[CONTRIBUTION FROM THE DIVISION OF ANALYTICAL CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

# The Electrokinetics of Hydrogen Evolution. III. Hydrogen Overvoltage at Electrodeposited Copper Cathodes[1]

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Hydrogen overvoltage measurements have been made in normal hydrochloric acid solution on copper electrodes prepared by electrodeposition from acidified copper sulfate solution. In slow runs taken over days, the slope and overvoltage of the Tafel line in the range $10^{-3}$–$10^{-6}$ a./cm.$^2$ were found to vary with time and electrode. A simple correlation of data on 19 runs and 9 electrodes was found in the constancy of the overvoltage/slope ratio at constant current density despite a threefold slope variation from 45 to 117 mv. The ratio at 22° is 4.33 ± 0.04 at $9.6 \times 10^{-5}$ a./cm.$^2$ This implies that a family of Tafel lines exists with a single zero overvoltage intercept on the current density axis of $-8.35 \pm 0.04$ which is a fundamental constant for this system. Heats of activation derived from temperature effects on three electrodes at 200 mv. are 21.6, 14.6 and 23.8 kcal./g. eq. The average temperature coefficient is $-2.4$ mv./deg. Electrodes prepared from cyanide solution showed similar constancy of the overvoltage/slope ratio. A theoretical discussion based on the Eyring rate equation leads to the conclusion that the average free energy of activation for 9 electrodes is constant to better than ±150 cal. in spite of slope variations. An attempt is made to interpret the significance of this result.

An attempt has been made to determine precisely the overvoltage of hydrogen on electroplated copper electrodes in a normal hydrochloric acid solution. The use of electroplated copper was justified by the ease of preparation in a reproducible fashion. Although careful attention was paid to the latest techniques for such measurements[2,3] reproducible results were not obtained.

Instead it was found that the copper electrodes not only varied among themselves with respect to their overvoltage–current density relations, but each electrode varied in its own behavior from day to day. Because of the care exercised in this experimental study, it was decided that these time variations were characteristic of the electrokinetic processes occurring on the metallic surface.

Since the electrodes were polarized for many hours and even days between runs, it was difficult to attribute this behavior to a permanent oxide coat.[4] The reduction of an oxide layer initially present might lead to some variability of surface. However, Frisby[5] has recently shown by electron diffraction studies that in the formation of cuprous oxide from copper at low temperatures, the orientation of the copper surface atoms is maintained.

Consequently a study of these time variations was made and as a result a very simple correlation of the data obtained with all of the electrodes used was discovered.

Previous workers have investigated the overvoltage characteristics of copper. Such early investigators as Knobel, Caplan and Eiseman[6] and Wirtz[7] used experimental techniques which are now known to be unsatisfactory. Even such recent investigators as Hickling and Salt[8] worked with rubber stoppers, sealing wax and without pre-electrolysis in their investigations on copper and consequently their data are of doubtful value. Azzam, Bockris, *et al.*,[4] have published a few graphs of the copper overvoltage relations. Altogether there is very little work of a trustworthy character available for copper.

## Experimental

The apparatus and techniques used in this study were similar to those described previously.[3,9] Some changes in the cell design were necessitated by the use of the electroplated copper cathodes. An examination of Fig. 1 will indicate the characteristics of the new cell. It will be observed that provision is made for operating in a pure hydrogen atmosphere. Here the electrolyte can be distilled, the *p*H and overvoltage measured internally and the electrolyte electrolytically pre-purified and reserved while the copper electrodes are being prepared.

The copper electrodes are prepared by electroplating a platinum disk 0.670 cm.$^2$ in area which had previously been mounted by sealing into a soft glass to Pyrex standard taper joint. For most of them the electroplating was done in an acid copper coulometer bath operated in the bright plating range.[10] The plating was performed in a vessel separate from the overvoltage cell at a current density of 9.0 ma./cm.$^2$ for two hours and at a temperature of 26 ± 1°. Electrolysis was halted abruptly. The completed electrode was repeatedly rinsed with distilled water and then transferred to the overvoltage cell.

Another group of electrodes was prepared from a cyanide-bath. The concentrations of the various reagents in this bath were as follows

| | |
|---|---|
| Copper(I) cyanide, g./l. | 22.5 |
| Sodium cyanide, g./l. | 30.0 |
| Anhydrous disodium carbonate, g./l. | 10 |

The solution was filtered before using. Electroplating was done at 3.0 ma. per sq. cm. at about 30° for 2 hours. The deposits obtained were smooth, dull and salmon colored. Considering the lower efficiency of this bath, the relative thickness of the plate is about one-sixth that from the acid copper bath. Thus a number of conditions have varied widely—the acid copper deposit being coarsely granular and shiny.

Overvoltage measurements were made as a function of current density and temperature. They were obtained by measuring the potential difference between the reversible hydrogen electrode and the working cathode with a *p*H meter. The meter used in measuring the current density was repeatedly calibrated using a precision resistor in series with it and measuring the voltage developed with the *p*H meter.

The electrolyte was hydrochloric acid (*p*H approx. 0), purified by distillation in hydrogen and subsequent electrolysis over copper. The electrodes used in the purification step were always discarded after use. The *p*H was meas-

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(2) J. O'M. Bockris, *Chem. Revs.*, **43**, 535 (1948).

(3) B. Post and C. F. Hiskey, THIS JOURNAL, **72**, 4203 (1950).

(4) A. M. Azzam, J. O'M. Bockris, B. E. Conway and H. Rosenberg, *Trans. Faraday Soc.*, **46**, 918 (1950).

(5) H. Frisby, *Compt. rend.*, **228**, 1291 (1949).

(6) M. Knobel, P. Caplan and M. Eiseman, *Trans. Electrochem. Soc.*, **43**, 55 (1923).

(7) K. Wirtz, *Z. physik. Chem.*, **B36**, 435 (1937).

(8) A. Hickling and F. W. Salt, *Trans. Faraday Soc.*, **36**, 1226 (1940).

(9) B. Post and C. F. Hiskey, THIS JOURNAL, **73**, 161 (1951).

(10) M. Thompson, "Applied Electrochemistry," The Macmillan Co., New York, N. Y., 1914.

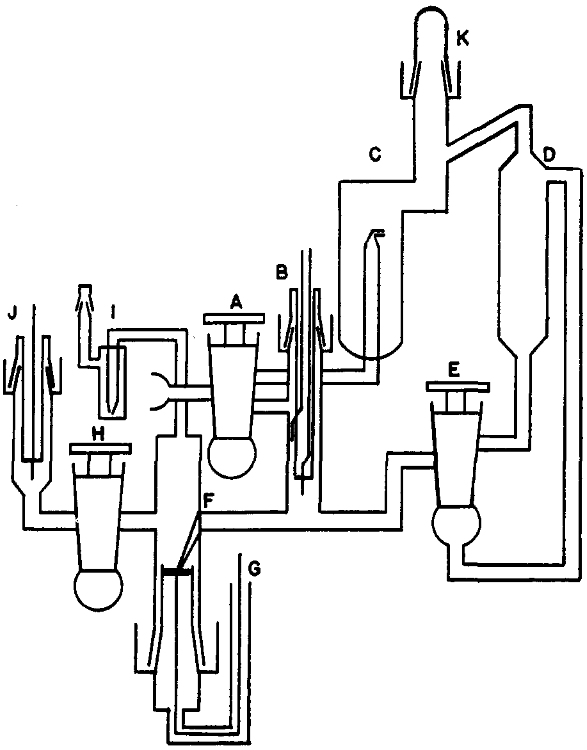

Fig. 1.—Overvoltage cell: A, attachment to hydrogen or vacuum line; B, reference electrode: upper Ag, AgCl; lower hydrogen; C, electrolyte stillpot; D, still receiver; E, stopcock between reservoir and stopcock; F, Luggin capillary; G, cathode: lead to back of sealed-in platinum disk; soft glass member of standard taper joint; H, stopcock between anode and cathode compartment; I, bubbler for hydrogen escape; J, anode; K, filling cap.

ured internally using a silver, silver chloride electrode in conjunction with a reversible hydrogen electrode. The anode was of bright platinum separated from the cathode by a closed stopcock. Hydrogen was obtained from a purification train. The cell was thermostated when desired. The working copper electrode was always maintained cathodic and in the standby condition had a current of about 4.0 μa. passing through it.

**Criteria for Good Data.**—The data obtained were considered satisfactory if a straight line was obtained for about two decades with relatively small "hysteresis," *i.e.*, difference between the "up" points (current increasing) and the "down" points (current decreasing). In initial runs, a difference of about 10 mv. was tolerated especially if it grew less in subsequent trials.

A further evidence of good data was believed to be the rapid attainment of the steady state reading at each point. For some measurements, especially at higher temperatures, this was less than a minute. Most of the data obtained have involved readings taken in two or three minutes at most. Another criterion of properly operating cells was their insensitiveness to hydrogen stirring. A further indication of a good electrode was its rate of solution in nitric acid. If impurities were absent the copper would dissolve very slowly. Finally, the rate of overvoltage decay served to indicate the presence or absence of appreciable amounts of depolarizers. If there were signs of instability; *i.e.*, large hysteresis after a day of running, or very large changes in overvoltage over short time intervals, the liquid in the cell was discarded, additional hydrochloric acid put in the still and fresh electrolyte distilled, purified by electrolysis over copper and used.

Once a "good" run was obtained, the cell was used for days without change. The next electrode was run, if possible, in the electrolyte reserved from the preceding run. The cell was not put through the entire preliminary cleaning (except where evidence of contamination was present) more than about once a month. It was felt that a greater purity of electrolyte was obtained in this fashion.

## Experimental Results

In Table I, data typical of those obtained in this study are presented for four electrodes plated from the acid bath. Each group of data obtained at any particular time consists of points taken as the current was increased, *i.e.*, upper values, and as the current was decreased, *i.e.*, lower values. In the case of electrode D only the points taken as the current was increased are given. The data for electrode E are presented in Fig. 2.

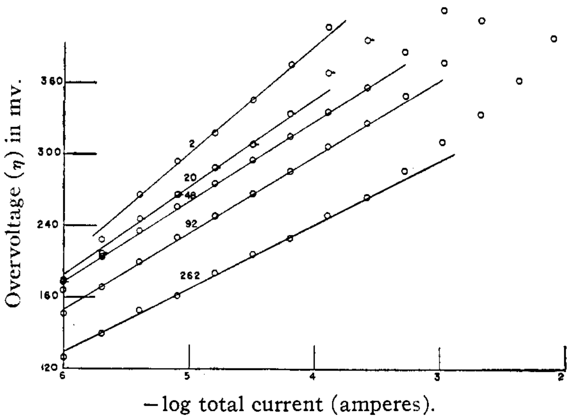

Fig. 2.—Time variation in overvoltage *vs.* total current for electrode E: area of electrode, 0.670 cm.$^2$; time in hours, 2, 20, 48, 92 and 262; corresponding slopes in mv. per decade: 91, 76, 67, 64 and 53, respectively.

Inspection of these data reveals a number of facts important to this study. In the first place all of the data show a difference between the overvoltage values obtained with current increasing and decreasing. This difference averages about 5 mv. with the current increasing limb having the higher value. In a few instances there was practically no hysteresis. A few of the plots have differences of as much as 10 mv. but data of this type were usually discarded. In the initial stages of this study the runs had much larger "hysteresis" effects. Altogether about one-half of all the data taken were considered too poor to use in this publication.

If the data presented are graphed with the absolute value of the overvoltage ($\eta$) against current density ($i$) on a semi-log plot, it is found that a Tafel line, $\eta = a + b \log i$ can be fitted to the individual runs. Individual overvoltage measurements in the main are within ±3 mv. of the Tafel line in the current density range of $10^{-6}$ to $5 \times 10^{-4}$ a./cm.$^2$. In the higher current density ranges there is a positive deviation but below about $5 \times 10^{-4}$ a./cm.$^2$ the effect is less than the uncertainty of any given overvoltage value. This deviation is due to an *IR* drop between the reference and working electrode.

Finally an inspection of Table I shows us that no single Tafel line occurs for these copper electrodes. Instead the values of the slopes as well as the values of the overvoltage for a fixed current density vary from electrode to electrode. In addition, for any particular electrode these quantities, *i.e.*, $b$ and $\eta$ in Tafel's equation, vary with time. In general $b$ and $\eta$ decrease with time of aging at the

TABLE I

OVERVOLTAGE (MV.) *vs.* TOTAL CURRENT

Electrode area = 0.670 cm.$^2$. All plated in acid bath

| **Electrode A** **Time (hr.) after introduction in cell** | | μa. | | | | | μa. × $10^{-2}$ | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $T$(°C.) | 1.0 | 2.0 | 4.0 | 8.0 | 16.0 | 0.32 | 0.64 | 1.28 | 2.6 | 5.2 | 10.4 | 20.8 | 40.2 | 80 |
| 0.5 | 27 | 161 | 189 | 210 | 230 | 250 | 270 | 290 | 313 | | | | | | |
| | | 159 | 181 | 202 | 221 | 241 | 262 | 285 | | | | | | | |
| 18 | 24 | 137 | 173 | 200 | 220 | 240 | 259 | 279 | 300 | 330 | | | | | |
| | | 137 | 169 | 193 | 214 | 234 | 251 | 270 | 296 | | | | | | |
| 19 | 25 | 139 | 170 | 196 | 213 | 233 | 251 | 270 | 292 | | | | | | |
| | | 133 | 168 | 191 | 212 | 232 | 250 | 270 | | | | | | | |
| Electrode B | | | | | | | | | | | | | | | |
| 0.5 | 26 | 150 | 180 | 208 | 229 | 248 | 268 | 289 | 312 | | | | | | |
| | | 158 | 181 | 210 | 229 | 242 | 260 | 281 | | | | | | | |
| 27 | 30 | 131 | 150 | 170 | 184 | 201 | 220 | 237 | 251 | 270 | 290 | 313 | | | |
| | | 124 | 140 | 160 | 179 | 200 | 218 | 231 | 249 | 267 | 287 | | | | |
| 44 | 30 | 137 | 150 | 163 | 181 | 199 | 212 | 230 | 249 | 263 | 291 | | | | |
| 51 | 30 | 120 | 142 | 162 | 181 | 200 | 216 | 230 | 249 | 269 | 290 | 321 | | | |
| | | 110 | 129 | 149 | 171 | 195 | 211 | 230 | 249 | 269 | 290 | | | | |
| 67 | 30 | 110 | 141 | 163 | 182 | 200 | 219 | 231 | 249 | 267 | 287 | 310 | | | |
| | | 109 | 129 | 150 | 171 | 193 | 214 | 231 | 250 | 269 | 286 | | | | |
| Electrode D | | | | | | | | | | | | | | | |
| 0.5 | 26.5 | 176 | 211 | 250 | 282 | 311 | 339 | 369 | 410 | 450 | 491 | | | | |
| 70 | 23 | 171 | 200 | 224 | 250 | 270 | 292 | 319 | 342 | 371 | 405 | 449 | | | |
| 90 | 37 | 159 | 179 | 199 | 220 | 241 | 262 | 286 | 310 | 332 | 359 | 388 | | | |
| Electrode E | See Fig. 2 | | | | | | | | | | | | | | |

TABLE II

OVERVOLTAGE (MV.) = TOTAL CURRENT

Electrode area = 0.670 cm.$^2$

| | | μa. | | | | | μa. × $10^{-2}$ | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Electrode | $T$ (°C.) | 1.0 | 2.0 | 4.0 | 8.0 | 16.0 | 0.32 | 0.64 | 1.28 | 2.6 | 5.2 | 10.4 |
| Electrodes prepared from acid solution | | | | | | | | | | | | |
| A | 26.5 | 161 | 189 | 210 | 230 | 250 | 270 | 290 | 313 | | | |
| A | 24 | 139 | 170 | 196 | 213 | 233 | 251 | 270 | 292 | | | |
| B | 26 | 150 | 180 | 208 | 229 | 248 | 268 | 289 | 312 | | | |
| B | 30 | 131 | 150 | 170 | 184 | 201 | 220 | 237 | 251 | 270 | 290 | 313 |
| C | 20 | 186 | 222 | 252 | 279 | 301 | 329 | 353 | 382 | 411 | 441 | 473 |
| G | 30 | 200 | 242 | 273 | 302 | 331 | 361 | 389 | 417 | 447 | 471 | 500 |
| D | 26.5 | 176 | 211 | 250 | 282 | 311 | 339 | 369 | 410 | 450 | 491 | |
| D | 23 | 171 | 200 | 224 | 250 | 270 | 292 | 319 | 342 | 371 | 405 | 449 |
| D | 37 | 159 | 179 | 199 | 220 | 241 | 262 | 286 | 310 | 332 | 359 | 388 |
| E | 27.5 | 178 | 212 | 250 | 278 | 302 | 329 | 359 | 400 | 450 | 519 | |
| E | 27.5 | 171 | 201 | 230 | 251 | 272 | 292 | 318 | 342 | 380 | 433 | |
| E | 24.3 | 188 | 210 | 230 | 250 | 269 | 289 | 309 | 329 | 351 | 380 | 415 |
| E | 21.2 | 169 | 191 | 213 | 233 | 251 | 270 | 289 | 309 | 329 | 351 | 380 |
| E | 22 | 130 | 150 | 169 | 182 | 200 | 216 | 230 | 248 | 264 | 287 | 310 |
| H | 30 | 267 | 300 | 332 | 368 | 401 | 438 | 472 | 510 | 548 | 582 | |
| I | 20 | 138 | 150 | 161 | 178 | 189 | 201 | 218 | 232 | 251 | 278 | |
| I | 20 | 130 | 141 | 157 | 170 | 183 | 199 | 211 | 230 | 250 | 270 | 299 |
| I | 22 | 120 | 135 | 150 | 166 | 180 | 195 | 210 | 228 | 246 | 263 | 287 |
| J | 23 | 150 | 181 | 208 | 229 | 250 | 269 | 290 | 315 | 341 | | |
| Electrodes plated from cyanide solution | | | | | | | | | | | | |
| K | 30.2 | 162 | 200 | 232 | 260 | 283 | 309 | 332 | 361 | 399 | 430 | |
| K | 30.4 | 151 | 200 | 231 | 260 | 287 | 312 | 340 | | | | |
| L | 32 | 140 | 181 | 217 | 247 | 272 | 299 | 323 | 351 | 389 | 419 | |
| L | 26.6 | 156 | 186 | 210 | 231 | 252 | 273 | 297 | 321 | 354 | | |
| L | 25.5 | 101 | 129 | 151 | 171 | 190 | 208 | 226 | 242 | 261 | 293 | |
| L | 27.4 | 99 | 119 | 139 | 158 | 172 | 189 | 206 | 221 | 241 | 260 | 281 |

standby current density. For electrode E time data were taken and they have been plotted to show this effect in Fig. 2.

At this stage of the investigation, it was apparent that at least two conclusions appeared possible to explain the effects observed. Either there were so many variables involved in making measurements of this sort that no reproducibility was to be expected or else it could be assumed that the overvoltage measurements were being done in a reasonably well controlled experiment with only the electrode surface as a variable. This electrode surface must be assumed to vary from plate to plate as well as with time of aging. Because it had been possible to measure hydrogen and deuterium overvoltages with considerable precision in these laboratories,[3,9] it was felt that in this case the erratic behavior of the data was due largely to the fact that a solid electrode was being used. Consequently it was decided to proceed with the investigation with the latter conclusion as a guide.

Accordingly a larger number of electrodes were prepared in the acid bath and their overvoltage characteristics recorded. Most of the more reliable data are listed in Table II. Here the data are assembled without regard for the time or conditions of aging of the electrode in the overvoltage cell. For comparative purposes, only "up" points are given.

To discover whether the behavior noted above was peculiar to the surface produced by the acid plating bath, additional electrodes were prepared from an alkaline cyanide bath. Data taken with these cyanide copper electrodes are also given in Table II. Again the slope and overvoltage are found to vary from run to run.

TABLE III

CALCULATIONS OF $(\eta/b)$ AT $T = 22°$ $(i = 9.6 \times 10^{-1}$ A./CM.$^2)$

| No. | Electrode | $b$(mv.) | $\eta$(mv.) | $\eta/b$ |
|---|---|---|---|---|
| | Electrodes prepared from acid solution | | | |
| 1 | A | 67 | 301 | 4.49 |
| 2 | A | 62 | 275 | 4.44 |
| 3 | B | 67 | 299 | 4.46 |
| 4 | B | 57 | 256 | 4.49 |
| 5 | C | 87 | 353 | 4.06 |
| 6 | G | 96 | 407 | 4.24 |
| 7 | D | 98 | 380 | 3.88 |
| 8 | D | 79 | 320 | 4.05 |
| 9 | D | 73 | 323 | 4.42 |
| 10 | E | 91 | 370 | 4.07 |
| 11 | E | 76 | 331 | 4.36 |
| 12 | E | 67 | 316 | 4.72 |
| 13 | E | 64 | 287 | 4.48 |
| 14 | E | 53 | 230 | 4.34 |
| 15 | H | 117 | 492 | 4.25 |
| 16 | I | 49 | 212 | 4.33 |
| 17 | I | 45 | 207 | 4.60 |
| 18 | I | 49 | 210 | 4.29 |
| 19 | J | 68 | 292 | 4.26 |
| | | | Mean value | 4.33 ± 0.04 |
| | | | Average deviation | ± 0.16 |
| | Electrodes prepared from cyanide solution | | | |
| 1 | K | 82 | 533 | 4.35 |
| 2 | K | 91 | 361 | 3.97 |
| 3 | L | 87 | 348 | 4.00 |
| 4 | L | 74 | 308 | 4.08 |
| 5 | L | 60 | 231 | 3.85 |
| 6 | L | 53 | 218 | 4.11 |
| | | | Mean value | 4.06 ± 0.05 |
| | | | Average deviation | ± 0.12 |

Now it is well known that those elements which are catalytic in hydrogenation and in hydrogen exchange reactions are generally of low overvoltage and with small slopes in their Tafel relations. Non-catalytic elements on the other hand usually possess large values of *b*. It was thought advisable therefore to attempt to relate the change of slope *b* in Tafel's equation to the change in overvoltage. To do this, the value of $\eta$ was computed at a fixed current density and at a temperature of 22°. A small correction for other temperatures was made as required using the temperature coefficient of $-2.4$ mv./° C. as found from experiments recorded below. The values of *b* were evaluated from graphical plots of the data. These values are summarized in Table III as well as values of the ratio $\eta/b$.

The most significant point to be seen in that table is the relative constancy of $\eta/b$. This term has a value of 4.33 with an average deviation of 0.16 for nineteen sets of data taken on nine different acid copper electrodes. For the six sets of data taken on the two cyanide copper electrodes a value of 4.06 was obtained. These results were obtained despite the fact that the slopes (*b*) of the Tafel relation varied threefold in the course of these measurements.

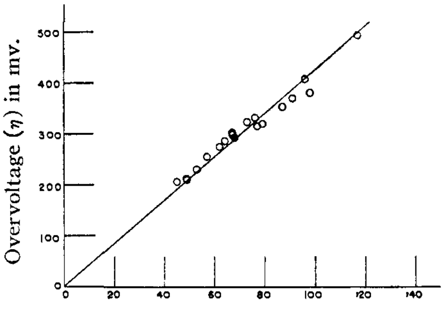

Fig. 3.—Overvoltage *vs.* slope: acid bath copper plates at a current density of $9.6 \times 10^{-5}$ a./cm.$^2$ and at a temperature of 22° in 1 *N* hydrochloric acid.

Quantitatively these data mean that when proper account is taken of the mechanism of the slow step involved in this discharge process, a characteristic term for all copper electrodes emerges.

**Temperature Dependence of Overvoltage.**—Measurements were now made of the temperature effect on the overvoltage. Any attempt to isolate the temperature variation of overvoltage had to be based on recognition of and correction for the temperature independent variations which were noted above. The experimental work on temperature variation was performed, however, before these factors were clearly known. Nevertheless, on the first electrode so run, *i.e.*, electrode B, extreme pains were taken with repetitive measurements to show that the temperature cycle was reversible. In addition a saturation pressure of hydrogen was maintained at all temperatures. For example, a duplicate run at 30° one day later gave an average deviation of $-3$ mv. from earlier ones. Re-runs were made also at 4 and 15° with results shown in Table IV.

TABLE IV

TEMPERATURE VARIATION OF OVERVOLTAGE ON COPPER

Electrolyte 1 $N$ HCl, area = 0.670 cm.$^2$, overvoltage (mv.) − total current

| | $\mu$a. | | | | | $\mu$a. × $10^{-2}$ | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1.0 | 2.0 | 4.0 | 8.0 | 16.0 | 0.32 | 0.64 | 12.8 | 2.6 | 5.2 | 10.4 |
| Electrode B, $p$H 0.09 | | | | | | | | | | | |
| 15.7 ± 0.3° | 160 | 180 | 200 | 216 | 230 | 248 | 262 | 280 | 302 | 332 | |
| 2/22/49 | 150 | 170 | 192 | 210 | 222 | 240 | 255 | 274 | 299 | | |
| 4.2 ± 0.3° | 179 | 199 | 217 | 232 | 250 | 266 | 281 | 309 | | | |
| 2/22/49 | 171 | 191 | 208 | 222 | 241 | 259 | 279 | | | | |
| Run repeated after $H_2$ stirring | 181 | 200 | 218 | 232 | 250 | 265 | 282 | 310 | | | |
| 4.2 ± 0.3° | 171 | 191 | 208 | 222 | 240 | 259 | 280 | | | | |
| Run repeated | 154 | 177 | 195 | 211 | 228 | 242 | 261 | 280 | 302 | 332 | |
| 15.3 ± 0.2 | 150 | 170 | 190 | 208 | 221 | 240 | 256 | 274 | 299 | | |
| 30.1 ± 0.3° | 131 | 150 | 170 | 184 | 201 | 220 | 237 | 251 | 270 | 290 | 313 |
| 2/22/49 | 124 | 140 | 160 | 179 | 200 | 218 | 231 | 249 | 267 | 287 | |
| 78.3 ± 0.2° | 121 | 121 | 126 | 130 | 139 | 150 | 162 | 179 | 198 | 218 | 242 |
| 2/23/49 | 120 | 121 | 122 | 129 | 134 | 148 | 161 | 178 | 201 | 218 | |
| 55.6 ± 0.2° | 101 | 109 | 120 | 137 | 151 | 168 | 181 | 200 | 219 | 239 | 260 |
| 2/23/49 | 101 | 109 | 119 | 131 | 145 | 161 | 178 | 197 | 219 | 240 | |
| Electrode D, $p$H −0.05 | | | | | | | | | | | |
| 8.2 ± 0.3° | 201 | 229 | 252 | 278 | 300 | 321 | 349 | 379 | 410 | 441 | 489 |
| 3/26/49 | 209 | 237 | 259 | 278 | 298 | 319 | 350 | 384 | 420 | 451 | |
| 22.7 ± 0.1° | 171 | 200 | 224 | 250 | 270 | 292 | 319 | 342 | 371 | 405 | 449 |
| 3/26/49 | 172 | 200 | 222 | 248 | 269 | 289 | 312 | 340 | 371 | 409 | |
| 37.0 ± 0.1° | 159 | 179 | 199 | 220 | 241 | 262 | 286 | 310 | 332 | 359 | 388 |
| 3/27/49 | 155 | 171 | 191 | 212 | 240 | 261 | 282 | 309 | 332 | 359 | |
| 64.5 ± 0.2° | 149 | 156 | 166 | 180 | 196 | 212 | 231 | 252 | 280 | 310 | 350 |
| 3/27/49 | 149 | 152 | 162 | 178 | 191 | 210 | 230 | 251 | 280 | 311 | 351 |
| 74.8 ± 0.3° | 149 | 150 | 153 | 161 | 172 | 186 | 201 | 221 | 244 | 271 | 310 |
| 3/27/49 | 139 | 141 | 149 | 156 | 167 | 181 | 199 | 219 | 241 | 270 | 310 |
| Electrode E, $p$H 0.04 | | | | | | | | | | | |
| 10.5 ± 0.5° | 218 | 250 | 272 | 292 | 312 | 338 | 362 | 401 | 460 | 553 | |
| 3/31/49 | 219 | 249 | 270 | 289 | 310 | 330 | 352 | 399 | 459 | | |
| 24.2 ± 0.1° | 188 | 210 | 230 | 250 | 269 | 289 | 309 | 329 | 351 | 380 | 415 |
| 3/31/49 | 162 | 190 | 219 | 241 | 260 | 279 | 298 | 320 | 340 | 372 | |
| Repeated at room temp. | 169 | 191 | 213 | 233 | 251 | 270 | 289 | 309 | 329 | 351 | 380 |
| 21.3 ± 0.1 | 159 | 180 | 208 | 230 | 250 | 268 | 281 | 302 | 331 | 348 | 379 |
| 4/2/49 | | | | | | | | | | | |
| 36.0 ± 0.1° | 135 | 151 | 171 | 189 | 207 | 223 | 243 | 261 | 281 | 305 | 330 |
| 4/2/49 | 131 | 150 | 168 | 182 | 202 | 224 | 244 | 262 | 282 | 308 | 329 |
| 49.7 ± 0.3° | 119 | 129 | 140 | 152 | 170 | 186 | 201 | 220 | 241 | 261 | 283 |
| 4/2/49 | 120 | 130 | 141 | 157 | 171 | 188 | 202 | 221 | 247 | 267 | 288 |
| 71.0 ± 0.5° | 115 | 118 | 120 | 128 | 133 | 148 | 161 | 178 | 193 | 211 | 231 |
| 4/2/49 | 110 | 111 | 114 | 121 | 131 | 148 | 162 | 180 | 198 | 212 | 233 |

Having apparently established the reversibility, electrodes D and E were run without checks, the emphasis being on getting all temperature data as quickly as possible. In the light of the slow time decay probable for electrodes of this slope, it was reasoned that serious errors should not occur.

Bowden and Agar[11] have given an expression for $i$ which may be written

$$\log i = (-\Delta H^* + \alpha F\eta)/2.3RT + \text{constant}$$

$\Delta H^*$ is the heat of activation and the slope of the Tafel line $b = 2.303\ RT/\alpha F$, defining $\alpha$. Therefore, the slope of the $\log i$ *vs.* $1/T$ plot at constant $\eta$ should yield values for the heat of activation $\Delta H^*$.

Such a plot has been made in Fig. 4 for an overvoltage value of 200 mv. Points were obtained from graphs of the data. The value of $\Delta H^*$ so obtained, using an average value for $\alpha$, were 21.6, 14.6 and 23.8 kcal./mole for electrodes B, D and E, respectively. Each of these plots shows a satisfactory agreement with a straight line plot although they vary widely among themselves. Thus the apparent precision for each $\Delta H^*$ determined appears to be of the order of ±1 kcal.

Values of $\alpha$ computed from $b$ are given in Table V and range from 0.75 to 1.30 for the three electrodes. In general $\alpha$ increases with temperature—for electrode E, it is almost exactly proportional to it but the other electrodes do not vary as regularly. At a current density of $10^{-4}$ a./cm.$^2$, the following average temperature coefficients are calculated: −1.9, −2.1 and −3.1 mv./deg. on electrodes B, D and E, respectively, at about room temperature. The mean value is −2.4 mv./deg.

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[11] F. P. Bowden and J. N. Agar, *Ann. Reports on Progress Chem.* (*Chem. Soc. London*), **35**, 90 (1938).

TABLE V

DERIVED FROM TEMPERATURE VARIATION DATA TABLE IV, VALUES OF $\alpha$

| Electrode B | | | Electrode D | | | Electrode E | | |
|---|---|---|---|---|---|---|---|---|
| $T$ (°K.) | $b$ (mv.) | $\alpha$(eq./mole) | $T$ (°K.) | $b$ (mv.) | $\alpha$(eq./mole) | $T$ (°K.) | $b$ (mv.) | $\alpha$(eq. mole) |
| 277.4 | 54 | 1.01 | 296 | 77 | 0.76 | 284 | 70 | 0.80 |
| 288.7 | 54 | 1.03 | 310 | 76 | .80 | 294 | 66 | .88 |
| 303.3 | 57 | 1.03 | 339 | 68 | .97 | 309 | 62 | .98 |
| 328.8 | 54 | 1.20 | 348 | 65 | 1.02 | 323 | 58 | .98 |
| | | | | | | 344 | 52 | 1.30 |
| | Mean | 1.07 | | Mean | 0.89 | | Mean | 1.01 |

## Theoretical and Discussion of Results

The Eyring absolute rate theory gives the following relation between current density and overvoltage.[12]

$$i = ce^{-\Delta F^*/RT}\, e^{\alpha F\eta/RT} \qquad (1)$$

Where $\Delta F^*$ is the free energy of activation, $c$ is fixed for a given temperature (and possibly $p$H), and $\alpha$ is an undetermined coefficient. From (1), one finds for the overvoltage

$$\eta = \Delta F^*/\alpha F - 2.3(RT/\alpha F)\log c + 2.3(RT/\alpha F)\log i \quad (2)$$

which is Tafel's equation.

The slope is given by

$$b = 2.3\ RT/\alpha F \qquad (3)$$

which defines $\alpha$. Solving (3) for $\alpha$ and substituting into (2) yields

$$\eta = b(\Delta F^*/2.3RT - \log c + \log i) \qquad (4)$$

In equation (4), at a fixed current density for a given electrode–electrolyte system, the term in parentheses is constant. Since $b$ is involved in questions of mechanism, in most theories it cannot vary independently of $\Delta F^*$. Then (4) requires that a single value of overvoltage corresponding to a single value of the slope at a given current density exist.

The assumption is now made that $b$ may vary independently of any of the variables in the parentheses including $\Delta F^*$. Then equation (4) predicts that a plot of $\eta$ *versus* $b$ will be a *straight line through the origin*. The experimental points graphed in Fig. 3 are in good agreement with a straight line drawn through the origin for the purpose of comparison. Furthermore, it now follows from (4) that, for varying $\eta$ and $b$, the ratio $\eta/b$ is constant. The experimental results have been given in Table III.

**The Tafel Line Intercept for Copper.**—When $\eta = 0$, let $i = i_0$, its value at the intercept. From (4) one finds a value which is *independent* of $b$.

$$\log i_0 = -(\Delta F^*/2.3\ RT - \log c)\ (b \neq 0) \qquad (5)$$

Equation (4) may be rewritten as

$$\eta = b(-\log i_0 + \log i) \qquad (6)$$

Equation (6) defines a *family of Tafel lines* for copper with *varying slope* but the *same intercept*! The value of $\log i_0$ is easily calculated to be −8.35 ± 0.04 and is a fundamental constant for this system.

The evaluation of $\eta/b$ has shown this ratio to be constant within limits. Since $\log i$ may be measured to a higher order of precision, $\log i_0$ is constant to the same order as $\eta/b$. Thus, all nine electrodes and nineteen runs for acid copper given in Fig. 3 and Table III fit equation (6) within the uncertainty given for the mean value of $\eta/b$. This is true experimentally, of course, only over the range of current density for which the Tafel line itself is valid.

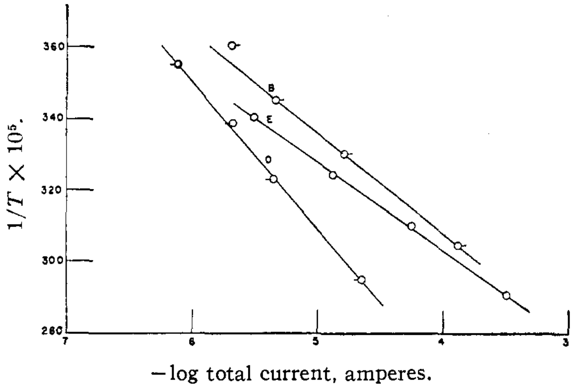

Fig. 4.—$1/T$ *vs.* −log total current. Acid bath copper electrodes B, E and D area 0.670 cm.$^2$; taken in 1 $M$ hydrochloric acid at $\eta$ = 200 mv.

**The Constancy of $\Delta F^*$.**—The average deviation for a single run of $\eta/b$ in Table III is ±0.16 unit. This may be ascribed to the experimental uncertainty in determining $\eta$ and $b$ separately or to real variations in the value of $\log i_0$. It is estimated that of the total average deviation, at most ±0.10 unit is due to variations in $\log i_0$ alone. This deviation may be accounted for in terms of variations in surface area (affecting $\log i$), variations in $\Delta F^*$, and the usual accidental errors. If the whole weight of the deviation is placed on the $\Delta F^*$ term alone, then at room temperature unit change in $\eta/b$ corresponds to 1380 calories change in $\Delta F^*$. Therefore, the maximum average deviation of $\Delta F^*$ in the above 19 runs is about ±150 calories.

**Universal Plot for Overvoltage Data.**—A plot of $\eta/b$ against $\log i$ is more satisfactory than the Tafel coördinates when $b$ is an additional variable. This will be a straight line of unit slope for all systems. Further, either the vertical or horizontal separation of these lines will be directly related to differences in $\Delta F^*$. At 25° each unit of separation represents 1380 calories difference.

**Significance of a Constant $\Delta F^*$ with Varying Slope.**—The constancy of $\Delta F^*$ implied by the constant ratio of $\eta/b$ is coupled with an almost threefold slope variation. The preparation of a surface of definite catalytic activity is generally difficult. Therefore, it may be argued that $\Delta F^*$ is independent of the catalytic nature of the surface. Evidence in further support of this view may be found in the data obtained with electrodes prepared from cyanide solution. Despite a physically different surface, the mean value of $\eta/b$ for these electrodes differed by only 0.27 unit from that for "acid copper." This difference may be reasonably accounted for by differences in real surface area. However, even if the entire difference is assumed to be in $\Delta F^*$, the two surfaces differ only by 375 calories. This corresponds to a difference of 16 mv. between the values of the mean Tafel lines for a slope of 60 mv.

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(12) H. Eyring, K. J. Laidler and S. Glasstone, *J. Chem. Phys.*, **7**, 1053 (1939).

Efforts to fit the results for copper into the framework of some one or another overvoltage theory have not been very successful. Setting aside questions of probability, it is possible to construct a logically consistent interpretation. This is presented below.

In Fig. 5, the usual type of energy diagram is given showing the initial (1), intermediate (2) and final (3) state for the formation of hydrogen.

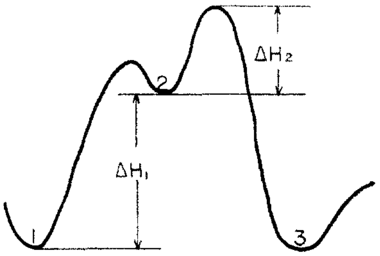

Fig. 5.—Energy diagram for hydrogen discharge: shown are the initial (1), intermediate (2) and final (3) states.

Suppose there is a Boltzmann distribution between material in solution (1) and the active intermediary (2) so that the concentration of active material, $c_2$, at site 2 is kept fixed. Then we have

$$c_2 = c_1 e^{-\Delta H_1/RT} \qquad (7)$$

where $c_1$ depends on the nature of the solution and may be taken here as temperature independent. $c_2$ might refer to adsorbed H atoms on the electrode surface. Now the application of the potential $\eta$ supplies energy $J\eta E$ so that (7) becomes

$$c_2 = c_1 e^{-(\Delta H_1 - J\eta F)/RT} \qquad (8)$$

In many theories, $J$ is set equal to $\alpha$ and $i$ is implicitly set proportional to $c_2$. Instead let us choose $J = 1$ which is consistent for example with the reaction

$$H_3O^+ + 1e \longrightarrow H + H_2O$$

Then it is still possible to obtain Tafel's equation if the rate limiting step in going from state (2) to (3) is written

$$i = kc_2^{\alpha} e^{-\Delta F_2/RT} \qquad (9)$$

where $\alpha$ is now the *order* of the reaction and $k$ is a proportionality constant whose temperature dependence may be ignored for the range with which we are concerned.

From (8) and (9) we find

$$\eta = \frac{RT}{\alpha F}\left(\frac{\alpha \Delta H_1}{RT} + \frac{\Delta F_2}{RT} - \ln c_1{}^{\alpha}k\right) - \frac{RT}{\alpha F}\ln i \quad (10)$$

This is Tafel's equation.

The total free energy of activation is $\Delta F_1 + \Delta F_2$. If $\Delta F_1$ is very large compared to $\Delta F_2$, the total $\Delta F$ remains substantially constant as the nature of the surface and $\Delta F_2$ change. The detailed kinetics of the rate-limiting step are thus made surface dependent. Variations in the order are equivalent to slope variations in the Tafel line.

The value obtained for the heat of activation depends upon the form of the equation assumed to represent $i$. A comparison of the equation of Bowden and Agar[11] (given in an earlier section) with equation (10) shows that

$$\Delta H^* = \alpha \Delta H_1 + \Delta H_2 \qquad (11)$$

where $\Delta H^*$ is the heat of activation as ordinarily derived. If $\alpha \Delta H_1 >> \Delta H_2$, then $\Delta H_1 \approx \Delta H^*/\alpha$.

Calculations of $\Delta H_1$ have been made for Cu neglecting $\Delta H_2$ and using the temperature data and $\alpha$ values given earlier. The results are 20.2, 18.1, 22.7 kcal./g. eq. for electrodes B, D and E, respectively. The agreement is better for the $\Delta H_1$ values than for the $\Delta H^*$ values given above. However, since $\alpha$ is close to unity for these electrodes, no drastic change has been effected.

The situation for Hg is quite different. Here $\alpha$ is about one-half and $\Delta H^*$ 21.7 kcal./g. eq.[3] Therefore, to the same approximation, $\Delta H_1$ is 43.4 kcal/g. eq. It has long been known that energies of the order of 50 kcal. were required in order to make atomic H a reasonable choice for the active intermediary. Further, the values of $\Delta H_1$ for Cu and Hg differ by a substantial amount as would be reasonable in view of the greater bonding of $H_2$ to Cu.[13-15] This is in marked contrast to the values of $\Delta H^*$ which are roughly the same for Cu and Hg.

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(13) E. B. Maxted and N. J. Hassid, *J. Chem. Soc.*, 31 (1931).

(14) G. B. Kistiakowsky, E. N. Flosdorf and G. B. Taylor, *Z. Elektrochem.*, **35**, 542 (1929).

(15) R. A. Beebe and H. S. Taylor, *J. Chem. Soc.*, **46**, 43 (1924).