

RECENT DEVELOPMENTS IN THE STUDY OF HYDROGEN OVERPOTENTIAL

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The present position of hydrogen overpotential studies is discussed. Owing to the large discrepancies still apparent among recent experimental determinations of overpotential, an outline of modern experimental technique and a critical survey of evidence regarding the effect of the different variables on hydrogen overpotential are given. The various suggested theories are described and critically compared with the experimental data.

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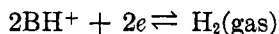
I. INTRODUCTION

The recent work of Frumkin (67, 71, 72) and his collaborators, of Eyring, Glasstone, and Laidler (57), and of Hickling (90, 95) has served to redirect attention to the unsolved problems of hydrogen overpotential and to emphasize

that considerable differences still exist between the theoretical views of modern authors. This is due primarily to the unexpected complexity of the phenomena and to the fact that only in recent years has experimental work been carried out which is relatively free from vitiating factors.

A full-length review (162) has not been devoted solely to this subject for many years, and the following is intended as a critical survey of the present state of the experimental and theoretical fields.

Hydrogen overpotential at a given current density of i amp./sq. cm. is defined as the difference between the potential of an electrode at which hydrogen is being evolved at i amp./sq. cm. and the potential of the reversible hydrogen electrode in the same solution. This potential difference may consist of three contributions: (1) that due to the ohmic potential difference between the electrode and the Luggin capillary (see below); (2) that due to concentration changes in the diffusion layer near the electrode surface; and (3) that associated with the activation energy of some stage of the reaction



(where B represents the solvation sheath round the proton). Hydrogen activation overpotential (31) is the specific term applied to the latter type of overpotential. In the following, hydrogen overpotential will generally be taken as synonymous with hydrogen activation overpotential on the assumption that, in the experimental arrangement, the two other contributions to the potential difference between working and stationary electrodes have been reduced to negligible proportions.

In the following, overpotential will be given its absolute sign, e.g., the hydrogen overpotential at a mercury cathode in dilute aqueous acid solution, at a current density of 10^{-3} amp./sq. cm., is about -1.04 v. Increase or decrease of overpotential means that the cathode potential becomes, respectively, more negative or less negative with respect to the reversible hydrogen electrode in the same solution.

II. THE TECHNIQUE OF MEASUREMENTS OF HYDROGEN OVERPOTENTIAL

A. ELECTROLYTIC CELL AND ITS USE

Typical designs of modern cells are shown in figures 1 (22) and 2 (107).

The essential requirements of a cell are that it should (i) maintain a hydrogen atmosphere against atmospheric oxygen, (ii) maintain catholyte separate from the anolyte and from the hydrogen electrode, and (iii) be provided with a suitable, preferably adjustable, "cathode tip" or Luggin capillary (125) to connect the cathode to the reference electrode. It is undesirable to grease taps and joints (123) which should be wetted with the solution and sealed to the outer atmosphere by solution-filled traps, able to withstand a vacuum (see figures 1 and 2). Outside the current density range of 10^{-8} to 10^{-2} amp./sq. cm. more specialized provisions (19, 32, 110) are necessary. Above the current density of 10^{-3} amp./sq. cm. it is not necessary to guard the solution from every trace of oxygen (19, 92).

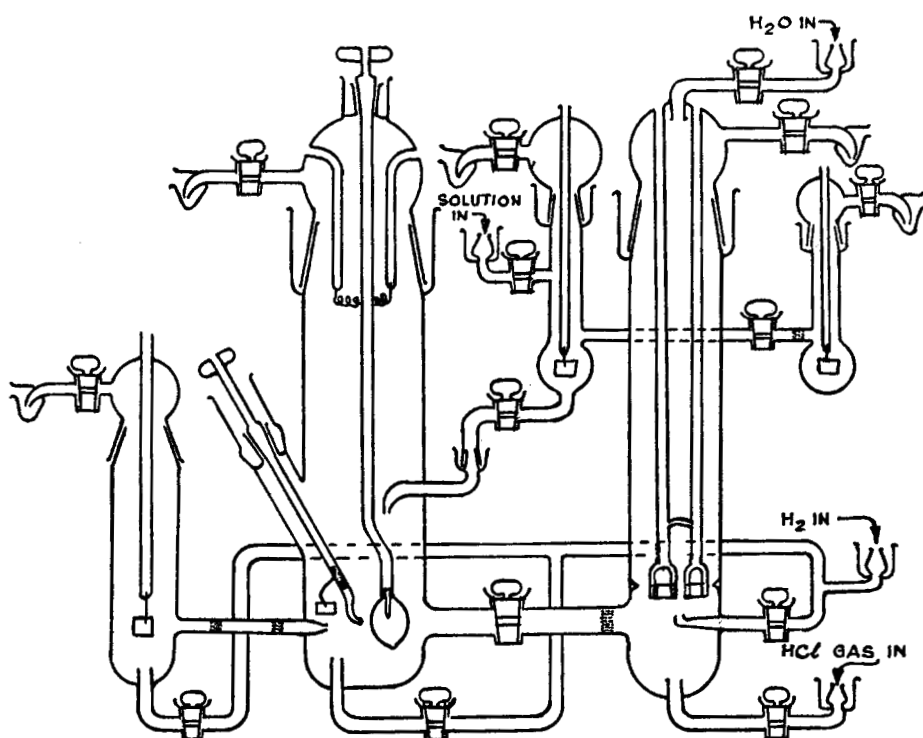


FIG. 1. Electrolytic cell for measurement of hydrogen overpotential

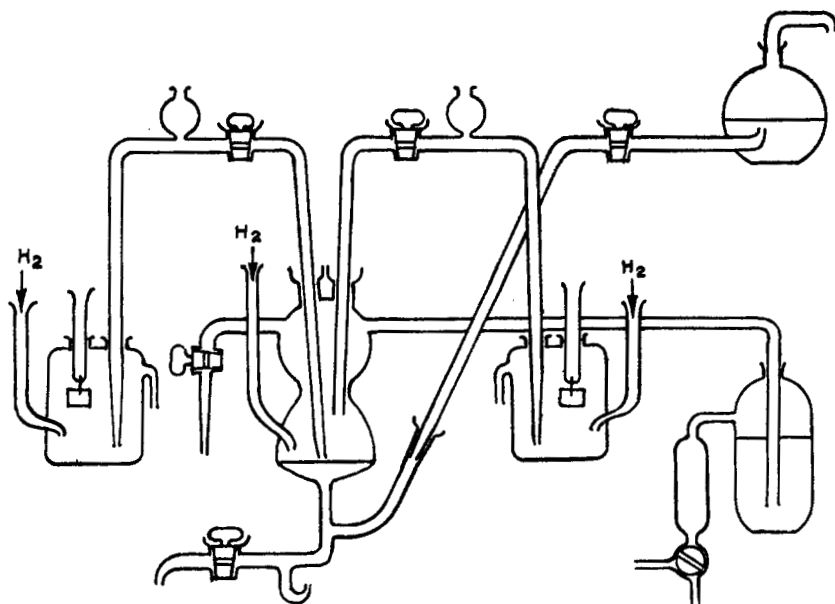


FIG. 2. Electrolytic cell for measurement of hydrogen overpotential

Cells, preferably cleaned with nitric-sulfuric acid mixture, should be washed with distilled water and then conductivity water for many hours before use. Drying agents for use with non-aqueous solvents, e.g., acetone, should be distilled before use to avoid the deposition of solid matter upon evaporation.

B. PREPARATION OF ELECTRODES

Mercury of appropriate purity can be obtained fairly easily by the double or triple distillation of mercury, first purified electrolytically by von Naray-Szabo's method (159).

Solid electrodes are difficult to prepare in a clean and reproducible state, and the many types of pretreatment described contribute considerably to the lack of agreement between the results of many authors. Chemical pretreatment is unsatisfactory, because products of the cleaning reaction may become occluded in the metal surface. It has been stated that relatively reproducible results can be obtained simply by washing with water and wiping the cathode surface with a filter paper (19); for soft metals scraping with a sharp knife can be employed (82, 106) if precautions (13) are taken (e.g., microscopic examination) to observe that no particles from the knife remain in the electrode.

Most former methods of preparation of solid electrodes have the disadvantage that they allow exposure of the cleaned surface to the atmosphere before immersion in the hydrogen-filled cell. Grease (1) and an oxide film may collect on the electrode in a few seconds and obscure the significance of, for example, the slow growth of overpotential with time.

Some kind of standard state of the electrode surface is clearly desirable and an attempt has been made to obtain this (Bockris and Conway (21)) by sealing the wire cathode in a stream of pure hydrogen (after prolonged preheating) into a narrow glass tube ending in a thin glass bulb. The cathode, thus annealed and preserved in a hydrogen atmosphere, is then introduced into the cell which is later filled with hydrogen and solution, after which the glass bulb (enclosing the hydrogen atmosphere round the electrode) is broken under the hydrogen-saturated solution (see figure 1). The method probably eliminates oxide films¹ and grease on the surface and avoids the difficulties involved in the attachment of solid electrodes to glass by cements. Effects of adhesives in solution have been stressed in work on electrode capacities (74) but insufficiently in work on overpotential. Bockris and Parsons (24) observed that not only organic but also many types of inorganic cements, though dissolving in aqueous acid solutions to the extent of only 10^{-6} gram-moles/liter in 12 hr., had an appreciable effect on overpotential at a current density of 10^{-3} amp./sq. cm. at platinized platinum electrodes.

The shape of the cathode is important because of the desirability of a uniform distribution of current density over all its parts. A plate is better in this respect than a wire, for which in most cell configurations the current lines tend to concentrate at the end nearest to the anode (79).

¹ Complete elimination thus of oxide films may be negated by the reaction $M + H_2O \rightarrow MO + H_2$, which possibly occurs for a very brief time after the electrode M contacts the solution.

C. PREPARATION OF THE SOLUTION

The apparatus should be of glass throughout, because no contact between the vapor of the solution and rubber bungs is desirable. The solvent used is distilled in hydrogen after other methods of preparation have been carried out. An appropriate criterion of the purity of the solvent is its electrical conductivity, which should be $< 10^{-6}$ mhos/cm. cube. The solution is preferably produced by dissolving a gaseous solute in the solvent. The solid source of the solute, e.g., potassium chloride of analytical reagent purity, should be heated to some 50°C . below its melting point in a hydrogen atmosphere for several hours to remove organic impurities present (107). The concentration of the gaseous solute is conveniently determined conductimetrically for both aqueous and non-aqueous solutions (25), the electrodes being in the vessel into which pass the solute gas and a vigorous stream of hydrogen for stirring purposes.

Non-gaseous solutes invariably contain appreciable quantities of heavy metal impurities and are therefore better avoided. Their use necessitates very thorough purification by repeated distillation and electrolysis.

After initial purification the solution still contains impurities, which are most efficiently removed by cathodic polarization (i.e., deposition, reduction, adsorption) on a cathode of the same material as the working cathode (72, 124). Cathodic "prepolarization" is continued on an auxiliary electrode of the material of the cathode under examination for many hours, often at fairly low current density. The exact conditions for satisfactory purification of a given solution with a given cathode material can only be finally established by experiment, the criteria of efficient purification being (i) reproducibility of results, and (ii) no further change in overpotential caused by further increase in the quantity of current passed through the solution (25). Few workers have used these more stringent methods for the preparation of solutions. In particular among modern workers, Hickling (90) does not consider the purification outlined above necessary for work at higher current densities. This may be relatively true with respect to depolarizers such as oxygen, but other active impurities in small traces may cause alteration in the slope of the overpotential-log current density line as well as in the actual values of the hydrogen overpotential (see figure 3) (123). Even at 10^{-1} amp./sq. cm., the overpotential on copper electrodes is some 5 cv.'s higher in prepolarized than in non-prepolarized solutions (19).

The method of preparation of alkaline solutions is less certain. Lukovtsev, Levina, and Frumkin (127) use sodium amalgam. It seems that this method may lead to the presence of mercury in solution unless cathodic prepolarization is carried out for a very considerable time.

The hydrogen used is preferably produced electrolytically. It may contain appreciable quantities of oxygen, hydrogen sulfide, carbon monoxide, and carbon dioxide and should be passed through appropriate absorbing agents (preferably not liquids) (24) and several liquid-nitrogen traps (124) before entry to the cell.

D. METHODS OF MEASUREMENT OF OVERPOTENTIAL

The so-called "direct method" consists in a direct comparison of the potential of the working electrode with that of some standard reversible electrode, in the

same solution as the former, by means of a potentiometer. Inclusion of an ohmic potential difference in the measured potential difference between working and stationary electrodes is avoided by pressing the Luggin capillary (diameter approximately 1 mm.) firmly against the cathode. This simple method suffers from several disadvantages: (i) part of the electrode surface is shielded from its share of the current lines; (ii) at high current densities the potential difference between the end of the tip and the electrode becomes significant. According to some (76, 81, 131) there is a gas film between electrode and solution at all current densities and the relatively high resistivity of this causes an appreciable ohmic overpotential to exist even at, say, 10^{-3} amp./sq. cm. This concept has been convincingly disproved (44, 59, 61). The presence of an oxide film on the

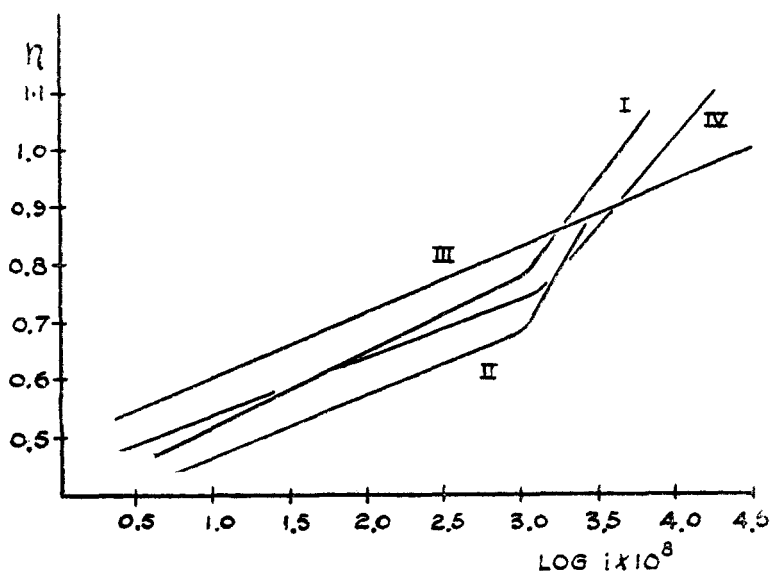


FIG. 3. Plot of hydrogen overpotential *versus* log current density. Curves I and II (II joins III) show the effect of grease on the taps of the electrolytic cell; curve IV shows the effect of other poisons. Curve III is from work in carefully purified solutions.

cathode surface may, however, lead to the setting up of a considerable ohmic overpotential similar to that which would be caused by a transfer resistance. In normal aqueous acid solutions, the direct method of measurement can be used up to a current strength of about 10^{-1} amp./sq. cm. and at higher current densities with the special precautions mentioned below.

The indirect or commutator method of measurement (131) involves the intermittent passage of current across the electrode-solution interface, measurements of potential being made in the periods when the current is not flowing, a procedure which thus eliminates ohmic overpotential. A disadvantage attaching to this method is that intermittent electrolysis may produce different conditions at the electrode surface compared to those occurring with continuous electrolysis. Further, the rapid decay of overpotential with time (5) makes it necessary to

measure the former very quickly and at a rapid succession of intervals, after the cessation of the polarizing current, so that extrapolation to zero time can be accurately made. Incorrect extrapolation consequent upon a too long interval before the first reading is recorded caused error in the earlier commutator method (76, 115, 143). More recently Hickling (88) has used an electronic interrupter, the essence of which is a thyatron valve in which the period of interruption is of the order of 5×10^{-5} sec. and which thus considerably facilitates a correct extrapolation. According to Frumkin (71), this commutator is also open to the criticism of incorrect extrapolation at current densities greater than 10^{-3} amp./sq. cm., owing to the extreme rapidity of the first stage of the exponential decay. Bockris (13), however, using the direct method of measurement and the same type of solution preparation as that used by Hickling and Salt (90), found agreement with results obtained using Hickling's commutator interrupter up to a current density of 10^{-1} amp./sq. cm., so that, because possible electrical errors from each method are of opposite sign, the validity of Hickling's commutator method seems confirmed up to this current density.

At very high current densities the rapid decay of overpotential causes the extrapolation from all modifications of the commutator method to be inaccurate, so that the direct method must be applied with the following precautions (19, 110): (i) A very small cathode area is used, thus reducing the ohmic overpotential (which depends on current *strength*) and also heating effects in the solution; (ii) very rapid rate of streaming of the electrolyte to reduce concentration polarization to negligible proportions; (iii) a configuration of the cathode, preferably a very short thin wire, which allows accurate calculation of the resistance between cathode tip and cathode. Some authors (90) consider this calculation to be inherently inaccurate, owing to the existence of an unknown specific conductivity in the diffusion layer; others (71) consider it permissible to use the bulk specific resistance. The latter view seems incorrect and the problem of an appropriate correction formula is very difficult because of the lack of information concerning the exact hydrodynamical conditions during rapid streaming.

Ferguson and Bandes (60) have recently reported a device for the convenient photographic recording of the variations of overpotential with time and rate of polarization, and this has been applied to the study of decay and of ohmic overpotential.

E. TECHNIQUE OF ESTABLISHMENT OF THE OVERPOTENTIAL-LOG CURRENT DENSITY RELATION (OR "TAFEL LINE")

The marked variation of the hydrogen overpotential on some metals with time (13, 90) makes it necessary to choose a time of polarization after which the potential difference between the working and stationary electrodes should be termed the overpotential. Workers who consider the time variation to be due to the electrodeposition of impurities, or to other secondary phenomena, have generally made measurements shortly after the commencement of polarization at a given current density. Some authors (116) state 1 min. to be this time. This procedure is satisfactory on metals for which the variation of overpotential with

time is relatively small. For some metals, however, it is considerable, so that this method of "quick runs" may vitiate a comparison of results obtained at various current densities.

The fact that intensive purification of the solution and prepolarization do not completely eliminate the variation of overpotential with time on mercury cathodes (71) and that it appears to be a function of the mode of preparation of the electrode surface, has led some workers (13, 90) to the view that this property is a primary characteristic of overpotential, in which case it appears to be more reasonable to take the overpotential after it has reached the steady state, i.e., after electrolysis lasting from a few minutes to several hours ("slow runs"). It has been claimed (90) that this method provides a standard condition under which all metals can be examined; its validity rests upon the unproved view that the variations with time are not due to true impurities.

A further discrepancy in technique is between authors who start polarization from the moment the electrode contacts the solution to the end of the experiment and those who cease polarization between each current density and allow the cathode potential to reach a "static potential" before polarizing at another current density. The latter method minimizes the possibility that polarization set up at one current density may affect the steady state set up at the next (90). Conversely, dissolution of the metal may take place during the resting periods between the various current densities.

III. THE EXPERIMENTAL FACTS OF HYDROGEN OVERPOTENTIAL

A. DISCREPANCIES BETWEEN THE RESULTS OF DIFFERENT WORKERS

Difficulties met in comparison of results of different workers are connected firstly with lack of rigor in purification of the solution, with a lack of comparability in the preparation of the electrode surface, and with factors connected with the time variations of overpotential. Thus, the large amount of work carried out by Frumkin and his coworkers has not been clarified by the earlier absence in their work of an attempt to deal with the problem of variation with time, which has more recently been admitted by them both for metals of low overpotential, e.g., nickel (120, 127) and palladium (73), and for mercury (71). In the following an attempt has been made to collect evidence from sources in which sufficient experimental detail is given to assess the reliability of the results.

Experimental results have been regarded as being concerned either with "electrode factors", e.g., time, or "solution factors," e.g., pH.

B. ELECTRODE FACTORS

1. *Effect of current density*

According to Tafel (153), over certain current density ranges and for certain electrodes, the relation between overpotential (η) and current density (i) is

$$\eta = a - b \log i$$

or

$$i = e^{(a-\eta)/b}$$

where a and b are constants (Tafel equation).

(a) Mercury at low current densities

The older results of Bowden and Rideal at 15°C. (35) are some 5 cv. lower in 0.2 N sulfuric acid than those of Jofa (102) in 0.1 N sulfuric acid over the range 10^{-6} to 10^{-3} amp./sq. cm. These latter data at 20°C. over the current density range 10^{-7} to 3×10^{-2} amp./sq. cm. are given by:

$$\eta = -1.426 - 0.113 \log_{10} i$$

Jofa (102) also measured overpotential in 0.1 N aqueous hydrochloric acid solution: If correction is made for differences in temperature of measurement, they agree to within about 9 mv. with those of Levina and Sarinsky (123). Below 10^{-7} amp./sq. cm. difficulties of measurement increase markedly because (i) the

TABLE 1
Values of i_0 obtained in aqueous acid solutions

WORKER	i_0 amp./sq. cm.	SOLUTION
Bowden and Rideal (35).....	3×10^{-12}	0.5 N H_2SO_4
Bowden and Kenyon (113).....	6×10^{-12}	0.2 N H_2SO_4
Jofa (102).....	5×10^{-13}	0.1 N H_2SO_4
Jofa and Mikulin (108).....	1.5×10^{-12}	0.25 N H_2SO_4
Jofa (107).....	1.8×10^{-12}	0.1 N HCl
Bockris and Parsons (24).....	5.2×10^{-13}	0.1 N HCl
Bockris and Parsons (24).....	1.3×10^{-12}	1.0 N H_2SO_4

region of the electrocapillary maximum is approached, so that the probability of adsorption of surface-active impurities is increased; (ii) the effect of traces of depolarizers is more marked; (iii) at current densities as low as 10^{-10} amp./sq. cm. the double layer takes an appreciable time to charge up. Bowden and Grew (32) tried to overcome difficulties (i) and (ii) by enclosing the cathode in glass and succeeded in confirming the linearity of the overpotential-log current density relation down to about 10^{-9} amp./sq. cm. Some deviations at lower current densities were observed, the cathode potential being more negative than that expected from the Tafel equation. If i of Tafel's equation = i_0 for $\eta = 0$, values of i_0 obtained in aqueous acid solutions at about 20°C. are as shown in table 1. Comparable results on mercury at low current densities are thus in good agreement.

Mituya (129) has also carried out experiments in the current density range 1.87×10^{-9} to 4.3×10^{-11} amp./sq. cm. In the rectilinear part of the Tafel line the observed value of b was 0.186 at 0°C. in 0.1 N hydrochloric acid, and the values of the overpotential are about 0.2 v. lower than those expected from other work. Insufficient precautions seem to have been taken by this worker for prevention

of the diffusion of platinum from the anode, which may have reached the cathode in his experiments, a fact which is probably the basis of the discrepancies in a and b of the Tafel equation between this and other work cited above.

(b) Mercury at high current densities ($> 10^{-3}$ amp./sq. cm.)

Work at high current densities is difficult for the following reasons: (i) ohmic overpotential tends to become marked, especially in dilute solution; (ii) the limiting current density may be approached in the absence of efficient aids to diffusion; (iii) excessive heating of the solution may occur; (iv) liquid mercury undergoes an oscillatory motion; this makes it preferable to use amalgamated copper electrodes upon which the overpotential is less than 10 mv. different from that on pure mercury at current densities greater than 10^{-4} amp./sq. cm. (19). The effect of (iii) can be minimized by using electrodes of small electrode areas (19, 110). The influence of concentration overpotential is more difficult to assess, owing to the uncertain values of the thickness of the diffusion layer in agitated solutions.

Frumkin (71) maintains that no limiting current density due to concentration overpotential occurs even at a current strength of 1 amp. in a well-agitated solution. Kabanov (110) used rapid shearing of the electrolyte, Hickling and Salt (90) agitation by passage of a rapid gas stream, and Dolin (45) mechanical stirring to minimize the contributions of concentration polarization. Resistance overpotential corrections were calculated by Kabanov (110), who measured the distance between cathode and electrode tip with a microscope and assumed that the appropriate specific resistance was that of the bulk of the solution, a procedure of doubtful validity. Corrections in Kabanov's work were of the same order as the measured overpotential at the highest current densities. Hickling and Salt (90) made use of an electronic commutator up to a current density of 10 amp./sq. cm.

Fairly large discrepancies exist between the results of Kabanov, which may be represented by the equation:

$$\eta = -1.42 - 0.14 \log_{10} i$$

and those of Jofa, for which the corresponding equation is:

$$\eta = -1.396 - 0.116 \log_{10} i$$

Kabanov's results on amalgamated mercury indicate that the Tafel equation is applicable on this metal up to a current density of 10 amp./sq. cm. (The points on the Tafel line show a scatter of 0.04 among themselves.) Conversely, Hickling and Salt (90) found that at current densities greater than 10^{-2} amp./sq. cm. the Tafel equation could no longer be used to express the results, a fact which indicated that the cathode potential was less negative (i.e., overpotential lower) than would have been so according to a linear Tafel line.

(c) Cathodes other than mercury at low current densities

According to Bowden and Rideal (35), the Tafel equation is applicable to the variation of hydrogen overpotential on silver, nickel, platinum, and carbon over

the current density range 10^{-7} to 10^{-3} amp./sq. cm., the b value for these metals being about 0.10–0.12 for the first three and 0.84 for carbon. Erdey-Grúz and Wick (51) found that on lead and tantalum the Tafel equation was applicable with the b values = 0.2 approximately. Kabanov and Jofa (106) found the b value for the Tafel line of lead in aqueous acid solution = 0.116; and Lukovtsev, Levina, and Frumkin (127) found that on nickel there were positive deviations² from the Tafel equation in the range 10^{-8} to 10^{-6} amp./sq. cm., but from 10^{-6} to 10^{-2} amp./sq. cm. this equation was applicable with $b = 0.10$. The Russian work on lead and nickel was carried out under stringently controlled conditions, with rigorous deoxygenation of the solution and electrolytic purification. Values of overpotential under apparently comparable conditions on the same metal from independent work are often discrepant by more than 0.1 v., and this is mostly due to the purity of the electrode material and solution.

Some investigation has been made of the hydrogen overpotential on catalytically active metals at low current density ranges where the logarithmic relation would be supposed from theory to break down. Volmer and Wick (157) find an approximately linear relation between current and potential near the reversible potential on platinum, gold, and iridium electrodes.

(d) Cathodes other than mercury at high current densities

Kabanov (110) determined the hydrogen overpotential on silver from 10^{-3} to 10^{-0} amp./sq. cm. and on platinum from 10^{-3} to 10^2 amp./sq. cm. in 5 *N* hydrochloric acid solution and obtained an apparent applicability of the Tafel equation with b values of 0.13 and 0.12, respectively.

In this work, no details are given with regard to cathode preparation; there is a considerable scatter of points around the Tafel line and the method of correcting for ohmic overpotential is crude.

Essentially different results were obtained by Hickling and Salt (90) on some eighteen of the more common metals in 1 *N* aqueous hydrochloric acid solution within the current density range 10^{-3} to 10^{-0} amp./sq. cm., using the commutator method and means of purifying the solution which did not include prepolarization. These workers found that the Tafel equation was applicable in the current density range studied only to comparatively few metals, i.e., bismuth, iron, nickel, tungsten, gold, and platinized platinum, whilst for other cathodes (particularly those of high overpotential) there were negative deviations from the Tafel lines which indicated an approach of the overpotential to a limiting value independent of current density. Values of the b factor, measured from the lower linear sections of the curves, showed that although for some cathodes $b \approx 0.1$, a large number of exceptions existed, the range covered by the b factor being 0.03–0.3 approximately (see table 2).

Bockris (13) measured the overpotential on copper, lead, nickel, molybdenum, columbium, tantalum, indium, and thallium, using the direct method and the same method of preparation of the solution and same current density range as

² Namely, deviations in the sense that the values of overpotential observed were greater than those expected from the Tafel equation.

Hickling and Salt. He obtained fair agreement with the results of Hickling and Salt for copper, lead, and nickel (i.e., metals examined by the latter workers) and observed a similar kind of negative deviation from the Tafel equation for indium, thallium, and tantalum as these workers observed for lead, tin, copper, etc.

It should be noted that these deviations from the Tafel equation at high current densities have only been observed in solutions which were not electrolytically purified. Work in electrolytically purified solutions at high current densities has not yet been reported. The position is therefore still uncertain.

(e) Experimental evidence on the b factor

The value of the b factor in the Tafel equation for different metals is controversial and of great importance to the theory of hydrogen overpotential. Values of b obtained by different authors in aqueous acid solution at the same intermediate current density ranges are in poor agreement, as is shown in table 2 (13), where values of b from recent work are tabulated. The average of these values

TABLE 2
Experimental values of b

METAL	b	METAL	b	METAL	b	METAL	b
Be.....	0.11	Cb.....	0.11	W.....	0.09	Hg.....	0.15
C.....	0.84	Mo.....	0.13	Pt (platinized)	0.02	Hg.....	0.12
Al.....	0.12	Rh.....	0.14	Pt (platinized)	0.08	Tl.....	0.08
Fe.....	0.12	Ag.....	0.12	Pt.....	0.3	Pb.....	0.3
Ni.....	0.11	Cd.....	0.25	Pt.....	0.19	Pb.....	0.23
Cu.....	0.16	In.....	0.25	Au.....	0.08	Bi.....	0.10
Cu.....	0.12	Sn.....	0.2	Au.....	0.12		

is 0.17 (or 0.14 if the result for C is neglected) and from this and the scatter of the values there is no clear support for the contention of some workers that b is a constant equal to 0.12 at 25°C. for all pure metals. Conversely, it is significant that in those few experiments where electrolytic purification of the solution and stringent elimination of oxygen have taken place, the b value found \approx 0.10–0.14 at intermediate current densities. Thus, several workers have reported b values for lead of 0.2–0.3; but Jofa and Kabanov (106) found that in carefully purified solutions the slope of the Tafel line was 0.12. There is as yet insufficient work in highly purified solutions to be able to assess the generality of this result. A first aim of most theories of overpotential is the theoretical interpretation of b . The most urgently needed experimental work appears to consist in determining its value in the most carefully purified solutions and on electrodes of very high purity.

2. Effect of temperature

The principal interest in measuring the temperature coefficient of hydrogen overpotential is to obtain the energy of activation, ΔH . Two different methods

may be used for the measurements (Agar (4)). The overpotential at a temperature T is measured against a reversible electrode either at the same temperature or at some other temperature, T_0 . Some uncertainty is involved in the latter method, owing to thermoelectric potentials in the bridge connecting the cell to the reversible electrode. According to Agar (4) this difference between the two resulting energies of activation is of the order of 1 kg.-cal.

Values of the temperature coefficient are of the order of a millivolt per degree and the energies of activation vary from about 5 to 20 kg.-cal. in various systems. The sparse data up to 1938 are recorded by Bowden and Agar (31). Since this time little fresh data on the energy of activation has been recorded.

Information on the variation of the coefficient b with temperature is contradictory. Bowden found b proportional to T (i.e., $\alpha = \text{constant}$) for mercury in 0.2 N aqueous sulfuric acid. This was confirmed by Jofa and Mikulin (108). In more concentrated acid solution, however, Jofa and Stepanova (109) found that b passed through a minimum between 0° and 80°C. Bockris and Parsons (24) observed that α increased slightly with increase of temperature in methanol solutions of hydrogen chloride. Hickling and Salt (93) found that in 1 N aqueous hydrochloric acid b decreased with temperature on some metals, e.g., tungsten. (It is also relevant to record that Stout (151) observed b constant with increasing temperature for the deposition of the azide ion, and Roiter and Jampolskaja (142) observed the same behavior of b in work on the electroreduction of oxygen.)

There is therefore little evidence to show that α is in general independent of temperature and indeed this would not be expected on theoretical grounds (24). No measurements exist in solutions containing capillary-active substances in known quantities. It would seem advantageous to extend the range of temperatures downwards by the use of non-aqueous solutions. This would be particularly useful for those metals which dissolve at higher temperatures.

3. Effect of change of state

An important experiment carried out by Bowden and O'Connor (33) showed that fusion of a gallium cathode caused the hydrogen overpotential at a current density of 10^{-4} amp./sq. cm. to increase considerably.

4. Effect of pressure

Harkins and Adams (85, 86) varied the pressure simultaneously over a mercury cathode and the reference electrode and found no effect on the overpotential. Goodwin and Wilson (80) found a decrease in overpotential on increase of pressure. Bircher and Harkins (10) repeated the work of Harkins and Adams and found that the *cathode potential* was independent of pressure, i.e., the overpotential decreased with increase of pressure. Harkins' work, of apparently excellent quality considering its early date, is confusing, as the earlier work of 1914 was published after the contradictory work of 1923.

Ipatiev (101) measured the overpotential on platinized platinum in acid and alkaline solutions with a mercurous sulfate electrode and pressures up to 100 atm. The potential of the cell was observed to increase with pressure but not in accord

with the normal logarithmic relation for the dependence of potential of a reversible electrode with pressure.

Cassel and Krumbein (40) found that the cathode potential was independent of hydrogen pressure in 1 *N* sulfuric acid and 1 *N* potassium nitrate solutions. Schmidt and Stoll (145) obtained a similar result for copper, nickel, lead, and silver cathodes in *N*/10 sodium hydroxide solutions but the results for iron, zinc, and tin cathodes were somewhat irregular.

The results for mercury cathodes are particularly contradictory, and the effect of partial hydrogen pressure in hydrogen-nitrogen mixtures was examined by Bockris and Parsons (24) in *N*/10 hydrochloric acid solutions. They found the cathode potential to remain constant with change of hydrogen pressure.

For many metals, therefore, most of the evidence indicates that the cathode potential is approximately independent of pressure.

5. *Effect of time*

(a) Build-up

Baars (6), and at about the same time Bowden and Rideal (35), reported the overpotential during the initial passage of current to be linearly dependent upon the quantity of electricity passed. For mercury this linear relation has a constant slope for nearly its whole length. For some other metals changes in slope occur, thus indicating that the charging up of the double layer is not the only process occurring during this initial increase of potential.

After this first build-up, which in oxygen-free solutions lasts about 0.25 sec. on mercury at a current density of 2.5×10^{-4} amp./sq. cm., the overpotential undergoes some more complex changes with time on some metals ("long-time" effects) which depend markedly on the properties of the metal (13, 90). Thus, for metals of high overpotential, such as lead and mercury, there is little further variation with time after the initial "short-time" build-up. With metals of low overpotential, however, considerable changes, usually increases, occur, and the overpotential may take several hours to reach a steady state. Such variations take place also in solutions which have been very stringently deoxygenated and electrolytically purified (73, 120, 127).

(b) Decay

Isolated observations made by Bowden and Rideal (35) and by Baars (6) led to the conclusion that the rate of decay of overpotential was proportional to $\log t$, where t is the time after cessation of the polarizing current. This was confirmed by Butler and Armstrong (39) for mercury and platinum cathodes, it being concluded from the relative rates of decay on these two cathodes that some electromotive atomic hydrogen existed on platinum, but not on mercury cathodes (at overpotentials less negative than -1 v.) during polarization in acid solution. Ferguson and Kleinhechsel (63) studied cathodes of platinum, palladium, gold, silver, zinc, cadmium, antimony, and nickel and found that the decay consisted of two parts: (i) a rapid potential drop completed in 0.01 sec., followed by (ii)

a slow decay towards the reversible potential. Increasing the speed of stirring increased the rate of decay. The work of Hickling and Salt (94) somewhat confirmed that of Ferguson and coworkers. The second potential decay is initially approximately proportional to $\log t$, as agrees with the earlier work, but deviates from this law after a few minutes. Frequent steps occur in the decay curves and these were shown—by examination of the effect of adding small quantities of the suspected salt—to be caused by trace metal impurities, deposited on the cathode, which reach their dissolution potential at the beginning of each step.

Frumkin and Aladjalowa (73) studied the build-up and decay of hydrogen overpotential on palladium in electrolytically purified solutions. These authors suggested that there is a quantitative connection between the build-up and decay processes, the fraction of the overpotential building up slowly after switching on the current being equal to the fraction decaying slowly. No such relation exists between the build-up and decay processes on a metal of high overpotential, e.g., lead, although these appear to be *qualitatively* similar to those on palladium (23).

6. Effect of electrode material

The dependence of the hydrogen overpotential upon the electrode material is a fundamental aspect of the phenomenon to which attention was paid by earlier workers, but which has more recently lacked emphasis. The approximate order of the metals, arranged according to their increasing hydrogen overpotential at 10^{-3} amp./sq. cm.³ in 1 *N* aqueous hydrochloric acid solution, is: platinum, rhenium, gold, tungsten, molybdenum, nickel, iron, tantalum, copper, silver, chromium, beryllium, columbium, bismuth, thallium, lead, tin, cadmium, mercury.

In general, metals with high melting points have a low overpotential and *vice versa*. Further, overpotential at a given current density increases with the metal in the same order as does the metal's power of catalyzing the reaction $\text{H} + \text{H} \rightarrow \text{H}_2$ (Bonhoeffer (26)).

It was pointed out by Bockris (13, 14) that if the hydrogen overpotential at a given current density on various metals and the thermionic work functions of the metals were both plotted against their atomic numbers, the overpotential showed a periodicity of a kind opposite in sense to the thermionic work function, i.e., metals with a large thermionic work function corresponded to those with a low hydrogen overpotential and *vice versa*. This dependence is shown in figure 4, where two definite groups and one less definite group are seen. It is notable that mercury does not fit into any of these groups. Statistical analysis shows that there are three distinct lines and that the two upper lines have significantly different slopes (18).

7. Effect of surface properties

Most workers have made small additions to knowledge of this factor, but few studies have been devoted to it, and interpretation of past results is uncertain

³ This current density is chosen for purposes of comparison because it avoids the controversies of measurements at very high or very low current densities.

owing to the unknown amount of impurity introduced into the surface during preparation.

In general, roughening lowers the overpotential. Conversely, polishing (35) tends to increase it. Scraping, i.e., removing the surface layers of a soft metal such as lead, generally reduces the overpotential somewhat from that in the unscraped (i.e., usually dirty) state. Annealing in hydrogen generally seems to increase the overpotential of the metals of lower overpotential (35). The so-called anodic activation (73) of electrodes, which consists in subjecting them to a preliminary anodic prepolarization, usually causes the overvoltage to be lowered.

Surfaces prepared by electrodeposition are associated with notably different absolute values of overpotential; the variation with time during polarization is also reduced (90). It is usual to plate onto copper or platinum; Bockris and Parsons (24) showed, however, that the overpotential depended to a significant

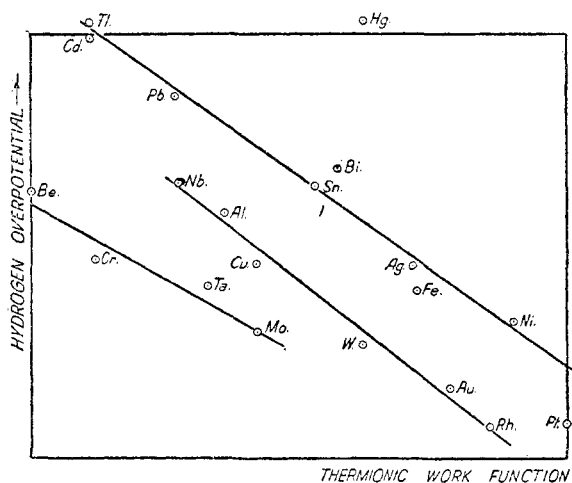


Fig. 4. Relation between hydrogen overpotential and thermionic work function

extent on the nature of the base metal for silver cathodes, so that some standard base metal, e.g., copper, must be chosen.

The effect of electropolishing the metal surface has been examined by Bockris and Azzam (19), who find that metals of high overpotential such as copper and lead are little affected by electropolishing but that for metals of lower overpotential, such as tungsten and nickel, electropolishing increases the overpotential by an order of about 0.1 v. at medium or high current densities.

8. Effect of diffusion through the cathode

Earlier work (e.g., particularly 47 and 130) on the transfer of hydrogen overpotential through a thin film of metal produced contradictory results, probably owing to the presence of impurities in solution which are known to affect adsorption markedly. Uhlig, Carr, and Schneider (155) found a transfer of potential after some minutes for electrodes consisting of iron-chromium alloys in partially deoxygenated sodium chloride solution. Conversely, Ferguson and Dupbernall

(62) failed to observe any transfer of overpotential through platinum and palladium plates and concluded that previous erroneous observations of a transfer had been caused by the porosity of the films to the solution by means of passage through the Smekal cracks.

Work in prepolarized solutions by Frumkin and Aladjalowa (73) showed an immediate transfer of a part of the overvoltage from the polarization to the diffusion side of a palladium electrode. The part of the overpotential transferred corresponded approximately to that component of it on palladium which varied with time (see figure 5; i. e., $\eta_{\text{transferred}}$ was found equal to $\eta_1 = \eta'_1$).

The situation with regard to this work is at present unclear. In work which avoids the undesirable presence of rubber and other adhesives for attaching the

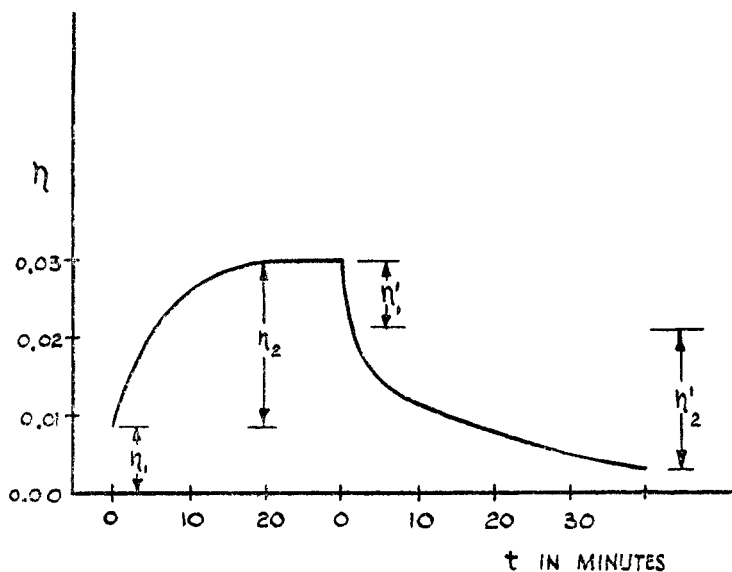


FIG. 5. Variation of overpotential with time on palladium electrode in acid solution at 10^{-4} amp./sq. cm. (73).

diffusion electrode to the glass of the cell it is extremely difficult to eliminate small leaks between the polarization and diffusion sides of the electrode. Frumkin and Aladjalowa attempted to overcome this difficulty by attaching the palladium electrodes to platinum and sealing this metal to glass. Work at Imperial College has shown that such seals are often the source of leaks (which give rise to transfers of a similar nature to those claimed by others) in these experiments.

Experiments on the transfer of overpotential are very important because they may give direct information on the "electromotive activity" of atomic hydrogen.

It may be that diffusion of hydrogen into the metal during electrolysis is more general than is often supposed. Thus, on nickel cathodes the evolution of hydrogen continues for several seconds after cessation of the polarizing current when the current density is greater than 10^{-3} amp./sq. cm. (17).

9. *Effect of shape and curvature of cathode*

According to Sederholm and Benedicks (146) overpotential is related to the radii of curvature of a curved electrode according to the empirical formula:

$$\eta = \eta_0 + K \log \left(1 + \frac{K'}{r} \right)$$

where η_0 is the overpotential on a plane surface, K and K' are constants, and r is the radius of curvature. The relation does not appear to have received specific test by other workers.

Baars (6) reported a dependence of overpotential upon the area of the electrode, but Hickling and Salt (90) could not confirm this.

10. *Effect of alloy formation*

Fischer and Barabanov (64) showed that deviations from a simple additive law existed in amalgams of cadmium, lead, and bismuth, and Cruatto and Da Via (43) found that for lead-antimony and lead-cadmium alloys in alkaline solution the overpotential rose with increase of the content of antimony or cadmium when two phases are present; in the presence of mixed crystals there is a rapid increase of overpotential with increase in antimony for lead-antimony alloys; and for lead-cadmium a decrease with increase in cadmium.

No general conclusions can be drawn from the available data. It must be questioned whether this field can be very profitable for overpotential research; changes in the structure in the surface caused by changing ratio of the components are difficult to separate from other effects of changes of composition.

C. SOLUTION FACTORS

11. *Effect of hydrogen-ion concentration*

Earlier work, particularly that of Bowden (28), was vitiated by the presence of impurities (123). Levina and Sarinsky (123) showed that in an acid concentration from 0.001 to 0.1 *N* the overpotential remains independent of the pH on mercury cathodes. Jofa (103, 104) found that at concentrations above 0.1 *N* in hydrochloric acid the overpotential becomes less negative with increasing hydrogen-ion concentration. This decrease with increasing hydrogen-ion concentration was also observed by Béthune and Kimball (8) in sulfuric and phosphoric acid solutions up to 9.65 *M* sulfuric acid and 5.65 *M* phosphoric acid. Bockris and Parsons (24) found that in methyl alcohol solutions of hydrogen chloride the hydrogen overpotential at a dropping-mercury electrode was affected by pH change to a larger extent than that in aqueous solution and the change with concentration began at a notably higher pH than in aqueous solutions.

On metals other than mercury the situation is not yet clear. On lead, Kabanov and Jofa (106) found that the overpotential was almost independent of the pH for the range 0.01–8 *N* sulfuric acid. At higher concentrations in sulfuric acid solution, the overpotential decreases with increasing concentration. A

similar change was noted in solutions of hydrochloric, hydrobromic, and perchloric acids, the changes with concentration being less than for mercury (104).

On nickel Lukovtsev, Levina, and Frumkin (127) found an independence of the pH only in the region 0.0003–0.001 *N*. At concentrations above 0.001 *N* the overpotential decreases with increasing hydrogen-ion concentration (see also Legran and Levina (121) and Sindjukov (148)).

Hickling and Salt (93) consider that for platinized platinum, tungsten, and mercury, the changes which occur upon increase of the concentration of hydrochloric acid from 0.1 *N* to 6 *N* have no fundamental significance. They observed, however, a large increase in overpotential at 10^{-1} amp./sq. cm. in 0.1 *N* hydrochloric acid solution on tungsten and platinum, a fact which they attribute to the existence of large concentration overpotential at this concentration, although it was not observed on mercury cathodes under the same concentration conditions.

Very little work has been done in alkaline solutions. On mercury cathodes it is particularly difficult, owing to the simultaneous deposition of sodium. Amalgam formation is unimportant at low current densities, according to Bowden and Kenyon (113).

12. *Effect of foreign salts*

Erdey-Grúz and Szarvas (49) measured the effect of various simple salts on the overpotential at mercury and found the mean activity of the salt (*a*) to be related to the overpotential in salt solution by the approximate empirical equation:

$$\eta = \eta_0 + K \log a$$

where η_0 is the overpotential in pure acid solution and *K* is a constant.

Levina and Sarinsky (123) examined the effect of lanthanum chloride on mercury cathodes and found that it caused a decrease in overpotential, although the slopes of the Tafel lines were not affected. Effects of low-valent halides are more complex and according to Jofa, Kabanov, Kutschinski, and Chystiakov (107) addition of potassium halide to hydrochloric acid solution decreases the *a* value of the Tafel equation particularly at low current densities, thus causing an inflection on the Tafel line (figure 6) (see also Kolotyrkin and Bune (119)).

On metals of low overpotential there is little data on the salt effect. Lukovtsev, Levina, and Frumkin (127) have shown that for nickel at low current densities in acid solution, lanthanum chloride causes a lowering of overpotential, but at higher current densities an increase. In alkaline solutions, a small lowering is produced in dilute solutions which becomes zero in concentrated solutions.

13. *Effect of solvent*

The first examination of the solvent effect under suitable experimental conditions was made by Levina and Silberfarb (124), who found that at a low current density on mercury a lowering of overpotential took place in alcoholic when compared with aqueous solutions. The *b* value remained unchanged. This

was confirmed by Novoselski (134). Bockris and Parsons (24) examined the solvent effect on mercury cathodes at low and intermediate current densities in $N/10$ methanolic hydrochloric acid and the corresponding methanol-water mixtures. The b values decrease up to 0.3 mole fraction of alcohol. At constant current density there is, on addition of methyl alcohol, an initial lowering of overpotential, which then remains constant until high alcohol concentration, when it again falls to the value in pure methanol solution, which is about 0.14 below that in aqueous solution. Similar results were observed at dropping mercury electrodes. Hickling and Salt (91) measured the overpotential on mercury at high current densities in solutions of hydrogen chloride in ethylene glycol, ethyl alcohol, and cyclohexanol. Contrary to the uniform results of

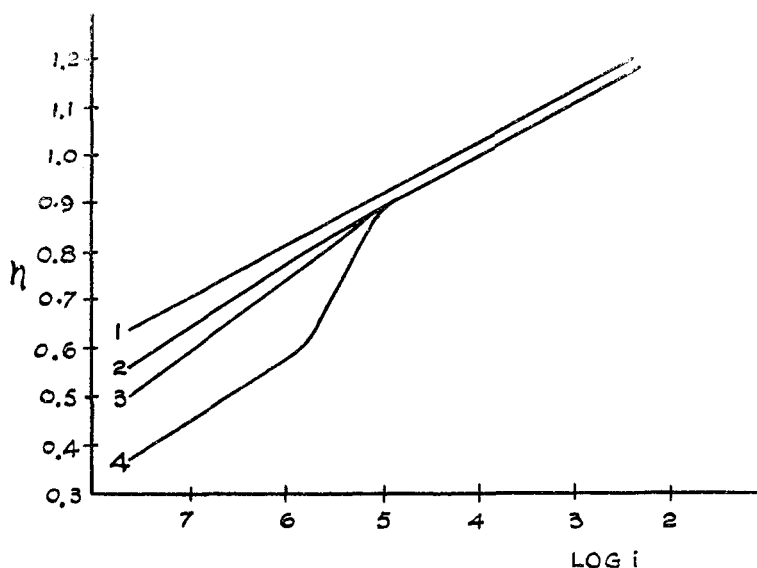


FIG. 6. Effect of salts on hydrogen overpotential. Curve 1, $N \text{ Na}_2\text{SO}_4 + 0.1 N \text{ H}_2\text{SO}_4$; curve 2, $N \text{ KCl} + 0.1 N \text{ HCl}$; curve 3, $N \text{ KBr} + 0.1 N \text{ HCl}$; curve 4, $N \text{ KI} + 0.1 N \text{ HCl}$.

the above authors, these workers found the overpotential to be greater in the non-aqueous than the aqueous solutions.

Hickling and Salt (91) also examined the solvent effect on lead, tin, tungsten, platinum, and lead at high current densities and found here also an increase with change of solvent. This result is probably due to the presence of sealing wax as a fixative for cathodes in the systems of these workers: its dissolution would cause a poisoning effect. Bockris *et al.* (12, 15, 23, 24) carried out an investigation of the solvent effect on lead, tin, copper, and nickel cathodes, using solutions of $1 N$ hydrochloric acid in the solvents methyl and ethyl alcohols, glycol, formic and acetic acids, ether, dioxane, and, where practical, a complete range of mixtures of these with water. In general it appears that on the metals of high overpotential—lead, tin, and, to a lesser extent, copper—there tends to be

a decrease of overpotential in the non-aqueous solvents which was greatest for methyl alcohol and least for ethylene glycol solutions, whilst on nickel the overpotential was little changed or somewhat increased. More complex effects occurred in mixed solvents, in which the overpotential passed through a maximum at intermediate composition in some systems. Measurements of the overpotential on twelve metals over the range 10^{-3} to 10^{-1} amp./sq. cm. in a 1 *N* solution of hydrogen chloride in methyl alcohol showed that on metals of low overpotential little change in *a* or *b* occurred; on metals of medium overpotential *b* was slightly decreased and *a* increased; and on metals of high overpotential *a* was decreased.

Pleskov (139) measured the hydrogen overpotential on nickel, mercury, and lead in liquid ammonia at -50°C. , but the results must be considered to be largely vitiated owing to the presence of visible films formed during electrolysis on the electrode surface of the last two metals. Results on nickel are difficult to compare with those in aqueous solution, owing to the large temperature differences involved.

14. *Effect of catalytic poisons and activators*

Several isolated studies of the effect of additives on overpotential have been carried out but systematic work is lacking. Kobozev and Nekrasov (118) found that mercurous chloride or hydrogen sulfide increased the hydrogen overpotential on platinum cathodes. Volmer and Wick (158) found that small amounts of arsenic trioxide brought about a lowering of overpotential on a platinum cathode, the *b* value in Tafel's equation being also lowered; higher concentrations, however, caused an increase in *a* and *b*. Knorr and Schwartz (117) found that arsenic trioxide raised the *b* value for a platinum cathode at all concentrations, which is the generally accepted result (see Von Naray-Szabo (160)). Varisikova and Kabanov (156) carried out an extensive study of the effect of additives on a spongy lead cathode in 2.8 *N* sulfuric acid. They found that alkylammonium derivatives were particularly effective in raising the hydrogen overpotential. Hickling and Salt (93) observed increases on mercury, tungsten, and platinized platinum cathodes caused by additives of carbon disulfide, arsenic trioxide, and mercuric chloride.

The converse phenomenon of additives which lower the overpotential is a rarer one. Semerano (147) observed that some alkaloids changed their polarographic half-wave potentials for the discharge of hydrogen from aqueous acid solutions to more positive values, and Bockris and Conway (20) found that certain alkaloids of the quinoline group caused a lowering of overpotential on mercury. The effect was decreased on tungsten and inverted on platinized platinum (see figure 7).

The situation in this field suffers particularly from a lack of systematic work on various cathode materials and correlation of the concentration of the additive with its activity. A connection between the structure of the additive and the threshold concentration at which the overpotential is affected should be obtained. Study of the dependence of activating or poisoning action on the structure of the additive, and adsorption measurements on poisoned electrodes, are necessary.

An interesting application of the study of poisons on hydrogen overpotential is in the field of inhibitors of acid corrosion. Bockris and Conway (22) have shown, by measurements of overpotential on iron cathodes by direct and commutator methods in solutions containing certain organic bases, that the presence of these inhibitors raises the true hydrogen overpotential. The mechanism of partial inhibition of the acid dissolution of iron is hence by a direct effect on the hydrogen overpotential and not by means of the mechanical protection of an adsorbed film, as had been suggested (42).

15. Effect of gaseous depolarizers, e.g., oxygen

In spite of frequent qualitative observations in the literature, few authors have undertaken quantitative work on the action of oxygen on hydrogen overpotential. Hickling and Salt (92) examined the effect of additions of oxygen to a solution containing a mercury (amalgamated copper) electrode: at current densities above

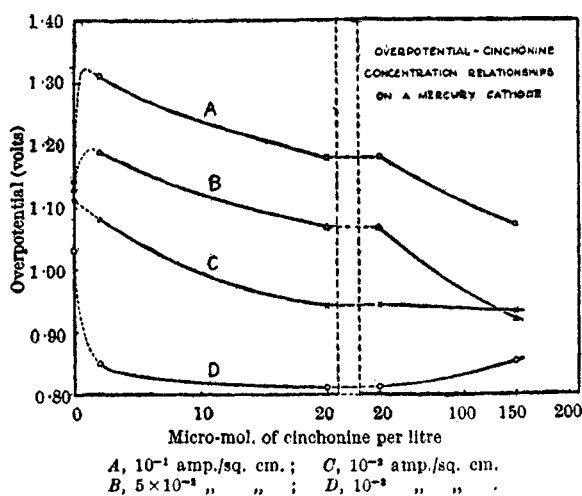


Fig. 7. Effect of cinchonine on hydrogen overpotential

10^{-3} amp./sq. cm. they found that the overpotential was almost independent of the amount of oxygen present, although this had a very considerable effect at current densities below 10^{-3} amp./sq. cm. Bockris and Azzam (19) found that oxygen still had a marked lowering effect (about 0.15 v.) on the overpotential at a current density of 10^{-3} amp./sq. cm. at a liquid mercury electrode and that the current density above which the effect of oxygen became negligible varied somewhat with the cathode material.

The effect of gaseous depolarizers other than oxygen does not seem to have been studied.

16. Effect of colloids

No recent measurements of the effect of colloids on overpotential appear to be recorded in the literature. Older work indicates an increase of overpotential on addition of colloidal material (128, 141).

17. *Effect of radiation*

Bowden (30) showed that the hydrogen overpotential on a mercury cathode was reduced by ultraviolet light. The threshold frequency was 4000 Å. and the effect depended on the potential. Preliminary attempts (133, 138) have also been made to examine the effect of supersonic waves on overpotential, but it seems likely that the small effects observed were caused by resultant decreases in concentration overpotential.

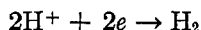
In a field yielding direct quantitative information on the kinetics of the reaction at the cathode, more work might have been expected. A comparison of the effect of light on cathodes evolving hydrogen and oxygen (the transfer of electrons here being activated in an opposite direction) would be of particular interest. A difficulty which might be expected in the experimental technique is that of heating effects, which may obscure the very small changes in potential due to light effects.

IV. THE THEORY OF HYDROGEN OVERPOTENTIAL

A. GENERAL EQUATIONS AT A WORKING HYDROGEN ELECTRODE

1. *Definition of currents at cathode and anode*

Suppose that \bar{v} is the velocity of the reaction:



and \bar{v} that of the reaction:



Then $F(\bar{v} - \bar{v})$ may be called the *net cathodic current*, i_c :

$$i_c = F(\bar{v} - \bar{v}) \quad (1)$$

Correspondingly, the net anodic current, i_a , is:

$$i_a = F(\bar{v} - \bar{v}) \quad (2)$$

From equations 1 and 2:

$$i_c = \bar{i} - \bar{i} \quad (3)$$

$$i_a = \bar{i} - \bar{i} \quad (4)$$

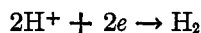
where the quantities \bar{i} and \bar{i} may be termed the *cathodic and anodic current*, respectively.

At equilibrium, $i_c = i_a = 0$

$$\bar{i} = \bar{i} = i_0 = \text{the exchange current} \quad (5)$$

2. *The Tafel equation*

For the reaction



let it be assumed, for conditions under which $\bar{v} \gg \bar{v}$, (1) that the velocity of the rate-determining stage is controlled by a process which can be undergone only by particles having more than some minimum (activation) energy and that such particles are Maxwellianly distributed; and (2) that the energy of activation of the reaction is affected by the electric field of the cathode by an amount proportional to some part ($E - X$) of the metal solution potential difference, where E is the potential difference of the metal solution and X may depend on the condition of the electrode surface, or the properties of the solution, etc. Let the proportionality factor for this effect of the cathode field be α .

Hence:

$$i = Ae^{-[U+(E-X)\alpha F]/RT} \quad (6)$$

where U is the "thermal part" of the energy of activation of the reaction and A is a collision factor characteristic of the mechanism of the reaction; A may depend on the concentration of some entities in the solution near the electrode and/or on the electrode surface.

$$E = K + X - \frac{RT}{\alpha F} \cdot \log_e i \quad (7)$$

But $\eta = E - E_r$, where E_r is the potential of a reversible hydrogen electrode under the same conditions, except for flow of current, as those for the irreversible electrode.

$$\eta = \left(K + X - \frac{RT}{F} \log_e a_{H^+} \right) - \frac{RT}{\alpha F} \log_e i \quad (8)$$

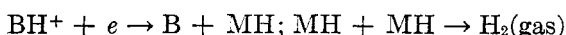
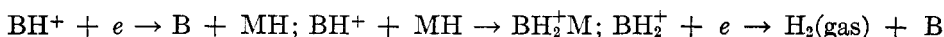
Or,

$$\eta = a - b \log_e i \quad (9)$$

where a is a term dependent in the general case on pH and $b = RT/\alpha F$.⁴ Hence, assuming only a Maxwellian distribution of the particles governing the slow stage of the reaction and an effect on the energy of activation proportional to some part of the cathode potential, overpotential is found to be logarithmically related to current density. It is stressed that no particular mechanism of overpotential is assumed in this deduction.

3. The reaction $2H^+ + 2e \rightarrow H_2$ at the working hydrogen electrode: principal theories of hydrogen overpotential (16)

If the solvent molecule with which the hydrogen ion is solvated is represented by B and the cathode material by M, the following are possible reaction paths occurring during the electrolytic evolution of hydrogen:



⁴ Numerical values of b quoted in this work are always to $2.303RT/\alpha F$.

Various stages in these reaction paths have been assumed to be rate determining, which assumptions give rise to the theories of hydrogen overpotential. Those of modern interest are set out below:

ORIGINAL AUTHORS	A: MAIN THEORIES	NAME OF MECHANISM
Smits (169).....	$\text{BH}^+ + e \rightarrow \text{B} + \text{MH}$	Slow discharge
Horiuti (96).....	$\text{BH}_2^+ + e \rightarrow \text{B} + \text{H}_2$	Molecular hydrogen ion
Eyring (157)....	$\text{B} + \text{B} + e \rightarrow \text{MH} + (\text{B-H})^- + \text{B}$	Prototropic transfer
Tafel (153).....	$\text{MH} + \text{MH} \rightarrow \text{H}_2 + 2\text{M}$	Catalytic
Horiuti (99).....	$\text{BH}^+ + \text{MH} + e \rightarrow \text{H}_2(\text{gas}) + \text{B} + \text{M}$	Electrochemical
	B: DUAL THEORIES	
Kobozev (118) ..	$\text{MH} + \text{MH} \rightarrow \text{H}_2(\text{gas}) + 2\text{M}$ $\text{BH}^+ + \text{MH} + e \rightarrow \text{B} + \text{H}_2(\text{gas}) + \text{M}$	Catalytic-electrochemical
Frumkin (69)....	$\text{BH}^+ + e \rightarrow \text{B} + \text{MH}$ $\text{BH}^+ + \text{MH} \rightarrow \text{H}_2(\text{gas}) + \text{B} + \text{M}$	Slow discharge-electrochemical

For a review of older theories, see reference 7. The above equations are incomplete expressions of the various theories and do not indicate the detailed mechanism of reaction.

The processes occurring at a cathode during the electrolytic evolution of hydrogen involve (i) the transport of the solvated ion BH^+ to a position in the double layer at the electrode-solution interface, where it can be regarded as adsorbed; (ii) neutralization of the proton, either by (a) electron transfer to the proton or (b) proton transfer to the electron-donating surface of the metal; (iii) desolvation of the proton; (iv) adsorption of hydrogen atoms produced in stage (ii) on the cathode surface; (v) desorption of the hydrogen atoms by (a) catalytic combination or (b) combination with a proton and an electron to form hydrogen molecules.

The above processes at the cathode can be divided into two parts: (I) the processes ii, iii, and iv; and (II) the processes v. Processes ii, iii, and iv constitute the discharge of hydrogen ions,—namely, the production of adsorbed hydrogen atoms from solvated protons or solvent molecules; processes v constitute the combination of hydrogen atoms and/or ions to form molecules.

Theories of hydrogen overpotential can therefore be divided into two ill-defined groups according to whether the rate-determining process is the *discharge* of hydrogen ions or the *combination* of entities on the electrode surface.

The principal modern contributions to the slow discharge theories can be divided into four subgroups.

(1) *General slow discharge theory* (Frumkin (66, 67, 71)): In this theory, the

discharge reaction $\text{BH}^+ + e \rightarrow \text{MH}$ is treated as a single process without detailed consideration of processes *ii(a)*, *ii(b)*, *iii*, or *iv* of the above. Frumkin states (66) that his version of the slow discharge theory does not distinguish between *ii(a)* or *ii(b)*.

(2) *The (energy level) slow discharge theory (Polanyi (100); Butler (37))*: The discharge reaction is considered without reference to a detailed mechanism but conditions for discharge are worked out energetically with reference to the molecular properties of proton, solvent, and metal.

(3) *Molecular hydrogen ion (Horiuti (96))*: According to this mechanism, the rate-controlling process is the neutralization of the H_2^+ (or BH_2^+) ion formed by combination of BH^+ with MH .

(4) *Prototropic transfer (Eyring (57))*: In this theory, the rate-determining step is the transfer of a proton from a solvent molecule in solution to a solvent molecule attached to the cathode surface. It is clear that this mechanism involves the discharge of hydrogen ions, as defined above; hence it is grouped under the heading "slow discharge."

The general slow discharge theories are ambiguous. Thus, it is claimed (2) that the processes of neutralization, desolvation, and adsorption take place simultaneously, so that no distinction can be made between them. This latter statement may be true at present, but there is no reason why the energetics of these different stages should not be considered in detail. Ambiguity also exists concerning the postulate that proton or electron transfer is rate determining. The general slow discharge theory may be subdivided into the groups: (i) slow neutralization (66, 67, 71), involving those theories in which neutralization by an electron can be regarded as the rate-determining reaction; and (ii) slow transfer, involving those theories in which proton transfer (37, 100) and prototropic transfer (57) are regarded as slow stages. The usefulness of this subdivision is lessened by the lack of clear definition of the slow stages postulated by Frumkin (66, 67, 71) and by Butler (37).

The main combination theories are divisible into two groups, in each of which there are treatments which differ only in detail.

(1) *Catalytic combination (Tafel, 153), Kobozev (118), Horiuti (99), Hickling (95))*: The rate-determining step is the second-order reaction between adsorbed hydrogen atoms.

(2) *Electrochemical mechanism (Horiuti (99), Frumkin (67))*: The rate-determining reaction is that between a solvated proton (BH^+), an adsorbed hydrogen atom, and an electron.

The concept of dual theories originated with Kobozev and Nekrasov (118), although this fact does not seem to be generally recognized. A dual theory may be defined as one in which the rate of the over-all reaction $2\text{BH}^+ + 2e \rightarrow \text{H}_2(\text{gas})$ is controlled by two processes having velocities of the same order and occurring simultaneously on the electrode surface.

For the general equation for the reaction $2\text{H}^+ + 2e \rightarrow \text{H}_2$ in which all of the above mechanisms are taken into account, see Bockris (16).

B. THE SLOW DISCHARGE THEORIES

1. *General slow discharge theory*(a) *Essential theory*

Smits's (149) suggestion in 1924 that neutralization was a slow stage in the evolution of molecular hydrogen was developed quantitatively by Erdey-Grúz and Volmer (50) in 1930 on the evidence of the charging curve data of Baars (6) and of Bowden and Rideal (35), which were not explicable on the Tafel mechanism. Erdey-Grúz and Wick (51) allowed for a non-symmetrical energy barrier at the electrode-solution interface in this treatment.

Gurney (83) developed the theory quantum-mechanically, supposing neutralization to take place by tunnel electrons at some distance from the cathode (see Fowler (65) for a review of this work). Gurney's theory is now rejected because: (i) Topley and Eyring (154) showed that the mechanism leads to energies of activation much higher than those observed; (ii) according to it, overpotential should be independent of the cathode material and its surface properties. Actually, overpotential at constant current density decreases with increasing work function of the metal (13, 14, 16) and depends markedly on surface properties. These latter objections do not necessarily apply to other slow discharge theories, some of which yield interpretation of the latter factors from the assumption of adsorbed hydrogen atoms on the electrode surface.

The above theories indicated that hydrogen overpotential depended on the pH; this is not so in dilute solution at mercury cathodes. Frumkin (66) avoided this difficulty by taking into account the difference in hydrogen-ion concentration in the bulk of the solution and in the electrical double layer. Assuming (i) that Stern's theory (150) of the double layer is valid, and (ii) that the solutions are dilute, then:

$$(C_{H^+})_{D.L.} = (C_{H^+})e^{-\psi F/RT} \quad (10)$$

$$\psi = \psi_0 + \frac{RT}{F} \log_e C_{H^+} \quad (11)$$

where $(C_{H^+})_{D.L.}$ is the hydrogen-ion concentration in the double layer, (C_{H^+}) that in the bulk, and ψ the potential at one ionic radius from the electrode surface, relative to the bulk. This was taken initially to be approximately the same as the electrokinetic potential.⁵

Equation 10 is correct if the solution near the cathode surface is far from saturation with hydrogen ions, which is usually so for negative polarizations, as follows from a calculation from the known capacity of the mercury-solution interface under these conditions (66).

Let E be the potential of the working electrode at a given current density. Then, if only the potential across the Helmholtz section of Stern's double layer is effective in controlling the rate of ionic neutralization at the electrode surface:

$$\vec{i} = k_1(C_{H^+})_{D.L.}e^{-[a_1(E-\psi)F]/RT} \quad (12)$$

⁵ Equation 11 is a rough approximation from Stern's theory. Equations 10 and 11 are not in agreement unless $(C_{H^+})_{D.L.}$ is independent of pH.

Similarly:

$$\vec{i} = k_2(C_H)e^{[\alpha_2(E-\psi)F]/RT} \quad (13)$$

where C_H is the concentration of hydrogen atoms at the electrode, k_1 and k_2 are rate constants, and α_1 and α_2 are constants the meaning of which is not clear.

If $E = E_r$, the reversible potential, equation 5 is true.

Evaluation of E_r from equations 5, 12, and 13 and comparison with Nernst's thermodynamic equation for E_r shows that:

$$\alpha_1 + \alpha_2 = 1$$

In general, if the rate of the neutralization reaction is i_c amp./sq. cm. of cathode surface, then:

$$\begin{aligned} i_c &= \vec{i} - \overleftarrow{i} \\ &= k_1(C_{H^+})_{D.L} e^{-[(E-\psi)\alpha_1 F]/RT} - k_2(C_H)e^{[(E-\psi)\alpha_2 F]/RT} \end{aligned} \quad (14)$$

At sufficiently high current densities $\vec{i} \gg \overleftarrow{i}$. Hence, from equation 14 and the equation for E_r :

$$\eta = \text{const.} - \frac{RT}{\alpha_1 F} \log_e i_c - \left(1 - \frac{1}{\alpha_1}\right) \frac{RT}{F} \log_e C_{H^+} + \left(1 - \frac{1}{\alpha_1}\right) \psi \quad (15)$$

Therefore, assuming equation 11:

$$\eta = \text{const.} - \frac{RT}{\alpha_1 F} \log_e i \quad (16)$$

For very low current densities the second term in equation 14 becomes appreciable and causes the Tafel line to become asymptotic to the log current density axis. The conclusion that at low current density overpotential is proportional to current density cannot be made from Frumkin's versions of the general slow discharge theories.

From equation 15 pH change has no effect on overpotential in pure solutions. This result depends upon the use of equation 11, which is inexact, and the more basic assumption that ionic adsorption potentials can be neglected. If an excess of neutral salt is added, ψ is a constant and hence at constant current density:

$$\eta = \text{const.} - \left(1 - \frac{1}{\alpha}\right) \frac{RT}{F} \log_e (C_{H^+}) \quad (17)$$

where the constant term is independent of pH.

For addition of neutral salts at constant pH and current density from equation 15:

$$(\eta + \psi) = \text{const.} \quad (18)$$

(b) Development of the general theory of slow discharge

Essin (55) generalized the theory in the form given by Erdey-Grúz and Volmer (50) by taking into account activity coefficients and concentration overpotential.

Recent developments have been mainly concerned with the interpretation of pH and salt effects on overpotential at higher acid concentrations.

In this connection, Jofa and Frumkin (105) attempted to allow for the effect of ion-solvent interaction in the double layer. These authors add to the energy of the transition state, equivalent in the elementary theory to $(\alpha(E - \psi) + \psi)F$, a term correcting for the difference in the activity coefficient of the hydrogen ion in the transition state to that in the bulk which occurs owing to changes in solvation at the electrode surface. Thus, the energy corresponding to the above term now becomes: $(\alpha(E - \psi) + \psi)F + RT \log_e f_T - RT \log_e f_{H^+}$, where f_T and f_{H^+} are activity coefficients of the hydrogen ion in the transition state and the bulk, respectively.

Hence:

$$i_e = k_1 \frac{f_T}{f_{H^+}} (C_{H^+}) e^{-[(\alpha(E - \psi) + \psi)F]/RT} \quad (19)$$

Let

$$f_T = f_{H^+}^{(1+\alpha')} \quad (20)$$

$$i_e = k_1 C_{H^+} f_{H^+}^{\alpha'} e^{-[(\alpha(E - \psi) + \psi)F]/RT} \quad (21)$$

Whence:

$$\begin{aligned} \eta = \text{const.} - \frac{RT}{\alpha F} \log_e i + \left(\frac{1 - \alpha}{\alpha} \right) \frac{RT}{F} \log_e C_{H^+} \\ + \left(\frac{\alpha'}{\alpha} - 1 \right) \frac{RT}{F} \log_e f_{H^+} - \frac{(1 - \alpha)}{\alpha} \psi \end{aligned} \quad (22)$$

If equation 11 is applicable, the variation of overpotential with pH can depend only on f_{H^+} . This is improbable, for if f_{H^+} is varied with constant anion content (e.g., in hydrochloric acid-potassium chloride mixtures) the overpotential remains constant. Further, changes in overpotential with pH found on mercury cathodes are dependent on the cathode potential, so that anions are probably present in the double layer (105). Hence, changes with pH arise mainly from the inapplicability of equation 11 in concentrated solution.

Of considerable interest to the slow discharge theories is the recent work of Fedotov (58) who showed, by means of capacities calculated from decay curves, that for mercury the usually accepted value of the double-layer capacity ($18-20 \mu F/\text{sq. cm.}$) is retained over the current density range 5×10^{-5} to 5×10^{-3} amp./sq. cm., i.e., at quite high overpotentials. This indicates that over this range of current densities there is no change in the amount of atomic hydrogen on the mercury surface. Frumkin (72) considers that this implies absence of hydrogen atoms from the surface of mercury polarized under these conditions, so that a slow combination mechanism cannot be important on mercury cathodes.

(c) Fundamental aspects of the general slow discharge theory

There is good qualitative agreement between this theory and experiments on mercury cathodes. In particular, a reasonable, though only qualitative, explanation of salt and pH effects is given. The following difficulties arise:

(i) The coefficient α receives no special interpretation (*cf.* Horiuti and Polanyi (100)), and the value of $\alpha = \frac{1}{2}$ is purely experimental and has no theoretical basis. On the basis of some other theories, however (e.g., that of Eyring (57) or Hickling (95)), a reasonable theoretical estimate can be given for α .

(ii) The theory does not lead to calculation of correct numerical values in contrast to other mechanisms (96, 99, 135).

(iii) The effect of adsorption of hydrogen atoms on the discharge process is undefined. On metals of high overpotential it appears that adsorbed hydrogen is supposed to be absent from the metal surface (*cf.* Frumkin's (72) conclusions to Fedotov's work, etc.) The theory is not then consonant with the connections between surface properties, work function, etc., and overpotential on other metals of high overpotential.

(iv) Discharge of many ions proceeds without marked overpotential. It is unclear why discharge of protons should be a slow stage.

2. The (energy level) slow discharge theory

Horiuti and Polanyi (100) first considered the discharge of protons ("proton transfer," according to these authors) in the light of energy level diagrams. They assumed adsorption of the hydrogen atoms formed from the discharged proton and were the first authors to point out that the state of adsorption of these could affect the rate of proton discharge so that the experimental connection between properties of the metal surface and overpotential became understandable without assuming necessarily that a surface-catalyzed reaction was rate determining.

Butler (37) developed the views of Horiuti and Polanyi and those of Gurney. The energy required to remove an electron from the lowest energy level of a hydrogen atom is the ionization potential, I . Electrons may hence pass from the cathode material to an adjacent hydrogen ion if $\phi < I$, where ϕ is the thermionic work function of the metal. In solution, the stabilizing solvation energy (L) and the repulsion energy (R) between water and the hydrogen atom must be taken into account, so that $\phi < I - L - R$ becomes the condition for neutralization. This is true if a zero potential difference exists at the metal-solution interface. If this potential difference is V , $\phi + Ve < I - L - R$ is the condition for neutralization. If the metal is one of low overpotential, the adsorption energy of hydrogen atoms on the metal is also added, so that $\phi + Ve < I - L - R + A$.

The condition for discharge can be illustrated by a plot of potential energy against distance (figure 8). AA represents the curve of L , the interaction energy of a proton and water raised by a distance corresponding to I ; BB represents the curve of R raised vertically by $\phi + Ve$. To combine the latter curve with a curve representing A to obtain a curve representing $\phi + Ve + R - A$, the distance between the center of the water molecule and that of a metal atom in the cathode is assumed to be the sum of the radii of these entities. CC represents the combined curves of $R - A$ raised by a distance corresponding to $\phi + Ve$.

Suppose C^1C^1 represents $\phi + Ve - R + A$ for the electronic level $\phi - \Delta\phi$; then the probability of finding an electron in this level is proportional to $e^{-\Delta\phi/RT}$. As C^1C^1 intersects AA at X^1 , an electron in the level $\phi - \Delta\phi$ can neutralize an

ion in the energy level E corresponding to X^1 . The probability of an ion having this energy is $e^{(E_0-E)/RT}$.

Hence:

$$i = \int_{E_0}^E e^{(E_0-E)/RT} e^{-\Delta\phi/RT} \text{const. } dE \quad (23)$$

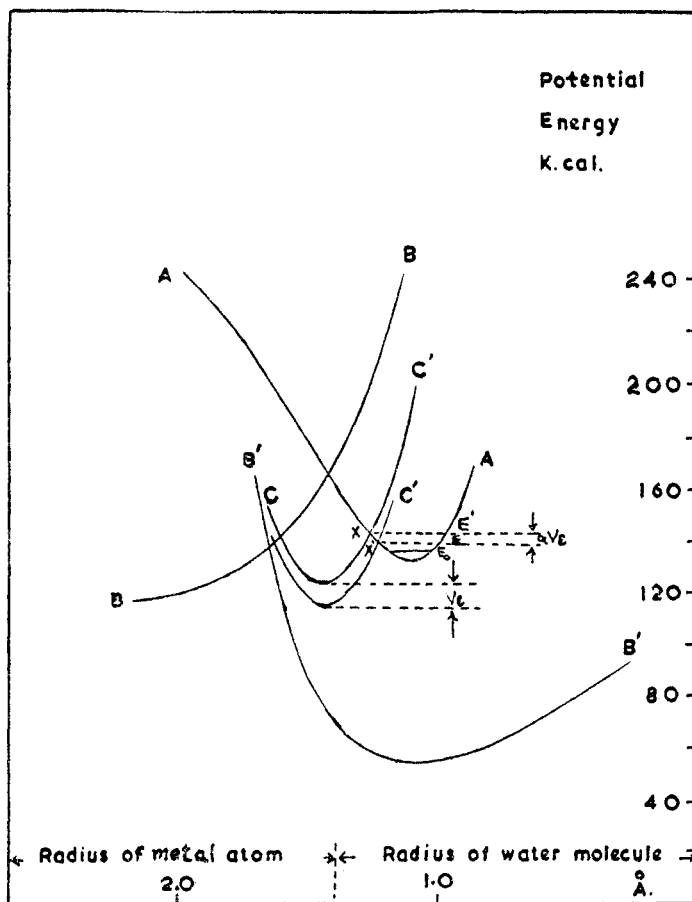


FIG. 8. Plot of potential energy against distance

But

$$\Delta\phi = -\frac{m_C - m_A}{m_A} (E^1 - E) = \frac{1}{\alpha} (E^1 - E), \text{ say.} \quad (24)$$

$$i = \int_{E_0}^E e^{(E_0-E)/RT} e^{(E^1-E)/\alpha RT} \text{const. } dE \quad (25)$$

Whence, with the relation

$$\frac{dE^1}{dV} = \alpha \quad (26)$$

the equation

$$V = a^1 - \frac{RT}{\alpha F} \log_e i \quad (27)$$

is obtained.

The slow discharge theory as given by Butler is particularly useful in providing a model for proton discharge. The following ambiguities exist: (i) the rate-determining stage implied is unclear; (ii) there is no attempt to deal with the effect of concentration factors and the structure of the electrical double layer. If V is assumed to be the absolute cathode potential and a concentration term is introduced into the equation for the current, then an incorrect dependence of overpotential on concentration is obtained (24). A rigorous kinetic treatment of the energy level slow discharge theory would be valuable.

3. Hydrogen molecule ion theory

Horiuti, Okamoto, and Hirota (96) suggested that the rate-determining stage at metals of high hydrogen overpotential was the neutralization of the BH_2^+ ion. This mechanism is analogous to the general theory of slow discharge. Attention has therefore been directed to gaining support for the suggestion of the existence of H_2^+ near a cathode during the evolution of hydrogen.

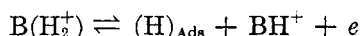
Consider a simple Helmholtz double layer, of capacity C .

$$-CE = e(n_{\text{H}^+} + n_{\text{H}_2^+}) \quad (28)$$

where E is the absolute electrode potential, e the electronic charge, and n_{H^+} and $n_{\text{H}_2^+}$ the numbers of H^+ and H_2^+ present per square centimeter of the electrode surface. Hence, the charge necessary to create a unit area of new surface is

$$q = e(n_{\text{H}^+} + 2n_{\text{H}_2^+}) \quad (28a)$$

n_{H^+} and $2n_{\text{H}_2^+}$ are calculated as a function of potential by consideration of the equilibrium



so that at equilibrium

$$F\eta = RT \log_e \frac{n_{\text{H}_2^+}}{n_{\text{H}^+} C_{\text{H}^+}} + C' \quad (29)$$

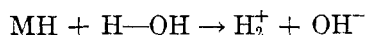
where C' is a constant.

Calculation of the charging current as a function of η on this basis (i.e., assuming the existence of H_2^+) agrees quantitatively with experimental results obtained by the authors with dropping-mercury electrodes, though these are somewhat at variance with the results of other workers. α is shown to be given by the relative inclination, at the point of intersections of the potential energy-distance relations for H^+ and H_2^+ and, when repulsion on the mercury surface is allowed for, turns out to be 0.6 in quite good agreement with experiment.

This theory is based upon an apparently reasonable quantitative calculation,

unlike the theory considered above. However, direct experimental support, which is based upon one type of measurement, must be considered to be slender.

It may be noted that an H_2^+ ion also appears in Heyrovsky's theory (87), which is based mainly upon polarographic data. Here, it arises from the combination of H_{Ads} with a solvent molecule:



No direct support for the existence of the H_2^+ ion is given.⁶

4. Slow prototropic transfer theory

(a) Essential theory

The theory of absolute reaction rates was applied by Eyring, Glasstone, and Laidler (57) to hydrogen overpotential as follows: If α is the fraction of the over-

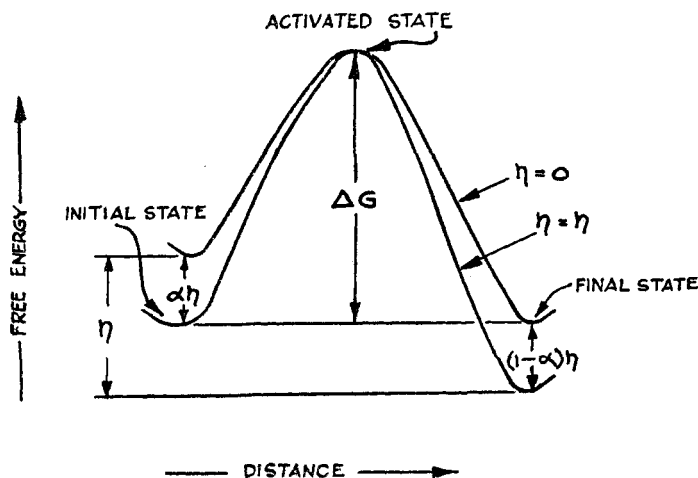


Fig. 9

potential which affects the velocity of the rate-determining reaction at the electrode surface in the direction of cathodic discharge (figure 9), then:

$$i_c = \frac{F}{N} \left[C_1 \frac{kT}{h} e^{-[\alpha\eta F + \Delta G_1^*]/RT} - C_2 \frac{kT}{h} e^{[(1-\alpha)\eta F - \Delta G_2^*]/RT} \right] \quad (30)$$

where C_1 and C_2 are the concentrations of the reacting entities in the rate-determining processes controlling the cathodic and anodic currents, respectively.

When

$$\vec{i} \gg \overleftarrow{i} \quad \eta = \frac{RT}{\alpha F} \log_e \frac{FC_1 kT}{Nh} - \frac{\Delta G_1^*}{\alpha F} - \frac{RT}{\alpha F} \log_e i \quad (31)$$

⁶ Difficulties exist in the interpretation of polarographic data on overpotential, mainly owing to the lack of information on current density in this work (75).

Or:

$$\eta = a - \frac{RT}{\alpha F} \log_e i \quad (9)$$

where a is a constant, independent of pH.

When η is so small that the term for the reverse process in equation 30 becomes appreciable, then

$$\eta = - \frac{NhRT}{F^2 C_1 kT} e^{\Delta G^\ddagger / RT} i \quad (32)$$

assuming that $C_1 = C_2$, $\Delta G_1^* = \Delta G_2^*$, and $\eta < 0.03$ v.

These general equations can now be applied to evaluating the slow stage of the reaction.

If $\eta = 0$, and $i = i_0$,

$$i_0 = \left(\frac{F}{N} C_1 \frac{kT}{h} e^{\Delta S^*/R} \right) e^{-\Delta H/RT} \quad (33)$$

or

$$i_0 = B e^{-\Delta H^*/RT} \quad (34)$$

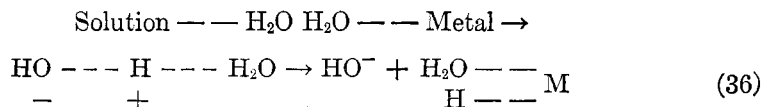
where

$$B = \left(\frac{F}{N} C_1 \frac{kT}{h} e^{\Delta S^*/R} \right) \quad (35)$$

The quantity i_0 is obtained by extrapolation from results on overpotential at low and medium current densities and ΔH can be calculated from a knowledge of the temperature coefficient. Hence, B is obtained from equation 35.

The authors conclude from a small number of experimental values of ΔH that B is substantially a constant independent of the cathode material or the pH of the solution. Exceptions are considered to be due to some extraneous factors, e.g., amalgam formation during hydrogen evolution on mercury cathodes in alkaline solution. It therefore follows that C_1 and ΔS are constant, i.e., that the concentration of the rate-determining entity is constant and independent of pH. This entity must therefore be water, which must therefore be involved in the rate-determining reaction.

It is postulated that the cathode is covered with a layer of water molecules, adjacent to which is another layer of water molecules, associated with the solution. The slow reaction is the transfer of a proton from a water molecule of the solution layer to one on the electrode layer, i.e.,



C_1 , the number of water molecules per square centimeter on the electrode surface, is approximately 10^{15} . ΔS may be roughly estimated, because from the above it

is clear that the limiting process is similar to the ionization of water and therefore the change in entropy should be of the same order, i.e., approximately -34 cal./gram-mole. Calculation of B with these values of C_1 and ΔS and the usual values of the other constants in equation 35 gives a value of the same order as the values calculated from experimental results by means of equation 34.

(b) Fundamental aspects of the slow prototropic transfer theory

This theory has the advantage of an apparently quantitative basis for its fundamental postulate. α is the fraction of ηF effective between the initial and the activated states of the discharge reaction and this leads with moderate logic to the value of $\frac{1}{2}$ for α .

Frumkin (69) has criticized the postulate that a layer of water molecules is attached to the cathode. It is difficult to assess the likelihood of this concept. Schaaf (144) concluded from observations of the effect of the vapor of water and alcohols on the thermionic emission from platinum that there was reversible physical adsorption but no chemical adsorption. Cassel and Salditt (41) found that at non-polarized interfaces with mercury, the adsorption of vapor was not primarily dependent on the dipole moment of the molecule but rather on its size and molecular refractivity (e.g., benzene was strongly adsorbed and water not at all). This evidence seems to be against a chemisorbed layer of water molecules attached to the electrode but it applies to non-polarized interfaces of the solid-gas type. At a polarized solid-liquid interface it seems unlikely that molecules of a strongly polar solvent would not orient themselves perpendicularly to the negatively charged cathode and even if no chemisorption occurred, this electrostatic attachment would meet the requirements of the model. It is relevant to note that the H/D conversion is poisoned by the presence of water on the catalyst (48).

The probable existence of a cathode and a solution layer of solvent molecules does not necessarily imply a symmetrical fall of potential from cathode to solution, upon which the value $\alpha = \frac{1}{2}$ is based. According to modern theories of the electrical double layer a diffuse section is present, and there seems no *a priori* reason to suppose that the potential governing the reaction at the cathode should act only over the non-diffuse portion. Further, it seems unlikely that the two solvent layers of the slow prototropic transfer theory should be strictly symmetrical, because on the solution side the molecules must take their places in the pattern of the solvent whilst on the cathode side they presumably act more as single entities. The explanation of the value $\alpha = \frac{1}{2}$ therefore seems to be oversimplified.

A more fundamental difficulty concerns the significance of η in equation 30 and following equations. η is assumed to be the overpotential but this is obviously incorrect, the kinetics of the rate-determining reaction at the cathode being a function of the cathode-solution potential difference. This difficulty, and also the fact that the type of double-layer structure assumed at the cathode-solution interface differs from that which is successful in explaining a number of

other (particularly electrokinetic) phenomena at electrode-solution interfaces, has been discussed by Kimball, Glasstone, and Glassner (114). They continue to regard η as the overpotential, and consequently have to postulate two different double layers at the electrode-solution interface, possessing two different energy barriers over which the proton must pass. The barrier nearest to the electrode is the higher and the overpotential is therefore established essentially across this inner layer, whilst variations in equilibrium potential caused by changes in hydrogen-ion concentration are established across the outer layer. Quantitative development of this is complex and uncertain. If proton discharge is assumed to be the slow stage, η is a function of pH, but if prototropic transfer is slow, η is independent of pH. The latter mechanism is therefore accepted. No account is taken of the changes in the structure of the double layer with pH, nor of ion-solvent interaction in the double layer. In discussions of η in this connection (38, 114) it was not realized that overpotential generally varies with pH and is

TABLE 3
Dependence of B on pH

SYSTEM	B	SYSTEM	B
<i>Hydrogen overpotential</i>			
Hg/0.2 N H ₂ SO ₄	1×10^2	Hg/0.1 N NaOH.....	2×10^{-2}
Ga/0.2 N H ₂ SO ₄	3×10^2	Pt (bright)/0.1 N NaOH.....	4×10^{-2}
Wood's metal/0.1 N H ₂ SO ₄	1×10^2	Hg/0.2 N D ₂ SO ₄	2×10^{-3}
Cu/N HCl.....	4×10^2	Pb/N HCl.....	3×10^0
Pt (bright)/0.2 N H ₂ SO ₄	2×10^2	<i>Oxygen overpotential*</i>	
Pd/0.2 N H ₂ SO ₄	1×10^2	Pt/0.2 N H ₂ SO ₄	5×10^2
		Pt/0.1 N NaOH.....	1×10^0

* An advantage of the slow prototropic transfer theory is that it yields an interpretation of oxygen overpotential by a reversal of the mechanism for hydrogen overpotential described above. *B* values calculated from oxygen overpotential should be the same and are therefore given here.

independent of it as an exception. The discussion concerning the significance of η in equation 30 thus appears misguided.

There are at present insufficient data (3, 29, 36, 97, 108, 111, 152) to allow of a definite estimation of the dependence of *B* on pH. In table 3 available results for various systems are given.

From these values there is little justification for the claim of the authors that *B* is constant and independent of the pH of the solution, as most of the "constant" values are in solutions of the same pH.⁷ Moreover, Butler (38) has shown that if in place of the equation

$$i_0 = Be^{-\Delta H^*/RT}$$

⁷ The values for mercury in 0.1 N sodium hydroxide are included here, it having been shown by Bowden and Kenyon (113) that amalgam formation is not important for this system at low current densities.

the equation

$$i_0 = (C_{H^+})B^1 e^{-\Delta H^*/RT}$$

is written, a slightly more constant value of B' is obtained than B .

Temperature coefficient data are available (108, 109) in concentrated hydrochloric acid solution for mercury cathodes over the concentration range 1–10 N . B values calculated from these results vary from 10^{-6} to 10^5 . The theory is therefore definitely incorrect in concentrated acid solution (17).

The acceptance at present of the slow prototropic transfer view as a general theory of overpotential is prevented by several difficulties. However, the *method* of attack presents advantages over others and as further data concerning i_0 , ΔH^* , and ΔS^* become available, it may be possible by this approach to make a convincing estimate of the slow stage effective for a given system.

C. SLOW COMBINATION THEORIES

1. Catalytic theory

The catalytic mechanism has been treated in two fundamentally different ways. It is possible to assume the applicability of the classical thermodynamic relations between electrode potential and concentration of "electromotively active" material, and, by correlating the concentration of the latter with the current, obtain a relation between η and current density. Or, purely kinetic methods may be used with the assumption of some effect of the electrode potential on the reaction rate. These two methods can be termed respectively the "quasi-thermodynamic" and the "kinetic" catalytic theories.

(a) Quasi-thermodynamic catalytic theory

(i) Essential theory

Tafel (153) considered the slow combination between two hydrogen atoms on the electrode surface to govern their surface concentration. The atomic hydrogen was assumed to be electromotively active, i.e., the electrode potential became more negative with increasing concentration of adsorbed atomic hydrogen. An equation analogous to the Nernst equation for the relation between reversible potential and ionic activity was assumed to apply, so that if n and n_r are the number of hydrogen atoms per square centimeter on an electrode across which passes a current density i and on the reversible hydrogen electrode, respectively, then, neglecting the anodic current:

$$E - E_r = \eta = \frac{RT}{F} \log_e \frac{1}{n} \quad (37)$$

$$\text{But } i = kn^2, \text{ if the reaction } MH + MH \rightarrow H_2 \text{ is of the second order.}^8 \quad (38)$$

⁸ The order of the reaction should be 2 or 1, according to whether the slow combination is $MH + MH \rightarrow H_2(\text{gas})$ or $MH + H \rightarrow H_2(\text{gas})$.

Hence

$$\eta = a - \frac{RT}{2F} \log_e i \quad (39)$$

where a is a constant at constant T . (40)

The theory has an obvious interpretation of the relation between the electrode material and overpotential: namely, that the overpotential is low for metals of good catalytic power and high for poor catalysts.

Equation 39 is clearly incorrect, because its b factor $= RT/2F$. In equation 38 if the order of the reaction is taken to be x , then $b = RT/xF$. If $b = 0.12$, $x = \frac{1}{2}$, a result which is improbable.

Two serious difficulties are met in Tafel's original theory: (1) the b value of the Tafel equation is one found for few metals; (2) there is no experimental foundation for applying the thermodynamic equation for electrode potentials to *adsorbed* hydrogen, although it is known to be valid with respect to gaseous hydrogen at reversible electrodes. To avoid the first difficulty, it has been suggested (77) that the concentration of the hydrogen atoms outside the electrode surface should be connected to the concentration of those adsorbed on it by an adsorption isotherm. This gives $b = mRT/F$, where m is about 1-6, so that a large range of experimentally observed values of b is satisfactorily interpreted. (If m be taken as 1-10, a range which is reasonable at an electrified interface, $b = 0.03$ -0.30 approximately.)

Hickling and Salt utilize essentially this method of accounting for b and express the electrode potential equation in terms of atomic hydrogen pressures, which are considered to arise as a result of the presence of (dissolved ?) atomic hydrogen at a pressure p_H .

Hence

$$E - E_r = \eta = -1.98 - \frac{RT}{F} \log_e p_H \quad (41)$$

where -1.98 is the standard electrode potential of the atomic hydrogen electrode.

Also,

$$i = k_1 n^2 \quad \text{and} \quad n = k_2 p_H^{1/m} \quad (42)$$

where k_1 and k_2 are constants. Therefore:

$$\eta = a - \frac{mRT}{2F} \log_e i \quad (43)$$

where a is a constant, at constant T , independent of pH.

For high current densities, when a certain degree of saturation of the electrode surface has been reached, Hickling and Salt suppose that an increasing proportion of the hydrogen evolution at the cathode takes place by the electrochemical mechanism. Further increase in current density then results in no further in-

crease in adsorbed atomic hydrogen, so that p_H , and therefore the overpotential, become constant (*cf.* the experimental position, page 536).

The theory of Hickling and Salt gives a satisfactory qualitative description of the effect of many "electrode factors" but is less useful in the treatment of solution factors, e.g., pH change. It retains the chief advantage of Tafel's theory—reasonable interpretation of a —and offers a more rational account of b than most other theories.

However, the pressure of atomic hydrogen corresponding to the overpotential of 1 v. according to this theory is $10^{-16.9}$ atm. and assuming the liberal depth of 100 layers of gaseous atomic hydrogen, this pressure is equivalent to about 10^{-4} atoms over each square centimeter of electrode surface (11). Such an anomalous concentration can hardly be explained on the grounds that it is a stationary concentration of rapidly moving atoms, for if z atoms per second pass through unit area travelling at x cm./sec., the concentration of atoms is $\frac{z}{x}$ atoms/cc. But if the current is i , $z = iN/F$; hence the concentration of atomic hydrogen is iN/xF per cubic centimeter. This should be approximately equal to 10^2 atoms/cc., which is the amount per cubic centimeter corresponding to the 10^{-4} atoms in the volume described above (i.e., for a mercury electrode at 10^{-3} amp./sq. cm.). Hence $x = 10^{13}$ cm./sec. (136). These results suggest that the literal physical meaning attributable to Hickling and Salt's model is limited.

(ii) Fundamental aspects of the quasi-thermodynamic catalytic theory

A considerable difficulty in these theories is the use of thermodynamic equations to represent the potential of electrodes on which the processes are not at equilibrium. The use of isotherms such as that of Freundlich is open to criticism on similar grounds.

The assumption of electromotive *atomic* hydrogen, in the theories of Tafel (153) and of Hickling and Salt (95) in the adsorbed and the dissolved state, respectively, is made without direct evidence. There is also little treatment of the double layer in these theories, so that it is not possible to express overpotential as a function of "solution factors."

Conversely, the slow combination theories described above provide a satisfactory qualitative model for the interpretation of overpotential (particularly "electrode factors") and related phenomena (e.g., electrolytic reduction). Their correct formulation does not seem possible upon a quasi-thermodynamic basis.

(b) Kinetic catalytic theory

This has been developed by Okamoto, Horiuti, and Hirota (99) for a nickel cathode by a detailed theoretical treatment, using the transition state method and taking account of the repulsive forces between the hydrogen atoms on the nickel surface.

The limiting condition for the existence of this mechanism on a given metal is clearly the level of the lowest adsorption state (*cf.* Topley and Eyring (154)). Upon the assumption that the adsorbed hydrogen is practically non-polar,

application of the transition state method to the reaction $\text{MH} + \text{MH} \rightarrow \text{H}_2$ shows that

$$\text{Rate of combination: } V = KG e^{-\epsilon_{\text{H}_2}/kT} \frac{1}{P^2} \quad (44)$$

$$\text{Rate of atomization: } V' = KG e^{-\epsilon_{\text{H}_2}/kT} \frac{n}{Q_{\text{H}_2}} \quad (45)$$

where G is the number of adjacent pairs of metal atoms at which atomization or combination occurs, ϵ_{H_2} is the minimum potential energy of H—H in the activated state, and n is the number of hydrogen molecules per unit volume.

$$Q_{\text{H}_2} = \frac{(2\pi mkT)^{3/2} 4\pi^2 I kT e^{-\epsilon_{\text{H}_2}/kT}}{h^5 \sinh \frac{h\nu_{\text{H}_2}}{2kT}} \quad (46)$$

$$K = \frac{kT}{h} (1 - \theta)^2 e^{-u^*/kT} \sum_{j=0}^{j=1-5} \frac{1}{2} \sinh \frac{h\nu_{\text{H}_2, i, j}}{2kT} \quad (47)$$

$$q = e^{(\epsilon_{\text{H}^+} + u\theta)/kT} \sum_{j=0}^{j=1-5} \left(\frac{1}{2} \sinh \frac{h\nu_{\text{H}_2}}{2kT} \right) \quad (48)$$

$$\frac{1 - \theta}{\theta} = \sqrt{\frac{Q_{\text{H}_2}}{n}} e^{F E / RT} \quad \text{and} \quad P = \sqrt{\frac{Q_{\text{H}_2}}{n}} e^{F E / RT} \quad (49)$$

where θ = the degree of saturation of chemisorbed atoms; $\epsilon_{\text{H}_2} = -109.12$ kg.-cal.; $\nu_{\text{H}_2, i, j} = 936, 87, 1704, 368, 626$ cm.⁻¹ = normal vibration frequencies of H—H in the activated state; $\nu_{\text{H}, i, j} = 417, 479, 1900$ cm.⁻¹ = normal vibration frequency of hydrogen in the adsorbed state; $\nu_{\text{H}_2} = 4417.2$ cm.⁻¹ = harmonic frequency of a hydrogen molecule; $I = 4.65 \times 10^{-41}$ gram-cm.² = moment of inertia of hydrogen molecule; $u = 5.65$ kg.-cal. = repulsive potential of adsorbed hydrogen due to surrounding hydrogen when $\theta = 1$; $u^* = 6.70$ kg.-cal. = repulsive potential of H—H in the activated state due to surrounding chemisorbed atoms.

The steady cathodic current is found to be:

$$i = 2KG e^{-\epsilon_{\text{H}_2}/RT} \left(\frac{1}{P^2} - \frac{n}{Q_{\text{H}_2}} \right) \quad (50)$$

Tests of this expression have been carried out on nickel electrodes by calculating from it and from the interchange reaction, G , and then comparing this with z , the number of available metal atoms per square centimeter for chemisorbed atomic hydrogen. The three values obtained are 4×10^{-14} , 2×10^{-14} , and 2×10^{-14} , respectively. Direct calculations of i are also in fair agreement with experiment at low current densities and α is calculated to be 0.7 (experimental value for nickel = 0.6 in acid solution).

Criticism may be made chiefly on the ground that, from this mechanism, limiting current density would be expected at fairly low current density. This

has not been observed. The assumption that the metal-hydrogen bond is non-polar is also doubtful, and if it is assumed to have a reasonable dipole moment the calculated value of α is erroneous (70).

Conversely, the theory yields quantitatively correct values of overpotential on nickel at low current densities and is the most comprehensive attempt at a rigorous quantitative kinetic theory of hydrogen overpotential hitherto made. The approach invites much further work.

2. Electrochemical theory

It was first suggested by Kobozev and Nekrasov (118) that the rate-controlling step at working hydrogen electrodes was under certain conditions the combination of solvated hydrogen ions with adsorbed hydrogen atoms and an electron to form gaseous molecular hydrogen. Horiuti and Okamoto (96) also utilized this mechanism. A concise treatment is given by Frumkin (67) as follows:

Let ψ be momentarily assumed equal to 0, C_{H^+} be the number of hydrogen ions adsorbed on the surface, n = the number of adsorption centers on the surface, and E the cathode potential.

The following reactions (i, ii, and iii) take place:



The rate of this process is given by

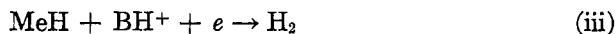
$$R_1 = k_1 \left(1 - \frac{C_H}{n}\right) C_{H^+} e^{-EF/2RT} \quad (51)$$

where C_{H^+} is the hydrogen-ion concentration in the bulk of the solution (and therefore, if $\psi = 0$, at the electrode surface). The author is followed here in assuming without theoretical justification that $\alpha = \frac{1}{2}$.



The rate of this process is:

$$R_2 = k_2 \frac{C_H}{n} e^{-EF/2RT} \quad (52)$$



$$R_3 = k_3 \frac{C_H}{n} - C_{H^+} e^{-EF/2RT} \quad (53)$$

In the stationary state, therefore, we have that

$$k_1 \left(1 - \frac{C_H}{n}\right) C_{H^+} e^{-EF/2RT} - k_2 \frac{C_H}{n} e^{EF/2RT} - k_3 \frac{C_H}{n} C_{H^+} e^{-EF/RT} = 0 \quad (54)$$

whence:

$$\frac{C_H}{n} = \frac{k_1 C_{H^+}}{k_1 C_{H^+} + k_2 e^{EF/RT} + k_3 C_{H^+}} \quad (55)$$

Also, according to the present assumption that reaction iii is the slow stage, we have that:

$$i = 2Fk_3 \frac{C_H}{n} C_{H^+} e^{-EF/2RT} \quad (56)$$

Let now C'_H/n be the concentration of atomic hydrogen on the electrode surface corresponding to equilibrium between hydrogen ions and atoms at a given potential E . Then

$$k_i \left(1 - \frac{C'_H}{n}\right) C_H e^{-EF/2RT} = k_2 \frac{C'_H}{n} e^{EF/2RT} \quad (57)$$

Hence

$$\frac{C_H}{n} = \frac{k_i C_{H^+}}{k_1 C_H + k_2 e^{EF/RT}} \quad (58)$$

For weak cathodic polarization

$$k_2 e^{EF/RT} > k_1 C_{H^+} \quad (59)$$

and hence:

$$\frac{C_H}{n} = \frac{C'_H}{n} = \frac{k_1}{k_2} C_{H^+} e^{-EF/RT} \quad (60)$$

From this and equation 56

$$i = 2F \frac{k_1 k_3}{k_2} C_{H^+}^2 e^{-3EF/2RT} \quad (61)$$

For stronger polarization

$$i = 2F \frac{k_3 k_1}{k_1 + k_3} C_{H^+} e^{-EF/2RT} \quad (62)$$

for which result the converse condition to that of expression 59 is taken.

Introducing the ψ potential in equation 62 and transforming:

$$\eta = k_4 + \frac{RT}{F} \log_e C_{H^+} - \psi - \frac{2RT}{F} \log_e i \quad (63)$$

where

$$k_4 = \frac{2RT}{F} \log_e 2F \frac{k_1}{k_1 + k_3} \quad (64)$$

is the absolute hydrogen electrode potential at unit activity.

The electrochemical mechanism has a satisfactory qualitative approach to most phenomena in hydrogen overpotential because it is essentially a combination of a general type of slow discharge and catalytic theories. Quantitatively, however, the agreement with experiment is unsatisfactory, e.g., it does not well interpret the pH and salt effects found by Legran and Levina (121) on nickel cathodes.

D. MISCELLANEOUS THEORIES

The older theory that a gas film of "contact resistance" at the electrode-solution interface is the cause of overpotential has received recent support from Porfirov (140) and Newbery (132).

Lemarchands and Juda (122), Phomotov (137), Bonnemay (27), and Karpen (112) have also contributed recent theoretical work which does not fall into the divisions made above.

E. DISCUSSION

1. *Quantities relevant to hydrogen overpotential and open to quantitative determination*⁹

Much of the past work on hydrogen overpotential has been vague, qualitative, and irrelevant to theoretical interest. *Quantitative* results of use as a numerical test of various theories should clearly be the aim of experiments. A summary of these follows:

(a) *α and the exchange current*: Changes of α are particularly important in giving information on *changes* of mechanism. Thus, for mercury cathodes, the value of α is approximately 0.5 in acid solution and 0.25 in alkaline solution (113), indicating the mechanism to be different in these two systems. It is possible, but unproved, that considerable deviations of α from 0.5 in aqueous acid solutions indicate the presence of impurities, particularly for high overpotential metals. i_0 gives a measure of the velocity of the reaction $2\text{H}^+ + 2e \rightarrow \text{H}_2$ at zero overpotential and provides a standard of comparison for this velocity on various metals.

(b) *λ , the net charge*: It can be shown (16) that if:

$$\lambda = \frac{RT}{F i_0} \left(\frac{\partial i}{\partial \eta} \right)_{i=0} \quad (65)$$

then λ is the net number of charges which cross the energy barrier during the elementary process in the reaction at the cathode. Determination of λ is hence diagnostic. Equation 65 is valid only if $\eta < 10$ mv. approximately; the determination of overpotential at current densities low enough for this is very difficult for metals of high overpotential.

(c) *Limiting current density*: The existence of a limiting current due to hydrogen activation overpotential, not concentration overpotential, would be expected from the catalytic theory. This limiting current may be differentiated from one due to concentration effects by (i) varying the concentration of the electrolyte, which would leave any limiting current due to activation overpotential relatively unchanged (19) (so long as the concentration is not changed sufficiently to alter the mechanism of the reaction) and (ii) examining several metals under the same conditions of high current density, when the limiting current due to activation overpotential would be expected to be different in each case.

(d) *Temperature coefficient and energy of activation*: Determination of the

⁹ In this and the following section only leading references are given.

energy of activation is of well-known importance in the determination of the mechanism of any reaction; it is of great cogence as a test of suggested mechanisms. Thus, the existence of *free* atomic hydrogen in solution near an electrode surface is improbable because the energy of activation for the overpotential is 5–20 kg.-cal./gram-mole. at the reversible potential, whereas the formation of free atomic hydrogen needs about 50 kg.-cal./gram-atom (4).

Further, the energies of activation combined with i_0 yield numerical values of B of equation 36, and thus a quantitative test of the prototropic transfer theory (19).

(e) *pH and salt effects*: Knowledge of these factors is useful because of the relations between the electrokinetic potential and overpotential which follow from the general slow discharge theories. In alkaline solutions, a difference in direction of the salt effect follows from the general slow discharge and slow prototropic transfer theories (4).

(f) *Decay*: Measurement of the decay of overpotential after cessation of the polarizing current yields information on the presence of adsorbed hydrogen on the surface of the cathode material. Its presence causes the slope of the overpotential-log time relation to be $< b$ of the Tafel equation (39).

(g) *Solvent effect*: Change of solvent from water to methyl alcohol, for example, affects the overpotential in a manner characteristic of the cathode material; the effect is quantitatively related to the slow discharge views and can therefore be used as a test of them. Change from a hydroxylic to, say, an ethereal solvent would cause considerable alteration in overpotential according to the slow prototropic transfer theory, owing to the absence of hydrogen bonding in the latter solvent (11).

Other quantitative electrochemical measurements, useful in elucidating the mechanism of the reaction of hydrogen evolution, are as follows:

(h) *Rate of single stages of the reaction at working hydrogen electrodes*: On cathodes of very low overpotential it is possible to determine separately the rate of the discharge reaction $BH^+ + e \rightarrow H + B$ as distinct from the rate of the over-all process of hydrogen evolution. Thus, on platinum in hydrochloric acid and sodium hydroxide solutions, the rate of the discharge process was considerably faster than that of the over-all process (45).

(i) *Capacity of the electrode-solution interface*: Measurements of capacities at the electrode-solution interface by various appropriate methods yield the following type of information: (a) D.C. transients can be used in conjunction with a cathode ray oscillograph for the determination of electrode capacities compared with that of mercury, which is supposed to have an ideal, smooth surface. By a not very certain argument (35), a comparison of the capacities, measured under the same conditions, of various metals per apparent square centimeter gives a measure of the ratio: true area/apparent area.

(b) Measurements of the capacity of the electric double layer with mercury or gallium and liquid alloys give clear information concerning anionic adsorption, which causes a shift in the electrocapillary curve in the anodic branch (78).

(c) Measurements of electrode capacity at various frequencies give informa-

tion on the adsorption of hydrogen or other entities on the electrode. Thus, if adsorbed hydrogen atoms are present, increasing frequency allows the hydrogen atom less time to arrange itself completely, so that the apparent capacity becomes less (53). Some evidence of adsorbed material can also be obtained from d.c. transients, where the initial linear section of the potential-time relation represents the charging up of the double layer, whilst the second is concerned with the adsorption of hydrogen atoms on the metal (52).

2. *Matters of contemporary interest in the interpretation of experimental results*

(a) *Current density*: The deviations from the Tafel equation at low current density, where the Tafel line becomes asymptotic to the log current density axis, and, over a certain range and on certain metals, the overpotential becomes approximately proportional to current density, can be directly interpreted on the basis of the principal theories. Possible deviations at high current densities are of greater interest. According to slow discharge views the Tafel equation should be applicable up to indefinitely high current density. According to the slow combination views, deviations should occur at current densities high enough to cause the surface to approach saturation. In Horiuti's catalytic theory this leads to positive deviations (owing to a limiting current caused by saturation at the surface) and in Hickling's catalytic theory to negative deviations from the Tafel equation (owing to participation of an electrochemical mechanism at high current density). Unfortunately, the experimental information is not yet available to test these very diagnostic theoretical expectations. It is definite that negative deviations occur at high current density, though it is not yet proved whether they persist in sufficiently purified solutions. If they do, either a change in mechanism at higher current density must be effective or the deviations may be connected with hydride formation; it is significant that where the negative deviations are most pronounced (i.e., on cathodes such as tin and lead) the tendency to form *gaseous* hydrides is most marked. It is also significant that some solid cathodes at which the deviations from linearity in the Tafel line occur, do not retain their original bright surface after electrolysis (19). The observed deviations may be due to the deposition of impurities. Should it be established that the Tafel equation is generally applicable even at very high current density, the slow combination mechanism could be discarded for this current density range. Conversely, should the coefficient b of the Tafel equation prove to be constant at all current densities above the lowest, then this itself is a puzzling fact, because it seems reasonable to expect some deviations from a constant value over large ranges in current density, according to all existing theories.

Four principal interpretations of α have been given: (i) as a factor representing the relative inclinations to the horizontal of the potential energy/distance relation of the hydrogen ion in solution and the adsorbed hydrogen atom (37); (ii) as the fraction of the potential of the cathode effective in influencing the rate of reaction

57¹⁰; (iii) as the order of the slow combination reaction (79); (iv) as the experimental coefficient in the Freundlich isotherm applied to hydrogen atoms very near to and adsorbed upon the electrode surface (95). The second and last of these interpretations have been shown to lead to rational values in agreement with experiment. In much theoretical work, α is tacitly assumed equal to $\frac{1}{2}$. The limitation $\alpha < 1$ follows from the first two interpretations, and as these are associated respectively with the energy level slow discharge and slow transfer theories it can be definitely concluded unambiguously that these theories are not applicable to electrodes for which $\alpha > 1$ (e.g., platinum).

Values of b over the range 0.03–0.3 approximately are observed for various metals at intermediate current densities and successful theories must clearly be capable of giving interpretation to these values, even if the scatter of values is shown to be due to impurities in the solution. The method of establishing the Tafel line probably influences b , owing to diffusion of atomic hydrogen into metals of low overpotential, which may have effect in slow measurement.

In summary, no clear generalizations concerning the mechanism of overpotential can yet be made from the variation in current density in pure solution, owing to lack of satisfactory work at very low and very high current densities. For metals for which $b < 0.058$, however, the slow discharge theories cannot be applicable.

(b) *Temperature*: The behavior of the constant α with temperature is of great interest. Although α may be constant for mercury cathodes with variation of temperature in aqueous solution, there is an increase in α with increase of temperature on metals of lower overpotential (e.g., tungsten). This behavior indicates the presence of adsorption on the cathode as an important factor in determining overpotential. Formally, if α is proportional to T (i.e., b constant), the change in potential affects the entropy but not the heat of activation (4).

(c) *pH and salt effects*: Quantitative agreement with Stern's theory regarding the electrokinetic potential at various concentrations is not achieved by the general slow discharge theories even in quite dilute solutions. It is possible that Stern's theory as used in these calculations (i.e., in an approximated form), and also inherently, is inadequate (9).

The effect of changes in pH and the effect of salts do not appear to be diagnostic for the slow discharge theory, as seems to have been generally considered, for the electrochemical theory can also be formulated with equations of the same form as that of the general slow discharge theory. Also pH and salt effects could probably be understood according to the catalytic theory if the polar nature of the metal-hydrogen bond were taken into account.

(d) *Time*: The linear build-up of overpotential during the first few tenths of a second after commencement of the polarizing current is strong evidence in favor of the slow discharge mechanisms. This linear build-up, however, does not occur on metals of low overpotential. Hickling (89) attempted to reconcile the linear

¹⁰ (i) and (ii) are analogous but not identical.

build-up of overpotential on metals of high overpotential with the slow combination theories by showing that the quantity of electricity needed to charge up the double layer was vastly more than that needed to establish an overpotential of 1 v., assuming that this overpotential is established according to the theory of this author. It has been shown above that this theory gives rise to results which lack physical meaning, so that this explanation of the linear increase of overpotential with time seems unsound.

The slower variations with time which occur after the charging up of the double layer is completed could be interpreted in terms of the slow discharge theory as due to the setting up of certain adsorption equilibria. The nature of such equilibria in pure solutions of non-capillary-active substances is unclear. The gradual reduction of a film of oxide by the evolved hydrogen is also a possible explanation of long time variations, particularly decreases with time. These explanations seem weak when applied to the large changes with time which occur for some metals, e.g., tantalum. It is significant that the variation with time depends upon the preparation of the electrode surface. This fact is not in consonance with an interpretation of time variation depending entirely on the deposition of impurities. According to slow combination theories, changes with time are a consequence of the "deactivation" of the "active centers" of the metal with use (161). Diffusion of hydrogen into the metal is probably also a cause of time changes, from which the noted lesser variation with time on electrodeposited metals, where the thin films of cathode material give little scope to the diffusion process, would follow. Both diffusion and deactivation theories agree with the facts that time variations are more extensive with metals of low overpotential.

Metals divide themselves into two rough classes with respect to long time variations: those of high overpotential, where the initial build-up of overpotential is linear with the amount of electricity passed and the variation after the first fraction of a second's polarization is small; and those of lower overpotential, where the build-up is not totally linear with the quantity of electricity passed and the final steady value of overpotential is not reached for some time.

(e) *Surface:* Activation of the surface of metal electrodes causes a decrease in overpotential, as would follow were the chief purpose of the metal that of a catalyst. Aging of the surface of the metal also causes an increase in the overpotential which leads to the same implication as the result of activation. The effects of electropolishing correspond to what would be expected from a slow combination viewpoint for the metals of low overpotential. Finally, the large increase in overpotential which occurs on melting gallium tends to indicate that here overpotential involves a catalytic phenomenon depending upon the "active center" present in a solid lattice.

Surface effects are in general satisfactorily interpreted according to the viewpoint of slow combination.

(f) *Transfer by diffusion:* If overpotential is transferred from the polarization to the diffusion side (where there is no incoming current) of an electrode, two conclusions can be drawn: (i) that there is a considerable concentration of atomic

TABLE 4
Experimental criteria for the determination of fundamental reaction mechanisms at a working hydrogen electrode

THEORY	α	λ	LIMITING CURRENT	B (VARIATION WITH pH)	pH EFFECT (IN PURE SOLUTION AND ON ADDITION OF SALT)	SOLVENT EFFECT	TRANSFER OF H BY DIFFUSION THROUGH THIN FILMS	EFFECT OF pH_2
Atomic hydrogen.	$0 < \alpha < 2$	2	Present	Varies	No effect	Depends on size of solvent molecules and their adsorption on cathode; for metals of low overpotential, increased in alcoholic solution	Present	Decrease of pH_2 makes more negative
Slow discharge....	$0 < \alpha < 1$	1	Absent	Constant for given metal	No effect in pure solution except at very high concentrations; in the presence of salt, less negative with decrease of pH	In alcoholic solution: lowered for metals of high overpotential. No effect for metals as platinum, nickel, etc., according to Butler's theory. Slightly lowered in alcoholic solutions according to Volmer and Frumkin	Absent	Same as above
Molecular hydrogen ion.....	$0 < \alpha < 1$	2	Absent	Varies	Same as above	Same as above	Absent	Same as above
Electrochemical...	$0 < \alpha < \frac{1}{2}$	2	Absent	Varies	Same as above	Same as above	Present	Same as above
Prototropic transfer.....	$0 < \alpha < 1$	1	Absent	Constant for all metals	No effect in pure solution; in presence of salt, unclear	Increased in alcoholic solution; large change expected in non-hydroxylic solvents	Absent	No effect

hydrogen adsorbed on the surface of the working electrode (polarization side); (ii) that adsorbed atomic hydrogen must be electromotively active.

(g) *Experimental criteria for the elucidation of fundamental reaction mechanisms at a working hydrogen electrode*: A tabulated summary of some experimental results expected according to the main theories is given in table 4.

V. SUMMARIZING REMARKS

1. Experimental work of a high standard on hydrogen overpotential is still lacking except for mercury. Accurate experimental information for a number of cathode materials is particularly needed on the following factors: (i) current density, particularly at very low and very high current densities; (ii) temperature; (iii) pH. Transfer of overpotential through metallic films and experiments on rates of single stages are also particularly important.

2. Slow discharge is not the general mechanism of hydrogen overpotential on various metals. The most important evidence supporting this conclusion arises from pH effects on metals of low overpotential, from the transfer of overpotential through metallic films, and by experiments on the individual velocities of various reactions at the cathode. On mercury cathodes, a slow discharge mechanism seems probable in acid solution. The detailed mechanism is still uncertain.

On metals of low overpotential, some form of slow combination mechanism seems probable.

3. It is unlikely that one mechanism of hydrogen overpotential is effective for all metals. The future task consists in a detailed examination of overpotential at the more important cathode materials to establish the mechanism individually, investigation being made of distinguishing factors such as those in table 4.

4. The theory of adsorption at solid-liquid interfaces and the detailed structure of the electrical double layer would repay extensive work. Detailed information regarding the diffusion of hydrogen through metals and the kinetics of the reactions of hydrogen on solid surfaces (particularly the energy of activation of these processes) would be of great use.

Some of the work which has been described above as necessary to further advances in the field of hydrogen overpotential is in progress at Imperial College.

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