by margins greater than ±1% and ±0.05%, respectively. While such margins of error serve to eliminate the data in Table III from use in quantitative evaluations, they are not sufficient to mask some clearly discernible qualitative trends.

The increasing trend in the figures in the rightmost column of Table III with increasing monomer conversion shows that *p*-chlorostyrene units continue to become attached to polymethylacrylate chains as polymerization progresses, in accordance with expectations. Reference to the third column of Table III discloses that, of the *p*-chlorostyrene which polymerizes, a larger fraction combines with polymethylacrylate when no catalyst is added to the reaction mixtures. In addition, this fraction decreases with increasing per cent. of monomer polymerized in the "thermal" polymerizations. In the peroxide-catalyzed runs, the fractions of combined poly-*p*-chlorostyrene are of about the same magnitude as the probable error, so that no trend can be detected.

The decrease in the fraction of combined poly-*p*-chlorostyrene at corresponding monomer conversions caused by the presence of benzoyl peroxide may be interpreted readily in terms of chain branching reactions of the type represented by equations 1 and 2. Application of currently accepted theories of free radical induced vinyl polymerization to the chain branching mechanism leads to the conclusion that the rate of entry of *p*-chlorostyrene into combination with polymethylacrylate, measured as a function of monomer conversion, should be proportional to the ratio of free radicals which have polymethylacrylate chains within the "free radical molecules" (*e.g.*, IIIa, R = $COOCH_3$, R′ = *p*-C_6H_4Cl) to total free radicals. An inverse relationship between this ratio and total free radical concentration can be derived; therefore, the introduction of benzoyl peroxide, which increases the total free radical concentration, should have the effect of reducing the ratio and with it the fraction of poly-*p*-chlorostyrene combined with polymethylacrylate.

Summary

The polymerization of *p*-chlorostyrene in the presence of polymethylacrylate gives polymers each of which, after saponification and dialysis, may be divided into three fractions on the basis of their solubility behavior in benzene and in water. Control runs, in which solutions of separately polymerized poly-*p*-chlorostyrene and polymethylacrylate are subjected to the same procedures, give relatively small amounts of fractions insoluble both in benzene and in water; therefore, the greater portions of such fractions formed in the "normal" runs must be the result of chemical interaction between *p*-chlorostyrene and polymethylacrylate. The experimental observations may be explained by assuming that growing poly-*p*-chlorostyrene chains undergo free radical chain transfer reactions with polymethylacrylate, with the result that polymer molecules consisting of polymethylacrylate chains having poly-*p*-chlorostyrene branches are formed.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Electrokinetics of Hydrogen Evolution. I. Hydrogen Overvoltage on Mercury[1]

BY BENJAMIN POST AND C. F. HISKEY

In this paper measurements of hydrogen overvoltage on mercury cathodes, in ordinary water, are presented and discussed. In a second paper measurements made in heavy water will be reported and compared with the above.

In 1905 Tafel[2] made the important observation that the overvoltage varied with the current density and that the relation could be expressed by an equation of the form

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

where η is the overvoltage, a and b are constants, and i is the current density. Much of the experimental work in this field since that time has been concerned with the determination of the values of a and b for a number of electrodes.

There is little agreement among the published results. In Fig. 1 are shown sets of typical measurements of hydrogen overvoltage on mercury cathodes at room temperature.

There is a similar lack of agreement concerning the nature and magnitude of the variation of overvoltage with temperature. Bowden's measurements[3] were long accepted as correct, but the results of recent investigations by Jofa and coworkers[4,5] and by Bockris and Parsons[6] differ significantly both from Bowden's results and from each other.

In this investigation efforts were first concen-

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[1] This paper is based on the thesis of Benjamin Post submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn, June, 1949. This material was presented before the Division of Inorganic and Physical Chemistry of the American Chemical Society at the Atlantic City meeting, September 19, 1949. This work was supported in part by an Office of Naval Research contract.

[2] J. Tafel, *Z. physik. Chem.*, **50**, 641 (1905).

[3] F. P. Bowden, *Proc. Roy. Soc.* (*London*), **126a**, 107 (1929).

[4] Z. A. Jofa and K. P. Mikulin, *J. Phys. Chem. U. S. S. R.*, **18**, 137 (1944).

[5] Z. A. Jofa and V. Stepanova, *ibid.*, **19**, 125 (1945).

[6] J. O'M. Bockris and R. Parsons, *Trans. Faraday Soc.*, **45**, 416 (1949).

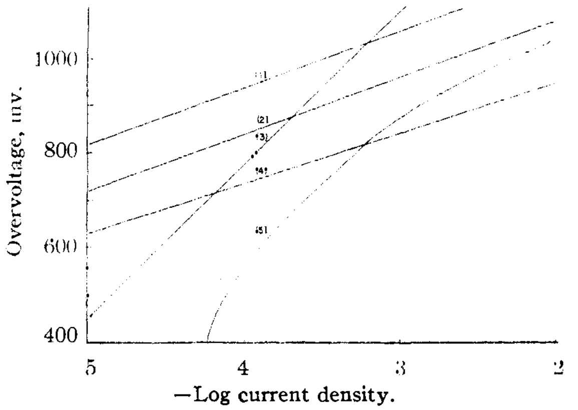

Fig. 1.—Overvoltage on mercury: (1) Jofa, *Acta Physicochim. U. R. S. S.*, **10,** 908 (1939); (2) Bowden, *Proc. Royal Soc.*, **126,** 107 (1929); (3) Harkins and Adams, *J. Phys. Chem.*, **29,** 215 (1929); (4) de Bethune and Kimball, *J. Chem. Phys.*, **13,** 53 (1945); (5) "Int. Crit. Tables," **6,** 339 (1929).

trated on the development of techniques for the measurement of hydrogen overvoltage on mercury surfaces in a reproducible manner. The behavior of overvoltage over a wide range of current densities and temperatures was then studied. From these data the values of the energy of activation of the slow step responsible for hydrogen overvoltage, and of various other constants, have been determined.

Experimental

Techniques.—Experimental work hinged upon the design and construction of electrolysis cells in which overvoltage measurements could be made in a reproducible manner.

The design finally adopted involved the use of a one-piece, all Pyrex glass electrolysis cell. Stills for both mercury and electrolyte were incorporated into the unit. Provision was also made for the evacuation and flushing with gas of component parts of the cell independently of one another. To minimize the possibility of contamination, ground glass joints at openings to the cell have been avoided in favor of openings which could be sealed with the torch after the addition of mercury and electrolyte to the cell.

A schematic representation of the cell is shown in Fig. 2.

The inclusion of the electrolyte still (D) as an integral part of the cell, together with the use of hydrochloric acid as electrolyte, makes possible the variation of the *p*H of the catholyte within wide limits without interrupting a run. To increase acidity of the catholyte it is only necessary to distil additional electrolyte into the cathode compartment (I).

To minimize a possible carry over to the cathode of depolarizers liberated at the anode during electrolysis, the latter is separated from the cathode by an ungreased mercury-well stopcock (K). This stopcock, wet with electrolyte during operation of the cell, cuts down diffusion of oxygen from anode to cathode to negligible proportions. The electrical resistance of typical stopcocks, using 0.1 *N* hydrochloric acid as electrolyte, was approximately 25,000 ohms.

A hydrogen reference electrode (H) is sealed into the cathode compartment. It is set within a capillary container which can readily be flushed and refilled with catholyte. During runs, the capillary tip is less than 1 mm. from the mercury surface. A larger separation leads to the inclusion in the measured overvoltage of an appreciable fraction of the *IR* drops of the working cell.[7]

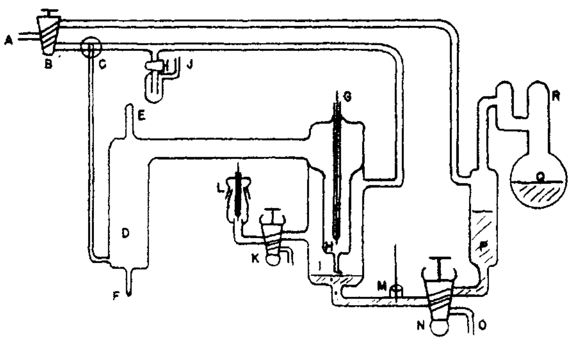

Fig. 2.—Overvoltage cell for mercury cathodes: A, to hydrogen and vacuum lines; B, three-way stopcock; C, three-way "T" stopcock; D, electrolyte still; E, filling tube; F, drain; G, to reference electrode; H, hydrogen reference electrode; I, cathode compartment; J, gas bubbler; K, three-way, ungreased, mercury-well stopcock; L, anode; M, lead to mercury cathode; N, three-way, ungreased, mercury-well stopcock; O, cathode compartment drain; P, mercury reservoir; Q, mercury still; R, filling tube.

The hydrogen reference electrode consists of a short length of thin platinum wire coated with platinum black in the usual manner. It is kept immersed in catholyte drawn up into the electrode container, except when hydrogen is bubbled through the solution in the cathode compartment. In most runs the electrode was quite stable for periods up to two or three weeks. When it showed signs of erratic behavior, the trouble was corrected by making the electrode anodic for two to three minutes, using a current of about 10^{-4} ampere, and then forcing the liquid from the reference container into the cathode compartment proper under hydrogen pressure. In the process hydrogen was passed over the reference electrode, the gas flow being continued for about one hour.

Provision is also included for prepurification of the electrolyte, after distillation into the cathode compartment, before the commencement of a run. This purification is achieved by prolonged electrolysis over mercury at current densities higher than any to be used during the runs. This mercury can readily be discarded and fresh mercury admitted to the cell. In this way traces of cationic impurities are plated out onto the mercury and eliminated from the cell.

At the beginning of a run, about 50 ml. of 4% hydrochloric acid solution are added to the electrolyte still. From 30 to 40 ml. of triply distilled mercury are added to the mercury still (Q). The openings (E and R) through which additions are made are sealed off with the torch. From 25 to 35 ml. of electrolyte, depending on the *p*H desired and the size of the cathode, are distilled into the cathode compartment in a stream of hydrogen. The mercury is then distilled, *in vacuo*, into the mercury reservoir. A source of potential is connected to the anode and cathode leads, and a few ml. of catholyte are forced under gas pressure into the anode compartment. About 10 ml. of mercury is then introduced into the cathode compartment. The cell is run at maximum current (usually 3 to 6 ma./sq. cm.). The catholyte is stirred by intermittent bubbling of hydrogen. After forty-eight hours the mercury in the cathode compartment is discarded via stopcock N, and fresh mercury is admitted to the cathode compartment to within 1 mm. of the capillary tip of the reference electrode container.

It was found that overvoltage readings were unsteady for several hours after introduction of the mercury. After twenty-four hours of electrolysis at approximately 10^{-5} amp./sq. cm., readings were generally stabilized.

Two cells were used in all the runs reported in this paper.

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[7] A. de Bethune, This Journal, **71,** 1556 (1949).

These differed only in the areas of the cathodes: 3.80 sq. cm. in one cell, and 5.47 sq. cm. in the other. The area of the cathode was considered equivalent to the inside cross sectional area of the cathode compartment. The latter was determined to ±0.02 sq. cm. by measurement of the inside diameter with precision calipers.

Potential measurements were made with a Beckman model G *p*H meter. This meter could be read to within 1 mv.; it was checked periodically against an external Weston standard cell.

During runs the overvoltage cell was immersed in a thermostatted bath whose temperature was regulated to ±0.1° with the aid of the conventional type of mercury thermoregulator.

Purification of Materials.—Mercury was distilled three times in all glass stills, under partial vacuum, with a fine stream of air bubbling through the mercury, and then transferred to the mercury still in the electrolysis cell.

Electrolytic tank hydrogen was used in these runs. It was purified by passing through a furnace filled with copper turnings heated to 450°. The gas train was of glass and copper construction. From the furnace the gas was passed through a Dry Ice-trap and then into the cell.

All glassware was cleaned before use by boiling with a mixture of 80% sulfuric acid and 20% nitric acid, rinsing with distilled water and drying.

Results.—There is fairly general agreement that overvoltage on mercury is independent of *p*H, in dilute solutions of pure acids.[8] Recently, however, de Bethune[7] reported that the overvoltage in 10^{-3} *M* hydrochloric acid is approximately 40 mv. higher than in 1 *M* solution.

In this investigation, which was substantially completed before publication of de Bethune's paper, measurements of overvoltage on mercury were made in solutions of hydrochloric acid at *p*H's of 1.0, 1.5 and 2.4. The results of these measurements, all made at 0°, are summarized in the equations

$$\begin{array}{lll}
\text{(a)} & (p\text{H } 1.0) & \eta = 1448 + 108 \log i \\
\text{(b)} & (p\text{H } 1.5) & \eta = 1446 + 108 \log i \\
\text{(c)} & (p\text{H } 2.4) & \eta = 1445 + 107 \log i
\end{array}$$

The differences among the three sets are within the range of experimental error. In this *p*H range the measurements show no significant variation of overvoltage with *p*H. All measurements reported in this paper, other than the above, have therefore been made in solutions of 0.1 *N* hydrochloric acid.

Because of the uncertainty surrounding the variation of overvoltage with temperature, measurements have been made at closely spaced intervals from 0.0 to 91.3°; these are reported in Table I. For reasons made clear in the Discussion, measurements made from 0.0° to 26.0° are dealt with separately from those made at higher temperatures; the former are plotted in Fig. 3, the latter in Fig. 4.

Reproducibility of Measurements.—In assessing the degree of reproducibility of the above measurements it is necessary to distinguish between measurements made during one run, and those made in separate runs, and in different cells.

In a single run, duplicate sets of measurements were made at each temperature, several hours or one day apart. All runs were also made in two cells, differing in electrode area.

For individual runs measurements were reproducible to ±2 millivolts. For separate runs, made in cells of differing electrode areas and using fresh batches of mercury and electrolyte, measurements were reproducible to ±5 millivolts.

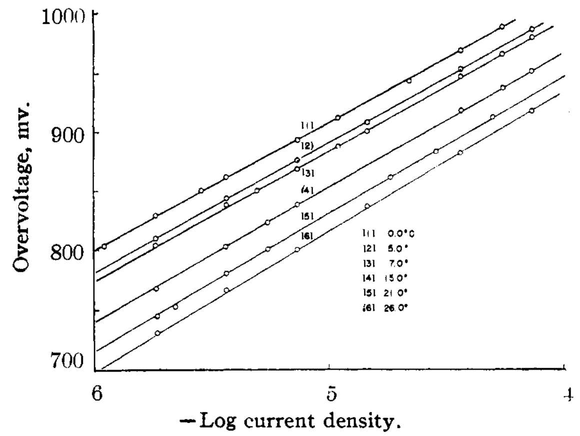

Fig. 3.—Overvoltage on mercury (0.1 *N* HCl).

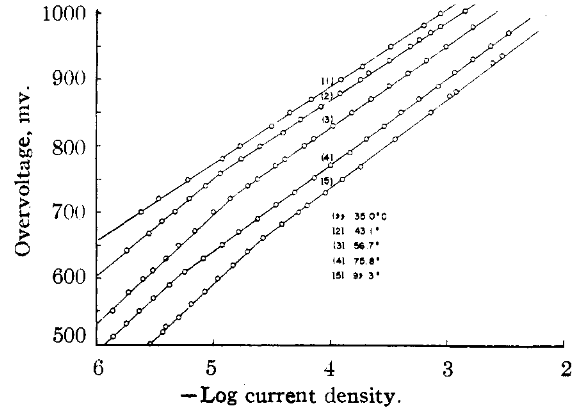

Fig. 4.—Overvoltage on mercury (0.1 *N* HCl).

Examination of Fig. 4 shows a break in the straight line portions of the η *vs.* log i lines at current densities near 10^{-5} amp./sq. cm. for temperatures above 35°. In this region stabilization of potential readings occurred slowly, often taking from 10 to 15 minutes. Readings below 10^{-5} amp./sq. cm., taken as current was being increased, were also from 5 to 6 millivolts lower than comparable readings taken as current was being reduced. At current densities above 10^{-5} amp./sq. cm. this "hysteresis" phenomenon disappeared; the up and down lines coalesced. The data in Table I for these temperatures (above 35°) are based on measurements made as current density was being reduced. Slopes of these lines were computed from results recorded at current densities in excess of 10^{-5} amp./sq. cm. Estimates of reproducibility are limited, for these higher temperature data, to measurements in this current density range.

Discussion

A. General Considerations

The relation between the current density (i), which is a measure of the rate of the reaction, and the overvoltage, may be written as

$$i = ce^{-(\Delta H - \alpha F\eta/RT)} \qquad \text{(I)}$$

where ΔH is the heat of activation of the slow step responsible for the overvoltage, α and c are constants, and the other terms have their usual significance.[3,9]

Usage with regard to ΔH varies. Bockris[6] and Agar[10] have defined a heat of activation, $\Delta H'$, such that $(\partial \ln i/\partial T)_\eta = \Delta H'/RT^2$. This

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(8) (a) A. N. Frumkin, *Acta Physicochim.*, *U. R. S. S.*, **18**, 23 (1943); (b) S. Glasstone, *J. Chem. Soc.*, **125**, 2646 (1924); (c) F. P. Bowden, *Trans. Faraday Soc.*, **24**, 473 (1928); (d) S. Lewina and V. Sarinsky, *Acta Physicochimica*, *U. R. S. S.*, **7**, 485 (1937).

(9) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., N. Y., 1941, pp. 584-588

(10) J. N. Agar, *Trans. Faraday Soc.*, **43a**, 85 (1947).

TABLE I

HYDROGEN OVERVOLTAGE ON MERCURY (0.1 *N* HCl)

Current density (i) in microamperes per sq. cm.; overvolgage (η) in millivolts

i	η
0.0°	
62.0	994
54.8	990
36.6	969
22.0	943
11.0	912
7.32	893
3.66	862
2.87	851
1.83	829
1.10	804
0.92	794
5.0°	
73.2	987
36.6	953
14.6	908
7.32	877
3.66	844
1.83	810
0.92	776
7.0°	
73.2	979
54.8	966
36.6	947
14.6	901
11.0	889
7.32	869
4.94	850
3.66	838
1.83	803
0.92	766
15.0°	
73.2	951
54.8	937
36.6	918
7.32	838
5.48	823
3.66	903
1.83	768
0.92	722
21.0°	
50.0	972
28.4	883
18.3	861
5.48	801
3.66	780
2.19	752
1.83	745
26.0°	
73.2	916
36.6	881
14.5	836
7.32	800
3.66	766
1.83	730
0.92	689
35.0°	
2260	1047
895	1000
645	980
336	950
190	920
126	900
69.7	870
46.3	850
31.8	830
17.4	800
12.1	780
6.05	750
3.42	720
2.42	700
1.00	652
43.1°	
1460	1003
1140	994
895	980
732	970
584	960
493	950
332	930
215	910
181	900
124	880
84.0	860
56.6	840
43.1°	
40.2	820
25.2	800
17.4	780
11.7	760
8.75	740
6.40	720
4.74	700
3.65	687
2.88	667
1.83	642
0.92	608
56.7°	
1700	980
1000	950
676	930
465	910
328	890
225	870
152	850
106	830
72.1	810
60.3	800
41.0	780
33.9	770
24.6	750
20.1	730
14.0	720
10.4	700
7.30	670
4.05	650
3.84	630
3.20	610
2.40	600
1.90	570
1.41	550
76.8°	
3370	970
2420	950
1680	930
1160	910
843	890
579	870
412	850
287	830
208	810
150	790
103	770
73.7	750
49.2	730
34.2	710
24.5	690
16.6	670
11.8	650
8.15	630
5.79	610
4.26	590
3.10	570
2.32	550
1.82	530
1.42	510
1.16	490
89.7°	
3050	934
2520	925
1580	899
1000	873
630	846
400	820
252	794
89.7°	
158	767
100	742
63.1	714
40.0	688
25.2	661
10.0	587
6.31	555
4.00	523
2.52	494
1.58	469
1.00	449
91.3°	
1210	880
1060	874
732	850
366	811
183	770
128	750
91.5	730
64.0	710
54.8	700
38.4	680
27.0	660
19.7	640
14.8	620
11.0	600
8.60	580
6.58	560
5.12	540
3.69	520
2.91	500
2.19	480
1.70	460
1.33	440
1.04	420

$\Delta H'$ is equivalent to $(\Delta H - \alpha F\eta)$, the numerator in the exponential of (I). It is the *net* heat of activation; it includes an overvoltage term, and different values of $\Delta H'$ will therefore be obtained for different current densities. Bockris[6] has reported such a variation of $\Delta H'$ with current density.

ΔH is here used in a more conventional sense. It determines the rate of the reaction only at the reversible potential; the imposition of an overpotential reduces the net heat of activation as indicated in (I) leading to an increase in the current. Significant changes in ΔH reflect changes in mechanism and not merely changes in the rate of reaction. Rearranging terms in (I) gives

$$\eta = \left[\frac{\Delta H}{\alpha F} - \frac{2.303RT}{\alpha F}\log c\right] + \frac{2.303RT}{\alpha F}\log i \qquad \text{(II)}$$

The "a" of Tafel's equation is equivalent to the bracketed term in (II). Tafel's "b," the slope of η *vs.* log i, equals $2.303RT/\alpha F$. Where α is constant, b varies linearly with the temperature; deviations from such a linear relationship reflect changes in α. Differentiation of (II) with respect to temperature yields an expression for the temperature coefficient of overvoltage

$$\left(\frac{\partial\eta}{\partial T}\right)_i = \frac{2.303R}{\alpha F}\log\frac{i}{c} \qquad \text{(III)}$$

Equation (III) is valid only where ΔH, α and c are independent of temperature. It shows explicitly the dependence of $(\partial\eta/\partial T)_i$ on the current density and its independence of temperature. Combining (I) and (III) gives

$$\left(\frac{\partial\eta}{\partial T}\right)_i = \frac{\alpha F\eta - \Delta H}{\alpha FT} \qquad \text{(IV)}$$

which relates the temperature coefficient of overvoltage to the heat of activation.[3]

B. Discussion of Experimental Results

Measurements made from 0–26° are shown in Fig. 3. Over this temperature range the value of b equalled $2.303RT/0.50F$, within the limits of experimental error, *i. e.*, α was substantially constant, equalling 0.505 ± 0.01.

Above 35° α was found to vary with temperature, rising to 0.55 at 91.3°. Values of b and α are shown in Table II.

TABLE II

VARIATION OF α WITH TEMPERATURE [$\alpha = 2.303\ RT/bF$]

T, °C.	Slope	α	T, °C.	Slope	α
0.0	108	0.50_0	35.0	118	0.51_6
5.0	110	$.50_0$	43.1	119	$.52_6$
7.0	111	$.50_0$	56.7	123	$.53_2$
15.0	114	$.50_0$	76.8	130	$.53_6$
21.0	116	$.50_4$	89.7	132	$.54_7$
26.0	117	$.50_6$	91.3	132	$.55_0$

It is evident, from (IV), that $(\partial\eta/\partial T)_i = 0$ where $\alpha F\eta = \Delta H$. Extrapolation of the lines in Fig. 3 results in their intersecting where $\eta = \Delta H/\alpha F$. This is illustrated in Fig. 5. The extrapolated lines intersect at $\eta = 1880 \pm 20$ mv. At this overpotential the current density equals 10^4 amp./sq. cm. This is the value of the constant c of equation (I), since, when $\Delta H = \alpha F\eta$, the exponential term equals 0, and $i = c$.

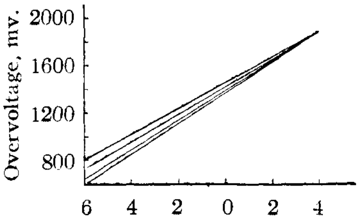

Fig. 5.—Intersection of plots of overvoltage *vs.* current density (0.0–26.0°).

The value of ΔH computed from $\Delta H = \alpha F\eta_{\text{int.}}$ is 21.7 ± 0.2 kcal. g. ion^{-1}. The temperature coefficient of overvoltage (for 0–26°) is accurately given by (III)

$$\left(\frac{\partial\eta}{\partial T}\right)_i = \frac{2.303R}{\alpha F}\log\frac{i}{c} = 0.40\log\frac{i}{10^4}$$

A simplified form of Tafel's equation may be written for the data in Fig. 3. By substituting the experimentally determined values of $\Delta H/\alpha F$ ($= \eta_{\text{int.}}$), α and c, in (I) and rearranging, we have

$$\eta = \eta_{\text{int.}} + \frac{RT}{\alpha F}\log\frac{i}{c} = 1880 + \frac{2.303RT}{0.50F}\log\frac{i}{10^4} \qquad \text{(V)}$$

The temperature independent term, $\eta_{\text{int.}}$, clearly bears a much more significant relation to the nature of the electrode than does the temperature dependent "a" of Tafel's equation.

ΔH may also be evaluated using equation (I). Values of log i at 900 and 800 mv. overvoltage for the temperatures shown in Fig. 3 are shown graphically in Fig. 6.

The slopes of the 900 and 800 mv. lines, determined by the method of least squares, are -2.50 and -2.72; these give values of ΔH equal to 21.8 and 21.7 kcal. g. ion^{-1}.

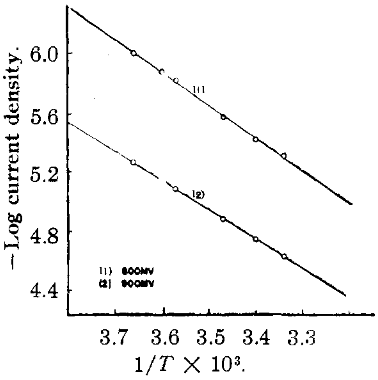

Fig. 6.—Variation of current density with temperature (0.0–26.0°).

For the temperature range 35.0 to 91.3° the mean value of $\alpha (= 0.535)$ was used to compute ΔH. The average deviation of values of α in this range from the mean is ± 0.010. Values of log i at 1000, 900 and 800 mv. are plotted in Fig. 7.

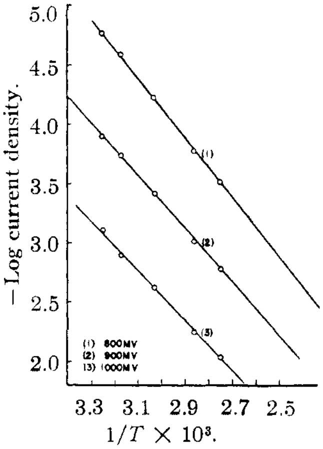

Fig. 7.—Variation of current density with temperature (35.0–91.3°).

The slopes of the lines are -2.06, -2.26 and -2.52, which yield values of 21.6, 21.4 and 21.4 kcal. g. ion^{-1} for ΔH. The assumption of a constant (mean) value of α for this temperature range involves an approximation of the order of 2% in the determination of ΔH.

C. Results of Other Workers

1. **Bowden**[3] measured overvoltage on mercury in 0.2 N sulfuric acid at 0, 36 and 72°. He found that b varied with temperature as indicated by the expression $b = 2.303RT/\alpha F$, where α equalled 0.50 ± 0.01. At 10^{-5} amp./sq. cm. $(\partial\eta/\partial T)_i$ equalled -2.6 mv. degree^{-1}. From a knowledge of the values of b at 0, 36 and 72° (108, 122 and 136) $(\partial\eta/\partial T)_i$ can be computed for other current densities: *i. e.*, at 10^{-6} amp./sq. cm. it equalled -3.0 mv. degree^{-1}. From the above Bowden found $\Delta H = 18.0$ kcal. g. ion^{-1}. Some limitations of Bowden's data may be noted here. The absolute values of

overvoltage which he reported are substantially lower than comparable values reported by more recent investigators.[4,5,7] His determinations of $(\partial\eta/\partial T)_i$ and of b were based on only four experimental points at each of three temperatures. He maintained his reference electrode at constant temperature while varying the temperature of his working electrode. Agar[9] has pointed out that this results in the inclusion, in the measured overpotential, of contributions due to the temperature coefficient of the reference electrode and the thermo junction potential between the reference electrode and the cathode. Agar has estimated that a correction of 1.7 kcal. g. ion^{-1} should be added to Bowden's value of 18.0 kcal. on this count alone.

2. **Jofa and Mikulin**[4] investigated the variation with temperature of overvoltage on mercury in 0.25 N sulfuric acid solution. Jofa had previously shown that, in relatively dilute solutions (0.1 to 0.2 N) of hydrochloric acid, hydrobromic acid and sulfuric acid, the overvoltage is independent of the acid concentration and the nature of the anion.[11] Comparisons between measurements made in 0.2 and 0.25 N sulfuric acid and those made in 0.1 N hydrochloric acid thus appear to be justified.

Jofa and Mikulin's measurements were made from 0.3 to 80 at 20° intervals, and at current densities from 10^{-6} to 10^{-2} amp./sq. cm. Their results may be summarized as follows: the slopes of η *vs.* log i increase regularly with temperature; α equals 0.50 up to 40° and rises to 0.51 at 60°, and to 0.52 at 80°: $(\partial\eta/\partial T)_i$ is essentially independent of the temperature and decreases regularly from −3.7 mv. degree^{-1} at 10^{-4} amp./sq. cm. to −2.5 mv. degree^{-1} at 10^{-3} amp./sq. cm. Results close to these were reported by Jofa and Stepanova[5] in their work with 1 N hydrochloric acid. The Tafel expression for Jofa and Mikulin's data for 20°, is

$$\eta = 1405 + 116 \log i$$

These values are about 80 mv. higher than Bowden's [3] and within 10 mv. of those reported in this investigation (see Table I). Values of ΔH computed from Jofa and Mikulin's data range from 20.7 to 21.6 kcal. g. ion^{-1}.

3. **Bockris and Parsons**[6] recently reported the results of measurements of overvoltage in 0.1 N hydrochloric acid at 10° intervals from 0–40°. They note that the slope of η *vs.* log i "does not appear to vary with temperature"; for all five temperature ranges studied, b equalled 116 ± 3. It follows from this that $(\partial\eta/\partial T)_i$ is independent of the current density. The value of $(\partial\eta/\partial T)_i$ is given as −3.0 ± 0.1 mv. degree^{-1} for the entire current density range investigated.

Values of $\Delta H_0'$ (the heat of activation at the reversible potential) were found to be 21.1 ± 0.6 kcal. g. ion^{-1}. It should be noted that different values of $\Delta H_0'$ were determined for each temperature and current density and that the result reported is a mean value for the region of measurement.

Bockris and Parsons report overvoltage values for 20° very close to those previously reported by Jofa.[4] The agreement is fortuitous in view of the different behavior of the two sets of data with respect to temperature variation. At temperatures other than 20° agreement between Bockris and Jofa is necessarily poor.

Summary

Techniques have been developed for the measurement of hydrogen overvoltage in a reproducible manner. Measurements of overvoltage have been made at current densities from 10^{-1} to 10^{-3} amp./sq. cm. and at temperatures from 0.0 to 91.3°. Reproducibility of measurements for individual runs is ±2 mv.; for separate runs, in different cells, reproducibility is ±5 mv.

The average of a series of determinations of ΔH was found to be 21.6 kcal. g. ion^{-1}; the average deviation of individual determinations from this mean is 0.2 kcal. This compares with values of 20.7 to 21.6 kcal. g. ion^{-1} computed from Jofa and Mikulin's data[4] and with 18.0 kcal., reported by Bowden.[3]

We found, as was previously reported by Bowden, and by Jofa and Mikulin, that the slopes of η *vs.* log i varied with temperature. Bockris and Parsons[6] have reported that the slope is independent of temperature.

Bowden had reported that α equalled 0.50 ± 0.01 for all his measurements; Jofa and Mikulin's data show an increase in α from 0.50 at 0 to 40°, to 0.52 at 80°. Our measurements indicate that α is constant at 0.50 from 0 to 26°, and then rises to 0.55 at 91.3°.

The overvoltage values reported by Bowden are about 80 mv. lower than values reported by Jofa and Mikulin. Over most of the current density and temperature ranges investigated our measurements agree with those of Jofa and Mikulin to within 10 or 15 millivolts.

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[11] Z. A. Jofa, quote by A. N. Frumkin, *Acta Physicochimica, U. R. S. S.*, **18**, 23 (1943).