneration after the electrode process, developed in Brdička's papers, is an important one, and was adopted in subsequent theories of catalytic hydrogen waves. According to Brdička, regeneration consists in addition of hydrogen ions to the product of electrochemical discharge of the catalyst under the influence of acids (proton donors).

Stromberg also reported[12] an increase in the catalytic wave with increasing concentration of proteins and cobalt salts, and interpreted this phenomenon in terms of the kinetics of the electrode reaction, finally arriving at an expression for the limiting current of the catalytic wave. Klumpar[23] put forward an empirical formula for the catalytic limiting current in terms of the concentration of cystine and cobalt salt in the solution.

Knobloch[14] made the first detailed studies of the influence of various factors on the catalytic hydrogen waves produced by nitrogen compounds (such as pyridine derivatives) in buffered solutions free from cobalt salts. He showed that the limiting current of a catalytic hydrogen wave is increased by decreasing the pH of the solution and by increasing its buffer capacity. In view of the similarity between the observed current–catalyst concentration curve and the Langmuir adsorption isotherm, Knobloch suggested that the current is limited by the amount of catalyst adsorbed on the surface, and identified the maximum current obtained at high catalyst concentrations with complete coverage of the electrode surface by catalyst particles. The influence of pH and buffer capacity is explained in terms of protolytic regeneration of the catalytically active cationic form of the catalyst: this process is also thought to bring about a decrease in hydrogen overvoltage by Heyrovský's mechanism, *i.e.* by increasing the rate of formation of H_2^+ molecule-ions from H and from the protons of the cationic form of the catalyst. Thus, Knobloch was the first to ascribe electrochemical activity only to the acidic (or cationic) form of nitrogen-containing catalysts.

The effect of catalyst concentration and proton donor concentration on catalytic hydrogen waves has been studied in detail[24,25] by examining the first quinine wave in solutions containing effectively only one proton donor — hydrochloric acid — and a supporting electrolyte of 1 *N* LiCl. As in other catalytic hydrogen waves, the catalytic current in quinine solutions increases with quinine concentration in a way (Fig. 1) reminiscent of the Langmuir adsorption isotherm. The asymptotic values of the wave height, and,

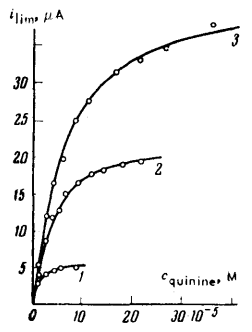


Fig. 1. Variation of limiting catalytic current with quinine concentration at different concentrations of hydrochloric acid (10^{-3} M): 1) 1.06; 2) 3.65; 3) 6.8.

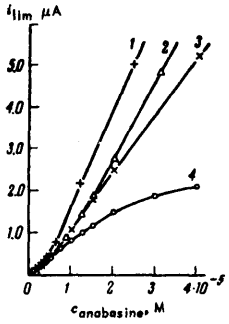


Fig. 2. Variation of limiting catalytic hydrogen current with anabasine concentration in acetate buffer solutions of ionic strength I = 0.5: 1) pH 4.46, Σc_{ac} = 0.2 M; 2) pH 5.0, Σc_{ac} = 0.1 M; 3) pH 5.0, Σc_{ac} = 0.2 M; 4) pH 6.0, Σc_{ac} = 0.1 M.

even more important, the quinine concentrations at which i_{lim} approaches the asymptote, were found[25] to depend on the concentration of hydrochloric acid in solution: the lower the concentration of HCl, the lower the limiting wave height, and the lower the quinine concentration needed to approach this limiting value (Fig. 1).

Hence, the limiting wave height is not due to full coverage of the surface of adsorbed catalyst. By comparing the limiting height of the catalytic wave with the diffusion current for hydrogen ion discharge, it can be shown that this limit arises from complete exhaustion of proton donors (in this case hydrogen ions) at the electrode surface. Its value corresponds to the limiting rate of supply of hydrogen ions by diffusion from the bulk solution to the electrode surface[24,25].

In the presence of an excess of proton donors and very low concentrations of catalyst, the height of the catalytic wave shows an unusual dependence on the concentration of catalyst in solution, increasing faster than linearly with catalyst concentration (see, for example, Fig. 2, taken from Ref. 26). This is a fairly frequent phenomenon: thus, some of the polarograms given in Kirkpatrick's paper[11] show catalytic hydrogen waves, for atropine and pilocarpine in buffer solutions, whose height increases faster than the alkaloid concentration.

The present writer, after examining available experimental data in the light of the ideas of Brdička, Knobloch, and Stromberg, put forward[24,27] a mechanism of catalytic hydrogen evolution which explains all the experimental facts. Equations which adequately describe the observed phenomena were derived by combining this scheme with Brdička and Wiesner's well-known views on the kinetics of current limitation, with Frumkin's theoretical considerations of the influence of double layer structure on electrode processes and of the mechanism by which organic substances are adsorbed at an electrode, and lastly with Delahay and Feike's data on adsorption kinetics.

3. Mechanism of Catalytic Hydrogen Waves in Solutions of Organic Bases

Catalytically active organic substances invariably exist in two forms: the acid form BH^+ and the basic form B (in the Brønsted sense), which are in mutual protolytic equilibrium:

$$B + DH^+ \underset{\beta\sigma}{\overset{\rho}{\rightleftharpoons}} BH^+ + D. \qquad (I)$$

The symbol DH^+ stands for the acids (proton donors) present in solution, D for their conjugate bases.

Various organic compounds catalyse hydrogen evolution by virtue of an unshared electron pair (*e.g.* on an atom of nitrogen, sulphur, oxygen, phosphorus, arsenic, etc.) which can add on a proton to give an 'onium' compound able to react electrochemically at the cathode. The electrochemical activity of 'onium' compounds arises not from their positive charge (which assists the movement of species towards the cathode, and their discharge[28]) but, rather, from the very nature of the 'onium' ion. If electron transfer to a protonated 'onium' form were due exclusively to the positive charge on the latter, the same process should occur, albeit at a more negative (200–300 mV) potential, even with the uncharged, unprotonated form of the catalyst. This is observed with charged and uncharged derivatives of aniline and phenol[29-31], and also with weak acids and their anions (see, for example, Refs. 32–40). However, electrons are not transferred to the unprotonated form of the catalyst, which justifies the above conclusion.

The catalytic activity of organic compounds is also unrelated to the mobility of hydrogen ions within the molecule: careful studies[18] of compounds in which the hydrogen is very labile have failed to reveal any catalytic activity.

Electron transfer to the protonated form of the catalyst

$$BH^+ + e^- \underset{\longleftarrow}{\overset{\text{electrode}}{\longrightarrow}} BH \qquad (II)$$

results in an unstable, uncharged species behaving like a free radical.

In the discharge of tetrasubstituted ammonium[41-43] or phosphonium[44] salts, or of trisubstituted sulphonium cations[45], the unstable products can dimerise, as is the case with *N*-alkylpyridinium salts[46-49], or alternatively they can be attacked at the carbon–heteroatom bond, giving the corresponding tertiary amines, phosphines, or sulphides respectively, as well as hydrocarbon radicals. The latter can be reduced at the cathode, react with the solvent, dimerise, or disproportionate.

When a protonated 'onium' cation is discharged, as in the catalytic evolution of hydrogen by the species BH (see reaction scheme II), the bimolecular reaction

$$2BH \xrightarrow{k_d} 2B + H_2 \qquad (III)$$

is apparently energetically more favourable than the splitting off of a hydrocarbon radical or a hydrogen atom, since it regenerates the catalyst in its basic form, and evolves molecular hydrogen. Because the reaction is bimolecular, its rate decreases very significantly with decrease in catalyst concentration, and can, in some cases, limit the rate of the overall process. This situation can arise under the conditions of the experiments summarised in Fig. 3. Reports[11,24,26] of a limiting catalytic current increasing faster than linearly with catalyst concentration can be

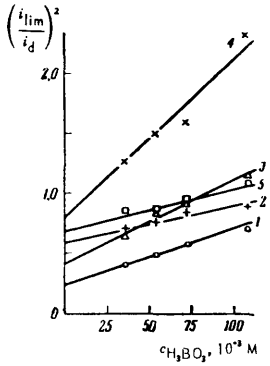


Fig. 3. Variation of $(i_{lim}/i_d)^2$ with concentration of undissociated H_3BO_3 in a borate buffer of pH 8.40 (ionic strength 0.5) for catalytic hydrogen waves produced by $\sim 0.5 \times 10^{-3}$ M solutions of: 1) pyridine; 2) 2-picoline; 3) 3-picoline; 4) 4-picoline; 5) 2,6-lutidine.

explained by postulating that the height of the wave is limited by a reaction which is of second order with respect to the catalyst.

Sometimes, as in the discharge of the anabasinium ion[50], bimolecular radical reactions of type (III) give rise to relatively stable HB–BH dimers as intermediates, which slowly decompose into two B species and evolve molecular hydrogen. The HB–BH dihydrodianabasine dimers become less stable at higher temperatures, and their formation (or, more precisely, their rate of decomposition) no longer affects the overall rate of process (III)[50].

B, the basic form of the catalyst produced by reaction (III), is again protonated by reaction (I), discharged by reaction (II), once again regenerated, etc., each cycle of reactions (I–III) converting two protons from DH^+ into molecular hydrogen by a catalytic electrochemical reaction. Thus each catalyst species can "reprocess" many species of the proton donor.

The catalytic hydrogen evolution current is determined by the rate of processes (I–III). Under limiting current conditions, when the rate of the electrochemical step (II) is high enough to discharge all BH^+ species present at the electrode surface, the height of the catalytic wave is determined by the rate of formation of BH^+ at the electrode. In most cases, this process is controlled by protonation of the basic form of the catalyst, a reaction whose overall rate constant, shown as ρ in scheme (I), is in reality the sum of the rate constants for all possible interactions between the catalyst and proton donors in solution:

$$\rho = k_1[DH^+]_1 + k_2[DH^+]_2 + \cdots + k_n[DH^+]_n. \qquad (1)$$

The equilibrium constant relating the basic and the acidic form of the catalyst, σ, is an important parameter of the catalytic system. As in other protolytic reactions, the value of σ is determined only by the acid dissociation constant of the protonated form of the catalyst and by the solution pH: unlike ρ, this constant is unaffected by the nature of the concentration of the buffer present in solution:

$$\sigma = \frac{[B]}{[BH^+]} = \frac{K_A}{[H^+]}. \qquad (2)$$

We shall now consider the relationship between the limiting catalytic current and solution composition which the suggested model of the catalytic wave predicts.

Consider first a process limited only by the rate of protonation (I), *i.e.* in which the rate of regeneration of the catalyst by reaction (III) is large enough. To simplify matters, we shall assume that the solution contains only one kind of proton donor:

$$\rho = k_{H^+}[H^+].$$

The further assumption, frequently justified in practice, is also made that the protolytic equilibrium lies on the side of the basic form of the catalyst, *i.e.* $\sigma > 1$, and that the rapid and complete regeneration of the catalyst produces a steady state, established very shortly after formation of the drop, in which the equilibrium concentrations of BH^+ and B are maintained even at relatively short distances from the electrode[51]. Under these conditions, the limiting catalytic current is given by the expression

$$i_{lim} = k_{H^+}[H^+]_s[B]_s sFa, \qquad (3)$$

where s denotes the mean area of the dropping electrode, F is the Faraday, and a is a proportionality factor equal to the thickness μ of the reaction layer if the catalyst were not adsorbed. For the so-called surface waves, discussed below, a is a factor which converts bulk concentrations into surface concentrations with allowance for catalyst adsorption. The subscript s indicates that the concentrations are to be taken close to the electrode surface.

In the catalytic cycle one hydrogen ion is consumed for every electron transferred. Hence the hydrogen ion concentration near the surface can be expressed, using the Ilkovič equation, as

$$[H^+]_s = [H^+]_0 - i_{lim}\kappa_{H^+}, \qquad (4)$$

where $[H^+]_0$ is the concentration of hydrogen ions in the bulk of the solution and κ_{H^+} the Ilkovič constant for hydrogen ions ($\kappa_{H^+} = i_d/[H^+]_0$).

The quantity $[B_S]$ is proportional to the catalyst concentration in solution c_{cat}, but if the catalyst is not adsorbed, and $\sigma \gg 1$, we may write $[B_S] = c_{cat}$. Thus, replacing $[B_S]$ by c_{cat} and inserting into Eqn. (3) the value of $[H^+]_S$ given by Eqn. (4), we find

$$i_{lim} = \frac{k_{H^+} sFac_{cat}}{1 + k_{H^+} sFac_{cat}} \kappa_{H^+}[H^+]_0. \qquad (5)$$

Eqn. (5) predicts, in agreement with experiment, a variation of catalytic limiting current with catalyst concentration of the same general form as the Langmuir adsorption isotherm: the reader can easily check that, as c_{cat} increases, the height of the catalytic wave tends towards a limit given by $\kappa_{H^+}[H^+]_0$, *i.e.* towards the diffusion current of hydrogen ions in the given solution.

The influence of the rate of reaction (III) on the height of the catalytic wave becomes appreciable at very low catalyst concentrations. Assuming that reaction (III) occurs only in the bulk reaction layer μ_d, in the limiting case, when the process is wholly determined by the rate of the

bimolecular reaction, the height of the catalytic wave can be expressed (after Brdička and Wiesner[52,53]) as

$$i_{\lim} = sFk_d \mu_d [BH]_s^2, \quad (6)$$

where k_d is the rate constant of the bimolecular reaction (III). The thickness of the reaction layer μ_d is given[54], for a bimolecular reaction, by

$$\mu_d = \sqrt{D/k_d[BH]_s}, \quad (7)$$

whence

$$i_{\lim} = sFk_d^{1/2} D^{1/2} [BH]_s^{3/2}, \quad (8)$$

where D is the diffusion coefficient of the catalyst.

Under conditions where the catalytic current is limited by the rate of the bimolecular reaction (III), $[BH]_s$ is proportional to c_{cat}, and Eqn. (8) requires that $i_{\lim}$ should vary with the 3/2 power of catalyst concentration. This behaviour is observed experimentally at very low values of c_{cat} (Fig. 2). The rate of process (III) increases rapidly with c_{cat}, and soon ceases to be the only rate-determining step. Under these conditions the limiting catalytic current departs from Eqn. (8).

The method of Brdička and Wiesner cannot give a general expression for the limiting catalytic current over a wide range of catalyst concentrations. Yet, it has been successfully applied[55] to particular catalytic hydrogen waves. Koutecký[51] has given a general solution of the problem, based on his so-called "exact" method, for the bulk chemical reactions (I) and (III) and the reversible electrochemical step (II).

The conclusions, and the experimental results, given above are only an illustration of the suggested mechanism of formation of the catalytic wave, and apply only to some of the simpler systems. In general, catalytic hydrogen evolution is a more complicated process, involving adsorbed catalyst species. It is powerfully affected by the structure of the electrical double layer at the electrode surface, and therefore also by the composition of the solution. Nevertheless, all the experimental data so far available on catalytic hydrogen evolution and the influence of various factors on this process can be satisfactorily explained on the basis of the suggested mechanism for the catalytic wave (*cf.* Mairanovskii *et al.*[56]).

II. BULK CATALYTIC HYDROGEN WAVES WITH A REVERSIBLE ELECTROCHEMICAL STEP IN BUFFERED SOLUTIONS

1. Reversible Catalytic Hydrogen Waves

Catalytic hydrogen waves in which the electrochemical step (II) is reversible were first observed[27,57] in pyridine solutions.

Reversibility of the electrochemical step during discharge of pyridinium ions was postulated[27] by analogy with the discharge of *N*-alkylpyridinium cations, which has repeatedly been shown[48,49,58] to be a reversible process, and later confirmed by the observation of a reaction pseudocapacity in impedance measurements[59] on a mercury electrode in pyridine solutions.

Electron transfer appears to proceed reversibly also in electrochemical processes involving other substances with an 'onium' structure, such as quaternary ammonium salts[60].

2. Bulk Nature of Catalytic Waves in Pyridine Solutions

When catalytic waves are limited by the rate of the preceding chemical reaction (I), the latter can occur either in the bulk of the solution adjacent to the electrode surface or at the surface itself, in which case adsorbed substances are involved. The waves can therefore be classified[31,61,62] into bulk, surface, and mixed waves, the third type referring to systems for which the bulk reaction and the surface reaction have comparable rates. The surface component of the kinetic current can become comparable with the bulk component at a surface coverage (by adsorbed catalyst in its electrochemically inactive form, B) as low as a few tenths of 1%. Since many of the compounds giving rise to catalytic hydrogen evolution are markedly surface-active, most catalytic waves are definitely of the surface type.

Waves in pyridine solutions are among the very few exceptions. Studies of their $i-t$ curves have shown, however, that catalytic pyridine waves associated exclusively with bulk effects can only be obtained[63,64] in the presence of a concentration of an indifferent electrolyte (greater than 0.2 *M* in the case of potassium salts[63]) high enough to inhibit the adsorption of pyridine. Very short drop times are also needed: they can be achieved by using a wiper to assist drop detachment.

3. Equations for Reversible Bulk Catalytic Hydrogen Waves in Buffered Solutions

We shall now apply the concept of a reaction layer to the commonest type of catalytic wave, in which the limiting current is determined only by the rate of the preliminary protonation reaction (I), and the rate of the subsequent bimolecular reaction (III) has no effect. If the preliminary reaction (I) takes place in the bulk, the thickness of the reaction layer is given by

$$\mu = \sqrt{D/\rho\sigma}, \quad (9)$$

where D is the appropriate diffusion coefficient.

The height of the catalytic wave is determined by the number of BH^+ species appearing per unit time in a layer of thickness μ:

$$i_{\lim} = sF\mu [B]_s \rho. \quad (10)$$

Making the frequently justified assumption that $\sigma \gg 1$, *i.e.* that the catalyst exists in solution mainly in its basic, unprotonated form, and that complete catalyst regeneration can rapidly set up a steady state at the electrode, we equate $[B]_s$ to the total analytical concentration of catalyst in solution c_{cat}. Using Eqn. (9), we obtain

$$i_{\lim} = sFc_{cat} D^{1/2} \rho^{1/2} / \sigma^{1/2}. \quad (11)$$

We now write an Ilkovič equation for the hypothetical difffusion current corresponding to normal, diffusion-limited discharge of the catalyst with $n = 1$:

$$i_d = 1.235\, sFc_{cat} D^{1/2} t^{1/2}, \quad (12)$$

where t is the drop time of the electrode. Then[55]

$$\frac{i_{\lim}}{i_d} = 0.81 \sqrt{\frac{\rho t}{\sigma}}. \quad (13)$$

Eqn. (13) readily leads, on the basis of experimental values of $i_{\lim}$, to the overall rate constant ρ for the protonation reaction, defined by Eqn. (1). An expression almost identical to Eqn. (13) has also been derived by an exact solution

of the depolarisation problem under the present set of conditions [*cf.* Eqn. (49) of Koutecký *et al.* [51]].

If the limiting current of the catalytic wave is significantly affected also by the rate of the subsequent reaction, the exact solution[51] gives the following expression for ρ:

$$\rho = \frac{(i_{lim}/i_d)^2 \sigma}{0.81^2 t \left\{1 - \left[\frac{3}{2} \times \frac{(i_{lim}/i_d)^2}{0.81^2 k_d c_{cat} t}\right]^{1/4}\right\}^2} \quad (14)$$

This expression tends towards Eqn. (13) as the rate of the bimolecular interaction of the electrode products increases, *i.e.* when c_{cat} or k_d increases. An expression similar to Eqn. (14) can also be deduced from the reaction layer concept [Eqn. (30) of Hanuš *et al.* [55]: this differs from Eqn. (14) only by the numerical coefficient 3/2 within the square bracket.

When the limiting catalytic current is determined by the bimolecular step (III), the exact solution of the depolarisation problem gives an expression for the limiting current [Eqn. (50) of Ref. 51] differing from Eqn. (8) only by a numerical factor of $\sqrt{2/3}$. Thus, the depolarisation problem for catalytic waves of this type can be solved by an exact and by an approximate method, with practically identical results.

The equation for the shape of a reversible, bulk catalytic hydrogen wave, under conditions of rate limitation by the preliminary protonation reaction and with $\sigma \gg 1$, can be derived[27,55] by introducing the values of $[BH^+]_s$ and $[BH]_s$ [*i.e.* the surface concentrations of the components of the redox system (II)] into the Nernst equation:

$$E = e_0 - \frac{RT}{F} \ln \frac{i^{1/3}}{i_{lim} - i}, \quad (15)$$

The characteristic potential ϵ_0, independent of catalyst concentration, corresponds to the point on the wave at which $i^{2/3} = i_{lim} - i$, and is given by

$$e_0 = E_0 - \frac{RT}{3F} \ln \left(\frac{sFD^{1/3} \rho^{1/3} \sigma^{1/3}}{k_d} \right), \quad (16)$$

where E_0 is the redox potential of system (II).

The exact solution of the depolarisation problem[51] gives the following expression for the half-wave potential in the present case:

$$E_{1/2} = E_0 + \frac{RT}{3F} \ln \frac{c_{cat} k_d}{3\sigma^2 \rho}. \quad (17)$$

However, a similar expression for $E_{1/2}$ can also be obtained[27,55] from Eqn. (15), putting $i = \frac{1}{2} i_{lim}$.

4. Experimental Test of the Equations for Reversible Bulk Waves in Buffered Media

The sharpest catalytic waves produced by pyridine and its homologues are observed[26,27,63,65] in borate and veronal buffer solutions (pH 7.5–10). Under these conditions the limiting catalytic current, as required by theory, is proportional to the area of the dropping electrode and independent of the height of the mercury column. The limiting step is protonation of the catalyst. Thus, an increase in the buffer capacity of the solution at constant pH and ionic strength must raise the limiting catalytic current (Fig. 3), since it increases the rate of protonation ρ. Increase in pH, *i.e.* in $\sigma = K_A/[H^+]$, has been found by many experimenters[27,56,65,66] to depress the catalytic wave [see Eqn. (11) or (13)].

In accordance with Eqn. (15), bulk catalytic hydrogen waves with a reversible electrochemical step are found to be asymmetrical. When plotted as E against $\log i^{2/3}/(i_{lim} - i)$, they give straight lines[27] with a reciprocal slope of ~ 59 mV. The $E_{1/2}$ values [see Eqn. (17)] are shifted[27] by about 20 mV in the positive direction by a tenfold increase in c_{cat}.

The half-wave potential of a reversible bulk wave becomes more negative at higher pH values, *i.e.* on increasing σ. As required by theory [see Eqn. (17)], $\Delta E_{1/2}/\Delta pH \simeq$ $\simeq$ -40 mV provided the pH is not too high (Fig. 4). At pH > 8.8, $E_{1/2}$ begins to increase more slowly with σ: this effect, which is associated with the structure of the double layer, is discussed in detail in the following sections.

The influence of the buffer capacity of the solution on the $E_{1/2}$ value of a reversible wave is the most revealing test of the suggested mechanism of the appearance of catalytic waves. A shift in $E_{1/2}$ towards less cathodic potentials is expected, for an increase in buffer capacity, in most systems where the rate is limited by preliminary protonation. This effect has been observed, for example, in the reduction of nitro-compounds in acidic media[67]. The theory of catalytic waves developed by Knobloch[14] and by von Stackelberg and Nürnberg[19] also requires a positive shift in $E_{1/2}$ with increase in buffer capacity. However, and in qualitative agreement with Eqn. (17), Fig. 5 shows that the $E_{1/2}$ value of reversible catalytic waves becomes about 20 mV more negative for a tenfold increase in ρ (*i.e.* when the buffer capacity of the solution is increased).

When pyridine is used as a catalyst, a clearly defined limiting catalytic current due to the bimolecular reaction (III) cannot be obtained[26]. This practical complication arises from the formation, below pH 7.0, of appreciable quantities of a catalytically active pyridine polymer[64]. Nevertheless, the catalytic pyridine wave has been studied down to pH 6.0 (acetate buffer), and it has been shown that under these conditions the current is mainly limited by the bimolecular reaction[26,66]. An approximate value for the rate constant of this reaction has also been obtained (5×10^8 litre mole^{-1} sec^{-1} at 25°).

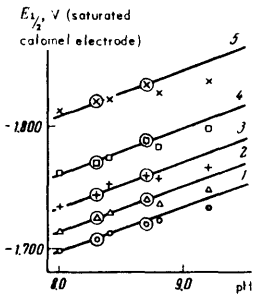


Fig. 4. Variation of $E_{1/2}$ of the catalytic wave with solution pH at catalyst concentration ~0.5×10^{-3} M and $\rho \simeq 1500$ sec^{-1}. Catalyst: 1) pyridine; 2) 3-picoline; 3) 2-picoline; 4) 2,6-lutidine; 5) 4-picoline. Single points — borate buffer solutions; circled points — veronal solutions.

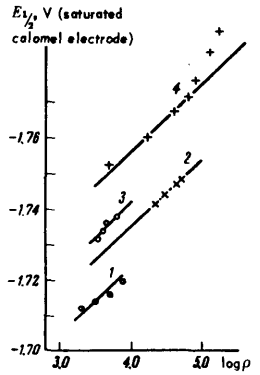


Fig. 5. Variation of $E_{1/2}$ of the catalytic wave in pyridine solutions with measured value of ρ: 1) veronal buffer, pH 8.3; 3) borate buffer, pH 9.0; 2) and 4) ammoniacal solutions of pH 9.0 and 9.5.

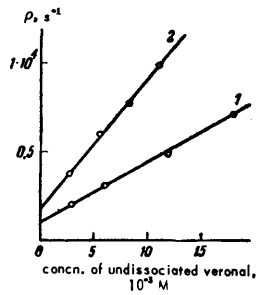


Fig. 6. Variation of ρ with concentration of undissociated veronal: 1) pH 8.30; 2) pH 8.70.

Limitation of a reversible catalytic wave by the rate of bimolecular regeneration can be demonstrated rather more clearly by using[26] the waves of 2,6-lutidine.

5. Evaluation of the Rate Constants for Catalyst Protonation. Influence of Double Layer Structure on Protonation in the Bulk Reaction Specie.

The value of ρ — the rate constant for catalyst protonation in the given solution — can be calculated from the limiting current of bulk catalytic waves by applying Eqn. (14). The hypothetical diffusion current i_d of the catalyst is calculated from the Ilkovič equation (assuming $n = 1$) or assumed equal to the diffusion current for the discharge of a compound having similar structure.

The value $k_d = 5 \times 10^8$ litre mole^{-1} sec^{-1} has been adopted[56,66] in calculations relating to pyridine waves. Its precision is quite low, but since the expression in braces in the denominator of Eqn. (14) is very close to unity, even large fluctuations in the value of k_d have little effect on the value of ρ.

The individual rate constants for catalyst protonation by different acids can be derived from the variation of ρ with the concentration of the appropriate proton donor, keeping the concentration of any other proton donors constant. Fig. 6, for example, shows the variation of ρ with the concentration of undissociated veronal, one of the components of the buffer mixture, at constant pH and ionic strength. The slope of the linear plots of ρ against the concentration of the acid component gives directly the rate constant for catalyst protonation under the influence of this particular proton donor. The individual rate constants for catalyst protonation determined in this way are found to increase with pH. The observed increase in rate constant is only apparent, however, and arises from the increasing effect of double layer structure at high solution pH[56].

The structure of the electrical double layer has an effect on the distribution of ions and on the rate of their migration in the layer of solution adjacent to the electrode[68-70]. Grabowski and Bartel[71] were the first to consider the influence of double layer structure on the preliminary protonation reaction, but the problem was later discussed in a more general way by a number of other workers[72-74].

If the reaction layer is much thicker than the diffuse part of the double layer, the effect of the double layer on the mean ionic concentrations within the reaction layer can be neglected. As the reaction layer shrinks, an increasing fraction of its thickness is occupied by the diffuse part of the double layer, and the influence of the double layer becomes more significant. With bulk catalytic currents the thickness of the reaction region decreases when the pH increases [*i.e.* when σ increases, see Eqn. (9)], and the effect of double layer structure becomes correspondingly greater. It has been shown[31,62,75] that the effect of the field surrounding the electrode is to lower the pH of the solution close to the cathode well below its bulk value. This explains the apparent increase in rate constant upon decreasing the thickness of the reaction layer.

On varying the solution pH at constant ionic strength, only the thickness μ of the reaction layer is altered, the effective thickness of the diffuse part of the double layer remaining constant. The relative thickness of the two layers can also be varied by altering only the thickness of the diffuse part of the double layer whilst keeping μ constant: this is done by varying the ionic strength of the solution at constant pH and buffer capacity. Calculation shows that the decrease in height of the catalytic pyridine wave observed[31] on increasing the ionic strength of the solution corresponds exactly to the change in the effect of double layer structure[76].

To find the true rate constants for catalyst protonation, free from errors due to electrode field effects, the experimentally observed values must be extrapolated to the region of very high μ, *i.e.* very low pH, where the effect of double layer structure is undetectable. The experimental, "apparent" values of individual protonation constants $k'_A = \Delta\rho/\Delta[DH^+]_A$ are found, by plots such as those of Fig. 6, to vary linearly with the reciprocal of hydrogen ion concentration[56,65,66]. The true protonation rate constants k_A are found by plotting k'_A against $1/[H^+]$ and extrapolating to $1/[H^+] \to 0$, as in Fig. 7 (taken from Ref. 56). The intercepts of the straight lines on the vertical axis gave the following true rate constants for pyridine[56,66]: $k_{H_3BO_3} = 9.0 \times 10^3$ and $k_{veronal} = 1.2 \times 10^5$ litre mole^{-1} sec^{-1}.

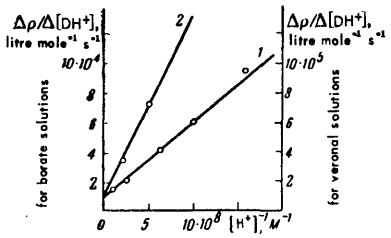


Fig. 7. Effect of $1/[H^+]$ on the observed individual rate constants for the reaction of pyridine with H_3BO_3 (curve 1) and veronal (curve 2).

The y-intercepts of linear plots of the type shown in Fig. 6 give the "apparent" values ρ_0', *i.e.* the sum of the rate constants for protonation under the influence of water and of hydrogen ions. To find the true ρ_0 values, free from errors due to double layer effects, ρ_0' must be divided by the ratio k_A'/k_A for the given solution. The rate constants for the protonation of pyridine by hydrogen ions ($k_{H^+} \simeq 2.5 \times 10^{10}$ litre mole^{-1} sec^{-1}) and by water ($k_{H_2O} \simeq$ $\simeq$ 7 litre mole^{-1} sec^{-1}) have been evaluated[56] from the variation of the corrected ρ_0 values with $[H^+]$.

The rate constant for the protonation of pyridine by different donors increases with the acid strength of the proton donors. As with other protolytic reactions, the individual protonation rate constants of pyridine are related to the dissocation constants of the acids K_A by the Brønsted expression (see, for example, Ref. 77)

$$k_A = p\,Q\left(\frac{q}{p}K_A\right)^{\alpha}; \qquad (18)$$

where Q and α are constants, and p and q are the so-called static factors, giving respectively the number of protons which can be removed from different atoms of the given acid or added to different atoms of its conjugate base. The value of α for the protonation of pyridine at 25° in a solution of ionic strength 0.5 has been found[66] to be 0.58

6. Effect of Temperature on Bulk Catalytic Waves in Buffered Solutions

The height of bulk catalytic hydrogen waves increases with temperature. The individual rate constants for the protonation of pyridine were evaluated[66], at various temperatures, from the variation of the limiting current with concentration of the acid component, and corrected for the effect of the double layer. When plotted against the reciprocal of temperature, these data afforded[66] the activation energies for the reactions between pyridine and boric acid (5.1 kcal mole^{-1}), veronal (6.4 kcal mole^{-1}), hydronium ions (~ 2.4 kcal mole^{-1}), and water (~ 6 kcal mole^{-1}).

The linear Brønsted plots [Eqn. (18)] for the protonation of pyridine, at different temperatures, all have the same slope, within experimental error, and are only slightly displaced parallel to one another[66].

7. Effect of Stirring on Catalytic Hydrogen Waves under Conditions of Polarographic Maxima of the Second Kind

The turbulence caused by the tangential motion of the surface of a dropping mercury electrode at relatively high drop rates can distort the diffusion layer, leading to an increase in the observed polarographic diffusion current. This phenomenon has been studied in detail by Frumkin and his coworkers[68], and has been termed a polarographic maximum of the second kind[78,79].

Stirring, under conditions of a maximum of the second kind, often increases the catalytic current[80] of bulk catalytic waves in pyridine solutions. The effect of stirring depends on the thickness of the reaction layer μ, reaching a maximum of almost twice the diffusion current at $\mu \simeq 100$ Å. Stirring effects are absent when the rate-limiting reaction occurs in a very thin layer (< 20 Å) or at the electrode surface itself (adsorbed reactants). In these circumstances the reaction layer is entirely within the interfacial layer of solution, which does not move with respect to the electrode.

III. REVERSIBLE BULK CATALYTIC HYDROGEN WAVES IN UNBUFFERED SOLUTIONS

In a neutral or alkaline unbuffered solution water is practically the only proton donor DH^+, with hydroxide ions as the conjugate base D, so that

$$\rho = k_1[H_2O] \text{ and } \rho\sigma = k_2[OH^-]_s. \qquad (19)$$

It follows from our mechanism of the process that each catalytic cycle of reactions (I–III) produces one OH^- ion. Using the Ilkovič equation to calculate their rate of removal from the electrode, and noting that $[OH^-]_S \gg [OH^-]_0$ when neutral or weakly alkaline solutions are electrolysed, we find

$$[OH^-]_s = i/\kappa_{OH^-}, \qquad (20)$$

where κ_{OH} is the Ilkovič constant for OH^- ions. The thickness of the reaction layer for the protolytic reaction (I) is determined, in this case, by the rate at which hydroxide ions can react with the active form of the catalyst BH^+. Hence, if μ is so small that the concentration of OH^- can be assumed constant throughout the reaction layer, the following expression for μ will apply:

$$\mu = (D/k_2[OH^-]_s)^{1/3} = (D\kappa_{OH^-}/k_2 i)^{1/3}, \qquad (21)$$

where D is the diffusion coefficient of the catalyst.

The limiting current can be found[57] by combining Eqns. (10) and (21) with Eqn. (19), and noting that $[B]_S = c_{cat}$:

$$i_{lim} = (Qc_{cat})^{2/3}, \qquad (22)$$

where

$$Q = k_1 sF[H_2O]D^{1/3}\kappa_{OH^-}^{1/3}/k_2^{1/3}. \qquad (23)$$

We see from Eqn. (22) that in unbuffered solutions the height of the catalytic wave should vary with the 2/3 power of catalyst concentration: this agrees well with experiment[63] (see Fig. 8).

An equation for the wave can be obtained by introducing the values of $[BH^+]$ and $[BH]_S$ into the Nernst equation:

$$E = \varepsilon_0^{\circ} - \frac{RT}{F}\ln\frac{i^{2/3}}{i_{lim}^{2/3} - i^{2/3}}, \qquad (24)$$

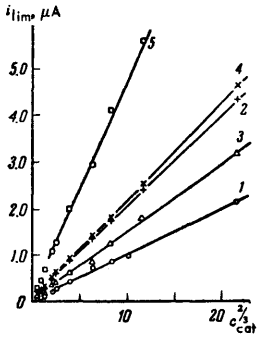


Fig. 8. Variation of limiting catalytic current with the 2/3 power of catalyst concentration (in 10^{-3} mole litre^{-1}) for waves in unbuffered solutions: 1) pyridine; 2) 2-picoline; 3) 3-picoline; 4) 4-picoline; 5) 2,6-lutidine.

which can be rewritten in the form

$$e_0^{\cdot} = E_0 + \frac{RT}{F} \ln \frac{k_d^{1/6} K_{OH^-}^{1/3}}{k_g^{1/6} (SF)^{1/6} D^{1/6}} + 59 \text{ mV}, \qquad (25)$$

if the current in Eqn. (24) is expressed in μA.

Fig. 9 shows the variation of the function

$$\log \frac{i^{5/3}}{i_{lim}^{3/2} - i^{3/2}},$$

with potential for catalytic waves produced at catalyst concentrations of the order of 2.4×10^{-2} M (the results for pyridine waves are reported at several values of c_{cat}). The upper part of the polarograms (above some current value which overcomes the small but finite buffer capacity of the KCl solutions due to traces of dissolved CO_2 and other impurities) is satisfactorily described by Eqn. (24), as

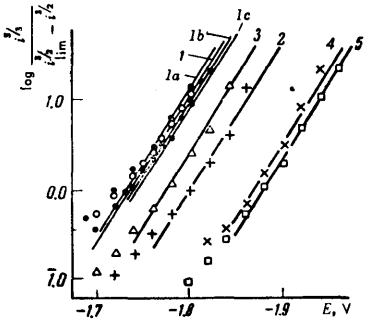


Fig. 9. Variation of $\log i^{5/3}/(i_{lim}^{3/2} - i^{3/2})$ with E for catalytic hydrogen waves with a base electrolyte of 0.5 M KCl in 24×10^{-3} M solutions of: 1) pyridine; 2) 2-picoline; 3) 3-picoline; 4) 4-picoline; 5) 2,6-lutidine. Curves 1*a*, 1*b*, and 1*c* correspond to pyridine concentrations of 16, 40, and 100 10^{-3} M.

shown by the fit of the experimental points on the straight lines calculated from this equation (Fig. 9). The function of current which appears in Eqn. (24) should be described by a single straight line, irrespective of catalyst concentration, for waves produced by a given catalyst. However, the results for different concentrations of pyridine (Fig. 9) show a slight shift towards negative potentials with increasing pyridine concentration. This may be due to an increase in pH in the bulk of the solution, caused by increasing the catalyst concentration, of which no account was taken in deriving the equations.

IV. SURFACE CATALYTIC HYDROGEN WAVES

1. Fundamental Relations

In catalytic waves purely of the "surface" type the catalyst undergoes the protonation reaction at the electrode surface whilst in the adsorbed state[61,81,82].

The surface catalytic current is proportional to the amount of catalyst adsorbed. Hence we can write, from the general mechanism of formation of catalytic waves limited by the rate of protonation,

$$i = sF(\rho_{surf}\Gamma - \rho_{surf}^{o}\Gamma'), \qquad (26)$$

whilst the limiting current is given by

$$i_{lim} = sF\rho_{surf}\Gamma, \qquad (27)$$

where Γ and Γ' are the amounts of adsorbed base (B) and acid (BH^+) respectively. Surface catalytic currents are found in practice[83] to have an irreversible electrochemical step. Therefore, the current should be calculable from the following formula, taken from the slow-discharge theory[68]:

$$i = sk_{el}\Gamma' e^{-\frac{\alpha FE}{RT}}. \qquad (28)$$

If the adsorption of the catalyst were independent of electrode potential, and equal to the value Γ^0 which corresponds to the potential of maximum adsorption E_{max}, the catalytic wave would be described [on the basis of Eqns. (26)–(28)] by the expression

$$E = E_{1/2} - \frac{RT}{\alpha F} \ln \frac{i^0}{i_{lim}^0 - i^0}, \qquad (29)$$

where the superscript zero denotes adsorption at E_{max}.

We shall suppose that the adsorption of the catalyst obeys the Langmuir isotherm

$$\Gamma_e = \Gamma_\infty \frac{\beta c_{cat}}{1 + \beta c_{cat}}, \qquad (30)$$

where Γ_e and Γ_∞ are the equilibrium and the maximum adsorption respectively, and β is the adsorption index. Adsorption equilibrium is not usually established during the lifetime of a drop[84], and we must write, for time t after the onset of drop formation,

$$\Gamma = y\Gamma_e. \qquad (31)$$

The extent of approach towards equilibrium (y) depends on the adsorption time, on the rate of supply of material to the electrode, and on the value of β.[84,85] Far from equilibrium, *i.e.* when $y \ll 1$, y varies approximately with the square root of the adsorption time[85]:

$$y \simeq kt^{1/6}. \qquad (32)$$

Using the results of an accurate calculation[84] on the rate of diffusion-limited adsorption on a dropping electrode, it can be shown (as in Fig. 10) that at constant c_{cat} and t the quantity y increases with β according to the equation[81]

$$y = 1 + \beta c_{cat} \quad (y \leqslant 0.55). \tag{33}$$

According to Frumkin[86], adsorption at an electrode decreases in the following manner as the potential changes from that for maximum adsorption:

$$\beta = \beta^0 e^{-\frac{1/2(C-C')}{RT\Gamma_\infty}\varphi^2} = \beta^0 e^{-a\varphi^2}, \tag{34}$$

where φ is the potential relative to E_{max} (*i.e.* $\varphi = E - E_{max}$), C and C' are the values of the double layer capacity of the electrode at zero coverage and at full coverage of the electrode by the surface-active substance.

Gouy and Butler, working with organic bases in neutral and in acid solutions, [87-89] have shown that the basic form of the catalyst has a significantly higher surface activity on mercury than the acidic form. Furthermore, the adsorbability at the cathode of the cationic form varies much less with potential than does that of the uncharged basic form[87]. Thus, the change in adsorption of the catalyst is largely determined by the change in adsorption of the basic form, particularly when equilibrium (I) lies far over to the left, even though the extent of adsorption depends also on the relative amounts of the two forms (*i.e.* on the pH).

Because of the decrease in adsorbability of the catalyst at more cathodic potentials, the observed catalytic current is smaller than i^0: $i/i^0 = \Gamma/\Gamma^0$, or, using Eqns. (30) and (31),

$$\frac{i}{i^0} = \frac{\mu\beta}{1+\beta c_{cat}} : \frac{\mu^0\beta^0}{1+\beta^0 c_{cat}}. \tag{35}$$

Introducing Eqns. (33) and (34), and confining ourselves to values of $y < 0.55$ (a condition nearly always satisfied at a dropping electrode in normal circumstances), we find

$$\frac{i}{i^0} = \frac{\beta}{\beta^0} = e^{-a\varphi^2}. \tag{36}$$

The characteristic, humpbacked curves given by surface catalytic hydrogen waves[81] can be described by combining Eqns. (29) and (36). The appearance of the hump on surface waves is illustrated in Fig. 11: the maximum

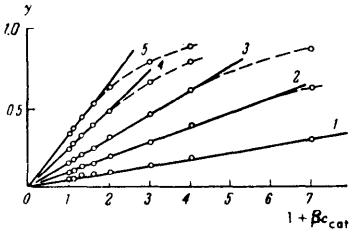


Fig. 10. Variation of y with $1 + \beta c_{cat}$ for different adsorption times on a dropping electrode (after Delahay and Fike[84]):
1) 0.2; 2) 0.5; 3) 1.0; 4) 2.0; 5) 4.0 s.

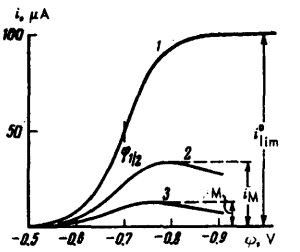


Fig. 11. Demonstration of the formation of humpbacked surface catalytic waves:
1) no allowance for change in adsorption with potential, Eqn. (29); 2) and 3) change in adsorption allowed for by putting a = 1.63 V^{-2} and a = = 3.27 V^{-2}, respectively, in Eqn. (36).

height i_M of the wave differs from the limiting current, but since i_M is, in most cases, proportional to i^0_{lim}, the former quantity, which is directly measurable, can be used for analytical purposes.

2. Experimental Test of the Equations for Surface Waves

The correctness of the above equations has been demonstrated[81] for the concrete case of the surface catalytic waves produced by anabasine and by quinine.

The surface catalytic wave, like all waves in which the rate of preliminary protonation is rate-determining, increases with the buffer capacity of the solution. The variation of the catalytic current in anabasine solutions with the concentration of undissociated acetic acid has been used[81] to calculate the rate constant for protonation of adsorbed anabasine under the influence of CH_3COOH: the value obtained was 2.9×10^5 litre $mole^{-1}$ sec^{-1} at a potential of -1.84 V relative to the saturated calomel electrode.

Polarisation of the adsorbed species by the electric field surrounding the electrode probably can affect[71] the rate constants for surface reactions.

Surface waves often show an interesting and unusual variation with h, the height of the mercury column above the dropping electrode. Whereas the limiting diffusion currents and the heights of the preliminary adsorption waves decrease with decrease in h, whilst bulk kinetic and catalytic currents are independent of h, it is frequently found[31] that waves limited by preliminary surface reactions increase as h decreases. This phenomenon is observed when adsorption equilibrium is not reached: under these conditions longer drop times (*i.e.* adsorption times) enable adsorption equilibrium to be approached more closely, and therefore raise the value of Γ.

The surface component of the kinetic current density often varies with time as required by Eqn. (32). This was demonstrated by analysing the second wave of the polarograms of maleic acid[90]. Vojíř[91,92] has reported an increase in the catalytic waves upon lowering the mercury reservoir.

Other workers[93,94] have observed similar effects for currents due to complexes of cobalt with amino-acids and proteins. Von Stackelberg and Fassbender[17] plotted $i-t$ curves during the lifetime of a single drop, and showed that the catalytic current is given by the approximate relation $i \simeq t^{\nu}$, where the value of ν is greater than unity in the presence of a high-molecular-weight catalyst. Inspection of their Fig. 2 suggests that ν can reach the value of $\sim 7/6$, which is accounted for by the combined effects of increase in electrode area (2/3) and increase in the amount of catalyst adsorbed [1/2, see Eqn. (32)].

Surface catalytic waves, like surface kinetic waves[90], are often practically unaffected by changes in temperature[50], since an increase in the protonation rate constant of the catalyst can be compensated by decreased adsorption of the catalyst on the electrode surface[31].

It is well known that addition of surface active compounds (SAC) to the polarographic solution can often cause a drastic decrease in the catalytic wave (see, for example, Knobloch[15] and Mairanovskii[61]). The effect is due to displacement of the catalyst from the electrode surface by the added SAC. The extent to which the SAC suppresses the catalytic wave depends, as expected, on the ratio of the SAC and catalyst concentrations and on their relative adsorbabilities.

If desorption of the SAC occurs before that of the catalyst and the desorption potential of the SAC is in the range of catalytic hydrogen evolution, the polarograms show a sharp increase in catalytic current coinciding with desorption of the SAC[95,96], which can be mistaken for a new wave. This is reminiscent of the formation of spurious reduction waves upon desorption of an SAC able to inhibit the electrode process[97] or to suppress the tangential flow of the mercury.

3. Mixed Bulk and Surface Catalytic Waves

All catalytic currents observed in practice must be the sum of a surface term and a bulk term: systems in which either of the two components can be neglected are extremely rare.

The surface component of the current increases as the ionic strength of the solution decreases[98] and becomes predominant in solutions containing only non-adsorbable cations[99,100] such as lithium ions[101].

The bulk and the surface components of the current usually give one common wave on the polarogram, even when two separate waves could have been expected. The large increase in concentration (at the electrode) of irreversibly discharged species, resulting from adsorption of these species, sometimes gives rise[102,103] to additional polarographic waves corresponding to discharge of the strongly adsorbed species. The non-adsorbed species (or, more accurately, those whose adsorption is weaker or energetically less favourable) are discharged at more negative potentials. Thus, the surface catalytic wave should be shifted towards potentials less cathodic than that of the bulk wave by the sharp increase in catalyst concentration near the electrode accompanying the flow of surface currents. On the other hand, the mode of adsorption of the electrochemically active species (its orientation on the electrode surface, for instance) can influence the rate constant of the purely electrochemical step. Thus, in the polarography of indoleninium salts[104], whose discharge mechanism is in many ways analogous to the transfer of an electron to a protonated catalyst species, the slope of the wave suggests that the irreversibility of the process increases with pH. This can be ascribed to more ready adsorption of the depolariser when in its basic, uncharged form. We may conclude, therefore, that adsorption can significantly alter the rate of the electrode process, and shift the half-wave potential both in the anodic and in the cathodic direction.

Bulk waves in solutions of pyridine and its homologues have a reversible electrochemical step: with surface catalytic waves, on the other hand, no reversible electrochemical process has so far been reported. It is interesting to note, however, that a reversible catalytic hydrogen wave has been obtained[83] by adding a high concentration of a strongly adsorbable compound to quinine solutions. This decreased the total height of the wave approximately 30-fold and made the half-wave potential slightly more positive than $E_{1/2}$ for a surface wave of comparable height. This suggests that the bulk component of the catalytic wave observed in quinine solutions is reversible, and can be detected at potentials less negative than those of the surface wave. It should be possible, therefore, under favourable conditions, to resolve the combined catalytic wave into a bulk and a surface step: the resolution has been achieved with catalytic currents in quinine solutions[61].

The double "hump" observed by von Stackelberg *et al.*[18] on catalytic waves obtained in solutions of the leuco form of Malachite Green and of β-naphthoquinoline may also indicate separation of the current into a bulk and a surface term.

4. Effect of Double Layer Structure on Surface Catalytic Waves

In systems showing surface catalytic hydrogen waves, changes in the structure of the double layer have an effect on the adsorbability of the catalyst, on the pH of the layer of solution adjacent to the electrode, and also (to some extent) on the dissociation constant of adsorbed catalysts. For example, the maximum height of the catalytic wave decreases almost by a factor of three[75], and the potential at the maximum becomes more positive as a result of the increase in double layer capacity [and therefore also in the value of a, Eqn. (36)], following an increase from 0.04 to 0.08 M in the total concentration of sodium ions at constant pH, buffer capacity, and catalyst (quinine) concentration.

The catalytic wave is greatly decreased by changing from solutions containing Li^+ to solutions containing Cs^+ salts[75]. The effects observed on exploring the sequence $Li^+ \rightarrow Cs^+$ include an increase in the superequivalent adsorption of cations at the mercury electrode[99,100], a decrease in the absolute value of the ψ_1 potential, and an increase in the capacity of the double layer [and therefore also in the value of a in Frumkin's Eqn. (34)].

The difference in pH between the bulk of the solution and the layer of solution adjacent to the electrode is a simple function of the ψ_1 potential only in the case of surface waves with preliminary protonation[31,62]. Thus it has been possible, in these systems, to make an almost quantitative allowance for the effect of changes in the concentration of potassium and sodium ions in solution on surface catalytic currents[75].

Some interesting observations by Pungor and Farsang[106-109] have also been explained[105] in terms of the effect of double layer structure. These workers reported that

the catalytic wave of quinine increases at first, and then decreases, when a tetraethylammonium salt is gradually added to the polarographic solution. Pungor and Farsang used phosphate buffer media, where the anions HPO_4^{2-} and $H_2PO_4^-$ are the main proton donors. Hence, low concentrations of the surface-active tetraethylammonium cation make the ψ_1 potential less negative and assist the approach of proton donors (phosphate anions) to the electrode. At higher concentrations, however, tetraethylammonium begins to displace the quinine from the electrode surface and lowers the catalytic current. Surface-active cations have a very similar effect on the surface recombination wave of anions[82,110,111].

5. Effect of Organic Solvents

Addition of organic solvents to catalytically active solutions lowers the catalytic currents[15,16,112-115].

Organic solvents, by suppressing the dissociation of proton-donor acids, raise the pH of the solution[116,117], lower the dissociation constant of the catalyst[112,116], and therefore cause σ to increase more relative to the change in pH. They also decrease the adsorbability of the catalyst very significantly — a very important effect with surface waves.

V. CATALYTIC WAVES DUE TO SULPHUR COMPOUNDS

1. Mechanism of the Process

Many organic compounds containing mercapto-groups show a marked tendency to give catalytic hydrogen waves, particularly in the presence of cobalt or nickel salts. Despite the many studies of catalytic waves in solutions of sulphur compounds (see, for example, the review articles listed in Refs. 5, 8, 9, 10, and the more recent experimental work[18,94-96,118-125]), some aspects of the mechanism of this process are still far from clear.

Brdička suggested[9,22] that hydrogen, being very mobile in the SH group, can be easily split off by the electrochemical reaction

$$RSH + e^- \rightarrow RS^- + H, \qquad (IV)$$

the resulting RS^- anions undergoing rapid protonation by the proton donors present in solution to regenerate the electrochemically active form RSH. A convincing argument in favour of this scheme was supplied by Brdička himself[9,126], who showed that the catalytic activity of thiols can be suppressed by adding salts of iodoacetic acid to the solution, the acid residue attaching itself to the sulphur in place of the labile hydrogen atom.

Mairanovskii and Neiman[127] found, in their study of the reduction of sulphones at a dropping electrode, that the reduction product (by a four-electron reaction) of *pp'*-dichlorodiphenylsulphone — probably *pp'*-dichlorodiphenyl sulphide — gives a catalytic wave despite the absence of an SH group. The authors conclude[127] that the catalytic wave of a sulphur-containing catalyst is formed by the same mechanism as the wave of a nitrogeneous base: the species undergoing discharge is a sulphonium ion, formed by protonation of the sulphide. Catalytic hydrogen evolution has been repeatedly observed with compounds containing sulphur as disubstituted sulphide (*e.g.* in solutions of ethylenebisthioglycollic acid[18] $HOOCCH_2SCH_2CH_2SCH_2COOH$ and also with the sulphides produced by two-electron electrolytic reduction of trisubstituted sulphonium ions[45]). The mechanism involving discharge of a sulphonium cation seems the more likely (see Frumkin and Andreeva[28]) from the point of view of electrical double layer effects. Considerations of double layer structure can also explain the suppression of catalytic activity resulting from interaction between the catalyst and iodoacetate ions: the product, being negatively charged, is prevented from reacting at the cathode.

The catalytic activity of cysteine is largely retained when its thiol hydrogen is replaced by a mercuribenzoate residue[21]:

$$RSH + ClHgC_6H_4COOH \rightarrow RSHgC_6H_4COOH.$$

This observation supports the sulphonium mechanism for the catalytic wave.

The available experimental data, however, do not justify a final choice between the two mechanisms for the catalysis of the hydrogen discharge process by substances containing mercapto-groups.

The reduction wave of Co^{2+} occurs below the potential of catalysed hydrogen evolution in solutions of sulphur compounds. This has led some workers to suggest[9,12] that the catalytically active centres are formed by adsorption of the organic catalyst on metallic cobalt, deposited on the mercury surface. Březina[128] refuted this view by showing that preliminary electrolysis of the solution with a static mercury cathode at a potential sufficient to discharge Co^{2+} does not give rise to catalytic hydrogen evolution: the accumulation of metallic cobalt in the electrode had no effect on subsequently measured polarographic waves. Hence, the catalyst is a complex involving cobalt ions and the organic compound.

We may assume that cobalt ions can form several complexes, of different composition[9], with any given thiol. Some of these will be so stable as not to participate in the electrochemical cobalt deposition reaction and will only take part in the catalytic hydrogen evolution. Stable Co^{2+} complexes, not decomposed at the cathode, are formed[129] by ethylenediaminetetraacetic acid, for example. Sunahara's report[121] that the height of the Co^{2+} discharge wave is decreased by adding cysteine to the solution also tends to confirm the formation, to some extent, of a complex between Co^{2+} and cysteine, which cannot be discharged with deposition of metallic cobalt.

Nevertheless, some metal ion discharge from the thiol complex must occur together with the catalytic evolution of hydrogen. This effect becomes noticeable at relatively low concentrations of the complex-forming ion. The shortage of these ions in the neighbourhood of the electrode, aggravated by their partial discharge, can give rise to a situation in which the catalytic current is a function of the diffusion of these ions from the bulk of the solution, and the observed catalytic wave shows some features of diffusion current. Some effects observed in cysteine solutions containing low concentrations of Ni^{2+} can be explained in this way[132]. The Ni^{2+} bound in catalytically active complexes is discharged relatively slowly, and the complex is therefore able to take part in the catalytic process several times before the Ni^{2+} is discharged. Hence, the catalytic current is several times larger than the diffusion current of Ni^{2+} ions[132]. The discharge of metal from the complex has recently been demonstrated[136] with the help of radioactive cobalt ions.

The increase in the catalytic activity of thiols resulting from complex formation with Co^{2+} is probably due to the gain of two charges by the catalyst, which must considerably assist electron transfer to such species.

Co^{2+} and Ni^{2+} ions increase the catalytic activity of pyridine[133] as well as that of sulphur compounds.

Organic compounds containing sulphur show a high surface activity at the mercury–solution interface. Their catalytic waves are definitely of the "surface" types, and are described by the equations for surface waves[81]. Sunahara[122] examined the waves produced by cystine and by some of its derivatives with blocked amino- (*NN*-diacetylcystine) or carboxy- (cystine diethyl ester) groups, and showed that blocking of the amino-groups leads to total loss of catalytic activity, whereas esterification has practically no effect on the catalytic wave. Thus, we may assume that the catalytic action of catalysts containing both amino- and mercapto-groups is mainly associated with the amino--groups, whereas the SH groups are primarily responsible for the adsorbability of the catalyst. This hypothesis accounts for Ivanov's observation[130] of a parallelism between the effectiveness of a catalyst as a maximum suppressor (*i.e.* its adsorbability) and the height of the catalytic wave at equal analytical concentrations. The adsorbability of catalysts, which determines the limiting catalytic current under otherwise identical conditions, increases with the size of the molecule and with the number of SH groups, whereas the number of amino-groups per unit weight of catalysts of similar structure is almost independent of the size of the catalyst molecule. This explains the rough proportionality, reported by Ito[131], between the increase in catalytic activity and the increase in the number of cysteine residues in the molecule of protein catalysts.

It is interesting to note that the normal falling off of catalytic waves in albumin solutions can be avoided by greatly increasing the concentration of albumin at constant concentration of buffer solution and cobalt ions (see, for example, Figs. 3 and 4 on pp. 115 and 117 of Brdička's article[3], and Basinski *et al.*[132]). It follows that under these conditions the rate of formation of the catalytically active complex is no longer determined by the concentration of the protein, and that protein desorption at more cathodic potentials does not cause a decrease in catalytic current.

2. The Splitting of Albumin Waves

Catalytic waves in albumin solutions containing cobalt ions, unlike the waves produced by many amino-acids, often have a characteristic "double hump" shape. A study[93] of this splitting of catalytic waves led to the suggestion that two catalysts, of different catalytic and adsorption properties, must be present in solution.

Numerous observations indicate that the catalyst responsible for the first albumin wave is the less adsorbable. Thus, addition of a surface-active substance such as gelatine decreases the height of the first step, but leaves the second step almost unchanged (see, for example, Fig. 4 of Marha's paper[134]). The smaller temperature coefficient of the first wave[135] also points to the same conclusion (on the assumption that the chemical reactions which determine the height of the two waves have similar activation energies).

Addition of ethylenediaminetetraacetic acid (EDTA) to Brdička's solution initially decreases the second wave (see Fig. 4 of Ref. 129). This is obviously due to the sequestering effect of EDTA, which lowers the concentration of Co^{2+} ions in solution, but it involves the further assumption that the Co^{2+} ions are more firmly bound to the protein in the catalyst responsible for the first wave than in the second catalyst.

If the solution contains a complexing agent with which cobalt can form a more stable complex than it can with the second catalyst (but less stable than with the first), the polarograms should retain only the first albumin wave. Ito[131] has observed this phenomenon by working with a solution of tris(ethylenediamine)cobalt.

Various chemical effects which influence the height of albumin waves, such as the effects of higher fatty acids[134] or of formaldehyde[137], can be explained in terms of blocking of catalytically active centres or of interaction with groups involved in complex formation, or alternatively by postulating a change in the adsorbability of the catalyst.

VI. CATALYTIC HYDROGEN WAVES AND THE STRUCTURE OF ORGANIC CATALYSTS

1. General Remarks

Knobloch[14] was the first to point out that the decrease in hydrogen overvoltage at a dropping mercury electrode caused by a series of heterocyclic catalysts increases in proportion to the acidity of the catalyst. Data for different classes of organic catalysts, obtained by von Stackelberg *et al.*[18], show that catalytic hydrogen evolution often increases with decreasing pK_A in a series of structurally similar catalysts. A qualitative explanation readily follows from the proposed mechanism for the catalytic wave. According to Shikata and Tachi's rule[138], discharge of the electrochemically active acidic form of the catalyst is facilitated by increasing the electronegativity of the residue attached to the group undergoing reduction[50]. But it is well known that the introduction of an electronegative group into an acid molecule also lowers pK_A.

The height of the catalytic wave, on the other hand, is usually greater when pK_A of the catalyst is large[14,139]. This is because, other conditions being the same, the protolytic equilibrium between the two forms of the catalyst (process I) is displaced towards the electrochemically active (acidic) form when pK_A of the catalyst increases.

2. Reversible Bulk Catalytic Waves in Buffered Solutions

The quantitative relationship between catalyst structure and the nature of the catalytic wave is most conveniently investigated by discussing bulk, reversible catalytic waves, in the absence of complicating adsorption phenomena. To this end, a study of the bulk catalytic waves produced by pyridine, the picolines, and 2,6-lutidine has been made[65].

Fig. 3 shows the variation of $(i_{lim}/i_d)^2$ with concentration of undissociated boric acid at a constant pH of 8.40. It can be seen that the slope of the linear plots, which is a measure of the rate of protonation, depends on the nature of the catalyst. Values of ρ were calculated from Eqn. (14) (for the method of evaluating k_d, needed in the calculation of ρ, see later), and were used to derive the individual rate constants shown in Table 1. In a series of structurally similar catalysts the protonation rate constant for a particular acid (k_A) should increase with pK_A of the catalyst, as required by Brønsted's relation.

When H_3BO_3 and veronal are used as protonating agents, $k_{H_3BO_3}$ and $k_{veronal}$ for the 2-methyl derivatives (see Table 1) are much lower than the Brønsted value owing to steric hindrance[140]. Thus, steric factors can have a profound influence on the height of catalytic waves.

When the buffer capacity of the solution is increased at constant pH, the $E_{1/2}$ value for the bulk catalytic waves of these compounds becomes more negative, the slope $\Delta E_{1/2}/\Delta \log\rho$ being approximately -20 mV as required by Eqn. (17). The half-wave potential becomes more negative also with increase in pH (see Fig. 4).

The standard redox potential E_0 for reaction (II) can be evaluated by means of Eqn. (17). By substituting the values[26,66] of k_d for pyridine and for 2,6-lutidine into Eqn. (17), E_0 values of -1.626 V and -1.715 V (w.r.t. the saturated calomel electrode) were obtained for the discharge of their ions. E_0 is related to pK_A by the expression

$$E_0 = \text{const} - \frac{2.3RT}{F} pK_A . \qquad (37)$$

The experimental data for pyridine and 2,6-lutidine give -1.302 V and -1.312 V respectively for the constant in Eqn. (37). In view of the limited accuracy of the measurements[26,66] of k_d, we may conclude that these values do not differ significantly, and that the k_d values themselves are correct to within a power of ten. Putting const = -1.307 V, the values of k_d for the picolines (Table 1) were obtained from Eqns. (17) and (37), and used to calculate ρ by means of Eqn. (14). The relationship between $E_{1/2}$ for the catalytic wave and pK_A for the catalyst is evident from Eqns. (17) and (37).

3. Bulk Waves in Unbuffered Media

The rate constants for the protolytic interaction of the pyridine homologues with water were determined[63] from the effect of catalyst concentration on the limiting currents of catalytic polarographic waves in unbuffered solutions (see Fig. 8). The rate constants for protonation by water (k_1) and deprotonation by OH^- (k_2) of the same series of compounds in 0.5 M KCl at 25° are listed in Table 2.

The k_1 values increase with pK_A of the catalyst, as required by the Brønsted equation for the protonation of bases of a given structure by a given acid:

$$\log k_1 = \log G + \beta pK_A . \qquad (38)$$

With the exception of 2-picoline, the k_1 values of the catalysts follow Brønsted's Eqn. (38) to an accuracy[63] of ±5%.

TABLE 1. Properties of pyridine and its methyl derivatives.

	Pyridine	2-Picoline	3-Picoline	4-Picoline	2,6-Lutidine
pK_A (25°C, 0.5 M KCl)	5.50	6.15	5.90	6.19	6.83
k_d, litre mole^{-1} s^{-1}	$5.0\cdot10^9$	$3.8\ 10^7$	$1.4\cdot10^8$	$\sim3\cdot10^8$	$1.5\cdot10^6$
E_0, V (sat. cal. el.)	−1.632	−1.670	−1.655	−1.673	−1.710
$k_{H_3BO_3}$, litre mole^{-1} × × s^{-1}	$7\ 10^3$	$1.5-2\cdot10^3$	$7-10\cdot10^3$	$1-2\cdot10^4$	~100
$k_{veronal}$, litre mole^{-1} × × s^{-1}	$1.3\ 10^5$	$4\ 10^4$	$1-2\cdot10^5$	$3-6\cdot10^5$	$\sim8\cdot10^3$
N-Methiodides in 0.5 M KCl					
$E_{1/2}$, (~0.5×10^{-3} M)	−1.522	−1.60	−1.560	−1.671	−1.698
$10^5 D$, cm^2 s^{-1}	1.05	1.05	0.95	1.00	1.10

TABLE 2. Some constants of pyridine, the picolines, and 2,6-lutidine in 0.5 M KCl at 25°.

Compound	pK_A	k_1, litre × × mole^{-1} s^{-1}	$10^{10}k_2$, litre × × mole^{-1} s^{-1}	$c_{0.5}''$, V ($c=24\times10^{-6}$ M, saturated calomel electrode)	E_0, V (saturated calomel electrode)
Pyridine	5.50	5.5	9.8	−1.733	−1.614
2-Picoline	6.15	10.1	4.0	−1.800	−1.675
3-Picoline	5.90	8.0	5.5	−1.775	−1.656
4-Picoline	6.19	12.5	4.5	−1.869	−1.699
2,6-Lutidine	6.83	2.6	2.1	−1.875	−1.732

With 2-picoline the error is 12%. The coefficients of Brønsted's equation for this particular reaction are: $\log G = -2.15$; $\beta = 0.5$.

Brown and his coworkers[140,141] showed that the rate constants for chemical reactions involving the nitrogen atom of pyridine derivatives with a CH_3 group in position 2 are significantly lower, as a result of steric hindrance, than the values predicted by the linear rule for free energy changes (see, for example, Pal'm[142]). For any given 2-substituted pyridine derivative, the steric effect increases with the size of the species attacking the nitrogen atom of the pyridine ring[141].

Steric effects are also apparent, as mentioned earlier, in the protonation of pyridine homologues by boric acid and by veronal. However, no steric hindrance is observed when the 2-methyl derivatives of pyridine are protonated by water: this may be due to the small size of the water molecule. Protonation of these compounds by hydronium ions is also free from steric hindrance effects[141].

An increase in the pK_A of the catalyst shifts the wave towards more negative potentials in unbuffered as well as in buffered solutions (see Fig. 9). The characteristic potentials ϵ_0'', listed in Table 2, are convenient for comparison purposes. Inspection of Eqn. (25) shows that ϵ_0'' depends primarily on the E_0 value of the redox system, which decreases linearly [see Eqn. (37)] with the pK_A of the species undergoing discharge.

E_0 can be determined by means of Eqn. (25) from experimental values of ϵ_0'' and of the rate constant. The E_0 values listed in Table 2, obtained in this way, are obviously less accurate than the values measured in buffered solutions (see Table 1).

4. Irreversible Surface Waves

The relationship between irreversible surface catalytic hydrogen waves and the structure of the catalyst is complicated by adsorption phenomena which increase the catalytic current, but can also displace the wave towards less cathodic potentials.

In a series of catalysts of comparable adsorbability, the half-wave potential $E_{1/2}$ (or the "half-maximum" potential, which is much easier to determine) varies with the pK_A of the catalyst according to one of the modified forms of Hammett's equation (see, for example, Pal'm[142] or Zuman[143]): the wave moves in the negative direction as pK_A increases. The limiting current, as already pointed out, increases with the pK_A of the catalyst. Numerous examples of this type of behaviour are to be found in some of the papers already mentioned[14,18,139].

Zuman and Kuik[144] have shown that the catalytic activity of pyrimidine in Co^{2+} solutions is increased by substituents in the 5-position in the following sequence: $OH < NH_2 < SH$. They attribute the higher activity to changes in acid properties and in the ability to form complexes with Co^{2+}.

Lamprecht *et al.*[21] established that the nature of the catalytic wave depends on the type of complex formed by the sulphur-containing catalyst and Co^{2+}. Thus, if complex formation involves, besides SH and SS groups, some neighbouring carboxy-groups, the catalytic wave occurs immediately beyond the discharge potential of cobalt, and shows the characteristic falling off observed in solutions of cysteine and Co^{2+}. If Co^{2+} in the complex is coordinated to sulphur and also to an NH_2 or NH group in the same molecule, the resulting wave is somewhat lower, and, instead of falling off, shows something in the nature of a limiting current plateau. If the molecule contains no ligand groups other than SH or SS, polarograms taken in ammoniacal cobalt solutions show only the rising section of the wave before the discharge potential of the base electrolyte, but no limiting current.

Stevančevič published some interesting observations[145] on the catalytic activity of quinoxaline-2,3-dithiol in Co^{2+} and Ni^{2+} salt solutions. The catalytic wave in nickel solutions is significantly lower than in cobalt solutions, and occurs at less negative potentials. Assuming approximately equal adsorbabilities for the complexes formed by quinoxalinedithiol with nickel and with cobalt ions, the observed difference between the catalytic waves must be attributed to a higher pK_A for the Co^{2+} than for the Ni^{2+} complex.

Toropova and Elizarova[146] showed that complex formation between sulphur compounds and Fe^{2+} (as well as Co^{2+} and Ni^{2+}) can give rise to catalytic activity. When metal ions which can attach themselves to a thiol more firmly than can Ni^{2+} are added to the polarographic solution, the height of the catalytic hydrogen wave decreases[146-148].

The dependence of the catalytic wave on the pK_A of the catalyst has been used[149] to evaluate, approximately, unknown pK_A values of catalytically active compounds.

When the catalysts differ in their surface activity, the height of the catalytic wave increases with the adsorbability of the compound[130,131]. Surface waves are extremely sensitive to slight changes in the structure of the catalyst: Zuman[150] reports that the second polarographic wave of *erythro*-phenylcysteine in ammoniacal $CoCl_2$ solution is almost twice as high as the corresponding wave of the *threo*-isomer.

5. Catalytically Active Organic Compounds

The catalytic activity of organic catalysts is determined by the ability of the catalyst to add on a proton and form an 'onium' compound. Thus, catalytic waves are observed in solutions of amines (but not tetrasubstituted amines!), thiols and sulphides, phosphines[92], and arsines[151-154]. Knobloch[15,155] has recently made a detailed study of the catalytic hydrogen waves produced by oxonium compounds (derivatives of chromone). Ryvolová[156] also observed catalytic hydrogen evolution in the presence of catalysts of the oxonium type (the products of electrochemical reduction of unsaturated diketones containing methoxycarbonyl groups). Zhdanov and Polievktov[157] described catalytic waves due to diphenylcyclopropenone in acid solutions.

VII. ALTERNATIVE THEORIES OF CATALYTIC HYDROGEN WAVES

A number of theories and schemes, differing from that presented here, have been put forward to account for the nature and mechanism of catalytic hydrogen waves. We shall consider them briefly in the present section.

One of the earliest theories was formulated by Brdička to explain the mechanism of catalytic waves in solutions of sulphur compounds. This worker visualised hydrogen being split off, at the electrode, from the SH group of the thiol, followed by protonation of the RS^- anion by acidic constituents of the solution. A short account of this theory has already been presented in Section V. Brdička's views are widely known, and are described in most polarographic textbooks: we shall not consider them further, except for pointing out that Brdička's theory is not applicable to catalytic waves due to nitrogenous organic bases.

Kirkpatrick[11], in his study of catalytic hydrogen evolution in the presence of many different alkaloids, proposed that the catalytic act consists in the capture of an electron from the electrode by the alkaloid, followed by transfer of the electron to a hydrogen ion in solution. According to Kirkpatrick, the catalytic activity of an alkaloid is determined by its "electron capacity", *i.e.* by its ability to extract electrons from the cathode.

Knobloch[14] applied Brdička's mechanism to the catalytic waves produced by heterocyclic and aromatic amines. Like Brdička, he assumed that the catalyst accelerates the formation of molecules from the atomic hydrogen evolved at the cathode and thus lowers the hydrogen overvoltage (in accordance with Heyrovský's theory[158] of hydrogen overvoltage). In his more recent paper[15], however, Knobloch adopts the mechanism for the formation of catalytic waves put forward by von Stackelberg and his coworkers[17-19].

Von Stackelberg's mechanism comes nearest to that proposed by the present author. According to von Stackelberg[17-19], the catalyst is active only when adsorbed on the electrode. By accepting a proton, it is converted into the electrochemically active cationic form, which is irreversibly discharged at the electrode, evolving hydrogen and regenerating the catalyst in its basic form. Von Stackelberg and his coworkers do not consider the mechanism of the last stage of the process, following the electrochemical act. Hence, with the exception of the last stage, von Stackelberg's mechanism is indistinguishable from the particular case of irreversible surface waves in the author's mechanism. Von Stackelberg's mechanism does not account for all the facts: as we saw in the previous Sections, there are catalytic processes other than irreversible surface waves. Protonation can occur in the layer of solution adjacent to the electrode, *i.e.* without involving adsorption of the catalyst, which is a prerequisite in von Stackelberg's theory, and electron transfer to a protonated catalyst species can occur fast enough to make the electrochemical stage reversible.

The view (held by von Stackelberg and his coworkers) that the catalyst can only be protonated by hydronium ions is probably erroneous. Other acids present in solution are thought to contribute to the process only after dissociation, with formation of hydronium ions:

$$HA \rightarrow H^+ + A^-, \qquad (V)$$

$$B + H^+ \rightarrow BH^+. \qquad (VI)$$

On the basis of these concepts, von Stackelberg and his coworkers[159-161] even tried to determine the rate constants for the dissociation of acids HA from the catalytic currents observed in solutions of these acids (and also, by applying the method of Rüetschi[162], from kinetic currents limited by the rate of protonation). However, the processes investigated by these workers were in fact limited mainly by the rate of the direct interaction of HA with B (see, for example, Refs. 33, 34, 82, 163–165).

Thus, the dissociation of water into its ions

$$2H_2O \rightarrow H_3O^+ + OH^- \quad (k = 2 \times 10^{-5}\ s^{-1}\ ^{166})$$

(an essential condition in von Stackelberg's theory) cannot possibly account for the catalytic currents observed in unbuffered solutions, which corresponds, as already pointed out, to the rate of protonation of the catalyst by water itself (for pyridine, $k_1 = 5.5$ litre mole^{-1} sec^{-1}).

If protonation of a catalyst by an undissociated acid of the type HA involved a preliminary dissociation stage, no steric hindrance would be observed in the protonation of 2-picoline and 2,6-lutidine by undissociated boric acid and veronal[63], since there is no hindrance when these compounds are protonated by water or by hydronium ions[141].

To conclude this brief survey of theories of the catalytic hydrogen wave, we shall discuss Frumkin's shrewd explanation[28,167] of the ease with which the cations of the catalyst are discharged (as compared with the discharge of hydrogen ions). Frumkin confines himself to discussing a situation in which the purely electrochemical reaction is the slowest step of the catalytic process, and the catalyst exists mainly as the electrochemically active action BH^+ both in solution and in the adsorbed state (*i.e.* $\sigma \ll 1$). Assuming that the discharge of BH^+ and H_3O^+ involves identical transfer coefficients α, Frumkin applies Brønsted's equation (relating the rate constant of an electrode process to the dissociation constant of the acid undergoing discharge) to the problem of calculating the rate constants for electron transfer to BH^+ and H_3O^+. It can be shown that BH^+ will be discharged faster than H_3O^+ in the same solution only if BH^+ is a cation and its specific adsorption is considerable. Then, and only then, does the effect of the electrical double layer structure favour the discharge of BH^+ significantly much more than the discharge of H_3O^+. The theory assumes, however, that the product of the electrochemical reaction is an adsorbed hydrogen atom, rather than a BH radical. Thus it cannot explain, among other things, the formation of reversible catalytic waves. The theory is likewise inapplicable to the case of $\sigma \gg 1$, *i.e.* to catalysts which exist mainly in their basic (unprotonated) form.

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NEW ASPECTS OF THE CHEMISTRY OF COMPLEXES OF SELENIUM AND TELLURIUM

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I. INTRODUCTION

The growing interest in the chemistry of rare and dispersed elements, which include selenium and tellurium, is connected with the development of new branches of technology — automation, telemechanics, and semiconductor technology.

In the Periodic System selenium and tellurium lie between sulphur, a typical non-metal, and polonium, a metal. This position determines the most important physical and chemical properties of these elements. As regards electrical conductivity, tellurium recalls a metal while selenium is a semiconductor. Selenium and tellurium and their compounds are widely used in semiconductor technology for the production of thermoelements, systems for stabilising temperature, and in radio technology.